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The Radiochemistry of Cobalt

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The Radiochemistry of Cobalt

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Subcommittee on Radiochemistry
National Academy of Sciences—National Research Council

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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 cobalt 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 cobalt which might be included in a revised version of the monograph.

CONTENTS

The Radiochemistry of Cobalt

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

1. W. J. Williams, "Analytical Chemistry of Cobalt," Talanta 1, 88-104 (1958).

2. B. S. Evans, "The Determination of Cobalt. A New Method of Volumetric Determination and a New Method for Its Determination in Steel," Analyst 62, 363 (1937).

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II. THE RADIOACTIVE NUCLIDES OF COBALT

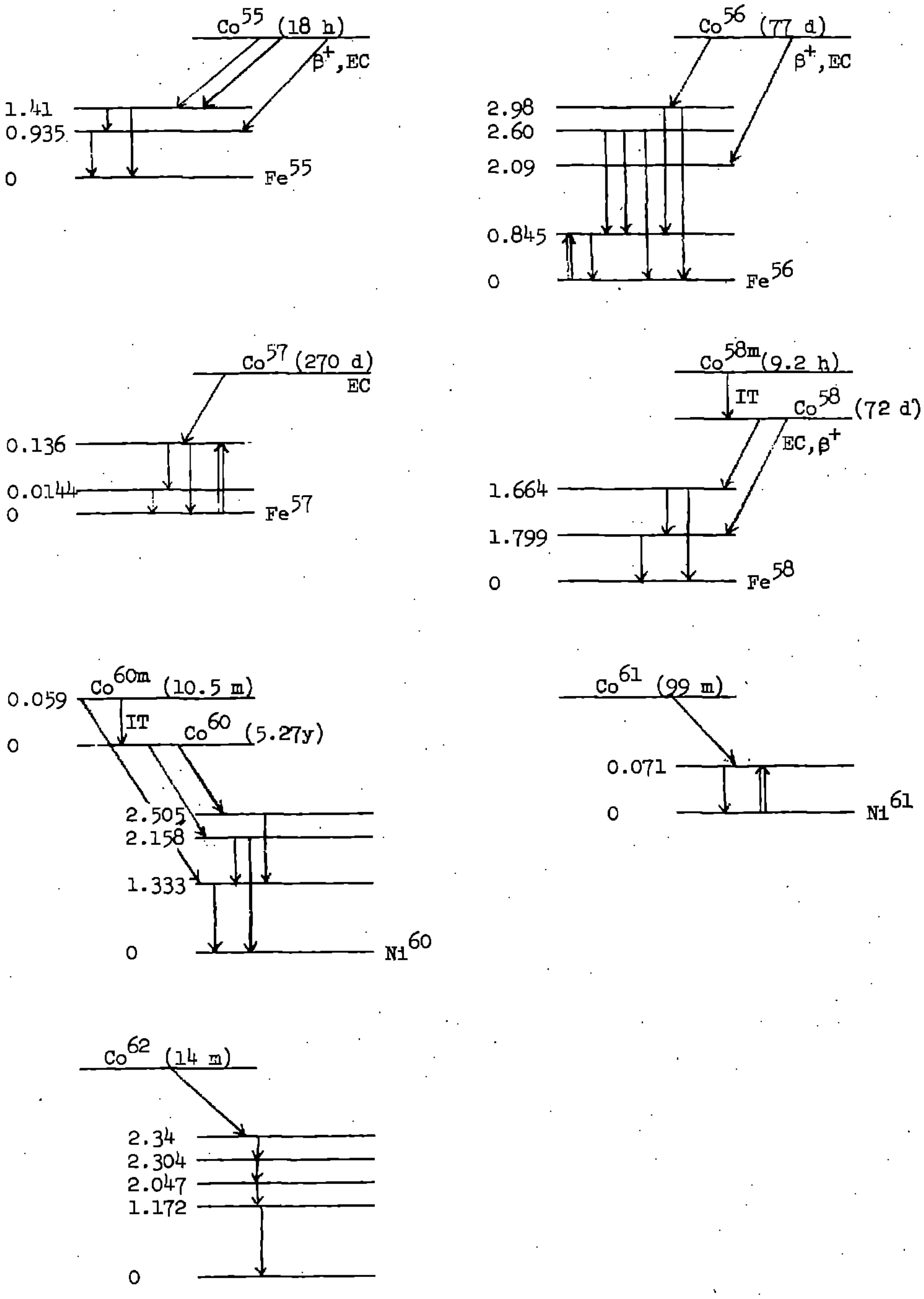
The radioactive nuclides of cobalt which are of interest to the radiochemist are given in Table I. This table has been compiled from information appearing in reports by Strominger, et al.,(1) and by Hughes and Schwartz.(2)

Table I. The Radioactive Nuclides of Cobalt

Radio-nuclide	Half-Life	Mode of Decay	Energy of Radiation, Mev	Produced By
Co^{54}	0.18 sec	β^+	>7.4	Fe-p-n
Co^{55}	18.2 hrs	β^+, EC	β^+: 1.5 γ: 0.477,0.935,1.41	Fe-d-n, Ni-γ-p2n Fe-p-γ
Co^{56}	72 day	EC, β^+	γ: 0.845,1.26,1.74 2.01,2.55,3.25	Fe-d-2n, Fe-α-np Co-p-p3n, Ni-d-α Ni-γ-pn
Co^{57}	270 day	β^+	β^+: 0.26 γ: 0.119,0.131	Fe-d-n, Fe-p-γ
Co^{58m}	9.2 hrs	IT	γ: 0.025	Mn-α-n, Co-d-p2n Co-n-2n, Ni-n-p Ni-d-2p, Fe^{58}-p-n Co-γ-n
Co^{58}	72 day	EC, β^+	β^+: 0.47 γ: 0.81 1.62 0.51 (with B^+)	Mn-α-n, Fe-d-n Fe^{58}-p-n, Fe-p-n, Fe-α-np, Fe-p-γ, Co-p-pn, Ni-n-p
Co^{60m}	10.1 min	IT, β^-	β^-: 1.56 γ: 0.059	Co-n-γ, Co-d-p Ni-n-p
Co^{60}	5.3 y	β^-	β^-: 0.306 γ: 1.33,1.17	Co-d-p, Co-n-γ Ni-d-α, Cu-n-α
Co^{61}	99 min	β^-	β^-: 1.42,1.00	Co-α-2p, Co-t-p Ni-γ-p, Ni^{64}-p-α Ni^{61}-n-p, Ni-d-αn Cu-γ-2p, Cu-γ-α
Co^{62}	13.9 min	β^-	β-γ: 1.3	Ni^{62}-n-p
Co^{62}	1.6 min	β^-	γ	Ni^{62}-n-p, Ni^{64}-d-α
Co^{64}	~5 min			Ni^{64}-n-p

The decay schemes(1) for the principal radionuclides of cobalt are shown in Figure 1.

Figure 1. Decay Schemes of the Cobalt Radionuclides



III. THE CHEMISTRY OF COBALT AND ITS APPLICATION TO THE RADIOCHEMISTRY OF THE COBALT RADIONUCLIDES

Radiochemistry is probably best described as being an analysis technique used primarily either (1) to assist in obtaining a pure radionuclide in some form so that an absolute measurement of its radioactivity, radiation energies, and half-life can be made, or (2) to determine the amount of radioactivity of a particular radioelement in a radionuclide mixture, or (3) to complete a radioactivation analysis being used to determine the concentration of a specific stable element in a particular sample material. In order to be an aid in accomplishing any one of the above interests, radiochemistry usually considers the isolation of the desired radionuclide by either carrier or carrier-free separation methods.

Generally, carrier methods are used most frequently in radiochemistry. They involve the addition of a small amount of inactive stable element to a solution of the irradiated material to serve as a carrier of the radionuclide of that element through the separation method. In carrier-free separations, i.e., those radiochemical techniques used mostly for absolute radioactivity measurements, it is required that the radioelement be isolated in a manner capable of giving either no amount or a minimal amount of stable element in the final form to be used in the radioactivity measurements.

In most instances, analytical radiochemistry is dependent upon more conventional ideas in analytical chemistry involving separations by such methods as precipitation, solvent extraction, chromatography, volatilization, and/or electroanalysis and the subsequent presentation of the isolated radioelement in a form suitable for a measurement of the radioelement's radioactivity. One major difference exists between carrier radiochemistry and more conventional techniques in that it is not always necessary to recover completely the added amount of carrier element, since a radiochemical analysis is designed to assure that the atoms of a radioactive element achieve an isotopic state with the atoms of the inactive element, and any loss of the radioactive species is proportional to the "loss" of carrier during the separation process.

Colorimetric, polarographic and similar analysis techniques are seldom used in radiochemistry, because they do not separate the desired radionuclide from contaminants (either radioactive or stable) in the mixture being analyzed. However, some of the developments used in these analysis techniques may be useful in radiochemistry.

Thus, the information that follows generally describes the behavior of cobalt and its compounds and how this behavior can be used in devising radiochemical analyses for the cobalt radionuclides. More detailed information can be obtained either from the references given in this section or from the references given in Section I of this monograph.

A. The General Chemistry of Cobalt

The chemical properties of cobalt are intermediate to those of iron and nickel. It forms compounds that chiefly exhibit a valence of +2 or +3. It also shows a valence of +1 in a few complex nitrosyls and carbonyls and a valence of +4 in some fluoride complexes.

In the simple cobalt compounds, the divalent forms are more stable. Cobaltous ion, Co^{+2}, is basic and is not easily hydrolyzed in an aqueous solution. A few simple cobaltic, Co^{+3}, salts, such as $Co_2(SO_4)_4 \cdot 18H_2O$ and CoF_3, are known. Most simple Co^{+3} compounds are unstable because Co^{+3} is a strong oxidizing agent and it cannot exist in aqueous media. The trivalent state of cobalt forms many complex ions, most of which are stable in aqueous media. In particular, such coordination complexes of Co^{+3} as the cobaltinitrates, the cobalticyanides, and the cobaltammines are most stable. On the other hand, cobaltous ions, Co^{+2}, in the complexed state are very unstable and can be readily oxidized to the Co^{+3} form by ordinary oxidants.

In its electrochemical properties,(3) cobalt is more active than nickel and is more noble than cadmium. Although this relationship exists in many irreversible systems, the relative degree of activity or nobility will vary. Latimer(4) reports that the reversible potentials for certain of the cobaltous-cobalt and cobaltic-cobaltous couples are as follows:

$$\begin{array}{ll}
Co^{++} + 2\ e^{-} = Co & E^{o} = -0.277\ v \\
Co(OH)_2 = 2\ e^{-} = Co + 2\ OH & E^{o} = -0.73\ v \\
Co(NH_3)_6 + 2\ e^{-} = Co + 6\ NH_3\ (aq.) & E^{o} = +0.42\ v \\
CoCO_3 + 2\ e^{-} = Co\ CO_3^{-} & E^{o} = -0.64\ v \\
Co^{+++} + e^{-} = Co^{++} & E^{o} = +1.842\ v \\
Co(OH)_3 + e^{-} = Co(OH)_2 + OH^{-} & E^{o} = +0.17\ v \\
Co(NH_3)_6^{+++} + e^{-} = Co(NH_3)_6^{++} & E^{o} = +0.10\ v \\
Co(CN)_6^{---} + e^{-} = Co(CN)_6^{-4} & E^{o} = -0.83\ v
\end{array}$$

The irreversible potentials of cobalt in various solutions have recently been measured by Akimov and Clark.(5) The cathodic deposition potentials of cobalt from various H_2SO_4 acid concentrations have been measured by Glasstone(6) and in H_2SO_4 and in NaOH by Newberry.(7) Verdieck, et al.,(8) have determined the deposition potentials of cobalt from chloride and bromide solutions. Schwabe(9) and El Wakkad and Hickling(10) report on the anodic behavior of cobalt.

1. Metallic Cobalt

Cobalt is more frequently obtained as a crude metal from the smelting of such ores as smaltite, $CoAs_2$, linnaeite, Co_3S_4, and cobaltite, CoAsS, which usually occur together either with nickel and silver ores of similar composition or with minerals containing iron, nickel and copper. Following a series of roasting processes in which a series of selected fluxes are used to remove the silver and other metallic arsenides, another roasting operation using sodium chloride converts cobalt, nickel, copper and the remaining silver to their respective chlorides. The mixture is extracted with water to separate the soluble chlorides. The metallic copper is removed from the aqueous solution by reduction and the hydroxides of cobalt and nickel are then precipitated. The nickel is removed from the mixture by forming the volatile carbonyl, $Ni(CO)_3$ in a separatory process involving a reduction of the nickel and reacting it with carbon monoxide. The resulting cobaltous oxide, CoO, may be reduced to the metal with carbon or with aluminum.(11)

Metallic cobalt is silvery white with a faint tinge of pink. It has a density of 8.9 and it melts at 1480°C and has a boiling point of 2900°C. The atomic weight of cobalt is 58.94.

Finely divided cobalt is pyrophoric. Cobalt in a more massive form is not attacked by air or water at temperatures below 300°C; above 300°C, it is readily oxidized in air. It combines with the halogens to form halides, but it does not combine directly with nitrogen; yet, it will form nitrides by decomposing ammonia at elevated temperatures. At temperatures above 225°C, it will react with carbon monoxide to form the carbide, Co_2C. It will combine with most of the other metalloids when heated or when it is in the molten state. It will form intermetallic compounds with other metals, such as aluminum, chromium, molybdenum, tin, vanadium, tungsten, zinc, nickel, and iron.

Dilute sulfuric, hydrochloric and nitric acids easily dissolve cobalt metal, but it is passivated by such strong oxidizing agents as the dichromates. Ammonium hydroxide and sodium hydroxide attack it very slowly.

2. The Simple Cobalt Compounds

Cobalt reacts less readily than iron with dilute acids. Its salts are either pink or blue in color. The pink color will change to blue either on heating, or on dehydration, or in the presence of concentrated acids. The most probable explanation for this color change is that divalent cobalt is pink as a cation, but blue as an anion.(12)

Cobalt compounds exhibit varied degrees of solubility in water and in other solubilizing agents. Table II lists the more common cobalt compounds and reports on their solubility in water and other agents.(13)

3. The Complex Compounds of Cobalt

As reported in Gmelins' Handbook,(14) Co^{+3} forms one of the largest groups of complex compounds known. The most numerous of these complexes are those of ammonia and the amines indicating that the most important donor atom is nitrogen. Carbon, oxygen, sulfur and the halogens are also

Table II. Solubility of Common Cobalt Compounds

Compound	Formula	Solubility in Water	Solubility in Other Reagents
Metal	Co	very insoluble	soluble in acids
Acetate (ous)	$Co(C_2H_3O_2)_2 \cdot 4H_2O$	very soluble	soluble in acids, alcohol
Acetate (ic)	$Co(C_2H_3O_2)_3$	hydrolizes readily	soluble in glacial acetic acid
Benzoate (ous)	$Co(C_7H_5O_2)_2 \cdot 4H_2O$	very soluble	
Bromate (ous)	$Co(BrO_3)_2 \cdot 6H_2O$	soluble	soluble in NH_4OH
Bromide (ous)	$CoBr_2 \cdot 6H_2O$	soluble	soluble in acids, ether, alcohol
Carbonate (ous)	$CoCo_3$	insoluble	soluble in acids
Chlorate (ous)	$Co(ClO_3)_2 \cdot 6H_2O$	very soluble	soluble in alcohol
Perchlorate (ous)	$Co(ClO_4)_2 \cdot 6H_2O$	soluble	soluble in alcohol, acetone
Chloride (ous)	$CoCl_2 \cdot 6H_2O$	very soluble	soluble in alcohol
Chromate (ous)	$CoCrO_4$	insoluble	soluble in acids, NH_4OH
Cyanide (ous)	$Co(CN)_2 \cdot 2H_2O$	insoluble	soluble in KCN, HCl, NH_4OH
Ferricyanide (ous)	$Co_3[Fe(CN)_6]_2$	insoluble	soluble in NH_4OH
Ferrocyanide (ous)	$Co_2Fe(CN)_6 \cdot 7H_2O$	insoluble	soluble in KCN

Fluoride (ous)	$CoF_2 \cdot 2H_2O$	soluble	soluble in HF
Fluoride (ic)	$Co_2F_6 \cdot 7H_2O$	insoluble	
Hydroxide (ous)	$Co(OH)_2$	slightly soluble	soluble in acids, ammonium salts
Hydroxide (ic)	$Co(OH)_3$	slightly soluble	soluble in acids
Iodate (ous)	$Co(IO_3)_2$	slightly soluble	soluble in HCl, HNO_3
Iodide (ous)	CoI_2	very soluble	soluble in alcohol, acetone
Nitrate (ous)	$Co(NO_3)_2 \cdot 6H_2O$	very soluble	soluble in alcohol, acetone
Oxalate (ous)	CoC_2O_4	insoluble	soluble in acids, NH_4OH
Oxide (ous)	CoO	insoluble	soluble in acids
Oxide (ous, ic)	Co_3O_4	insoluble	soluble, in H_2SO_4 only
Oxide (ic)	Co_2O_3	insoluble	soluble in acids
Orthophosphate (ous)	$Co_3(PO_4)_2$	insoluble	soluble in H_3PO_4, NH_4OH
Phosphide	Co_2P	insoluble	soluble in HNO_3
Sulfate (ous)	$CoSO_4 \cdot H_2O$	soluble	
Sulfate (ic)	$Co_2(SO_4)_3 \cdot 18H_2O$	soluble	soluble in H_2SO_4
Sulfide, mono-	CoS	slightly soluble	soluble in acids, alcohol
Sulfide, di-	CoS_2	insoluble	soluble in HNO_3, aqua regia

(Table continued on following page.)

Table II (Continued)

Compound	Formula	Solubility in Water	Solubility in Other Reagents
Sulfide, sesqui- (ic)	Co_2S_3	insoluble	decomposes in acids
Tartrate (ous)	$CoC_4H_4O_6$	slightly soluble	soluble in dilute acids
Thiocyanate (ous)	$Co(SCN)_2 \cdot 3H_2O$	soluble	
Tungstate (ous)	$CoWO_4$	insoluble	soluble in hot conc. acids
Ammonium cobalt orthophosphate (ous)	$NH_4CoPO_4 \cdot H_2O$	insoluble	soluble acids
Ammonium cobalt sulfate (ous)	$(NH_4)_2SO_4 \cdot CoSO_4 \cdot 6H_2O$	soluble	soluble acids, alcohol
Potassium cobalt carbonate acid (ous)	$KHCo_3 \cdot COCO_3 \cdot 4H_2O$	decomposes	
Potassium cobaltinitrite	$K_3Co(NO_2)_6$	slightly soluble	soluble mineral acids
Potassium cobalt malonate (ous)	$K_2Co(C_3H_2O_4)_2$		
Potassium cobalt sulfate (ous)	$K_2SO_4 \cdot CoSO_4 \cdot 6H_2O$	soluble	
Potassium cyanocobaltate(III)	$K_3Co(CN)_6$	soluble	insoluble aluminum
Potassium cyanocobaltate(II)	$K_4Co(CN)_6$	soluble	insoluble aluminum and ether
Potassium sodium nitrocobaltate(III)	$K_2NaCo(NO_2)_6 \cdot H_2O$	0.07	insoluble aluminum
Sodium nitrocobaltate(III)	$Na_3Co(NO_2)_6$	slightly soluble	soluble dilute acid, alcohol

important donor atoms. The coordination number of Co^{+3} is six, and most of the trivalent cobalt complexes are stable. In contrast, Co^{+2} has a coordination number of either 4 or 6, and the Co^{+2} complexes are relatively unstable towards oxidation. The ammine complexes can be easily oxidized in air, and the cobaltocyanides are oxidized rapidly in air or in water.

Many aquo-halo complexes are known and exist in varied shades of red and blue. The aquo complex, $[Co(H_2O)_6]^{+2}$ is pink, but when a halide is introduced into the system, a blue-colored complex anion, $(CoX_4)^{-2}$ is produced. Usually, the blue color is more intense and it can completely mask the color of a larger concentration of the pink complex. This phenomenon apparently results from the fact that cobaltous halides are normally pink in dilute aqueous solutions, but when heated or in concentrated solution will turn blue. Table III lists some of the cobalt complexes(13) showing their solubility in water and various solvents.

4. The Organometallic Compounds of Cobalt

Cobalt, like iron and nickel, does not appear to produce true organometallic compounds in that such reactions proceed largely with hydrocarbon evolution, metal deposition, abnormal coupling and other unusual reactions.(15) Kharasch and Fields(16) in their investigation on the effects of metallic halides on Aryl-Grignard Reagents and organic halides explain that these effects require transitory intermediate organocobalt compounds of the type RCoX. Briggs and Polya(17) have reacted α- and β-naphthylmagnesium halides with cobaltous halides to produce complex condensates of the type, $C_{10}H_7CoX_3$. $RCoX_3$ compounds have also been prepared by methyl-, ethyl-, n-propyl-, and i-propylmagnesium iodide and phenylmagnesium bromide reactions upon cobaltous halides.(18) Biscyclopentadienylcobalt and bisindenylcobalt compounds have also been prepared.(19) These compounds are readily oxidized to monovalent cations and their salts are usually colored, water-soluble compounds.

B. The Analytical Chemistry of Cobalt

As pointed out elsewhere in this monograph, the use of a known amount of inactive cobalt carrier in a separation method almost always makes it

Table III. Some Complex Cobalt Compounds[*]

Complex Compound	Formula	Solubility	
		In H_2O	In Other Solvents
Diamminecobalt(II) chloride	$CoCl_2 \cdot 2NH_3$	soluble	
Hexamminecobalt(II) chloride	$[Co(NH_3)_6]Cl_2$	soluble	soluble NH_4OH
Aquopentamminecobalt(III) chloride (roseo)	$[Co(NH_3)_5H_2O]Cl_3$	soluble	slightly soluble HCl
Chloropentammine-cobalt(III) chloride (purpureo)	$[Co(NH_3)_5Cl]Cl_2$	slightly soluble	conc. H_2SO_4
Hexamminecobalt(III) chloride (luteo)	$Co(NH_3)_6Cl_3$	soluble	
Hexamminecobalt(III) perrhenate	$[Co(NH_3)_6](ReO_4)_3 \cdot 2H_2O$	very slightly soluble	

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[*] Cobalt also forms polynuclear complexes. In these compounds 2, 3 or 4 cobalt atoms are linked by OH, O_2 or NH_2.

possible to obtain the cobalt carrier in a weighable form in the final stage of the separation procedure used. Two things are achieved if this is done. The radionuclide is concentrated into a small mass for the radioactivity measurements, and the carrier is obtained as a weighable compound which can be used to determine any loss of the "carrier" during the analysis.

The choice of acceptable gravimetric forms for a cobalt determination is extensive and somewhat controversial. Duval(20) in his thermogravimetric investigations states that there are at least 30 gravimetric methods available for the determination of cobalt. In his evaluation of these methods, he indicates that the most suitable compounds for determining cobalt are cobalt ammonium phosphate, $CoNH_4PO_4 \cdot H_2O$;(21,22) potassium cobaltinitrate, $2K_2Co(NO_2)_6 \cdot 3H_2O$;(23) silver hexacyanocobaltate, $Ag_3Co(CN)_6$;(24) cobalt tetrathiocyanatomercurate, $CoHg(CNS)_4$;(25-29) cobalt anthranilate, $Co(NH_2 \cdot C_6H_4 \cdot CO_2)_2$;(30,31) cobalt 5-bromoanthranilate, $Co(NH_2 \cdot C_6H_3Br \cdot CO_2)_2$;(32) cobalt 3-amino-2-napthoate, $Co(C_{10}H_6NH_2CO_2)_2$;(31) cobalt-α-nitroso-β-naphthylamine, $Co(C_{10}H_7ON_2)_3$;(33) cobalt oxine, $Co(C_9H_6ON)_2$;(34,35) cobalt oxide, Co_2O_3, obtained by the ignition of the phenylthiohydantoic acid complex;(36) or cobaltic oxide, Co_3O_4, obtained by the ignition of yellow mercury oxide complex.(37) Anand and Dechmukh(38) report that cobalt tellurite, $CoTeO_3$, is also a good gravimetric form for determining cobalt. Williams(39) records that the precipitation of cobalt as the metal by the reduction of Co_3O_4 with hydrogen is a recommended gravimetric form. However, certain limitations exist in that the reduced metal is very pyrophoric and sometimes contains appreciable quantities of unreduced oxide.

Very often when one of these gravimetric forms is employed, it is preceded by one of several other methods of chemical separation such as solvent extraction, ion exchange, precipitation, or electrolysis. The information that follows generally reports on current ideas used in isolating and determining cobalt. A combination of several isolation methods may be used. However, it should not be inferred that it is always necessary to radiochemically separate the desired cobalt isotope in a precipitable form for the radioactivity measurements. Sometimes it would be sufficient to accept and use, for example, an aliquot of the eluate from an ion-exchange separation column or one of the phases obtained in solvent extraction, or a portion of a paper chromatogram in the radioactivity measurements.

Williams(39) also provides an excellent summary of the advances made in the analytical chemistry of cobalt. The authors of this monograph feel that much of this information is pertinent to the separation techniques that follow and they have attempted to emphasize much of the information given in this particular review.

1. Separations by Precipitation

The separation of cobalt from other elements can be effected with hydrogen sulfide, ammonium sulfide, basic acetate, succinate, barium carbonate, zinc oxide, potassium hydroxide and bromine, ether-hydrochloric acid, and cupferron.(40) CoS can be coprecipitated with SnS_2 and carried down when low-solubility sulfides are precipitated in dilute or concentrated mineral acids.(40) Special care must also be taken to prevent its coprecipitation with zinc sulfide; however, the addition of a small amount of acrolein and gelatin to the solution before its treatment with hydrogen sulfide will reduce the coprecipitation effects.(41)

Britton(42) has shown that if there is a sufficient difference between the values of pH at which two metal hydroxides are precipitated with ammonium hydroxide, the metals may often be separated by maintaining the pH of the solution at such a value so that the weaker one will be precipitated first. Buffer solutions, usually weak acids or one of their salts, and heating are used to effect the hydrolysis. Such metals as chromium, zinc, uranium, aluminum, tin, iron (as Fe^{+3}), zirconium and titanium precipitate at lower pH values than cobalt, which precipitates at a pH of 6.8. Magnesium, silver, manganese, mercury, and some of the rare earths precipitate at pH values greater than 7.0.

Cobalt cannot easily be separated from such elements as iron, aluminum, copper and nickel by ammonium hydroxide. Lundell and Knowles(43) report that even though small amounts of cobalt are involved and double precipitations made, the amount of cobalt retained by the hydroxide precipitate of iron and aluminum is appreciable. Iron may be effectively removed from cobalt (and nickel) as ferric phosphate if the precipitation is made from an acetic acid solution.(44) Titanium, zirconium and hafnium can be separated from cobalt as phosphates by treating an acetic acid solution of the ions (pH 3.5) with ammonium phosphate.(44,45) Cobalt can be separated from iron, aluminum, titanium, and zirconium by precipitating them with an aqueous suspension of zinc oxide.(46) Chromium, vanadium, and tungsten can also be removed by a zinc oxide precipitation after the solution has been oxidized with nitric acid.(47) Chromium and such elements as aluminum, arsenic, molybdenum, tungsten and vanadium can be separated from cobalt by precipitations with sodium peroxide in the presence of bromine or some other oxidizing agent.(48) Chromium can also be separated from cobalt by precipitating CoS in the presence of ammonium tartrate.(49) Iron, nickel and zinc sulfide also precipitate. Cobalt does not form a cupferrate and can be separated from such elements as iron, titanium, vanadium, zirconium, tin, antimony, and bismuth by forming the cupferrates of these elements.(50) The cobalt can be recovered either by filtration or by solvent extraction.

Burgess,(51) von Knorre,(52) and Mayr and Feigl(53) report on the use of α-nitroso-β-naphthol (sometimes called 1-nitroso-2-naphthol) in glacial acetic acid to separate cobalt from such elements as aluminum, beryllium, lead, cadmium, manganese, mercury, arsenic, antimony, zinc, calcium, magnesium and moderate amounts of nickel. Phosphates, arsenates, and ammonium salts do not interfere whereas nitric acid must be absent before the precipitation is made. Iron, copper, bismuth, silver, chromium, zirconium, titanium, vanadium, and tin also interfere. If a considerable amount of nickel is present, the cobaltinitroso-β-naphthol precipitate, $[C_{10}H_6O(NO)]_3Co$, should be ignited, dissolved in hydrochloric acid and a reprecipitation made. The interferences from large amounts of nickel can also be eliminated by making an initial separation of nickel by adding an alcoholic solution of dimethylglyoxime to an acetic acid-sodium acetate solution of the ions.(54) The cobalt ions are soluble, and the nickel dimethylglyoxime precipitate can be removed by filtering the mixture. If cobalt is to be determined in the presence of large amounts of manganese by a precipitation with α-nitroso-β-naphthol, much of the manganese can be removed by precipitating it as the dioxide by adding potassium chlorate to a boiling nitric acid solution.(55) The manganese dioxide is separated from the mixture by filtration.

The traditional method of determining cobalt in ferrous metals is based upon its precipitation with α-nitroso-β-naphthol, but Bogshaw(56) reports that nitroso-R-salt is a much more reliable reagent. Nitrosonaphthol has also been used in separating cobalt (as both the stable and radioactive species) from neutron-irradiated steel.(57) The nitrosonaphthol precipitates, i.e., of the $[C_{10}H_6O(NO)]_3$ types, may be dried and weighed in that form, or they may be ignited to the oxide, Co_3O_4, or converted to the sulfate, $CoSO_4$, before weighing.

Cobalt may also be separated as the sulfide, CoS, from a basic solution and can be converted to ammonium cobalt phosphate, $NH_4CoPO_4 \cdot H_2O$, which after washing can be ignited to the pyrophosphate, $Co_3P_2O_7$, for weighing.(21,22,58) However, traces of cobalt are often found in the filtrate. As an alternative, the sulfide, CoS, can be directly ignited to the oxide, Co_3O_4.

According to Hillebrand and co-workers,(40) the method most often employed to separate cobalt from interfering elements is the converse of the cobaltinitrite method for potassium, i.e., the potassium nitrite method. In this method, first suggested by Fischer,(59) an excess of potassium nitrite in acetic acid is added to quantitatively precipitate the cobalt. Some recent applications of the use of potassium nitrite in separating cobalt include those reported by Brooksbank, et al.,(60) Kallmann,(61) and Smith, et al.(62) Brooksbank, et al.,(60) have used potassium cobaltinitrite dried at 110°C as the weighing form of cobalt separated from neutron-irradiated aluminum-base alloys. Kallmann(61) has used tartaric acid to complex interfering elements (especially nickel) in separating cobalt by the potassium nitrite method. Smith, et al.,(62) report on the use of potassium nitrite to separate radioactive cobalt from radioactive corrosion products. With regard to the use of this method, Broughton, et al.,(63) report that explosive reactions can occur if the cobaltinitrite solution is reheated after standing for some time. Horowitz(64) postulates that these explosions result from the formation of nitralic acid salts. It should be noted here that Kallman(61) suggests that the cobaltinitrite method is good for separating cobalt from other metals, but the final gravimetric determination of cobalt should be made by some other method.

Baker and McCutchen(65) report on the use of quaternary ammonium hydroxide as a precipitant for cobalt. Cobalt can also be precipitated from a hot solution with N-benzoylphenyl-hydroxylamine(66) and converted to $CoSO_4$ as the weighing form. Nickel will interfere in this separation. Also, copper is an interference; however, it can be removed by a precipitation at pH 4 in the presence of the reagent; cobalt (and nickel) require a pH from 5.5 to 6.5 for a precipitate to result. Bivalent cobalt can be separated from ferrous materials by precipitating it with acridine(67) from a hydrochloric acid solution containing excess ammonium thiocyanate. Cobalt can be separated from tungsten by treating a neutral or slightly alkaline solution with tartaric acid, ammonium thiocyanate and an excess of pyridine.(68)

Andrew and Gentry(69) have recently evaluated the advantages and shortcomings of methods proposed for the analysis of cobalt. As a result, they consider the tetraphenylarsonium cobaltothiocyanate method the best method. The precipitation of cobalt as the tellurite(38) by a measured excess of potassium tellurite and its determination gravimetrically as the cobalt tellurite, $CoTeO_3$, was also considered to be a favorable method.

Cobalt can be separated from strong acid solutions by treatments with sodium nitrite(70) to form $Co(NH_2)_6 \cdot Co(NO_2)_6$. The sodium nitrite oxidizes Co(II) to Co(III) to form $Na_3Co(NO_2)_6$. After the mixture is carefully shaken to remove the nitrite formed through interaction of excess acid with the $NaNO_2$, an excess of a saturated cold solution of $Co(NH_3)_6Cl_3$ is added dropwise to form a yelloy insoluble crystalline precipitate. Cobalt can be determined in the presence of nickel, calcium, copper, strontium, zinc, manganese, mercury, lead, cadmium and barium by this method. The ions of potassium and ammonium are major interferences.

As a preliminary study in an investigation concerned with the decontamination(71) of radioactive laboratory waste water by coprecipitation, the behavior of very small quantities of radioactive ions with different voluminous precipitants was studied. The radioactive ions of $PO_4(III)$, Co(II) and Cs(I) were precipitated from solution by the use of iron oxyhydrate, aluminum oxyhydrate, copper ferrocyanide and iron ferrocyanide reagents. In this report, data is given on the dependence of such factors as pH, precipitant concentration, and equivalent ratio of the precipitant compounds formed in the case of each precipitant used.

Rubeanic acid(72) will precipitate cobalt (as well as copper, nickel, zinc, and cadmium) from interfering ions found after the acid dissolution of rock specimens. Cobalt can be separated from nickel by forming a stable cyanide complex in acid solution.(24) After decomposing the $K_2Ni(CN)_4$, silver nitrate is added to the solution and the resulting precipitate of $Ag_3Co(CN)_6$ can be dried at 136° and weighed.

Other precipitation methods studied for the separation of cobalt include those based on the use of such reagents as mercuric chloride-ammonium thiocyanate,(25-29) dinitroresorcinol,(73) anthranilic acid,(30,31) 5-bromoanthranilic acid,(32) 8-hydroxyquinoline,(34,35) phenylthiohydantic acid,(36) diphenylthiohydantoin,(74) mercuric iodide-ammonium hydroxide,(75) benzoquinaldinic acid,(76) isonitrosodimedone,(77) and benziminazole.(78) Each of these methods have their merits; however, in some instances, the analysis conditions influence the ease with which a separation of cobalt can be obtained.

2. Separations by Electrodeposition

According to Williams,(39) many investigators consider the electrodeposition methods as the best methods where large amounts of cobalt are involved and high accuracy is desired. There are many diverse methods and each method considers variables concerned with such factors as the chemical composition of the electrolyte, the time of electrolysis, current density, temperature, type of electrode, rate of stirring and the pH of the solution. In almost all cobalt electrolytic methods and depending on the sample, electrolysis may be preceded by an isolation of the cobalt from interfering elements either by precipitation,(79) with such agents as zinc oxide, α-nitroso-β-naphthol, or phosphate ions, or by anion-exchange resins.(80)

Most electrolytic separations for cobalt are based upon the use of ammonical solutions as electrolytes. In order to prevent anodic deposits of cobalt and the oxidation of the cobaltous-ammine ions, small amounts of reducing agents such as hydrazine sulfate(81) and sodium bisulfite(82) are added to the solution during electrolysis. Brophy(83) reports on the use of such agents during an analysis at a high current density. Other variations, concerned with the use of reducing agents, as well as current density and time required for deposition, have been reported by Young and Hall,(44) Kallman,(61) and Scott and Furman.(84)

Lingane and Page(85) have shown that cobalt and nickel can be separated electrolytically by utilizing an aqueous pyridine solution with hydrazine to depolarize the platinum anode. The nickel is removed at a controlled potential of -0.95 volt and a solution pH of from 5 to 7, after which the cobalt is deposited at -1.20 volts without any interferences.

Torrance(86) first reported that cobalt could be deposited upon an anode at pH 5 as Co_2O_3. Salyer and Sweet(87-89) have also shown that hydrated cobaltic oxide could be deposited on an anode. Solutions containing a known amount of radioactive Co^{60}(5.3y) were used in this work and the concentration of cobalt deposited upon the anode determined by an isotope dilution technique.

The determination of small amounts of cobalt by internal electrolysis has been reported by Schleicher.(90) Also, information on the use of a rotating mercury electrode in determining cobalt has been presented by Tutundzic and Stojkovic.(91)

3. Separations by Solvent Extraction

Solvent extraction methods used as separation methods for other analysis techniques can often be adapted for use in radiochemistry and can be quite useful in separating the desired cobalt radionuclide from a sample by either a carrier-free or carrier radiochemical method. Morrison and Freiser(92) have recently reviewed the applications of ion association and chelate complex systems to the determination of most of the elements. Some of these systems are applicable for use as separation processes in the radiochemistry of the cobalt radionuclides.

a. <u>Ion Association System</u>

Kitahara(93) and Bock and Herrmann(94) have shown that cobalt (Co^{+2}) will not extract with ethyl ether from HF solutions of varying concentrations. Sn^{+2} and Sn^{+4} are completely extracted; As^{+3}, Sb^{+3}, Se^{+4}, and Mo^{+6} partially extract; cobalt (as well as Ni^{+2}, Cr^{+3}, Mn^{+2}, K^{+1}, Ti^{+4}, Zr^{+4}, Ga^{+3}, Ag^{+1}, U^{+6}, Bi^{+6}, Te^{+4}, Cd^{+2}, and Os^{+6}) do not extract.

Garwin and Hixson(95) have shown that cobalt (Co^{+2}) can be separated from nickel by extracting 10 <u>M</u> HCl and 0.85 <u>M</u> $CaCl_2$ solutions with 2-octanol.

Bock, et al.,(96) have shown that less than 0.1% Co^{+2} will be extracted by ethyl ether from a metal bromide solution (0.1 <u>M</u> to 6 <u>M</u> HBr); whereas, Sb^{+5}, Fe^{+3}, Hg^{+2}, Au^{+3}, In^{+3}, Tl^{+3}, are quantitatively extracted. Varying amounts of Ga^{+3}, Sn^{+2}, Sn^{+4}, Sb^{+3}, Se^{+4}, and Mo^{+6} will extract depending upon the HBr concentration. Cu^{+2}, Ni^{+2}, Zn^{+2}, Cd^{+2}, V^{+5}, and Te^{+4} do not extract appreciably. In another study,(97) the extractability of certain metal bromides from aqueous solutions containing HBr and/or NH_4Br with methyl isobutyl ketone and methyl ethyl ketone as solvents have been studied. Fe^{+3} can be separated from Mn^{+2}, Al^{+3}, Co^{+2}, and Ni^{+2} under these conditions.

Co^{+2} (Mn, Ni, Cr, V, Al, Fe^{+2}, Ti, Zr, Pb, Th, Ga, Be, U and the noble metals) do not extract into ethyl ether from 6.9 <u>M</u> HI solutions.(98) Sb^{+3}, Hg^{+2}, Cd^{+2}, Au^{+3}, and Sn^{+2} extract quantitatively into ethyl ether under the same conditions.

Oxygen-containing solvents can be used in the solvent extraction of Co^{+2} (as a blue complex) from NH_4SCN solutions of various concentrations. Co^{+2} (as well as Be, Zn, Co, Sc, Ga, In, Ti^{+3}, Fe^{+3}, Sn^{+4}, and Mo^{+4}) extract into ethyl ether(99) or amyl alcohol(100) and can be separated from such elements as Al^{+3}, V^{+4}, U^{+6}, Li^{+1}, Cu^{+2}, Cd^{+2}, Hg^{+2}, Ge^{+4}, As^{+3}, As^{+5}, Sb^{+3}, Bi^{+2}, Cr^{+3}, Ni^{+2}, and Pd^{+2}. These elements only partially extract or do not extract at all. Co^{+2}, Ni^{+2}, and Cu^{+2} form water-insoluble cyanate complexes in a NH_4SCN system that can be dissolved in and extracted with chloroform.(101)

Co^{+2} (as well as Ni^{+2}) precipitates at the interface in extracting alkaline aqueous solutions that contain Cu, Mn, Fe, Pd, and Ru with 5% $C_9H_{19}COOH$ (n-capric acid) in ethyl acetate.(102) Cu^{+2} is quantitatively extracted under these conditions; Mn, Fe, Ni, Co, Pd, and Ru interfere. When butyric acid in benzene is used, only Cu, Mn, and Fe extract.

Methyldioctylamine and tribenzylamine have been used to extract Zn from cobalt (and other metals of the first transition series) in dilute HCl solutions.(103) Only 0.4% Co and >99% Zn was extracted from a 2 M HCl solution by a solution containing 8 g of methyldioctylamine (MDOA) per 100 ml of trichlorobenzene. At a higher HCl concentration (10 N), 85.4% of the cobalt and 100% of the zinc extracted. Solutions of MDOA in xylene and in chloroform also quantitatively extract zinc from cobalt under the same conditions. These studies also include an investigation of the extraction of Cr^{+3}, Mn^{+2}, Fe^{+3}, Ni^{+2}, and Cu^{+1} under the same conditions. Varied degrees of extraction and separation of these elements from cobalt (and zinc), depending upon conditions and organic agents used, were found.

Acid solutions and extractions with high molecular weight amines(104,105) have been used to separate iron from cobalt. Only negligible amounts of Co (as well as Zn, Al, Na, Mg, Ca, Ni, Cu, Mn, and Cr^{+3}) are extracted under these conditions.

Cobalt (Co^{+2}) anionic thiocyanate complexes, as well as those of Fe^{+3}, Mo^{+5}, and Cu^{+2}, have been shown to form salts with triphenylmethylarsonium chloride that are extractable into o-dichlorobenzene.(106,107) A mixture of 35% amyl alcohol-65% ether can be used to extract the thiocyanate complex of cobalt to separate cobalt from other elements.(108) Iron, nickel, copper, and zinc also form thiocyanates that are partially extracted in this system. The extraction of Fe^{+3} can be prevented by adding citric acid or reducing the Fe^{+3} to Fe^{+2}. Nickel, copper, and zinc do not interfere in the determination of cobalt as the nitroso-R salt complex since cobalt can be extracted as a thiocyanate from a slightly acid solution with polyethylene glycol and methylene chloride;(109) iron, nickel, and zinc do not extract. The cobalt thiocyanate complex can also be extracted with acetylacetone.(110)

Potratz(111) has shown that at least 95% of the cobalt tetraphenylarsonium chloride formed in an acid solution can be extracted into chloroform. The use of a 50% KSCN and NH_4F mixture masks Fe^{+3} and U^{+6} and prevents their extraction. The reduction of Cu^{+2} to Cu^{+1} and the use of 10% KI solution eliminates the copper interference. None of the other metals interfere.

The heterocyclic polyamine, 2,2',2"-terpyridyl,forms a cobalt complex which can readily be extracted into nitrobenzene.(112) Cu, Fe, and Ni interfere in this system.

b. Chelate Compound Systems

Acetylacetone in chloroform does not form an extractable chelate(113) with either Co^{+2} or Ni^{+2} in highly acid solutions; however, the Co^{+3} chelate can be easily extracted(114,115) and this system can be used to separate cobalt from nickel. Other metals, such as Fe, Mn, V^{+4}, Zn, and Zr also extract under these same conditions (pH 6-9).

Cobalt can be extracted from aqueous solutions with 8-quinolinol (oxine) in chloroform.(116,117) Masking agents such as cyanide(118,119) can retard the extraction of Fe, Cu, Mo, and Ni. It has also been shown(120) that the use of sodium ethylenediaminetetraacetate, EDTA, as a masking agent in oxine extractions inhibits the extraction of Co (and Al, Fe^{+3}, Mn and Ni) at pH 8 or above. When calcium ethylenediaminetetraacetate is used, it is possible to completely inhibit the extraction of Co (as well as Al and Mn) at a pH of 6. In an earlier study,(121) it was shown that a solution containing 1% 8-quinolinol in chloroform will extract up to 10 mg of Co from aqueous solutions having a hydrogen ion concentration in excess of pH 3.5. Al^{+3} and Ni^{+4} interfere in these extractions. Cobalt will not extract below a pH of 3.5; whereas, Fe, Cu and Bi do.

In a thermodynamic study of some coordination complexes of metal ions with diprotic nitrogen compounds,(122) the formation constants of cobalt were determined. The acid dissociation constants of 2-hydroxymethylnaphth-[1,2]-imidazole and 2-hydroxymethylnaphth-[2,3]-imidazole and the stability constants of the divalent element chelates of these compounds have been studied.(123) The acid dissociation constants of 4-hydroxybenzothiazole and the formation constants of its chelates with Co(II), Mn(II), Cu(II), Zn(II), Cd(II), Pb(II), and Mg(II) have also been studied.(124)

The order of increasing stability of the metal chelates Cu > Pb, Ni, Co > Zn > Cd > Mn > Mg is similar to the stability sequence generally obtained for divalent metals.

Cobalt can be separated from nickel by extracting the nickel dimethylglyoxime into chloroform.(100,125) If the extraction is made in an alkaline solution, the extraction of cobalt can be retarded if the cobalt chelate is formed as $Co(NH_3)_6^{+3}$.(100) Cobalt (as well as Zn, Cu, Mn, Ti and Al) will not, but Ni and Fe^{+2} will, form chloroform extractable complexes with dimethylglyoxime in the presence of pyridine.(126) Similar separations of cobalt from nickel are possible if the Ni complexes of cyclohexanedionedioxime(127) and furildioxime(128,129) are extracted into either chloroform, o-dichlorobenzene, ethyl ether or ethyl acetate.

Co^{+3} in an acid medium will form an extractable complex with α-nitroso-β-naphthol.(130,131) The cobalt complex of α-nitroso-β-naphthol can be extracted from a phosphoric acid-sodium citrate solution with chloroform.(132) The red 2-nitroso-1-naphthol complex of cobalt can be extracted into either benzene(133) or isoamyl acetate.(134) Cobalt also forms chloroform-extractable complexes with isonitrosoacetophenone ($C_6H_5COCH{=}NOH$).(135) In this system, cobalt will extract from an acid solution but nickel will not.

Cobalt (as well as Fe, Cu, Ni, Cr, and other metals) can be separated from palladium by extracting the α-nitroso-β-naphthol palladium complex, in the presence of EDTA, into benzene or toluene.(136)

Cobalt cupferrate can be extracted from a dilute acetic acid solution with ethyl acetate or ether.(137)

Cobalt (and Cu, Pb, Hg, Mn, U^{+6} and Zn) will not react with N-benzoylphenylhydroxylamine in an acid solution having a pH of 4;(138,139) however, water insoluble complexes of Sn, Ti, Zr, V^{+5}, Mo^{+6}, and W^{+6} are formed under these conditions and will extract.

The ability of Ni^{+2} to form a complex with 3-hydroxyl-1,3-diphenyltriazine in the pH range of 4.4-7.0 suggests that a separation from cobalt is possible.(140) The Ni^{+2} complex is soluble in benzene and in chloroform.

Cobalt (as well as Ni, Bi, Cd, Cu, Pd, Pt, Sn^{+2}, U^{+6}, Fe^{+2}, Hg, Th, Pb, Zn, La, Ce^{+4}, In, Sc and Eu) forms a complex with 1-(2-pyridylazo)-2-naphthol that is insoluble in water.(141) However, it is soluble in both amyl alcohol and carbon tetrachloride.

Sandell(142) reports that cobalt dithizonates can be extracted from solutions at pH 7 to 9 with CCl_4 or $CHCl_3$; nickel extracts only from a weakly basic solution. For example, in the analysis of biological samples, Co has been separated from Fe, Te, Cr, V and other metals that do not form dithizonates by extracting a basic solution (pH 8) with chloroform.(143,144) The organic solution of the dithizionate is quite stable to dilute mineral acids.

Lacoste, et al.,(145) report that cobalt reacts with sodium diethyldithiocarbamate and can be extracted with chloroform from solutions having a pH of 6-8. Ni and Fe^{+3} also extract under these conditions.

Cobalt xanthate can be extracted from an ammoniacal solution with ether.(146,147) Ni and Fe xanthates are only extractable with chloroform from a weakly acid to neutral solution.(147)

2-mercaptobenzothiazole forms water-insoluble salts of Co (and Bi, Cd, Cu, Au, Pb, Hg, Ni, Tl, and Zn) that are extractable into alcohol or ether.(148)

Cobalt forms a chloroform-extractable complex with thiosalicylideneethylenediimine.(149) This complex and the Tl^{+1}, Br, Cu, Ag, Hg, Pd^{+2} complexes are stable in HCl or ammonia. The Ni, In, Te^{+4}, Sn^{+2}, Sb^{+3}, Cd, Pb, Au^{+3}, Pt^{+2}, Pt^{+4} complexes are stable in HCl but not in ammonia. The Zn complex is unstable in both HCl and ammonia. The Al, Fe^{+2}, Fe^{+3}, Mn and Ga complexes do not react in either system.

The cobalt-phenylthiourea complex will not extract from dilute HCl solutions into either ethyl or amyl acetate.(150) Ni, Cr^{+6}, Fe^{+3}, Au^{+3}, Os^{+4}, Pu^{+3}, Rh^{+3} and Ir^{+4} behave in a similar manner. Pd^{+2} is quantitatively extracted while Pt^{+4} and Cu are only partially extracted.

Co (as well as Ni, Cr, Zn, As^{+3}, Sn^{+4} and Hg) can be separated from Sb and Bi by forming the antipyrine (phenazone) complexes of Sb and Bi and extracting them into chloroform.(151)

4. Separations by Chromatography

a. With Inorganic Absorbents

The separation mechanisms of metal cations from aqueous solutions upon inorganic absorbents, such as alumina and clays, have been reviewed by Sacconi,(152) Zechmeister,(153) Smith,(154) and Pollard and McOmie.(155) With regard to the separation of Co^{+2} from other metal cations by use of alumina columns, Schwab, et al.,(156) Sacconi,(152,157-160) Venturello,(161) and Tanaka and Shibato(162,163) have described this work. Sacconi(152) has also shown that the complex ions of cobalt, the cobaltammines, can be separated on alumina. Cobaltous-tartaric acid and cobaltous-dioxan complexes and their separation from other metal cation complexes have also been studied by the use of alumina columns.(163,164) Erametsa(165) reports that cobaltous-dithizone complexes can be absorbed from CCl_4 upon alumina and has proposed a method of separating these complexes from other metal dithizone complexes. Boch(166) has shown that Co^{+2} and other metal dithizonates absorbed on an alumina column could be eluted with acetone. Tanaka, et al.(167,168) also used a similar system to detect as little as 0.001 parts per million of Co. Paulais(169) has separated cobalt α-nitroso-β-naphtholates from those of Fe^{+3}, Ni^{+2} and Cu^{+2} by use of a chloroform solution on alumina. Berkhout and Jorgen(170) also used this method to determine cobalt in cast iron, steels and Ni-base alloys; King, et al.(171) have used it to determine trace cobalt in animal feeds.

When metal ion solutions containing cobalt are complexed with nitroso-R-salt(172) and then passed through an alumina chromatographic ion exchange column, a separation of cobalt from copper, chromium, nickel and iron is effected. The elution of the cobalt complex may be measured colorimetrically. This technique has been applied to metal alloys without prior separation of any of the components.

The use of $Al(OH)_3$ as an absorbent has been investigated by Fricke and Schmah.(173) They have been able to separate cobalt from iron and copper by this method. Flood(174) has studied the glycine complexes of Cu, Ni and Co on Al_2O_3-inpregnated paper and found that it was possible to separate cobalt by varying the glycine concentration. Zolotavia(175) and Vanyarkho and

Garanina(176) have used $Al(OH)_3$-impregnated paper to separate Co^{+2} from other metal cations.

Cobalt has been separated from copper by inorganic chromatography using clays, such as kaolinite, bentonite, and montmorillonite, as the absorbent.(177) When a column is developed with water, Cu^{+2} is strongly absorbed on the column while cobalt flows rapidly down the column as a pink band. Silica gel has also been used as an absorbent and Milone and Cetini(178) carried out extensive studies on the separation of Co^{+2} from the other transition elements by use of this absorbent system. Sen(179,180) has used asbestos and $CaSO_4$ as media for the separation of Co from other elements. Silica gel impregnated with sodium silicate has also been used to separate Co^{+2} from other elements.(181)

Cobalt and copper diethyldithiocarbamates(182) can be separated from each other on an activated silica column. After the chromatographic separation, the dithiocarbamates were converted to the corresponding complexes and determined photometrically.

b. With Organic Absorbents (Other than resins and paper)

Powdered 8-hydroxyquinoline has been used as an inert support for aqueous solutions in the separation of Co^{+2} from other cations and anions.(183) Robinson(184,185) has also used 8-hydroxyquinoline columns to study the separation of cobalt from other cations contained in aqueous solutions of copper alloys and alloy steels. Co^{+2} elutes as a red-yellow band under these conditions and some interferences from the various components that gave yellow-colored bands (such as WO_4^{+2}, Ag^{+2}, Bi^{+3}, MoO_4^{+2}, Zn^{+2}, and UO_2^{+2}) were observed.

Cobalt has been separated from mixtures containing Fe^{+3}, Cu^{+2}, and Ni^{+2} by use of columns of 8-hydroxyquinoline, naphthaquinoline and cupferron mixed with potato starch.(186) Dimethylglyoxime, dimethylglyoxime-calcium carbonate, and dimethylglyoxime-magnesium carbonate columns have been used to separate nickel and cobalt(187) In another study, Labruto and d'Alcontres(188) have shown that complex cyanides can be absorbed upon activated charcoal. $K_3Co(NO_2)_6$, $K_4Fe(CN)_6$, and $K_2Hg(CN)_4$ are completely absorbed; whereas, about 99% of the $K_3Cu(CN)_4$ and 97% of the $K_2Cd(CN)_4$ are absorbed. The cobalt complex was easily separated from these other cyanide species by an elution method.

Since pectin and pectic acid(189) disperse or dissolve in water, they undergo ion exchange in aqueous systems as polyelectrolytes rather than as ion exchange material in the accepted sense. DiGeacoma and Respoli,(190) using alcoholic solutions, have shown that pectin columns could be used to separate cobalt ions from cupric ions. Gels, containing such salts as sodium arsenite, borax and sodium silicate, have been used to separate Co from mercury and lead.(191,192) Cobalt (and nickel) as complex amines(193) can be identified and determined by the formation of colored ring products on agar gel. Cobalt forms a yellow-brown ring with nucleonic acid while nickel forms a blue ring.

c. With Ion Exchange Resins

Kennedy and Davis(194) have shown that the anion exchange resin, Deacidite H, and organic solvents (such as acetone and dimethylformamide) can be used to separate mixtures of cobalt, lithium, and copper (as chlorides) and nickel (as nitrate). The anion adsorption by the basic form of the tertiary amine resin takes place through complex formation with the resin fundamental groups and both the cationic and anionic species are adsorbed upon the resin in equivalent proportions. When the crosslinking of Deacidite H is greater than 2%, a sharp reduction in the adsorption of cobalt chloride is noted. Adsorption of these species is also influenced by the nature of the solvent; it is much greater from acetone than from dimethylformamide.

Kraus and others(195-199) have studied the behavior of anions on strongly basic exchangers of the polystyrene-divinylbenzene type where the adsorption and elution of the element is defined in terms of molar hydrochloric acid. With respect to the separation of cobalt, the elution constants of Co^{+2}, Ni^{+2}, Mn^{+2}, Cu^{+2}, Fe^{+2}, and Zn^{+2} were studied using a Dowex-1 column and various HCl concentrations. Cobalt has an adsorption maximum at intermediate hydrochloric acid concentrations and will elute from the column with hydrochloric acid concentrations of 4.5<u>M</u> or less. Atteberry, et al.(200) used a strong base anion exchanger and HCl of varying concentrations as the eluant to completely separate Co^{+2} from Mn^{+2}, Fe^{+2}, Ni^{+2}, Cu^{+2}, Zn^{+2}, Cd^{+2}, Ag^{+1}, and Sb^{+2}. Blasius and Newger(201) have shown that Co^{+2} could be adsorbed upon either Permutit ES or

Dowex-2 resin at 80°C and easily separated from Fe^{+3}, Mn^{+2}, Al^{+3}, and Ni^{+2}. After each of these species were removed with varying concentrations of HCl, the Co^{+2} was removed from the column with water. Hicks, et al.(202) have also shown a similar behavior for Co^{+2} on Dowex-2 resin and its separation from many other elements by elutions with varying concentrations of HCl. Moore and Kraus(199) used Dowex-1 and 9 M HCl as the eluant to separate Co^{+3} (and Fe^{+3}) from such elements as Al^{+3} and Cu^{+3}.

Herber and Irvine(203) have used elutions with varying concentrations of HBr (no greater than 7 M) from a Dowex-1 column to separate radioactive Co^{60} in carrier-free and macro amounts from irradiated Cu, Zn, Ga, and Ni. The elutions were identical with those for HCl.

Neutron-irradiated biological ash has been analyzed for radioactive cobalt by an anion exchange resin system(204) and radioactive cobalt in environmental materials has been separated from radioactive ruthenium, zirconium, niobium, neptunium, cobalt, iron zinc, strontium, rare earths, chromium, and cesium by use of 8% cross-linked Dowex-2 (200-400 mesh) resins columns.(205) In each separation, varying concentrations of HCl were used as the eluants. Samsahl(206) used short anion exchange resin (Dowex-2, 200-400 mesh) columns coupled in series and saturated with chloride, citrate, and hydroxide ions to separate radioactive elements present as impurities in a water cooled nuclear reactor. Molybdenum and tungsten were quantitatively retained on the chloride form; other elements pass through to the citrate resin, where iron, cobalt, zinc, and nickel are adsorbed as complex ions. Manganese and chromium pass through and are finally precipitated on the hydroxide form.

Anion exchange in nitrate solutions is similar, in many respects, to that in chloride solutions. Nelson and Kraus(207) have shown that the non-adsorbable group in nitric acid includes most of the elements which are non-adsorbable in hydrochloric acid. However, the nitrate complexes of the divalent transition elements, i.e., Co(II), Cu(II), and Zn(II), are less stable than the corresponding chloride complexes.

Cobalt has been separated from solutions of soft magnetic alloys,(208) stainless steel(209) and other ferrous materials(210,211) by use of an anion exchange resin. After the separation, the cobalt was determined by an EDTA titration. Zeigler and Rittner(212) report that the cobalt(II) cyanate complex can be adsorbed by the ion exchanger, Dowex-1 (8% crosslinkage). Separations of cobalt are possible for cobalt-nickel ratios of 1 to 50. The cobalt was determined in the eluate by photometry.

Amberlite IRA-400 resin and HCl as an eluant have been used to separate Co (and Mo and Ag) from TcO_4^{--}.(213) Dowex-50 columns and 1 M NaCl and 3 M NaCl eluants have been used to separate the cis and trans isomers of dinitrotetrammine cobalt (III).(214)

Cobalt, but not nickel, is strongly adsorbed on ANEX-L resin(215) from greater than 9 M HCl solutions, and it may be eluted from the resin with water. Fe, Cu, Pb, Zn, Cd, and Sn do not separate from cobalt under these conditions.

Metal cations can be conveniently separated into groups by elution from an 8% crosslinked Dowex-50 (100-200 mesh) resin column with ethylenediammonium perchlorate solution.(216) Co^{+2} can be eluted from the column with a 0.1 M solution of the eluant.

Cobalt can be separated from cadmium(217) by eluting the cadmium from the mixture adsorbed on an 8% crosslinked AG-50W resin column with 0.5 N HCl. Cobalt is retained on the resin.

d. With Chelating Ion Exchange Resins

To increase the selectivity of ion exchange resins toward closely related cations, resins have been prepared which incorporate chelating compounds into the resin structure.(218) The equilibrium adsorption of several divalent cations over the pH range 1 to 10 has been measured for these resins and, for comparison, for two commerical cation exchangers. The chelating resins showed a capacity comparable to that of the commercial resins, and, in general, superior selectivity for metal ions. For example, the 8-quinolinol resin was very effective in separating cobalt from copper.

e. With Paper and Similar Materials

Co^{+2} has been separated from other inorganic ions by use of paper chromatographic techniques and such solvents as water(219), butanol-HCNS,(220) ether-mineral acids,(221) alcoholic KCN,(222) tetrahydrofuran-HCl,(223) butanol-HCl,(224,225) and nicotine.(226) Some of the reagents that have been used to detect cobalt in the presence of other cations on a paper chromatogram include

H_2S,(227) organic chelating compounds,(224,228) quercetin,(229) phenylthiosemicarbazide(230) and benzidine.(231) Daylight and ultraviolet light have been used to observe these reactions.(224,232) Alcoholic solutions of dimethylglyoxime have also been used as a reagent in paper chromatography to determine cobaltous ions.(233)

Pollard, et al.(234) have studied the behavior of Co^{+2} and other cations on paper chromatograms by use of complex-forming mixtures (such as acetylacetone, pyridine, and acetoacetic ester), butanol-HNO_3, butanol-acetic acid, and water as solvents. Lederer (235) and DeCarvalho(236) have studied the separation of many of the cations, including Co^{+2}, using alcohol-HCl mixtures as solvents. Walker and Lederer(237) have studied cationic separations of cobalt with binary alcohols mixtures and HCl as solvents. Ketone-HCl,(238) butanol-HBr,(239) alcohol-HNO_3(240) mixtures and other organic liquids(239) have also been used as solvents in similar studies.

Lederer and Lederer(241) report that a mixture of methyl n-propylketone-acetone and HCl can be used as a solvent to separate cobalt from iron, nickel, and manganese on a paper chromatogram. Shibota and Uemura(242) used acetone-HCl as a solvent for the same separation. Similar studies have been made by Airan,(243) Airan and Barnabas(244) and Tweari.(245) In all instances, rubeanic acid was used as the reagent for detecting the cobalt on the chromatogram.

Several ketonic solvent mixtures (such as acetone-water-HCl) have been used for the separation of cobalt from nickel, manganese, copper, iron, titanium, vanadium and uranium.(246) Cobalt (as well as Fe^{+3} and Ni^{+2}) has been separated from aluminum,(247) from nickel,(248) from copper,(249) and from iron, titanium, aluminum, vanadium and nickel(250) by paper chromatography. Lacourt(251) also has reviewed the general applications of paper chromatography to the separation of cobalt from other metals and its subsequent determination by other analysis techniques.

Paper chromatography has also been used to separate and identify radioactive Co^{60} (5.27 y) in an Fe^{59} (45 d) solution.(252) Co^{60} as a carrier-free tracer has been separated from an irradiated manganese target by use of paper chromatography and acetone-HCl as the solvent.(253)

Burstall, et al.(254) have used cellulose chromatographic columns composed of wood pulp, cotton linters, or filter paper to separate and determine cobalt, nickel and copper in steel. Methylpropylketone, and methylpropylketone - acetone-water-HCl mixtures were used as solvents. A cellulose column has also been used by Anderson and Lederer(255) to quantitatively separate Co (and Ni, Cu and Fe) from thallium. Butanol-1 N HCl was used as the solvent.

Filter paper columns impregnated with 8-hydroxyquinoline also have been used to separate cobalt from other metals.(256) Dioxan, pyridine, chloroform, acetone, methanol, propanol, and butanol were used as the solvents in this work.

Cobalt (as well as copper and nickel) amine and ethylenediamine complexes(257) can be separated from each other by paper chromatography(258) by eluting with solvents composed of mixtures of ether, methanol, water and concentrated hydrochloric acid. A good separation of copper from cobalt and nickel was achieved. The behavior of six Co(III) complexes(259) was also studied using butanol-HCl, butanol-ammonia, butanol-acetic acid, acetone, HCl and water as solvents for the paper chromatographic separation. Cobalt complex behavior on paper chromotographic columns has also been investigated using NH_2Cl solutions at varying concentrations.(260)

Weidman(261) reports on the use of paper chromatography to separate nickel from cobalt. A sharp separation was obtained by using n-tributylphosphate in hydrochloric acid-methanol (in the ratio of 2:1) as the solvent.

Singh and Dey(262) have investigated the separation of Co(II) from Cd(II), Cu(II) and Ni(II) by use of paper strip chromatography and using aqueous ethanol as the solvent. No satisfactory separation of Ni(II) and Cd(II) from Co(II) was possible due to the spreading and overlapping of zones.

Frierson, et al.(263) used a two solvent system composed of butyl alcohol in concentrated HCl and 3-methyl-2-butanone in acetone and HCl to separate cobalt, nickel, copper and zinc ions by paper chromatography.

Berg and Strasser(264) used cyclohexane, methanol and dioxan as solvents to separate cobalt(III), copper(II) and nickel(II) acetylacetone chelates by paper chromatography.

Majumdar and Singh(265) report on the use of a electro-chromatographic technique for the separation of cobalt, zinc, manganese, and nickel in the presence of a number of electrolytes. Separation sequences of Mn-Co-Ni, Ni-Co-Mn, Zn-Co-Mn, and Mn-Co-Zn were observed. In this work, a quarternary separation using potassium cyanide solution at a pH of 6.0 gave the sequence, Ni– Zn– Co– Mn. A slight spreading of the zinc band into that of the cobalt occurred for these conditions.

IV. DISSOLUTION OF SAMPLES CONTAINING RADIOACTIVE COBALT

Most materials containing radioactive cobalt isotopes can be dissolved in a manner similar to that used for non-active sample materials containing cobalt. Hillebrand, et al.(266) report that cobalt minerals and ores, metals and alloys, etc., can be broken up and/or dissolved by a preliminary attack with hydrochloric acid, followed by the addition of nitric acid. Any insoluble residue resulting from this processing can be fused with potassium pyrosulfate and sodium carbonate. Some ores, such as those containing silver, can be best attacked by the use of nitric and sulfuric acid mixtures. In extreme cases, fusion with sodium peroxide can be employed. Biological materials are best dissolved by wet-ashing, i.e., digestion with H_2SO_4-$HClO_4$-HNO_3 mixtures while being heated.(267) Gorsuch(268) also reports on wet or dry oxidation techniques for determining cobalt and other trace elements in organic and biological materials.

Any one of these methods of sample dissolution can be adapted for use in the radiochemistry of the cobalt radionuclides. However, it is considered most practical to add the <u>inactive</u> cobalt carrier (if an isotopic carrier method is being followed) to the mixture before dissolution begins. This should assist in achieving an exchange of the cobalt carrier with the desired cobalt radionuclide.

V. SAFETY PRACTICES

No matter what method is used to decompose a sample, adequate safety precautions should be followed. The toxicology of most elemental compounds have been reported by Pieters and Creyghton(269) and it should be consulted for information on handling cobalt-containing materials safely.

Safety practices in handling radioactive sample materials are always important in radiochemistry. The discharge of radioactivity by explosion, evolution, spilling, etc., into a laboratory area can be hazardous and can result in widespread contamination. Thus, some source of information on safe-handling practices in processing radioactive samples should be consulted before a radiochemical analysis for the cobalt radionuclides is undertaken. One such source is that which is given in the Oak Ridge National Laboratory's Master Analytical Manual.(270) Many other similar sources of information exist and should be consulted.

VI. COUNTING TECHNIQUES FOR THE RADIOACTIVE COBALT ISOTOPES

The analysis of sample materials containing the cobalt radionuclides may be completed either by a direct (nondestructive) measurement of the radioactivity of the particular cobalt radionuclide in the radioactive sample or by obtaining the radionuclide in some suitable form following a radiochemical processing of the radioactive sample. The use of either technique is dependent upon the cobalt radionuclide being measured and the sample material being analyzed. The radionuclide's half-life, the type of radiations it emits as it decays, and the energy of its radiations, as well as the radioactivity induced into the other elements in the sample matrix, must be considered in selecting the method to be followed.

Table I of this monograph shows the nuclear characteristics of each of the known radioactive isotopes of cobalt. The chief radionuclides of cobalt usually encountered by the radiochemist are Co^{60m} (10.5 m), Co^{58} (72 d), and Co^{60} (5.27 y). These isotopes are produced as a result either of a nuclear particle reaction on the stable isotope of cobalt (Co^{59}) or on the stable isotopes of other elements. The radioactivity of any of these cobalt radionuclides can be analyzed and measured by standard Geiger-Mueller, gamma scintillation and proportional counting technique.(271-274)

The nondestructive analysis technique has been used most frequently in determining the cobalt radionuclides in neutron-irradiated materials usually being analyzed by a radioactivation analysis method.(275,276)

For example, Schonken(277) has reported on the use of a nondestructive gamma spectrometry method to detect and determine the Co^{60} (5.27 y) radioactivity (and subsequently the stable Co^{59} content) in neutron-irradiated biological materials. Bate and Leddicotte(278) have used a nondestructive gamma spectrometer method employing the complement-subtaction technique to determine cobalt (as Co^{60}, 5.27 y) and nickel (as Co^{58}, 72 d) in such materials as soils, vegetation, water, and metals and alloys. Salmon(279) has also measured the Co^{60} content (and hence the Co^{59} content) of stainless steel by a neutron radioactivation method involving nondestructive gamma spectrometry. In another gamma spectrometer method, Leddicotte and Guss(280) have determined the cobalt content of Inconel by a nondestructive measurement of the Co^{60} radioactivity. In this same investigation, it was also possible to measure the Co^{58} (72 d) radioactivity produced as the result of the n,p reaction upon Ni^{58} with good precision and accuracy in order to determine the neutron flux of the reactor facility used for the irradiation. In similar neutron flux measurements, the Co^{60} and Co^{58} induced in neutron threshold detectors have also been measured by a nondestructive technique.(281)

Emery(282) has determined the cobalt content in alloys and animal tissue by a nondestructive gamma-spectrometer measurement of the Co^{60m} (10.5 m) radionuclide. Westermark and Fineman(283) have also used a similar technique to determine the Co^{59} content of stainless steel.

The radiochemical separation methods reported in Section VII of this monograph have most frequently been concerned with the assay of radioactive Co^{60}. However, it should be noted that Kaiser and Meinke(284) have used the Co^{60m} radionuclide following a rapid radiochemical separation to determine cobalt in animal tissues. Likewise, Mullins, et al.,(284) have measured the radioactivity of Co^{58} in order to determine stable nickel in a variety of sample materials by a neutron radioactivation analysis method involving radiochemical separations similar to those described by Leddicotte(286,287) and reported as Procedures 17 and 18 in Section VII.

VII. COLLECTION OF DETAILED RADIOCHEMICAL PROCEDURES FOR THE COBALT RADIONUCLIDES

The detailed radiochemical procedures presented in this section have evolved from each investigator's choice of ideas and techniques similar to those expressed in Section III of this monograph. Carrier-free and carrier methods are considered only in this presentation. However, the Co^{60} tracer-isotope dilution techniques, reported by such investigators as Salyer and Sweet(87-89) and Eristavi, et al.,(287) could be considered by other investigators in their work with the cobalt radionuclides.

Only a few applications of carrier-free separations for the cobalt radionuclides have been noted in the literature.(252,253,298,305) Typical of these procedures are those presented herein as Procedures 19 and 22. However, it should be possible to use any of the ideas and techniques from the solvent extraction or chromatography investigations cited in this monograph to serve as a means of obtaining carrier-free cobalt radionuclides.

Most of the carrier radiochemical procedures have been originated either for use in the preparation of radioactive cobalt tracers(204,288) (see Procedures 1-10), the separation of Co^{60} from fission products(62,205,289) (see Procedures 11-13), or in the use of radioactivation analysis.(275,276) In particular, in radioactivation analysis, carrier radiochemical methods have been used in analyses concerned with the determination of microgram and submicrogram amounts of cobalt in biological materials,(204,284,290-296) metals and alloys,(60,296,299-305) meteorites,(306-308) rocks and minerals,(307,309,310) and marine sediments.(307,311) Procedures 14 to 24 are typical of the separation methods used in these investigations. Similar procedures have been used by Hall,(291) Tobias, et al.,(292) Benson,(293) Dale,(294) Koch, et al.,(295) Albert, et al.,(300) Riezler,(301) Talbot, et al.,(302) and Cornand and Gillis(304) in their use of radioactivation analysis to determine trace cobalt in such sample materials as tissues and metals and alloys. Procedures 15 and 16 described herein are unique in that they use radioactive Co^{60} carriers. The reports by Westermark and Fineman(283) and by Kaiser and Meinke(284) should be consulted for additional information on this application.

In each of the radiochemical procedures that follow, special information regarding the procedure's use, the type of nuclear bombardment, the type of material analyzed, separation time, etc., appears as part of each procedure. Whenever possible, an evaluation of each procedure is made with regard to its usefulness in the decontamination of other radioactive species from the radioactive cobalt isotopes.

PROCEDURE 1

Procedure Used In: Preparation of radioactive cobalt tracers

Method: Ion exchange

Element Separated: Co^{60} (5.27 y)

Type of Material Analyzed: Neutron irradiated targets and cobalt targets for cyclotron production of radioiron(204)

Type of Nuclear Bombardment: Neutron and deuteron

Procedure By: Helwig, et al(204) (Adapted from studies by Kraus and others(195-199))

Chemical Yield of Carrier: Quantitative

Time of Separation: Short

Degree of Purification: Excellent from Fe^{59}

Equipment Required: Ion exchange columns

Procedure:

1. To a solution of the target material, add cobalt and/or iron carrier. Evaporate to dryness. Dissolve residue in 5 M HCl and transfer the solution to the resin column (Note 1).

2. Elute the cobalt from the resin column with a 20-ml volume of 5 M HCl. Collect the effluent in a suitable container (Note 2).

3. Evaporate the cobalt effluent to a small volume and mount for counting (Note 3).

Notes:

1. Dowex-1, 200-400 mesh, resin packed in a Pyrex glass column, having a cross section of 1.13 cm^2 and a bed 13 cm long. Column conditioned with 5 M HCl.

2. Further elution of the column with a volume of 0.5 M HCl removed Fe^{59}.

3. The Co^{60} gamma radioactivity was determined by counting liquid samples in 1 dram vials with a sodium iodide crystal counter.

PROCEDURE 2

Procedure Used In: Preparation of radioactive cobalt tracers

Method: Solvent extraction and precipitation

Type of Material Bombarded: Nickel (as separated isotopes)

Type of Nuclear Bombardment: a. 37" cyclotron (protons)

b. 60" cyclotron (protons and deuterons)

Procedure by: Lilly (Reported by Meinke(288))

Separation Time: 10 minutes

Chemical Yield of Carrier: ~ 90%

Decontamination: Factor of 5

Equipment Required: Standard

Procedure

1. Dissolve Ni foil, weighing 3-5 mg., in a 10 ml beaker containing 0.5 ml of hot 6 N HNO_3. Take to dryness on a preheated hot plate.
2. Add 3-4 drops of hot conc. HCl and take to dryness. Repeat.
3. Add 2 mg Co as the chloride sol'n and warm slightly. Transfer to a 50 ml separatory funnel and dilute to 10 ml with H_2O.
4. Add 5 gms of solid NH_4SCN and shake until all of the crystals are dissolved. Extract Co from this sol'n by shaking with an equal volume of ethyl ether-amyl alcohol (1:1).
5. Draw off the H_2O layer from this extraction and discard it.
6. Add 10 ml of 6 N NH_4OH to the organic layer in the separatory funnel to destroy the complex and reextract the Co.
7. Draw off the ammoniacal layer into a small beaker, heat to boiling, and ppt CoS by adding NH_4HS sol'n. Prepare this ppt for counting as desired.

PROCEDURE 3

Procedure Used In: Preparation of radioactive cobalt tracers

Method: Precipitation

Type of Material Bombarded: Copper or Nickel

Type of Nuclear Bombardment: 184" cyclotron (neutrons, deuterons)

Procedure by: Lilly (Reported by Meinke(288))

Separation Time: 4 hours

Chemical Yield of Carrier: ~ 90%

Decontamination: 10^2

Equipment Required: Standard

Procedure

A. Cobalt from Cu(10 gms) + neutrons - 184"

1. Dissolve Cu target in 50-100 ml of hot 6 N HCl containing 5 ml of 30% H_2O_2. Boil off excess H_2O_2 and add 25-50 mg Co and 5 mg Ni as the chloride sol'ns. Dilute the sample to ~ 1 liter and add NH_4OH until the sol'n is neutral or very slightly acidic.

B. Cobalt from Ni (1-2 gms) + deuterons - 184"

1. Dissolve Ni target in the least possible volume of conc. HNO_3. Convert nitrates to chlorides by adding successive portions of conc. HCl and taking to a low volume. Add 25-50 mg Co and 75 mg Cu as the chloride sol'ns. Dilute the sample to ~ 500 ml and add NH_4OH until the sol'n is neutral or very slightly acidic.

In each of the above cases, continue as follows:

2. Add conc. NH_4HSO_3 sol'n., 1 ml at a time, until all of the Cu is reduced (as shown by the lack of any localized blue color when a few drops of conc. NH_4OH are added). Add solid NH_4SCN dissolved in a small amount of H_2O until ppt'n is complete.

(3) Coagulate the CuSCN ppt by heating and filter it through a double thickness of 42 Whatman paper in a large glass funnel. Discard the ppt.

(4) Boil the filtrate to expel SO_2 and then add 3 ml of conc. HCl per 100 ml of volume.

(5) Add a freshly prepared hot sol'n of alpha-nitroso-beta-

naphthol, made by dissolving 10 gms of the salt in 100 ml of 50% acetic acid, as long as a ppt is produced.

(6) Filter the ppt through retentive paper. Wash it well with warm 6 N HCl, and then with warm H_2O until free from acid. Ignite the ppt until all of the paper is burned off.

(7) Dissolve the CoO in HCl and add 100 mg Cu and 25 mg Ni as the chloride sol'ns. Adjust the acidity as in step (1) and repeat steps (2) through (6) above.

(8) Convert this CoO to $CoCl_2$ by treating it with anhydrous Cl_2 at 650°C for 30 minutes.

(If desired, part of the CoO in step (7) may be dissolved in HCl and the cobalt fraction purified still further by adding Cu and Ni hold-back carriers and repeating the procedure.)

Remarks:

The above procedure was designed for preparing a sample for analysis in the calutron. In case a small spectrograph is to be used, the amount and final form of the Co may need changing.

PROCEDURE 4

Procedure Used In: Preparation of radioactive cobalt tracers

Method: Precipitation

Type of Material Bombarded: Copper

Type of Nuclear Bombardment: 60" cyclotron (37 Mev alphas, 9.5 Mev protons, 19 Mev deuterons)
184" cyclotron (388 Mev alphas, 348 Mev protons, 194 Mev deuterons)

Procedure by: Batzel (Reported by Meinke(288))

Separation Time: 40 minutes

Chemical Yield of Carrier: 30-40%

Decontamination: $\sim 10^2$

Equipment Required: Standard

Procedure

1. Dissolve copper in minimum amount of concentrated HNO_3, and boil to dryness or with HCl to destroy HNO_3. Add 5 mg of Co carrier and 1-2 mg of the neighboring elements to serve as holdback.
2. Remove copper as sulfide from a 1 N HCl solution. Wash the precipitate with 1 N HCl saturated with H_2S.
3. Boil supernate to remove H_2S and neutralize with KOH. Make 2-3 N in acetic acid. Saturate about 5 cc of water with KNO_2 and add 0.3 cc of acetic acid. Heat and add to the hot solution of cobalt.
4. Allow to settle for 5 minutes in a steam bath. Cool, and centrifuge. Wash with a 5% KNO_2 solution acidified with acetic acid.
5. Dissolve the ppt in concentrated HCl; add 1 mg each of holdback carriers and reprecipitate.
6. Weight as the potassium cobaltinitrite.

PROCEDURE 5

Type of Material Bombarded: Uranium metal foil

Type of Nuclear Bombardment: 184" cyclotron (full energy particles; high energy fission)

Procedure by: Folger (Reported by Meinke$^{(288)}$)

Separation Time: 2.5 hours

Chemical Yield of Carrier: ~50%

Decontamination: From 10^4 to 10^8

Equipment Required: Standard

Procedure

(1) Uranium target is dissolved in conc. HCl (plus a small amt. conc. HNO_3 to clear up the sol'n) or in conc. HNO_3 (should be >10N). Use ~1/4 (or more) of target sol'n for aliquot. Add 10-20 mg Co carrier and make basic with NH_3.

(2) Centrifuge and wash ppt twice with sat'd aqueous NH_3. Combine supernatant and washings.

(3) Scavenge twice with $Fe(OH)_3$, twice with $BaCO_3$ & $SrCO_3$ (add sat'd Na_2CO_3 and check pH to be sure sol'n is basic enough, ~pH 10).

(4) Make 0.7 - 0.8 <u>N</u> in HCl. Scavenge with CuS, CdS, Re_2S_7 (for Tc) HgS, PdS_2 (1-2 mg of carriers).

(5) Make basic with NH_3 and ppt CoS with H_2S. Wash to remove all NH_4^+. Dissolve in 1 cc conc. HNO_3. Dilute to ~4<u>N</u> HNO_3 and scavenge with 1-2 mg AgCl twice.

(6) Make basic with KOH to ppt $Co(OH)_2$ (upon heating goes to $Co(OH)_3$). Centr. and wash. Dissolve ppt in 3 cc 2-3 <u>N</u> Hac. Add 2 mg Ni holdback and heat.

(7) Add 3-4 cc 6 <u>N</u> HAc sat'd with KNO_2 hot (Caution! Beware of foaming over). Digest 10 min hot. Chill in ice bath to retard bubbles and centrifuge $K_3Co(NO_2)_6 \cdot 1\ 1/2\ H_2O$ (yellow).

(8) Wash, and dissolve in conc. HCl (with heating - green sol'n is obtained).

(9) Repeat steps (3) through (8). Then repeat (6) and (7).

(10) Wash twice with H_2O, EtOH, Et_2O. Filter, dry at 110° C for 5 min. Weigh as $K_3Co(NO_2)_6 \cdot H_2O$.

Remarks:

(1) In step (6), the $Co(OH)_2$ ppt becomes grey-brown on heating in the water bath. This does not interfere with the procedure.

(2) For additional information, see Scott, "Standard Methods of Chemical Analysis," D. Van Nostrand Co., Inc., New York, Ed. 5 Vol. I, pp 305-14.

PROCEDURE 6

Procedure Used In: Preparation of radioactive cobalt tracers

Method: Precipitation and solvent extraction

Type of Material Bombarded: Copper or Nickel

Type of Nuclear Bombardment: a. 60" cyclotron (neutrons)
b. 184" cyclotron (deuterons)

Procedure By: Lilly (Reported by Meinke(288))

Separation Time: 1 hour

Chemical Yield of Carrier: ~ 90%

Decontamination: 10^2

Equipment Required: Standard

Procedure:

A. Cobalt from Ni (separated isotopes) + p,d,n - 60"

1. Dissolve Ni foil, weighing 3-5 mg., in a few drops of conc. HNO_3 and boil off HNO_3 with successive portions of HCl. Add 2 mg Co, 2 mg Fe and 5 mg Cu as the chloride sol'ns.

2. Dilute to 50 ml with H_2O and heat to boiling. Ppt $Fe(OH)_3$ by adding NH_4OH in excess and coagulate the ppt well by heating. Filter the $Fe(OH)_3$ ppt through No. 42 Whatman paper in a glass funnel and wash with a small amount of 1% NH_4Cl sol'n. Make the filtrate slightly acidic with HCl. Add conc. NH_4HSO_3 sol'n dropwise until all of the Cu is reduced (as shown by the lack of any localized blue color when a few drops of conc. NH_4OH are added). Add solid NH_4SCN dissolved in a small amount of H_2O until ppt'n is complete.

3. Coagulate the CuSCN ppt by heating and filter it through a double thickness of No. 42 Whatman paper in a glass funnel. Discard the ppt. Boil the filtrate to a volume of 10 ml to expel SO_2 and transfer to a 50 ml separatory funnel.

B. Cobalt from Cu (50-100 mg) + d - 184"

1. Dissolve Cu target in conc. HCl containing a few drops of conc HNO_3. Boil off the excess HNO_3. Add 2 mg Co, 2 mg Fe, and 2 mg Ni as the chloride sol'ns.

2. Dilute to 50 ml with H_2O and heat to boiling. Ppt $Fe(OH)_3$ by adding NH_4OH in excess and coagulate the ppt well by heating. Filter the $Fe(OH)_3$ ppt

through No. 42 Whatman paper in a glass funnel and wash with a small amount of 1% NH_4Cl sol'n. Make the filtrate slightly acidic with HCl. Add conc. NH_4HSO_3 sol'n dropwise until all of the Cu is reduced (as shown by the lack of any localized blue color when a few drops of conc. NH_4OH are added). Add solid NH_4SCN dissolved in a small amount of H_2O until ppt'n is complete.

3. Coagulate the CuSCN ppt by heating and filter it through a double thickness of No. 42 Whatman paper in a glass funnel. Discard the ppt. Boil the filtrate to a volume of 10 ml to expel SO_2 and transfer to a 50 ml separatory funnel.

C. <u>Cobalt from Cu (0.1-0.5 gms) + n - 184"</u>

1. Dissolve Cu target in 10 ml of hot 6 <u>N</u> HNO_3 in a small beaker and boil off HNO_3 with successive portions of HCl. Add 2 mg Co and 2 mg Ni as the chloride sol'ns.

2. Add H_2O and HCl so as to give a volume of 25-30 ml with 0.3 <u>N</u>-0.5 <u>N</u> HCl. Heat to boiling and pass in H_2S to ppt CuS. Coagulate the ppt by heating and filter it through a small <u>fine</u> sintered glass filter. Wash the ppt with a small amount of H_2O and discard it.

3. Boil the filtrate to a volume of ~ 10 ml and then transfer it to a 50 ml separatory funnel.

In all three of the above cases continue as follows:

4. Add 5 gms of solid NH_4SCN and shake until all of the crystals are dissolved. Extract Co from this sol'n by shaking with an equal volume of ethyl ether-amyl alcohol (1:1).

5. Draw off the H_2O layer from this extraction and discard it.

6. Add 10 ml of 6 <u>N</u> NH_4OH to the organic layer in the separatory funnel to destroy the complex and reextract the Co.

7. Draw off this ammoniacal layer into another 50 ml separatory funnel and make it slightly acidic with HCl. Add 2 mg Ni as the chloride sol'n and repeat the extraction as in step (4) above.

8. Draw off the H_2O layer and discard it. Treat the organic layer with NH_4OH as described in step (6) above.

9. Draw off the ammoniacal layer into a 50 ml beaker, boil to a volume of 5 ml, and ppt CoS by adding NH_4HS sol'n. Prepare this ppt for counting as desired.

PROCEDURE 7

Procedure Used In: Preparation of radioactive cobalt tracers

Method: Precipitation and solvent extraction

Type of Material Bombarded: Arsenic

Type of Nuclear Bombardment: 190 Mev deuterons

Procedure By: Hopkins (Reported by Meinke(288))

Separation Time: 1 hour

Chemical Yield of Carrier: ~ 70%

Decontamination: ~ 10^2

Equipment Required: Standard

Procedure:

1. Dissolve As in minimum $HNO_3 + H_2O_2$, add 2 mg Se and Ge carrier, 5 mg Co.

2. Make alkaline with NH_4OH, pass in H_2S rapidly for 1 minute only. Centrifuge immediately.

3. Dissolve in minimum conc. HCl, add 1 mg Cu, ppt CuS from hot 1 N HCl.

4. Add other carriers, evaporate to small volume, make 6 N HCl, extract 4 times with equal volume ethyl ether.

5. Evaporate to near dryness, add H_2O to 2 ml volume, and an equal volume of solid KSCN. Extract 4 times with 2 ml amyl alcohol.

6. Extract out of amyl alcohol with 4 ml 1 N KOH.

7. Dissolve in HCl and reppt hydroxide with KOH.

8. Dissolve in minimum acetic acid, dilute to 4 ml, saturate with KCl, and add KNO_2 until pptn of $K_3Co(NO_2)_6$ is complete.

PROCEDURE 8

Procedure Used In: Preparation of radioactive cobalt tracers

Method: Electrodeposition

Type of Material Bombarded: Copper

Type of Nuclear Bombardment: 60" cyclotron (19 Mev deuterons)
184" cyclotron (194 Mev deuterons)

Procedure by: Stewart and Softky (Reported by Meinke(288))

Separation Time: 4-6 hours

Chemical Yield of Carrier: 90-100%

Decontamination: 10^5

Equipment Required: Stainless steel strip electrodes, electrolysis cell, platinum discs, and stirrers, 2 ampere d.c. rectifier unit.

Procedure:

1. Dissolve Cu foil in minimum dilute HNO_3. Add 1 mg. Co, Ni, and Mn carriers as nitrates, and 2 drops conc. H_2SO_4. Dilute to about 20 ml with distilled water.

2. Electrodeposit copper on stainless steel strip cathode set into beaker in which the foil was dissolved, using a rotating Pt spiral anode at 2-3 volts, 1-2 amperes.

3. When solution is water white, remove the electrodes, add 1 ml conc. H_2SO_4 and evaporate to SO_3 fumes to remove HNO_3.

4. Dilute to 35-50 ml and saturate with H_2S to precipitate residual Cu. Filter. Boil filtrate to expel H_2S, add 2 mg Cu carrier as chloride and repeat.

5. Boil filtrate 5 minutes to expel H_2S, make solution slightly ammonical, then add 1-2 ml 1% dimethylglyoxime in ethanol to ppt NiDMG. Filter. Wash ppt with hot water.

6. Acidify filtrate with HNO_3 and evaporate to SO_3 fumes to destroy alcohol. Add a few drops of conc. HCl and again take to SO_3 fumes to insure removal of NO_3^-.

7. Transfer solution to a 30 ml tower electrolysis cell fitted with a 1" Pt disc cathode, make strongly ammonical, and electrolyze at 1-2 amperes for about 30 minutes, using a slowly rotating Pt anode. Cobalt deposits as a smooth adherent plate on the cathode. MnO_2 deposits at the same time on the anode.

8. When Co is completely deposited, replace the electrolyte with distilled water while the current is still on. Remove the anode quickly to prevent sol'n of the MnO_2, pour off the water, and rinse the cobalt plate with alcohol.

Remarks:

(In step (5) if solution is too strongly ammonical at this point, NiDMG will be incompletely precipitated.)

(In step (7) NH_4OH should be added periodically during the electrodeposition. Current should be kept lower than 2 amperes to give a smooth adherent plate.)

PROCEDURE 9

Procedure Used In: Preparation of radioactive cobalt tracers

Method: Precipitation

Type of Material Bombarded: Copper foil

Type of Nuclear Bombardment: a. 60" cyclotron (deuterons)
b. 184" cyclotron (deuterons)

Procedure By: Stewart-Softky (Reported by Meinke(288))

Separation Time: 1 hour

Chemical Yield of Carrier: ~ 80%

Decontamination: 10^6

Equipment Required: Standard

Procedure:

1. Dissolve copper in minimum dilute HCl + a few drops of 30% H_2O_2. Boil off peroxide. Add 2 mg Fe and Co carriers as chloride.

2. Precipitate $Fe(OH)_3$ with excess NH_4OH. Filter and wash with NH_4OH (dilute).

3. Acidify filtrate to about 0.1 N HCl, add a few drops of NH_4HSO_3 to reduce Cu^{+2} to Cu^+ (decolorized solution) and warm to near boiling. Add NH_4SCN crystals until no further precipitation of CuSCN takes place. Let

settle for 15 minutes. Filter through No. 42 filter paper. Wash precipitate with a 1% solution of NH_4SCN.

4. Add sufficient conc. HCl to filtrate to make about 1 N acid and heat to near boiling. Add 5-10 ml of a freshly prepared solution of α-nitroso-β-naphthol reagent. (10 g α-nitroso-β-naphthol in 100 ml 50% acetic acid.) Let stand 30 minutes to insure complete precipitation of cobalt.

PROCEDURE 10

Procedure Used In: Preparation of radioactive cobalt tracers

Method: Solvent extraction and precipitation

Type of Material Bombarded: Copper foil

Type of Nuclear Bombardment: a. 60" cyclotron (deuterons)
b. 184" cyclotron (deuterons)

Procedure By: Stewart-Softky (Reported by Meinke[288])

Separation Time: 1 hour

Chemical Yield of Carrier: 80-100%

Decontamination: 10^5

Equipment Required: Standard

Procedure:

1. Dissolve copper foil in 6 N HCl and a few drops of 30% H_2O_2. Boil off the peroxide. Add 2 mg Fe, Zn, and Co carrier as chlorides.

2. Precipitate $Fe(OH)_3$ with excess NH_4OH, centrifuge and pour off supernatant. Dissolve precipitate in HCl and repeat. Add 2nd supernatant to the original.

3. Make solution about 0.1 N with HCl. Add a few drops of NH_4HSO_3 to reduce Cu^{+2} to Cu^{+1} (shown by decolorized or pale yellow solution). Warm to near boiling. Add NH_4SCN crystals until no further precipitation of CuSCN takes place. Let settle for 15 minutes. Filter through Whatman No. 42 filter paper directly into a separatory funnel. Wash precipitate with a 1% solution of NH_4SCN containing a little NH_4HSO_3.

4. Add 5 g NH_4SCn to the solution in the separatory funnel and extract $(NH_4)_2Co(SCN)_4$ with a 1:1 amyl alcohol-diethyl ether solution. Add 2 ml conc. HCl and 1 g NH_4SCN and repeat extraction until solvent layer is colorless (2-3 extractions are usually sufficient). Re-extract cobalt from the combined solvent layers with 6 $\underline{N}$ NH_4OH.

5. Make solution acid (pH 2-3) with HCl and add an additional 1 mg of Zn as $ZnCl_2$. Saturate with H_2S to precipitate ZnS, centrifuge and decant supernatant into another cone. Make slightly ammoniacal and warm to coagulate CoS precipitate.

Remarks:

It was found that Zn extracted partially from the saturated thiocyanate solution with the alcohol-ether mixture.

PROCEDURE 11

Procedure Used In: Separation of cobalt radioactivity from radioactive corrosion products (mixed with fused salts of uranium)

Method: Precipitation

Radionuclide Separated: Co^{60} (5.27 y)

Types of Materials Bombarded: Inconel and fused salts(62)

Type of Nuclear Bombardment: Neutron

Procedure By: Smith, R. R., et al(62)

Separation Time: Short

Chemical Yield of Carrier: ~ 70%

Decontamination: Good from iron, chromium, and fission products

Equipment Required: Standard

Procedure:

1. Add 2 ml standardized Co carrier (2.00 mg/ml) to fused salt solution (Note 1). Add NH_4OH until $Al(OH)_3$ precipitates. Centrifuge; transfer supernate to new centrifuge tube.

2. Dissolve precipitate in a minimum quantity of conc. HNO_3. Neutralize with NH_4OH and add excess NH_4OH. Centrifuge; combine supernate with initial supernate.

3. Dissolve $Co(NH_4)^{++}$ complex by adding sufficient glacial acetic acid. Then add excess 3 M HAc. Dilute to 25 ml with water.

4. Add 6 ml of 3 M HAc saturated with KNO_2 to the solution. Digest 10 minutes in an ice bath. Centrifuge; discard supernate. Wash the precipitate twice with 30 ml of water. Discard washes.

5. Dissolve precipitate in several ml of conc. HCl. Boil off decomposition products. Add Cs and Ba carriers and dilute to 25 ml with water.

6. Precipitate cobalt hydroxide with 10 ml of saturated KOH solution. Wash precipitate with water. Centrifuge; discard wash liquid.

7. Dissolve cobalt hydroxide precipitate in 3 ml of 6 M HAc. Add Zr and Cr holdback carriers. Dilute and add 3 M HAc saturated with $KNO_2 \cdot K_3Co(NO_2)_6$ precipitates.

8. Centrifuge. Wash twice with water and twice with absolute ethanol. Weigh after drying. Mount, compute carrier yield, and count (Note 2).

Notes:

1. Aluminum nitrate solution is used to dissolve the fused salt.
2. Gamma pulse analysis used to measure Co^{60} radioactivity.

PROCEDURE 12

Procedure Used In: Separation of radioactive cobalt from fission products

Method: Ion exchange

Element Separated: Co^{60} (5.27 y)

Type of Material Analyzed: Natural materials (waters, soils, vegetation)(205)

Type of Nuclear Bombardment: Neutron reaction products

Procedure By: Boni, A. L.(205)

Chemical Yield of Carrier: > 95%

Time of Separation: Several hours

Degree of Purification: $> 10^4$ from Fe^{59}, Zn^{65}, Cr^{51}, Cs^{137}, Sr^{89}, Ru^{106}, Np^{239}, Zr^{95}, Nb^{95}, and rare earth radionuclides.

Equipment Required: Standard

Procedure:

1. Prepare samples in following manner:

   a. Water - evaporate to dryness and dissolve residue in 3 N HCl - 0.1 N HF mixture.

   b. Soils (muds) - leach with 3 N HCl -- 0.1 N HF mixture (Note 1).

   c. Vegetation - fire in a muffle furnace and then dissolve the ash or leach it with 3 N HCl -- 0.1 N HF mixture (Note 1).

2. To the dissolved or leached sample material, add a known aliquot of Ru^{+4}, Cr^{+3}, Fe^{+3}, Co^{+2}, Cs^{+1}, Ce^{+3}, Nb^{+5}, Ba^{+2}, Sr^{+2}, Zr^{+4}, and Zn^{+2} carrier solutions to it (Note 2). Then add 1 ml of a 0.2 gram per ml thioacetamide solution to the mixture. Digest and allow the precipitate to settle. Repeat the thioacetamide addition. Remove thioacetamide precipitate (Ru^{+4}) either by centrifugation or filtration (Note 3).

3. Evaporate the supernatant liquid (or filtrate) to dryness and then add 2 ml of conc. HNO_3 and transfer the slurry to a 50-ml centrifuge tube. Add 25 ml of fuming HNO_3 to the tube; cool the solution under cold tap water. Digest the mixture for 15 minutes. Centrifuge and decant supernatant liquid to new centrifuge tube (Note 4).

4. Evaporate the supernatant liquid to dryness and then add 5 ml of distilled water to dissolve the residue. Heat, if necessary. Add 5 ml of 0.2 N H_2SO_4 - 0.6 N HF mixture to the solution. Digest for 15 minutes; then centrifuge the mixture and pour the supernatant liquid directly on to a

previously prepared Dowex-2 resin column (Note 5) washed with 15 ml of a 0.1 H_2SO_4 - 0.3 $\underline{N}$ HF solution. Wash the precipitate (Note 6) with 5 ml of the same acid solution, centrifuge the slurry, and add the supernatant directly to the resin column. Allow the liquid to pass through the resin column into a 100 ml beaker.

5. Wash the resin by adding 40 ml of a 0.1 $\underline{N}$ H_2SO_4 - 0.3 $\underline{N}$ HF solution in 5-ml aliquots to the column and combine the wash effluent with the sample effluent. Cautiously evaporate the combined effluents to dryness (Note 7).

6. Dissolve the residue in a minimum of conc. HCl. Heat, if necessary. Quantitatively transfer the solution to another prepared Dowex-2 resin column (Note 5) that has been washed with 15 ml of conc. HCl. Allow the solution to pass through the resin column, collecting the effluent in a 50-ml beaker. Wash the resin by the addition of 40 ml of conc. HCl in 5 ml aliquots and combine the effluent with that of the sample (Note 8).

7. Continue the resin column elution with 40 ml of 8.5 $\underline{N}$ HCl - 0.5 $\underline{N}$ HF solution. Collect this effluent (Note 9).

8. Elute the Co^{60} from the resin by adding 30 ml of 5 $\underline{N}$ HCl. Collect this fraction in a 50-ml beaker (Note 10).

9. Evaporate the cobalt fraction to a small volume. Transfer to a plastic sample vial and count the Co^{60} radioactivity by a gamma scintillation counter (Note 11).

Notes:

1. More than 99.0% of the radionuclides are leached by this process.

2. A total of 20 mg of Co^{+2} are added; all others range from 1-20 mgs each.

3. The radioactivity of this precipitate can be assayed.

4. The strontium nitrate precipitate obtained here can be further processed and the radioactivity of Sr^{89} measured.

5. Ion exchange column: 17 cm long x 0.9 cm I. D., with stopcock and 50-ml capacity reservior. Resin: 8% cross-linked Dowex-2 in the chloride form; 200-400 mesh.

6. Following wash process, this precipitate may be processed for rare earth radionuclides.

7. At this point, the resin column is processed for Zr-Nb radioactivity (see Boni(205)).

8. This fraction contains Cs^{137} and Cr^{51}.

9. This fraction contains Np^{239}.

10. The resin column retains Fe^{59} and Zn^{65}. If required, it can be further processed (see Boni(205)).

11. In this instance, a scintillation well counter, equipped with a 1.75 inch diameter x 2 inch NaI(Tl) crystal having a 5/8 inch diameter x 1.5 inch central well, was used.

PROCEDURE 13

Procedure Used In: Decontamination of Fission Product Solutions.

Method: Precipitation - solvent extraction - electrodeposition

Radionuclide Separated: Co^{60} (5.27 y)

Type of Material Analyzed: Fission Product Solutions

Type of Nuclear Bombardment: $Co^{59}(n,\gamma)Co^{60}$

Procedure by: Burgus, W. W. (Reported by Kleinberg(289))

Chemical Yield of Carrier: 70-75%

Time of Separation: 2-5 hours

Degree of Purification: Excellent from stable nickel and from fission product radionuclides.

Equipment Required:

a. Standard laboratory plus plating equipment described under "Preparation and Standardization of Carrier" given below.

b. Plating cells: 5 mil Pt square cathode (preweighed), mounted on brass plate and held in position by 7/8" ID glass cylinder, with gasket between platinum and glass cylinder; rotating Pt anode; d-c source; resistance in series with current source and cell. (One plating cell each per sample and standard.)

Reagents: Standard, except for

a. Amyl alcohol - ethyl ether mixture: equal parts by volume, and

b. Cobalt carrier as prepared and standardized in the procedure.

Procedure:

A. Preparation and Standardization of Carrier

Dissolve 49.3 gm of $Co(NO_3)_2 \cdot 6H_2O$ in H_2O, add 1 ml HNO_3, and dilute to 1 liter with H_2O.

Pipet 5.0 ml of the above carrier solution into a 125-ml Erlenmeyer flask and add 5 ml of H_2O and 3 ml of conc. H_2SO_4. Carefully boil down to copious SO_3 fumes to remove NO_3^- ion. Cool, dilute to 8 to 10 ml and allow the solution to come to room temperature. Cautiously neutralize with conc. NH_4OH, then add 1 ml in excess and allow to cool to room temperature. Transfer the solution quantitatively to plating cell and dilute to 15 ml. Add about 2 gm of solid $(NH_4)_2SO_4$, introduce rotating anode, and stir until the $(NH_4)_2SO_4$ has dissolved. Plate out Co with continual stirring. The current is initially kept at 0.10 amp at about 3 volts. During the first 1/2 hour of plating the current is gradually increased to 0.20 amp, which current is maintained for the remainder of the plating process. (The optimum plating time is at least 3 hours.) The cell is dismantled, the plate removed and washed several times with distilled H_2O and once with ethanol. It is then air-dried and weighed.

Four standardizations, with results agreeing within about 0.2% are usually made.

B. Radiochemical Procedure

1. To the sample in a 40-ml centrifuge tube, add sufficient H_2O to bring the volume to 20 ml. Add 3 ml of standard Co carrier and 1 ml of Ni carrier. Precipitate Co and Ni hydroxides by the addition of 10 M KOH (Note 1). Centrifuge and wash the hydroxides with 15 ml of H_2O, discarding the supernate and washings.

2. Dissolve the precipitate by warming with 3 ml of 6 M $HC_2H_3O_2$. Dilute to 25 ml with H_2O and cool to room temperature.

3. Precipitate $K_3Co(NO_2)_6$ by addition of reagent made by saturating 6 ml of 3 M $HC_2H_3O_2$ with KNO_2. Allow about 3 min for complete precipitation. Centri-

fuge, discard the supernate, wash the precipitate once with 30 ml of H_2O, and discard the washings.

4. Dissolve the $K_3Co(NO_2)_6$ by the addition of several milliliters of conc. HCl. Boil off the decomposition products. Add 1 ml of Ni carrier and dilute to 25 ml.

5. Precipitate Co and Ni hydroxides with 10 $\underline{M}$ KOH as before (Step 1). Dissolve the hydroxides as in Step 2.

6. Repeat Step 3.

7. Dissolve the $K_3Co(NO_2)_6$ in 4 or 5 ml of conc. HCl, boiling down almost to dryness. Add 2 drops of Pd and 4 drops of Cu carriers. Dilute to 20 ml and make about 0.1 $\underline{M}$ in HCl. Heat to boiling and pass in H_2S for 5 minutes. Filter onto No. 40 Whatman filter paper, catching the filtrate in a 125-ml Erlenmeyer flask and discarding the sulfide scavenging precipitate.

8. Boil out H_2S from the filtrate. Add 2 drops Pd and 4 drops of Cu carriers and dilute to 20 ml. Make 0.1 $\underline{M}$ in HCl, heat to boiling and pass in H_2S for 5 min. Again remove sulfides by filtration (Step 7).

9. Boil out H_2S from filtrate. This will require concentration almost to dryness (Note 2). Dilute to 25 ml and transfer quantitatively to 40-ml centrifuge tube. Add 4 drops of Fe carrier and precipitate $Fe(OH)_3$ by addition of conc. NH_4OH, adding about 0.5 ml of NH_4OH in excess. Centrifuge and discard $Fe(OH)_3$ scavenge, retaining the supernate.

10. Acidify the supernate with HCl. Add 4 drops of Fe carrier and remove $Fe(OH)_3$ again by the addition of conc. NH_4OH (0.5 ml excess). Centrifuge and discard the precipitate.

11. Repeat Step 10.

12. Acidify the supernate from 10 with conc. HCl, adding 1 ml in excess. Transfer to 125-ml separatory funnel. Add 15 gm of NH_4SCN and shake until all the solid has dissolved. Extract the Co-SCN complex into 50 ml of amyl alcohol-ethyl ether mixture. Wash the organic layer twice with 10 ml of NH_4SCN solution. Discard washings.

13. Back-extract the Co into 20 ml of H_2O to which 4 to 6 ml of conc. NH_4OH has been added. Discard the organic layer and transfer the aqueous layer to a 40-ml centrifuge tube.

14. Precipitate CoS from solution by passing in H_2S for 1 min. Centrifuge and discard the supernate.

15. Transfer the CoS precipitate with 5 to 10 ml of H_2O to a 125-ml Erlenmeyer flask. Add 10 ml of conc. HNO_3. Boil nearly to dryness (1 to 2 ml). Add 3 ml of conc. H_2SO_4 and heat to SO_3 fumes. Cool and add 5 to 10 ml of H_2O (slowly). Cool again. Neutralize with conc. NH_4OH and add 1 ml in excess. Add 2 gm of $(NH_4)_2SO_4$, transfer to plating cell and electroplate Co on a weighed Pt foil. (For a circular foil about 7/8" diameter begin plating at 3 or 4 volts and 0.10 amp. After the first 1/2 hour increase current to 0.20 amp. Plate for 2-1/2 to 3 hours.) After plating, wash with distilled water and then with ethanol. Dry at room temperature, weigh, and count. The counting procedure is dependent on the isotope involved.

Notes:

1. The purpose of the initial precipitation by means of KOH is to remove the Co from the strongly acid solution. For as complete a precipitation of $K_3Co(NO_2)_6$ as possible, mineral acids and oxidizing agents must be absent.

2. The H_2O is removed by boiling to prevent precipitation of Co as CoS when the $Fe(OH)_3$ scavenging step is made.

PROCEDURE 14

Procedure Used In: Radioactivation analysis

Method: Ion exchange with carriers

Element Separated: Co^{60} (5.27 y)

Type of Material Analyzed: Stainless steel, its corrosion products, and other elements, present as impurities in a water-cooled nuclear reactor.(206)

Type of Nuclear Bombardment: $Co^{59}(n,\gamma)Co^{60}$

Procedure By: Samsahl(206)

Chemical Yield of Carrier: Quantitative

Degree of Purification: Excellent

Equipment Required: Neutron source and standard laboratory equipment

Procedure:

The information given by Samsahl(206) in the section of his report entitled "Experimental" is considered to be rather concise and informative for use as the detailed Procedure for this radiochemical separation method. It reads as follows:

Experimental

The experiments were performed with irradiated (Note 1) metallic chromium, molybdenum and tungsten and salts of the cations, Na^{+1}, Mn^{+2}, Fe^{+2}, Co^{+2}, Ni^{+2}, Cu^{+1}, Zn^{+2}, and Sr^{+2}. The samples were individually brought into solution with hot 1:1 HCl containing a few drops of H_2O_2 and taken to dryness on a water bath. Subsequently, the residues were dissolved in water and diluted to a suitable strength of gamma activity. Carriers were added in amounts of about 5 mg of appropriate cation per 100 ml of solution. No carriers were added to the solutions of tungsten and molybdenum. Then 20 ml portions of a single gamma emitter solution were added to four ion exchange columns consisting of Dowex-2 (200-400 mesh) resin in the citrate, chloride and hydroxide forms, and Dowex-50 (200-400 mesh) in the hydrogen form. Each column consisted of 10 ml of water sedimented resin contained in a 2.5 cm diameter glass filter crucible (Note 2). The active solutions were sucked through at a rate of about 4 milliliters per minute and the columns washed with two 5-ml portions of water and drained by suction. Finally, the crucibles were placed directly at a definite geometry on the top of a gamma scintillation detector and the radioactivity assayed with a single channel pulse analyzer.

The activity of the Dowex-50 resin was measured and used as a standard for the estimation of the percent absorption on the other resins. The eluate was controlled for possible gamma activity.

Notes:

1. Irradiated in the Swedish R-1 reactor. Samples of irradiated steel and D_2O were also processed by this method.

2. Samsahl's report(206) should be consulted for a description of the ion exchange column and other information.

PROCEDURE 15

Procedure Used In: Radioactivation Analysis

Method: Solvent extraction and precipitation

Element Separated: Co^{60m} (10.5 m)

Type of Material Analyzed: Reactor Steel(283)

Type of Nuclear Bombardment: $Co^{59}(n,\gamma)Co^{60m}$

Procedure By: Westermark and Fineman(283)

Chemical Yield of Carrier: 60-90% (as a radioactive carrier)

Separation Time: 30 minutes

Decontamination: Good; some interference from Mn^{56} (2.6 h)

Equipment Required: Neutron source and standard laboratory equipment

Procedure:

1. Dissolve the irradiated steel turnings (Notes 1 and 2) in 10-15 ml of boiling 7 M HCl and 1 ml of radioactive Co^{+3} carrier solution (Note 3). After the sample has been put into solution, cool the solution to room temperature and transfer it to a separatory funnel (Note 4).

2. To the separatory funnel, add 1 ml of conc. HCl and 7.5 ml of ethyl ether. Shake the mixture and allow the two phases to separate. Discard the organic phase (Note 5) and collect the aqueous phase in another funnel and then add another volume of ether and shake the mixture.

3. Allow the phases to separate and transfer the aqueous phase to a 200 ml beaker. Boil the solution to remove any ether contained from the aqueous solution and then add hot 40 ml of nitrosonaphthol solution (Note 6).

4. Cool the mixture and then filter through a porcelain filter crucible. Wash the precipitate with water and mount for a measurement on a gamma scintillation spectrometer (Note 7).

5. Determine the amount of stable cobalt in the test sample by comparing the amount of Co^{60m} (10.5 m) radioactivity (Note 7) measured in it with that found in a comparator, or standard, cobalt sample (Notes 8 and 9). The amount of Co^{60} (5.27y) observed becomes a measure of the chemical recovery of the experiment (Notes 3 and 7).

Notes:

1. These irradiations were made in the D_2O - moderated reactor, RI, belonging to AB Atomenergi, Sweden. Neutron flux equal to about 6×10^{11} n/cm^2/sec. Limit of measurement about 5ppm of cobalt.

2. Sample weights of 0.1 - 0.2 g were irradiated.

3. Prepared by dissolving 1 g of irradiated cobalt in conc. HCl and diluting to 100 ml with water. Inactive cobalt content equal to 10 mgs per milliliter; radioactive Co^{60} content equal to 0.1 microcuries per milliliter. This carrier solution is used to determine the chemical yield of the experiment.

4. Use a very small amount of water to effect the transfer; solution should be 6-8 M in HCl.

5. The ether extraction removes stable and radioactive iron from the solution.

6. Prepared by dissolving 1 gram of nitroso-naphthol in 40 ml of glacial acetic acid and diluting to 80 ml with water. The solution should be freshly

prepared as required. If the solution is cloudy, it should be filtered.

7. In this instance, a 2-mm thick NaI crystal and a pulse height analyzer was used for the radioactivity measurement.

8. The standard is a filter paper on which about 0.05 ml of a solution of Co in dilute HNO_3 (1 g Co/liter) has been evaporated with an infrared lamp. The test sample and the standard sample were irradiated not more than 10 mm apart in the reactor.

9. The 0.059 Mev gamma photopeak is used to measure the Co^{60m} (10.5 m) radioactivity. The 1.17 and 1.33 Mev gamma photopeaks are used to measure the Co^{60} (5.27y) radioactivity.

PROCEDURE 16

Procedure Used In: Radioactivation Analysis

Method: Solvent extraction and precipitation

Element Separated: Co^{60m} (10.5 m)

Type of Material Analyzed: Tissue and Vitamin B_{12} solutions(284)

Type of Nuclear Bombardment: $Co^{59}(n,\gamma)Co^{60m}$

Procedure by Kaiser and Meinke(284)

Chemical Yield of Carrier: 40% (as a radioactive carrier)

Separation Time: 15 minutes

Decontamination: Good

Equipment Required: Neutron source and standard laboratory equipment

Procedure:

A. Irradiation of Samples

1. Samples weighing 0.275-0.300 g were allowed to air dry at room temperature for 24 hours and then placed in envelopes prepared from 4-mil thick polyethylene film. The envelopes were closed by heat sealing.

2. The sealed samples were then irradiated in the "rabbit" of the pneumatic tube system of the Ford Nuclear Reactor of the University of

Michigan (Note 1) along with suitable monitoring foils (Note 2) for a period of 30 minutes at full reactor power.

B. Radiochemical Separation

1. During the irradiation, a nickel crucible was prepared containing 10 mg of Co^{+3} carrier solution plus a known amount of Co^{60} (5.27 y) tracer (Note 3). Three sodium hydroxide pellets were added to the solution and the mixture heated to near dryness. After cooling the solution, 10 grams of Na_2O_2 were added to the crucible and melted.

2. At the end of the irradiation, the irradiated sample was transferred from the polyethylene envelope to the crucible and was fused in the melt mixture for 1 minute (Note 4). After cooling the mixture, (Note 5) the melt was dissolved in 50 ml of distilled water (Note 6) and then 15-20 ml of glacial acetic acid were added slowly to the solution (Note 7).

3. This mixture at a pH of 5-6 was transferred to a 150-ml separatory funnel containing 25 ml of 8-hydroxyquinoline solution (3% solution in chloroform) and shaken for 1 minute. The layers were allowed to separate and the aqueous layer discarded.

4. The cobalt was then extracted from the organic layer by adding 10 ml of 9 M HCl to the separatory funnel and shaking for 1 minute.

5. After the layers separated, the organic layer was discarded and cobalt precipitated from the HCl solution by the addition of Na_2O_2. This precipitate was collected on a filter chimney (Note 8), washed with water, and mounted for measurement on a gamma spectrometer.

C. Radioactivity Measurements

1. The amount of Co^{60m} (Note 8) was determined from the area under the 0.059 Mev photopeak.

2. The amount of Co^{60} retained (Note 3) on the precipitate was determined by measuring the 1.17 and 1.33 Mev photopeaks. This measurement was used to determine the chemical yield of the experiment.

3. Using the data obtained from the measurement of the gold foils (Note 2), data for the activation cross section for the reaction $Co^{59}(n,\gamma)Co^{60m}$ and the

half-life of Co^{60m} and the absolute measurement of the Co^{60m} radioactivity, the amount of stable cobalt was determined.

Notes:

1. Thermal neutron flux equal to about 10^{12} n/cm^2/sec when the reactor is operating at full power of 1 megawatt. The lower practical limit of detection for cobalt for these conditions was 5×10^{-8} gram.

2. Gold foils, weighing between 0.5 and 1.0 mg were wrapped in plastic envelopes and scotch taped to the inside cap of the "rabbit." Following the irradiation the foils were dissolved in 4 ml of aqua regia and diluted to 10 ml with distilled water. An aliquot of this solution was placed on a filter paper and mounted for measurement of the 0.411 Mev gamma ray of Au^{198} on the spectrometer. Comparison with other measurements made with calibrated gold foils permitted normalization of all irradiations to a neutron flux of 1×10^{12}.

3. Added to determine chemical yield of experiment.

4. CAUTION: A cover must be used on the crucible since the reaction may be quite violent.

5. The outside of the crucible was cooled by dipping it into a beaker of cold water. By manipulating the crucible during this cooling process, the melt was made to solidify into a thin readily dissolved coating.

6. 50-70 ml of liquid nitrogen were added to cool the solution to room temperature.

7. The solution was again cooled with liquid nitrogen.

8. 10-15 ml of 0.1 M HCl was added to prevent foaming.

PROCEDURE 17

Procedure Used In: Radioactivation analysis (Note 1)

Method: Precipitation

Element Separated: Cobalt

Type of Material Analyzed: Biological materials,(290) metals and alloys,(60,296) etc.

Type of Nuclear Bombardment: $Co^{59}(n,\gamma)Co^{60}$ (Co^{60}: 5.27 y)

Procedure by: Leddicotte, G. W. (Reported by Leddicotte(297,298))

Chemical Yield of Carrier: 60-70%

Time of Separation: 3 hours

Degree of Purification: Greater than 10^5 from all other radioactive elements

Equipment Required: Neutron source and standard laboratory equipment

Procedure

A. Irradiation of Sample Material

1. Irradiate known amounts of test (Note 2) and comparator (Note 3) sample in a neutron flux of at least 5×10^{11} n/sec/cm^2 for 1 week or longer (Note 4). Use small quartz tubes, polyethylene bottles, or aluminum foil to contain the samples during the irradiation.

B. Preparation of Irradiated Samples for Analysis

1. The Comparator Sample

a. After the irradiation, quantitatively transfer the comparator sample (Note 3) to a 25 ml volumetric flask. Dissolve it in 10 ml of 12 M HCl and dilute to volume with water. Pipet 0.5 ml aliquot of this solution into a 50 ml glass centrifuge tube. By means of a volumetric pipet, add to the same tube 1 ml of standard cobalt carrier of known concentration (Note 5). Mix well and continue with Step b in Part 2, below.

2. The Test Sample

a. After the irradiation, transfer the sample to a 50-ml centrifuge tube. Pipet 1.0 ml of standardized cobalt carrier into the same tube and dissolve the sample in a minimum amount of 12 M HCl. Add 10 mg. each of the following holdback carriers: Cu, Fe, Ni, Zr, Sr, and Na.

b. Adjust the solution to 1 M HCl and saturate the solution with H_2S. Heat gently to coagulate the Cu_2S, centrifuge, and transfer the supernate to another 50 ml glass centrifuge tube. Discard the precipitate. The supernate is boiled with 3 ml of 16 M HNO_3 and 3 ml of bromine water to oxidize the Fe^{++} to Fe^{+++}. Cool the solution and add 6 M NH_4OH until there is no further precipitation of $Fe(OH)_3$. Centrifuge and transfer the supernate to another 50 ml glass centrifuge tube. Discard the precipitate.

c. Saturate the supernate with H_2S and precipitate CoS_2 and NiS. Heat gently to coagulate the precipitate and centrifuge. Discard the supernate and wash the precipitate twice with 10 ml portions of hot water. Dissolve the precipitate in 1 ml of 16 M HNO_3 and dilute to 15 ml with H_2O. Boil to remove excess H_2S.

d. Make the solution basic with 1 M KOH to precipitate $Co(OH)_2$, centrifuge and discard the supernate. Wash the precipitate with dilute KOH solution (1 part of 1 M KOH to 10 parts water). Dissolve the $Co(OH)_2$ in 3 ml of 3 N acetic acid; add Ni holdback carrier and dilute to 10 ml with water. Heat to near boiling and add slowly 5 grams of solid KNO_2 until $K_3Co(NO_2)_6 \cdot H_2O$ begins to form. Digest for 15 minutes in a hot water bath to complete the precipitation of $K_3Co(NO_2)_6$. After precipitation is complete, cool and then centrifuge the mixture. Discard the supernate and wash the precipitate several times with 10 ml portions of nitrite wash (5% KNO_2 acidified with acetic acid). Discard each wash solution.

e. Slurry the precipitate in 10 ml of nitrite wash and filter with suction through a tared filter paper (Whatman No. 50) that is held in a Hirsch funnel. Wash with 5 ml portions of water, alcohol and ether. Dry at 110° C for 5 minutes. Weigh as $K_3Co(NO_2)_6 \cdot H_2O$, and prepare for measurement (Note 6).

C. Measurement of the Radioactivity of Co^{60} and Calculation of Inactive Cobalt Content of the Original Sample

1. The analysis of Co is completed by measuring the Co^{60} by counting on a gamma scintillation spectrometer. Cobalt-60 has a half-

life of 5.27 years and decays emitting gamma radiations of 1.17 and 1.33 Mev. The sum peak of Co^{60} is 2.5 Mev and can be used if necessary.

2. Following the radioactivity measurements, the observed radioactivity is corrected for loss of "carrier" during the experiment and sample weights of both the test and comparator sample. A comparison of these corrected radioactivities becomes a measure of the stable cobalt content of the test sample:

Per cent of stable cobalt in test sample

$$= \frac{Co^{60} \text{ in test sample}}{Co^{60} \text{ in comparator sample}} \times 100$$

NOTES:

1. This procedure has also been used to prepare radioactive Co^{58} tracer, produced by the nuclear reaction $Ni^{58}(n,p)Co^{58}$. Co^{58} decays with a half-life of 72 days and emits 0.47 Mev positrons.

2. At least 0.10 gram portion of solid samples should be used.

3. Use Co-Al alloy (0.15% cobalt) for cobalt comparator; approximately 25 mg portions of the alloy should be used.

4. The Graphite Reactor was used for this irradiation. The sensitivity of the method is such that 5×10^{-8} grams of cobalt can be determined. The sensitivity can be improved by use of higher neutron fluxes.

5. As $Co(NO_3)_2 \cdot 6H_2O$, standardized to 10 mgs of cobalt per milliliter of solution.

6. By comparing the final weight of the $K_3Co(NO_2)_6 \cdot H_2O$ precipitate obtained here with the theoretical yield expected for the amount of cobalt carrier added, it is possible to determine the chemical yield of the experiment. The chemical yield correction is then used to determine the amount of cobalt-60 recovered during the separation process.

PROCEDURE 18

Procedure Used In: Radioactivation Analysis

Method: Ion Exchange

Element Separated: Co^{60} (5.27 y) and/or Co^{58} (72 d)

Types of Material Analyzed: Metals and alloys(296)

Type of Nuclear Bombardment: $Co^{59}(n,\gamma)Co^{60}$
$Ni^{58}(n,p)Co^{58}$ (See Note 1)

Procedure By: Leddicotte (Reported by Leddicotte(298)) (See Kraus(195-199))

Chemical Yield Carrier: 60-70% (sometimes used as a carrier-free separation method)

Time of Separation: 2 hours

Degree of Purification: $> 10^5$ from all other species except Co^{58}

Equipment Required: Neutron source and standard laboratory equipment

Procedure:

A. Irradiation of Sample Material

1. Irradiate known amounts of test (Note 2) and comparator (Note 3) sample in a neutron flux of at least 5×10^{11} n/sec/cm^2 for 1 week or longer (Note 4). Use small quartz tubes, polyethylene bottles, or aluminum foil to contain the samples during the irradiation.

B. Preparation of Irradiation Samples for Analysis

1. The Comparator Sample

a. After the irradiation, quantitatively transfer the comparator sample (Note 3) to a 25 ml volumetric flask. Dissolve it in 10 ml of 12 M HCl and dilute to volume with water. Pipet 0.5 ml aliquot of this solution into a 50 ml glass centrifuge tube. By means of a volumetric pipet, add to the same tube 1 ml of standard cobalt carrier of known concentration (Notes 5 and 6). Mix well, then evaporate to near dryness; add sufficient acid to make the solution 10 M in HCl (Note 7). Mix well and continue with Step b in Part 2 below.

2. The Test Sample

a. After the irradiation, quantitatively transfer the sample to a 50-ml centrifuge tube and by means of a volumetric pipet, pipet 1.0 ml of standardized cobalt carrier (Notes 5 and 6) into the same tube and dissolve the sample in a minimum amount of 12 M HCl. Mix well, then evaporate to near dryness. Add sufficient acid to make the solution 10 M in HCl (Note 7).

b. Transfer the solution to a anion exchange resin column (Note 8).

c. Elute the column with at least 25 ml of 10 M HCl (Note 7). Collect the effluent and discard it.

d. Elute the Co^{60} (or Co^{58}) from the column with at least 25 ml of 4-5 M HCl. Collect the effluent in a suitable container (Note 9).

e. Evaporate the cobalt effluent to a small volume and mount for counting (Note 10).

C. Measurement of the Radioactivity of Co^{60} and Calculation of Inactive Cobalt Content of the Original Sample

1. The analysis of Co is completed by measuring the Co^{60} by counting on a gamma scintillation spectrometer. Cobalt-60 has a half-life of 5.3 years and decays emitting gamma energies of 1.17 and 1.33 Mev. The sum peak of Co^{60} is 2.5 Mev and can be used if necessary.

2. Following the radioactivity measurements, the observed radioactivity is corrected for loss of "carrier" during the experiment (Note 11) and sample weights of both the test and comparator sample. A comparison of these corrected radioactivities becomes a measure of the stable cobalt content of the test sample (Note 12).

Per cent of stable cobalt in test sample

$$= \frac{Co^{60} \text{ in test sample}}{Co^{60} \text{ in comparator sample}} \times 100$$

Notes:

1. This procedure has also been used to prepare radioactive Co^{58} tracer, produced by the nuclear reaction $Ni^{58}(n,p)Co^{58}$. Co^{58} decays with a half-life of 72 days and emits 0.47 Mev positrons and 0.81 Mev and 1.62 (~ 1%) Mev gamma radiations in its decay. The positron decay is accompanied by annihilation gamma radiations of 0.51 Mev. This procedure has also been used to determine trace nickel in sample materials. In that work, the observed Co^{58} radioactivity is a measure of the stable nickel content of the sample.

2. At least 0.10 gram portion of solid samples should be used.

3. Use ~ 25 gms of Co-Al alloy (0.15- cobalt) for cobalt comparator for determination of stable cobalt.

4. The graphite reactor was used for this irradiation. The sensitivity of the method is such that 5×10^{-8} grams of cobalt can be determined. The sensitivity can be improved by use of higher neutron fluxes.

5. As $Co(NO_3)_2 \cdot 6H_2O$, standardized to 10 mgs of cobalt per milliliter of solution.

6. If this procedure is used in a carrier-free separation, omit the addition of cobalt carrier.

7. 12 M HCl can also be used here.

8. Dowex-1, 10% crosslinkage, 50-100 mesh, resin packed in a Pyrex glass column, 0.5" in diameter x 12" long. Column conditioned with 10 M or 12 M HCl.

9. Further elution of the column with a volume 0.5 M HCl will remove Fe^{59} radioactivity, if present.

10. Quantitative recovery of cobalt carrier assumed here. If desired, solution may be processed in the manner described in Steps b through e of Section B-2 of Procedure 17 of this Monograph.

11. Not required if cobalt carrier is not used.

12. Does not apply if Co^{60} or Co^{58} is being prepared.

PROCEDURE 19

Procedure Used In: Radioactivation Analysis

Method: Precipitation

Element Separated: Co^{60} (5.27 y)

Type of Material Analyzed: Sodium potassium alloys(299)

Type of Nuclear Bombardment: $Co^{59}(n,\gamma)Co^{60}$

Procedure by Smales, A. A.(299)

Chemical Yield: Quantitative

Separation Time: Several hours

Decontamination: Complete from other radioactive species

Equipment Required: Neutron Source and Standard Laboratory Equipment

Procedure:

1. Dissolve irradiated alloy in methyl alcohol (Note 1) and then acidify the solution with hydrochloric acid.

2. To the solution, add 20 mgs of cobalt carrier and 5 mgs of Fe^{+3}. Boil the solution gently on a hotplate for ten minutes.

3. After cooling, dilute the solution to 250 ml with water; then add a slight excess of a suspension of zinc oxide in water. Digest for ten minutes; filter through a 15-cm Whatman No. 541 filter paper. Discard the precipitate.

4. Boil the filtrate and add dropwise 7.5 ml of a solution containing 1 gm of α-nitroso β-naphthol in 15 ml of glacial acetic acid. Boil for two minutes; filter through an 11-cm Whatman No. 31 filter paper. Discard the filtrate. Wash the precipitate thoroughly with hot water; dry and ignite the filter paper and contents in a silica crucible, at 800°C.

5. After cooling, dissolve the ignited residue in 5 ml of hydrochloric acid (specific gravity 1.18), by warming gently on a hot-plate. Transfer the solution to a 50 ml centrifuge tube, add 1 ml of a solution containing 1 mg of ferric iron and a slight excess of ammonium hydroxide (specific gravity 0.88). Boil gently; filter through a 9-cm Whatman No. 40 filter paper into a 150 ml beaker. Wash the precipitate with 5 ml of hot water. Discard the precipitate.

6. To the filtrate, add KOH solution (4 grams KOH in 10 ml H_2O) and boil gently until all the ammonia is driven off. Transfer the solution and precipitate to a centrifuge tube with water. Centrifuge and decant the washings.

7. Dissolve the precipitate in 5 ml of 3 <u>M</u> hydrochloric acid (Note 2). Then add 5 ml of glacial acetic acid and dilute to 25 ml with water. Precipitate $K_3Co(NO_2)_6$ by adding solid KNO_3 until precipitation is complete. Digest for five minutes; then centrifuge; discard the supernatant liquid.

Wash the precipitate with water and ethyl alcohol, centrifuging after each wash. Discard the washes.

8. Transfer the precipitate to a tared counting tray and evaporate to dryness under an infra-red lamp. Weigh the sample as potassium cobaltinitrite and determine the chemical yield.

9. Count the sample and standard under a normal end-window Geiger-Mueller counter. Correct for self-absorption, background, and chemical yield.

10. Check the radiochemical purity by absorption measurement.

Notes:

1. Irradiated material dissolution was made in a dry box under a nitrogen atmosphere.

2. Heat mixture gently until a solution is obtained.

PROCEDURE 20

Procedure Used In: Radioactivation Analysis

Method: Precipitation

Element Separated: Co^{60} (5.27 y)

Type of Material Analyzed: Nickel cathodes(303)

Type of Nuclear Bombardment: $Co^{59}(n,\gamma)Co^{60}$

Procedure By: Debiesse, et al(303)

Chemical Yield of Carrier: Not indicated

Separation Time: Not indicated

Decontamination: Excellent

Equipment Required: Neutron source and standard laboratory equipment

Procedure:

1. Following an irradiation in the Chatillion reactor for 180 hours, the samples were dissolved in hydrochloric acid and inactive cobalt and the Co^{60} precipitated with α-nitroso β-naphthol.

2. The precipitate was collected and washed and the 0.308 Mev beta

radiations from Co^{60} measured by means of a Geiger-Mueller counter.

Cobalt concentrations of the order of 0.28% cobalt in the nickel cathodes were determined by this analysis method.

PROCEDURE 21

Procedure Used In: Radioactivation Analysis

Method: Precipitation (chiefly)

Element Separated: Co^{60} (5.27 y)

Type of Material Analyzed: Sodium metal(304)

Type of Nuclear Bombardment: $Co^{59}(n,\gamma)Co^{60}$

Procedure By: Grand, et al(304) using radiochemical separation procedures reported by Meinke(288) and Kleinberg(289). (See Procedures 3-11 and 13)

Chemical Yield of Carrier: As indicated in adapted procedures(288,289)

Separation Time: Several hours

Decontamination: Excellent from Na^{24} (15 h), Mn^{54} (300 d), Ta^{182} (112 d), and Cr^{51} (27 d)

Equipment Required: Neutron source and standard laboratory equipment

Procedure:

1. Samples and cobalt monitors irradiated in Materials Testing Reactor.

2. The radiochemical procedure involved complete solution of the sample, addition of inactive carriers and treatment with HF-HNO_3-H_2SO_4 mixture and H_2O_2. Following this treatment, gross separations of the elements were made by adaptations of procedures reported by Meinke(281) and Kleinberg(282).

3. A known weight (about 50 mg) of the separated material was mounted in a reproducible manner on a plastic holder using a trace of collodion as a binder. The samples were counted on standard β-counting equipment.

4. Limits of measurement for this analysis: 0.002 ppm.

PROCEDURE 22

Procedure Used In: Radioactivation analysis

Method: Ion exchange

Element Separated: Co^{60} (5.27 y)

Type of Material Analyzed: 18/8 steel(305)

Type of Nuclear Bombardment: $Co^{59}(n,\gamma)Co^{60}$

Procedure By: Monnier, et al(305) (Note 1)

Chemical Yield of Carrier: Carrier-free

Degree of Purification: Excellent from stable chromium, manganese, nickel, silicon, carbon, molybdenum, and iron. Only radioactive contaminant obtained in separation was Co^{58} (72 d) produced by the reaction $Ni^{58}(n,p)Co^{58}$. Interference easily resolved by gamma spectrometry.

Equipment Required: Neutron source and standard laboratory equipment

Procedure:

A. Irradiation of Samples

1. Irradiate test samples (Note 2) in a neutron source for a predetermined time (Note 3).

2. After the irradiation, dissolve the sample in 15 ml of HCl and dilute with water to a 100-ml volume to obtain a 9 M HCl solution.

3. Take a 1 ml aliquot of this solution and mix with 10 ml of 9 M HCl. Transfer this solution to an ion exchange resin column (Note 4).

4. Elute the column with a 11-ml volume of 9 M HCl (Note 5).

5. Continue the elution with an additional 20-ml of the 9 M HCl solution (Note 5).

6. Change the molarity of the eluting reagent to 4 M HCl and continue elution until 32-ml of the 4 M HCl has passed through the column (Note 5).

7. Change the molarity of the eluting reagent to 0.5 M HCl and continue elution until a 10-ml volume has passed through the column.

8. Evaporate this solution to dryness in the presence of 1 ml of 5% NaCl solution. Then measure its radioactivity.

9. Measure the Co^{60} (and Co^{58}) gamma radioactivity by means of a 5 cm x 5 cm NaI crystal and a pulse height analyzer.

10. Obtain the Co^{60} disintegration rate in the test sample by comparing the gamma radiations at 1.17 and 1.33 Mev with those observed in a calibrated

Co^{60} standard (Note 6) measured under the same counting conditions.

11. Calculate the amount of stable cobalt in the test sample by the absolute method of calculations (Note 7).

Notes:

1. See Leddicotte(298) for additional information on separation of Co^{60} (and Co^{58}) by an ion exchange technique.

2. At least 0.40 gram of 18/8 steel was irradiated.

3. The pile at the University of Geneva (Switzerland) was used for these irradiations. Length of irradiation about 45 days.

4. 8% cross-linked Dowex-1 ion exchange resin was used. Dimensions of column: 12 cm high x 6 cm in diameter. Column was conditioned with 9 M HCl.

5. This volume was collected in a suitable container and its radioactivity measured on a γ-spectrometer. Showed presence of radioactive contaminants from activation of Cr, Fe, etc.

6. In this instance, a Co^{60} solution obtained from the Isotope Division, Atomic Energy Research Establishment (AERE), Harwell, England.

7. In this method, the following equation was used:

$$W = \frac{AM}{(6.02 \times 10^{23})(f)(\sigma_{ac})(\theta)(S)(D)}$$

where

W = weight of element, gram

A = Co^{60} radioactivity, disintegrations per second

M = atomic weight of stable cobalt

f = the neutron flux, neutrons/cm^2/sec

σ_{ac} = the activation cross-section of the reaction, $Co^{59}(n,\gamma)Co^{60}$, barns or 10^{-24} cm^2 per target atom

θ = abundance of Co^{59}

S = a factor for the production of Co^{60} during the irradiation time, t. Usually expressed as the relationship, $1-e^{-\lambda t}$, where $\lambda = 0.693/\text{half-life of } Co^{60}$.

D = a factor for the decay of Co^{60} equal to $e^{-\lambda t^1}$; t^1 = length of time from reactor discharge to counting time and $\lambda = 0.693/\text{half-life of } Co^{60}$.

PROCEDURE 23

Procedure Used In: Radioactivation analysis

Method: Precipitation

Element Separated: Co^{60} (5.27 y)

Type of Material Analyzed: Iron meteorites (306)

Type of Nuclear Bombardment: $Co^{59}(n,\gamma)Co^{60}$

Procedure By: Goldberg, et al, (306) adapted from a procedure by Young and Hall (44)

Chemical Yield of Carrier: Quantitative

Degree of Purification: Excellent

Equipment Required: Neutron source and standard laboratory equipment

Procedure:

1. Place the samples in a suitable container for irradiation (Note 1).

2. After the irradiation, dissolve approximately 0.3 g of the meteorite in a minimum amount of aqua regia.

3. Add 10 ml 6 M HCl, then dilute volume three-fold.

4. Heat and pass in H_2S until precipitation is complete.

5. Filter and wash precipitate with H_2S wash solution. Discard precipitate (Note 2).

6. Boil the solution to eliminate H_2S.

7. Add sodium phosphate reagent to the solution (Note 3).

8. Add conc. NH_4OH to solution until a pH of 5.5 is reached (Note 4).

9. Add glacial acetic acid until a pH of 3.5 is reached (Note 5).

10. Readjust pH to 3.5 with concentrated ammonium hydroxide.

11. Bring solution to boil, allow to settle, then filter through a fritted Buchner.

12. Wash with acetic acid wash solution at least five times (Note 6).

13. Make filtrate acidic with HCl (Note 7).

14. Add freshly prepared α-nitroso-β-naphthol reagent (Note 8).

15. Digest at low heat, cool, and filter.

16. Wash precipitate several times with hot 5% HCl, then several times with hot water.

17. Dry the precipitate in platinum crucible and ignite in muffle oven at 800°C (Note 9).

18. Dissolve the residue in 1:1 H_2SO_4 and transfer to a weighed porcelain crucible.

19. Evaporate carefully, then ignite at 550°C in a muffle oven.

20. Cool and weigh residue as cobalt sulfate.

21. Mount for counting on suitable radiation counter (Note 10).

Notes:

1. Authors do not indicate size of sample irradiated, place of irradiation, and length of irradiation.

2. Acid-sulfide insoluble salts removed in this step.

3. Reagent: 34.05 g of tri-sodium phosphate heptahydrate in one liter of water. 10 ml of reagent precipitates 0.05 g of iron. The solution is usually cream-colored after addition of the reagent, although it may be a clear yellow solution if the acid concentration is high.

4. Solution will be blue-grey.

5. Solution will be grey-white.

6. Reagent: 25 ml conc. acetic acid in 1000 ml of water.

7. 3 ml of 6 M HCl for every 100 ml of solution.

8. Reagent: 10 gram of α-nitroso-β-naphthol (Eastman Kodak) in 100 ml of 1:1 acetic acid. Approximately 0.5 g of α-nitroso-β-naphthol are required for every 0.01 g of cobalt. The cobalt precipitate is brick-red. If copper is present, the precipitate is brown.

9. The ignition should not take place at a temperature greater than 900°C or less than 750°C.

10. No specific information given on radioactivity measurement method or method of resolving data. Concentrations of cobalt as small as 0.53% were determined by this method.

PROCEDURE 24

Procedure Used In: Radioactivation Analysis

Method: Precipitation

Element Separated: Co^{60} (5.27 y)

Type of Material Analyzed: Meteorites,(307,308) rocks and minerals,(307,309,310) marine sediments(307,311)

Type of Nuclear Bombardment: $Co^{59}(n,\gamma)Co^{60}$

Procedure By: Smales, et al(307)

Chemical Yield of Carrier: Quantitative

Time of Separation: Several hours

Degree of Purification: Excellent

Equipment Required: Neutron source and standard laboratory equipment

Procedure:

A. Irradiation of Sample Materials

1. Irradiate known weights of test (Note 1) and standard (Note 2) samples in a neutron flux (Note 3) for at least one (1) week.

B. Radiochemical Separation

1. After irradiation, transfer the samples to 150-ml beakers and add standardized nickel, copper, and cobalt carriers (Note 4) and 5 ml of HCl (sp. gr. 1.18). Heat gently on a hot plate until the solids have dissolved (Note 5).

2. Allow the solution to cool and then dilute it to 80 ml with water; add 100 mg of Fe^{+3}, as ferric ammonium sulphate solution, 10 ml of a 10 percent solution of sodium nitrate, 5 ml of 40 percent w/v solution of ammonium citrate and ammonium hydroxide in slight excess. Precipitate the nickel by adding slowly 10 ml of a 1 percent w/v solution of dimethylglyoxime in methanol, and collect the precipitate on a Whatman No. 541 filter-paper (Note 6).

3. To the filtrate add dilute nitric acid until the solution is just acid, and then heat to 80° C and add 10 ml of a freshly prepared 1% solution of thionalde in methanol. Place the beaker on a hot-plate, stirring until coagulation of the precipitate is complete, and then collect it on a Whatman No. 541 filter-paper (Note 7).

4. To the filtrate from the copper thionalde precipitation add 20 ml of HNO_3 (sp. gr. 1.42) and evaporate to dryness. Then add 10 ml of H_2SO_4 (sp. gr. 1.84) and evaporate to fumes of sulphuric acid. Add additional quantities of HNO_3 and treat strongly to destroy completely all of the organic matter. After cooling the solution, dilute it to 250 ml with water, add a suspension of zinc oxide in water until precipitation occurs and then a slight excess, and set aside for 10 minutes before collecting the precipitate on a 15-cm Whatman No. 541 filter-paper. Discard the precipitate.

5. Heat the filtrate, and add dropwise 5 ml of a 10 percent solution of 1-nitroso-2-naphthol in glacial acetic acid, and boil for 2 minutes. Collect the precipitate on an 11-cm Whatman No. 31 filter-paper, and wash it thoroughly with hot water. Discard the filtrate.

6. Transfer the precipitate to a silica crucible. Ignite the crucible and its contents in a muffle furnace at 800° C. Cool and then dissolve the oxide residue in 5 ml of HCl (sp. gr. 1.18), warming if necessary. Make a "scavenging" precipitation by adding a few milligrams of ferric iron, precipitating it with ammonium hydroxide. Collect the precipitate on a Whatman No. 541 filter-paper. Discard the precipitate.

7. To the filtrate add 10 ml of a 40% w/v solution of KOH and carefully boil the solution until all the ammonia is expelled. Centrifuge the mixture; discard the supernatant liquid.

8. Dissolve the precipitate in 5 ml of 3 M HCl solution, transfer it to a 150-ml beaker, and add 15 ml of water, 5 ml of glacial acetic acid, and 5 ml of 60% w/v solution of potassium nitrite. Digest the solution for 5 minutes, then centrifuge. Discard the supernatant liquid.

9. Wash the precipitate with water and ethanol. Then, by slurrying it with a small amount of ethanol, transfer it to a weighed aluminum counting tray. Dry the tray and its contents under an infra-red lamp. Determine the chemical yield by weighing as potassium cobaltinitrite.

C. Co^{60} Radioactivity Measurement and Determination of Stable Cobalt

1. Count all samples and standards on suitable radiometric equipment, make any corrections necessary for background, self-absorption, and chemical yield. Calculate the stable cobalt content of the test samples by comparing the Co^{60} radioactivity found in both the test and standard samples (Note 8).

2. Check the radiochemical purity of the samples either by decay, by beta-absorption curves, or by gamma-ray spectrometry.

Notes:

1. Samples of varied weights were sealed in short lengths of polyethylene tubing.

2. Portions of a mild steel sample containing 0.016 percent cobalt were used as standard samples. These were also sealed in short lengths of polyethylene tubing. After the irradiation, dissolve the standards in $HCl-HNO_3$. To the solution add 10.0 mg of cobalt in solution and treat as for the test samples.

3. The "self-serve" and thermal column positions of the Harwell Pile were used for these irradiations.

4. Carriers used contained 10.0 mg of nickel in the form of nickel nitrate solution, 20.0 mg of copper as copper sulphate solution and 10.0 mg of cobalt as cobalt nitrate solution.

5. This treatment is adequate for the dissolution of the marine sediments. Meteorite and rock samples were dissolved in the following manner: "To these samples add 5 ml of HNO_3 (sp. gr. 1.42) and 10 ml of $HClO_4$ (sp. gr. 1.70) and evaporate to fumes of perchloric acid. Allow to cool, and then add 5 ml more of the HNO_3 and 10-20 drops of 40% w/w hydrofluric acid. Evaporate to fumes of perchloric acid; cool, and then add 5 ml of aqua regia and again evaporate to fumes of perchloric acid. If necessary, repeat this

treatment should any insoluble residue remain at this stage. Then, proceed with Step 2 of Part B of the Procedure."

6. This precipitate may be processed for nickel (See Smales, et al(307)).
7. This precipitate may be processed for copper (See Smales, et al(307)).
8. At least 10^{-8} gram of cobalt can be determined by this method.

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