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Chapter 48

Analytical Chemistry of Cobalt

by

John M. Dale and Charles V. Banks

Institute for Atomic Research and Department of Chemistry,

Iowa State University, Ames, Iowa

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Chapter 48

Analytical Chemistry of Cobalt

I. Introduction

A. History

The chemistry and metallurgy of cobalt is considered to have been initiated in the middle of the sixteenth century. However, the first man-made object to contain cobalt dates back to about 1400 B.C. (190). This was a deep-blue glass stone discovered in Nippur, Mesopotamia. Analysis of the glass showed the presence of about 0.93% of cobalt(II) oxide.

In the early part of the sixteenth century, a supposedly worthless ore was found in the mines of Saxony. This ore failed to yield copper through roasting and gave off fumes of arsenic which injured the miners health. Due to these difficulties and to the inability to refine the speiss obtained from smelting the ore, the miners called the material "kobold." This was the name of the gnome which the miners felt caused them endless trouble. In the middle of the sixteenth century it was discovered that when these ores were roasted to eliminate sulfur and arsenic, they could be fused with sand to give a beautiful blue glass called smalt (201).

Georg Brandt, assay master of the Royal Mint of Sweden, in 1742 was able to separate a new metallic element from the above mentioned ore by fire assay. He named it cobalt

after the mineral from which it had been extracted. The elemental character of cobalt was firmly established in 1780 when Torbern Bergman was able to obtain cobalt in small amounts from blue cobalt glass (190).

The manufacture of cobalt blue in Saxony was continued until about 1880. A few years prior to this time, cobalt mines were opened in New Caledonia. These mines were the principal source of cobalt until the large silver-nickel-cobalt ore deposits were discovered in Canada around 1904.

Prior to World War I, the oxide was the marketable form of cobalt and practically all of this was used as glaze and coloring on china, pottery, porcelain, and glass (201). The war caused an increased interest in ferrous alloying metals. This along with the rapidly-expanding Canadian industry was greatly responsible for the development of methods to produce the metal. Cobalt subsequently appeared on the world market from the Belgian Congo (1924), Morocco (1930), Rhodesia (1933), and several other countries including the United States (4).

The uses of metallic cobalt steadily increased until at the present time, approximately 75% of the cobalt mined is used in the metallic state (185, 201).

B. Occurrence

1. Nature

The average cobalt content of the lithosphere has been estimated to be in the range of 0.001 to 0.002% (160, 201). This is approximately 5 to 10% of the amount attributed to nickel. The cobalt to nickel ratios in acidic and basic minerals are about

1:2 and 1:10, respectively (126).

Cobalt occurs in meteorites either alloyed with iron and nickel or as the oxide. It has been identified in the spectrum of the sun. Other places of occurrence are in natural surface waters, sea water, soils, and in plants and animals. Animal tissues have been found to contain 1×10^{-5} to $7.5 \times 10^{-5}\%$ cobalt which is approximately twice the concentration of nickel found (126).

Cobalt ores occur in veins along with other minerals and also in surface concentrations of decomposition products of the weathering of basic igneous rocks (131). The kinds of rock in which these veins occur include crystalline limestone, clay-slates, conglomerates, quartzite and schists.

Approximately sixty cobalt-bearing minerals have been recorded (131, 201). Some of the more important minerals and their composition are listed in Table 48.I.

The chief world source of cobalt is the Union Miniere du Haut-Katanga in the Katanga province of the Congo. This region accounted for a little over 50% of the world mine production of cobalt in 1958 (185). The continent of Africa accounts for almost 70% of the world mine production of cobalt when the ores of Morocco and Northern Rhodesia are included.

The United States and Canada produce approximately 25% of the total cobalt ores mined. Several other countries have minor cobalt deposits which have a very small effect on the world market.

2. Industrial products

The two leading uses of cobalt are in permanent magnet

Table 48.I

Principal Minerals of Cobalt (131, 201)

Sulfides

Carrollite	CuCo_2S_4 or $\text{CuS} \cdot \text{Co}_2\text{S}_3$
Linnaeite	Co_3S_4 or $\text{CoS} \cdot \text{Co}_2\text{S}_3$ where some cobalt may be replaced by nickel, iron, or copper.

Arsenides

Smaltite	CoAs_2
Safflorite	$(\text{Fe}, \text{Co})\text{As}_2$
Skutterudite	CoAs_3

Sulfo-Arsenide

Cobaltite	CoAsS or $\text{CoS}_2 \cdot \text{CoAs}_2$
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Oxidized Minerals

Asbolite	$\text{CoO} \cdot x \text{MnO}_2 \cdot 4\text{H}_2\text{O}$, an impure mixture of manganese and other oxides containing variable proportions of CoO .
Heterogenite	A hydrated oxide of cobalt containing copper, nickel, iron, or manganese.
Sphaerocobaltite	CoCO_3
Erythrite	$\text{Co}_3\text{As}_2\text{O}_8 \cdot 8\text{H}_2\text{O}$ or $3\text{CoO} \cdot \text{As}_2\text{O}_5 \cdot 8\text{H}_2\text{O}$

alloys and in high strength, high temperature alloys. Permanent magnet alloys may contain from 3 to 36% cobalt. The ranges in the high strength, high temperature alloys are from approximately 10 to 30% cobalt in the Fe-Cr-Ni-Co alloys and nickel base alloys to 34 to 66% in the cobalt alloys (184). Cobalt also appears in some tool and wear-resisting alloys.

Cobalt is used in low-expansion alloys, constant modulus alloys, spring alloys, electrical resistance alloys, and alloys for glass-to-metal seals. Application of cobalt alloys have also been made in osteosynthesis and dental prosthesis.

Cobalt compounds are used in various industries. Cobalt sulfate is employed in the ceramic industry for decolorizing clay. The blueing of glass is obtained by an addition of cobalt oxide. Certain enamels may contain a small percentage of cobalt oxide. Organic salts of cobalt are used as driers for paints, inks, and varnishes. The petroleum industry uses cobalt compounds as catalysts for certain processes (4).

Some deficiency diseases in stock animals have been attributed to a lack of cobalt in the diet. Consequently, cobalt sulfate or chloride has been mixed with fertilizers, added directly to the feed, or to the salt-block licks.

C. Toxicology and industrial hygiene

Although sensitivity to cobalt is uncommon (144), dermatitis has been produced by powdered cobalt (167). The sensitivity is, however, less than that to nickel. A survey of workers exposed to cobalt metal dust on the whole showed no difference in health from workers of

similar type industry where cobalt was not present (43, 44). However, pulmonary symptoms among workers handling cobalt and cobalt compounds have been tentatively attributed to the metal (34). Three cases of pneumoconiosis were found in one plant where the concentration of cobalt in the air ranged from 1 to 2 mg. per cubic meter (133).

Inhalation of anhydrous cobalt(II) acetate dust is known to have caused nausea, vomiting, colicky pain, corrosion of the mucous membranes of the mouth and pharynx, and moderate intestinal hemorrhages (144, 187). Irritation of the cornea may be caused by certain cobalt ores (187). Cobalt salts or their aqueous solutions may cause erythematous papular eruptions of the skin. The cobalt carbonyls have been reported to be less hazardous than nickel carbonyl because they are less toxic and have a lower volatility (94). The hazardous properties of several other cobalt compounds have been listed (164).

Although cobalt is not considered as toxic as most of the heavy metals, precautions should be observed wherever the dust of metallic cobalt or soluble cobalt compounds is produced.

The toxic action of cobalt taken internally has been found to be low. Intravenously, it has been observed to cause paralysis of the extremities, enteritis, and death (42). The amount of injected cobalt retained by the tissues is very small, the highest concentrations being found in the glandular organs (26). Cobalt which appears naturally in

foods is generally excreted by normal processes (26, 93).

Radiation hazards have been discussed and several references given (70). The half life of Co^{60} which emits beta particles and gamma rays is 5.2 years. The permissible levels are 3 microcuries in the body, 10^{-6} microcuries per cc. in air, and 2×10^{-2} microcuries per ml. in water (164).

II. Properties

A. Physical properties

Cobalt when polished is a lustrous white metal which is similar to iron in appearance. It is harder and stronger than iron or nickel but it is not very malleable. The malleability and ductility are increased appreciably with the introduction of a small amount of carbon.

Cobalt exists in at least two allotropic modifications. At ordinary temperatures, the stable form is α -cobalt in which the atoms are arranged in a close-packed hexagonal lattice. In this respect, cobalt differs from iron and nickel in that their normal crystal structure is of the cubic system. Upon heating, cobalt undergoes a transformation at about 440°C . Above this temperature the stable form is β -cobalt which has a face-centered cubic lattice (cubic close packing).

Both forms of cobalt are ferromagnetic. The metal becomes paramagnetic at 1115°C . Table 48.II lists some of the physical properties of cobalt.

Table 48.II

Physical Properties of Cobalt (36, 137, 201)

Atomic number	27		
Atomic weight	58.94		
Melting point	1495°C.		
Boiling point	2900°C.		
Density (20°C.)	8.90 g./cc.		
Specific heat (20°C.)	0.099 cal./(g.)(°C.)		
Thermal expansion (30 to 100°C.)	0.0000143/°C. (approx.)		
Thermal conductivity (20°C.)	0.165 cal./(sec.)(cm ²)(°C./cm)		
Heat of fusion	58.4 cal./g.		
Electrical resistivity (20°C.)	6.24 microhm-cm		
Crystal structure	α Co $a = 2.5059 \text{ \AA}$ $c = 4.0695 \text{ \AA}$ β Co $a = 3.5368 \text{ \AA}$		
Curie point	1115°C.		
Tensile strength (cast, unannealed)	34,400 psi.		
Stable isotopes	59		100%
Radioactive isotopes	54	β^+	0.2 sec.
	55	$\beta^+, \text{E.C.}, \gamma$	18.0 hr.
	56	$\beta^+, \text{E.C.}, \gamma$	77 da.
	57	$\text{E.C.}, \gamma$	270 da.
	58	$\text{E.C.}, \beta^+, \gamma$	72 da.
	60	β^-, γ	5.3 yr.
	61	β^-, γ	1.65 hr.
	62	β^-, γ	13.9 min.

B. Chemical properties

1. Oxidation states

The principal oxidation states of cobalt are +2 and +3. It is present as Co(II) in practically all of its simple compounds while simple Co(III) compounds are almost nonexistent. Cobalt(III) is the principal oxidation state in complex ions, the few known complexes of Co(II) being fairly unstable. Other oxidation states which have been characterized are Co(IV), Co(I) and Co(0).

Cobalt exhibits a zero oxidation state in the carbonyls, $[\text{Co}(\text{CO})_4]_2$ and $[\text{Co}(\text{CO})_3]_4$ (37). At suitable temperature and pressure, $[\text{Co}(\text{CO})_4]_2$ may be obtained by passing carbon monoxide over the finely divided metal (136). However, the yields of this reaction are low and better results are obtained if the cobalt(II) sulfide (79) or iodide (78) is used. Reduction of $\text{K}_3[\text{Co}(\text{CN})_6]$ to $\text{K}_4[\text{Co}(\text{CN})_4]$ has been carried out by means of excess potassium in liquid ammonia (76). Water decomposes this compound with evolution of hydrogen. Compounds such as $\text{Na}[\text{Co}(\text{CO})_4]$ (13) and $\text{Co}(\text{CO})_4\text{H}$ (100) in which cobalt might be considered to be present in the -1 oxidation state may be obtained from the parent carbonyl.

The existence of Co(I) has been confirmed polarographically (84). Cobalt(II) cyanide complexes in the presence of KCN have been electrolytically reduced with almost quantitative yields to complex cyanides of Co(I) (183). Most Co(II) salts will react with aromatic isonitriles in alcoholic solution to form $[\text{Co}(\text{CNR})_4]\text{X}_2$ where X may be iodide, perchlorate, chlorate, or nitrate. Under mild reducing conditions, this compound will

form $[\text{Co}(\text{CNR})_5]\text{X}$ (125). Anhydrous Co(II) halides may be converted to $\text{Co(NO)}_2\text{X}$ by treatment with nitric oxide (77).

The "simple" salts of Co(III) are apparently limited to the fluoride, sulfate, and acetate. The solid compounds may be obtained in each case by electrolytic oxidation of the Co(II) salt in an aqueous solution of a large excess of the appropriate acid (175). They are decomposed by water.

Barium cobaltate(IV) is formed when a 2 to 1 molar mixture of barium hydroxide or barium carbonate and cobalt(II) hydroxide is heated in oxygen at 1050°C . (166). The fluorination of mixtures of potassium chloride and cobalt(II) chloride results in the formation of a complex of tetrapositive cobalt, K_3CoF_7 (101). Careful air oxidation of an ammoniacal solution of cobalt(II) nitrate results in the formation of a μ -peroxo complex of Co(III) , $[(\text{NH}_3)_5\text{Co}-\text{O}-\text{O}-\text{Co}(\text{NH}_3)_5]^{+4}$ (9). Further careful oxidation gives a complex, $[(\text{NH}_3)_5\text{Co}-\text{O}-\text{O}-\text{Co}(\text{NH}_3)_5]^{+5}$, in which cobalt may be regarded as being present as Co(III) and Co(IV) . Since no structural distinction can be made between the two cobalt atoms, the electron deficiency could be considered as being distributed over a larger section of the complex (61).

Some of the standard potential values of cobalt are listed in Table 48.III.

2. Reactions of cobalt

a. Cobalt metal

Cobalt dissolves upon heating in dilute hydrochloric or sulfuric acid undergoing dissolution less readily than iron. It is dissolved more rapidly in hot, dilute nitric acid. Strong

Table 48.III

Standard Potential Values of Cobalt (114)

	E° (volts)
$\text{Co}^{++} + 2\text{e}^{-} \rightleftharpoons \text{Co}$	-0.277
$\text{Co}(\text{OH})_2 + 2\text{e}^{-} \rightleftharpoons \text{Co} + 2(\text{OH})^{-}$	-0.73
$\text{Co}(\text{NH}_3)_6^{++} + 2\text{e}^{-} \rightleftharpoons \text{Co} + 6\text{NH}_3(\text{aq})$	-0.42
$\text{CoS}(\alpha) + 2\text{e}^{-} \rightleftharpoons \text{Co} + \text{S}^{-}$	-0.90
$\text{CoCO}_3 + 2\text{e}^{-} \rightleftharpoons \text{Co} + \text{CO}_3^{-}$	-0.64
$\text{Co}^{+++} + \text{e}^{-} \rightleftharpoons \text{Co}^{++}$	1.842
$\text{Co}(\text{OH})_3 + \text{e}^{-} \rightleftharpoons \text{Co}(\text{OH})_2 + \text{OH}^{-}$	0.17
$\text{Co}(\text{NH}_3)_6^{+++} + \text{e}^{-} \rightleftharpoons \text{Co}(\text{NH}_3)_6^{++}$	0.1

oxidizing agents tend to passivate cobalt. It is not readily oxidized on exposure to moist air at ordinary temperatures, while at elevated temperatures cobalt reacts with oxygen to form Co_3O_4 . Sulfur and the halogens also react at high temperatures to give CoS , CoX_2 , and in the case of fluorine, some CoF_3 . The effect of several different solutions on cobalt has been studied (202, 203). Other reactions of cobalt metal have been covered (87, 131).

Cobalt in finely divided form is able to absorb from 50 to 150 volumes of hydrogen. The volume is dependent upon temperature and the purity of the metal formed when reduced from the oxide (131).

b. Cobalt compounds

Alkali hydroxides precipitate the cobalt(II) ion from oxygen-free aqueous solutions at a pH of 6.8. The hydroxide occurs in a blue or pink form depending on the conditions of precipitation (85). A flocculent dark-blue precipitate is formed upon addition of hydroxide ion to a cooled solution of a cobalt(II) salt. On standing, or more readily by heating, the blue form changes to a pink form which may be obtained directly by adding the cobalt(II) solution to the alkali. The difference in color has been attributed to particle size. The presence of sugar or non-volatile organic acids prevents the precipitation of the hydroxide. Cobalt(II) hydroxide is readily soluble in dilute acids with the formation of a pink solution while a deep-blue solution is obtained upon warming the compound in a solution of excess alkali. In contact with air, the cobalt(II) hydroxide gradually turns brown due to oxidation to the hydrated cobalt(III)

oxide. In alkaline solution, oxidizing agents such as bromine or hydrogen peroxide convert cobalt(II) hydroxide to cobalt(III) hydroxide. This will not redissolve in solutions of ammonium hydroxide-ammonium chloride or in sodium cyanide.

In the absence of ammonium salts, ammonium hydroxide will precipitate a blue basic salt. The precipitation is not complete due to the ammonium ion released during the reaction (127). If sufficient ammonium chloride is present, a yellow solution is obtained which on exposure to air turns red due to the formation of cobalt(III) ammonia complexes (181). Ammonium and alkali carbonates produce red basic salts of varying composition. The normal carbonate, $\text{CoCO}_3 \cdot 6\text{H}_2\text{O}$, is formed upon addition of alkaline carbonate in the presence of an atmosphere pressure of carbon dioxide (175).

The anhydrous oxide, CoO , may be obtained by igniting the hydroxide or carbonate in the absence of air. The compound absorbs oxygen at ordinary temperatures and subsequent heating gives higher oxides (115).

All of the cobalt(II) halides have been characterized (131). The solubility in water increases from the moderately soluble fluoride to the very soluble iodide. These may be obtained by the reaction of the elements at high temperatures. From aqueous solution they are obtained as the hydrates as are all of the soluble salts of cobalt(II).

Hydrogen sulfide completely precipitates the cobalt(II) ion from solutions made basic with ammonium hydroxide as a black amorphous cobalt(II) sulfide ($\alpha\text{-CoS}$) (151). If oxygen is

excluded from the reaction, the precipitate formed is relatively soluble in cold dilute hydrochloric acid. Otherwise the material becomes quite insoluble upon standing for 10-15 minutes. When air is not excluded or if the sulfide is exposed to air, an oxygenated compound is formed which is no longer completely soluble in dilute hydrochloric acid (11). No precipitate is formed with hydrogen sulfide in the presence of mineral acids. In acetate solutions a crystalline sulfide (β -CoS) is formed which is practically insoluble in cold dilute hydrochloric acid. The amorphous sulfide tends to form colloidal dispersions which may be flocculated by boiling with acetic acid. Cobalt sulfide is readily soluble in concentrated nitric acid or in agua regia. The sulfur which separates out is oxidized further to sulfate by continued treatment with nitric acid. Cobalt(II) sulfide is precipitated from ammoniacal solutions by ammonium thioacetate. Sodium thiosulfate produces no precipitate in acid solutions while a partial precipitation of CoS occurs when a solution of Co(II) ion is boiled with this reagent.

The addition of an alkali cyanide to a neutral solution of a Co(II) salt precipitates the trihydrate, $\text{Co}(\text{CN})_2 \cdot 3\text{H}_2\text{O}$. An excess of cyanide ion converts this to a soluble cobalt(II) cyanide complex which upon warming is oxidized to a cobalt(III) cyanide complex. The hexacyanoferrate(II) ion precipitates Co(II) as the green $\text{Co}_2\text{Fe}(\text{CN})_6$ and the hexacyanoferrate(III) ion gives the brownish-red $\text{Co}_3[\text{Fe}(\text{CN})_6]_2$. These are relatively insoluble in hydrochloric acid.

In the presence of sufficient Co(II) ion, soluble chromates will precipitate a brownish-red basic cobalt(II) chromate from neutral solution. Oxalates precipitate a pink Co(II) oxalate which is practically insoluble in water. A red cobalt(II) phosphate, CoHPO_4 , is formed upon addition of disodium hydrogen phosphate to a solution of Co(II) ion. Soluble arsenates and arsenites also precipitate the Co(II) ion. All of these precipitates are soluble in mineral acids or ammonium hydroxide. Other cobalt(II) compounds have been covered (131, 151, 175).

3. Complexes of cobalt

Cobalt(II) is able to form some complexes, however, the number is very small in comparison with that of cobalt(III). The complexes of cobalt(II) are normally tetravalent, some hexavalency does occur, while the cobalt(III) complexes are always hexavalent. Magnetic data indicates that cobalt(II) complexes with coordination numbers of four and six usually use outer orbital bonding (170). Cobalt(II) has a strong affinity for nitrogen donors.

The number of ammonia molecules taken up by cobalt(II) salts does not normally exceed six and may be less. The hexammines are ionic compounds containing the octahedral structure $[\text{Co}(\text{NH}_3)_6]^{+2}$. The tetrammines are nonelectrolytes indicating coordination of the anions of the salt $[\text{Co}(\text{NH}_3)_4\text{X}_2]$. The diammines which are also nonionic are apparently of a planar structure (69) giving rise to cis and trans isomerism. Other nitrogen containing compounds including amines and substituted amines may replace ammonia in the complexes. The cobalt(II)

ammine complexes are not appreciably stable and are decomposed by water.

Complexes of cobalt(II) with oxygen donors are less stable than with nitrogen. Some of the complexes which have been characterized are the carbonato-compounds, $K_2Co(CO_3)_2 \cdot 4H_2O$ (5); oxalato complexes, $K_2CoOx_2 \cdot H_2O$ (28, 31, 39); and the nonelectrolytic β -diketone complexes.

With excess cyanide ion, cobalt(II) forms a pentacyano-complex, $[Co(CN)_5]^{-3}$ (151), which is unstable due to its tendency to be oxidized to the cobalt(III) complex, $[Co(CN)_6]^{-3}$ (15). Other complexes include the tetravalent thiocyanates, $K_2[Co(CNS)_4]$ (90), and the complex cobalt(II) halides (175).

Cobalt(III) has a very strong tendency to form complex compounds. Normally the most stable complexes are those in which cobalt is bonded to nitrogen. These are followed by the complexes in which cobalt is bonded to carbon (in the cyanides), oxygen, sulfur, and the halogens in order of decreasing stability (175). The relative stability, however, will depend also on the whole molecule of which the donor atom is a part and the nature of the other ligands bonded to the cobalt.

A large majority of the known cobalt(III) complexes are ammines. The number of ammonia molecules may vary from six to two, the hexammine complex being the most stable. The stability of the complex, $[Co(NH_3)_6]^{+3}$, is decreased if a hydrocarbon is substituted for a hydrogen atom of the ammonia molecule. This effect is more than compensated for if the ligand contains more than one nitrogen atom thereby permitting chelation. The

nitrogen atoms, however, must be positioned in the molecule in such a manner to permit formation of an unstrained ring. Hence the ethylenediamine complex, $[\text{Coen}_3]^{+3}$, is more stable than the parent complex, $[\text{Co}(\text{NH}_3)_6]^{+3}$. The six coordination positions may be filled by different combinations of ammine, water, and negative groups, e.g., $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})(\text{NO}_2)_2]^{+1}$ (175).

The hexacyanocobaltate(III) ion shows greater stability than the corresponding complexes of chromium(III), manganese(III), or iron(III). The complex may be formed by passing oxygen through a solution of a cobalt(II) salt in the presence of excess cyanide. The complex forms precipitates with the heavy metals whereas the hexacyanocobaltate(III) salts of the alkali metals are soluble. Evaporation of a solution of the potassium salt of the complex with nitric or sulfuric acid and extraction of the residue with water gives hexacyanocobalt(III) acid.

Other complexes which have been characterized include the isothiocyanato-, nitrito-, nitro-, nitrato-, β -diketone-, carbonato-, oxalato-, dithiooxalato-, malonato-, sulfato-, sulfito-, halo-, and bridge complexes. These complexes have been discussed (175) with the inclusion of the original references.

III. Sampling of cobalt-bearing materials

The principles and methods of sampling are covered in Chapter 4, Part I, of this treatise. Sources of specific sampling information for various types of material are tabulated.

IV. Separation and isolation of cobalt

A. Decomposition of sample

1. Metals

Methods of dissolving metals and alloys are available from several sources (3, 120, 127, 169). Cobalt metal dissolves slowly in hot, dilute hydrochloric or sulfuric acid while dissolution in hot, dilute nitric acid is more rapid.

Most of the ordinary cobalt alloys will dissolve in nitric acid. Others such as those of cobalt, chromium, and tungsten require other methods. Several fusion methods have been described (169); however, the most suitable method involves the use of perchloric acid. Dissolution is facilitated by first reducing the particle size of the sample to approximately 100 mesh. A mortar of sufficient hardness should be used so as to not contaminate the sample. The sample in a covered beaker is then treated with 1:1 perchloric acid and heated to fumes after which the cover is removed and the solution is fumed strongly. Hot water is added with stirring and the insolubles are allowed to settle. The solution is filtered and the insoluble material which contains tungsten(VI) oxide is washed with hot dilute hydrochloric acid followed by cold water. The insoluble materials are washed into the original beaker and the tungsten precipitate is dissolved by heating with a small amount of concentrated ammonium hydroxide. The solution is filtered through the same filter paper and the insolubles are washed with hot water, the filtrate being reserved for the determination of tungsten. The residue is thoroughly washed back into the beaker with hot dilute

hydrochloric acid followed by water. The filter paper is reserved for combination with the solution containing the tungsten. The residue is treated again with perchloric acid as described above, the corresponding solutions being combined with those from the first treatment. This is repeated until all of the material is in solution.

Ferro-cobalt is taken into solution by first treating the sample with concentrated nitric acid. After the action has ceased, an equal volume of (1:1) sulfuric acid is added and the solution is fumed to dryness. The salts are taken up with dilute sulfuric acid (1:20) and the solution is boiled until all of the salts are dissolved. This procedure may also be used for metallic cobalt.

Cobalt-base alloys are taken into solution by first treating the sample with concentrated hydrochloric acid until most of the sample has dissolved. Nitric and perchloric acids are added and the solution is evaporated to fumes of perchloric acid. The solution is cooled, diluted with water, and boiled to remove the free chlorine.

Alloy steels including stainless steels are dissolved in aqua regia by heating gently until only the carbides and silica remain as the precipitate. The solution is diluted with water and filtered. The paper is washed with dilute hydrochloric acid (1:50) and then thoroughly with water. Cobalt is in the filtrate.

2. Minerals, ores, and refractories

Methods of decomposition of minerals, ores, and refractories have been tabulated (120). Acids and fluxes necessary for the

dissolution of specific materials are included.

Prior to the dissolution of ores, the material is ground to a fine powder. The majority of cobalt ores contain cobalt as an arsenide or sulfide both of which may usually be dissolved with concentrated nitric acid, aqua regia, or a mixture of nitric and sulfuric acids. Hydrochloric acid is obviously not used for silver-bearing ores.

For the dissolution of silicate rocks containing cobalt, the following method may be used (161). The finely powdered basic rock (0.25 gm.) or acid rock (0.5 gm.) is weighed into a platinum dish, a few milliliters of water added, followed by 0.5 ml. of 70% perchloric acid and 2.5 ml. hydrofluoric acid. The mixture is evaporated to dryness, the residue taken up in 0.5 ml. perchloric acid and 2 or 3 ml. of water, and the solution is again evaporated to dryness. The residue is treated with 1 ml. of concentrated hydrochloric acid and 5 ml. of water, and heated to bring all of the soluble material into solution. Five milliliters of 10% sodium citrate solution is added, the solution is neutralized with concentrated ammonium hydroxide using litmus paper, and a few drops of ammonium hydroxide is added in excess. If an appreciable amount of residue is left at this point, it is filtered, washed with water, and ignited. The ignited residue is fused with approximately 0.1 gm. of Na_2CO_3 and cooled. This is taken up with excess dilute hydrochloric acid and heated. Three milliliters of sodium citrate is added, the solution made slightly ammoniacal, and combined with the original solution.

Cobalt oxides are treated with concentrated hydrochloric acid and heated in a covered beaker until most of the acid has evaporated. The solution is evaporated to dryness at a low heat, sulfuric acid (1:1) is added and the solution is fumed to dryness. The material is taken up with sulfuric acid (1:1) followed by water and the solution is boiled. If a large amount of insoluble material remains, it is filtered, ignited in a platinum crucible, and treated with hydrofluoric and sulfuric acids to volatilize any silica. After fuming, the solution is diluted and added to the main solution.

Refractory materials are treated with nitric acid after which the insoluble material is filtered off. This is washed with ammonium acetate, ignited, and fused with a mixture of sodium and potassium carbonates. The cooled fusion mixture is taken up with hot water and hydrochloric acid and all of the solutions are combined.

B. Selective separation methods

1. General methods

Separation of the hydrogen sulfide group may be made in the usual manner with the following precautions. Tin(IV) carries down some cobalt as a mixed sulfide while tin(II) does not. It is reported that this difficulty may be overcome by making the precipitation from a hot 1 M solution of hydrochloric acid containing acrolein (48). Coprecipitation of cobalt with zinc sulfide also occurs. This is prevented by adding acrolein before treating with hydrogen sulfide after which gelatin is added to promote coagulation of the colloidal zinc sulfide (21).

Cobalt is commonly classed with the elements which are not precipitated by ammonia. However, part of the cobalt will always be found in the ammonia precipitate under ordinary conditions of precipitation. It has been found that 2 mg. of cobalt is almost completely retained by 100 mg. of the hydroxides of aluminum, iron, titanium, zirconium, and thorium (142). Therefore, it is nearly impossible to completely separate cobalt from large amounts of these metals by this method even though repeated precipitations are made. A good separation is possible if potassium cyanide is added before the precipitation of iron but cyanide is objectionable for the subsequent determination of cobalt (119).

Zinc oxide has been extensively used for precipitating interfering elements prior to the determination of cobalt (80, 82, 119, 142, 169, 201). A suspension of zinc oxide has a pH of about 5.5 and is useful for precipitations in solutions containing sulfuric acid or sulfates. After separation of the hydrogen sulfide group, zinc oxide is commonly employed for the separation of cobalt from such elements as trivalent iron and chromium. For example, an oxidized solution of steel from which most of the acid has been evaporated is shaken with an increasing number of small portions of a freshly prepared suspension of zinc oxide (50 g. per 300 ml. of water). The addition of the suspension is continued until the supernatant liquid has a milky appearance after the precipitate has settled. The precipitate contains all of the phosphorus, aluminum, titanium, vanadium, chromium, iron, arsenic, zirconium, tin, tungsten, uranium, and most of the

molybdenum, copper, and silicon. Almost all of the manganese and cobalt will be in the filtrate. Small quantities of lead, molybdenum, silicon, copper, and antimony will be in the filtrate if they were present in the sample in large amounts and also any unoxidized iron and tungsten. A complete description of the elements which are precipitated by zinc oxide has been made (119). Some cobalt is retained in the iron precipitate and it is therefore necessary to make two precipitations, three precipitations being required for very accurate work (201). It has also been stated that it is difficult to make sure that the last traces of iron have been removed from solution (204) and that the method does not lend itself to precise control. After separation, cobalt cannot be determined directly by electrolysis and precipitation with α -nitroso- β -naphthol is normally carried out. This limits the amount of cobalt to approximately 50 mg. Beyond this amount, it is difficult to ensure complete precipitation of the cobalt without contamination from occlusion (204).

Some texts list a method whereby the zinc oxide separation is carried out in a volumetric flask and an aliquot of the supernatant liquid is taken for analysis. It has been reported that this practice may be unsatisfactory even for routine work (204).

A separation of cobalt from iron has been described whereby iron is precipitated by sodium phosphate (141). This method with some alterations has been applied to the determination of cobalt in materials containing a high percentage of cobalt

(201, 204). Separation is carried out after removing silica, barium, and lead by dehydration with sulfuric acid. Elements such as copper, bismuth, arsenic, antimony, and molybdenum are eliminated with hydrogen sulfide. At a pH of 3.5, phosphate precipitates aluminum, zirconium, titanium, and uranium with the iron while manganese, vanadium, chromium, nickel, and cobalt remain in solution. Zinc may be removed with phosphate by careful adjustment of the pH. Interference from chromium and vanadium may be eliminated by a sodium hydroxide separation. It should be noted that uranium phosphate tends to occlude cobalt and a double precipitation should be made if a large amount of this element is present. This method gives a filtrate in which cobalt may be determined directly by electrolysis. If nickel is present, it will be plated out with the cobalt. In this case, the deposit is dissolved and the nickel is determined with a vic-dioxime such as 1,2-cycloheptanedionedioxime or dimethylglyoxime, the cobalt being obtained by difference.

Several other separation methods have been compiled (80, 169) and the difficulties and objections to certain methods have been discussed (23, 40, 165).

2. Solvent extractions

The subject of solvent extraction in analytical chemistry has been recently reviewed (138). Several compounds have been used as extractants for cobalt. These include acetylacetone (138), 1-nitroso-2-naphthol (186, 188), isonitrosoacetophenone (107), diethyldithiocarbamate (111), diphenylthiocarbazone (161), cupferron (7), 1-(2-pyridylazo)-2-naphthol (22), 8-quinolinol (135),

2,2',2''-terpyridyl (134), potassium thiocyanate (12, 18), tetraphenylarsonium chloride (138), triphenylmethylation chloride (33,35), and potassium xanthate (24, 110).

Acetylacetone forms chelates with a large majority of the metals giving complexes which are in many cases soluble in organic solvents (138). The fact that Co(III) forms an extractable complex while Co(II) does not, permits a separation from several metals including Ni(II) which is likewise not extracted. The metals which form extractable complexes with the reagent are extracted from an approximately neutral solution with either acetylacetone or an acetylacetone-chloroform mixture. The Co(II) in the aqueous phase is then oxidized with hydrogen peroxide to Co(III) which is quantitatively extracted subsequent to acidification to pH 1.

From 0.5-10 μ g. of cobalt in approximately 20 ml. of sample solution may be determined colorimetrically after an extraction using 1-nitroso-2-naphthol (19). The extraction is accomplished from a solution of pH 5.0-7.0 with a 1% solution of the reagent in a mixture of carbon tetrachloride and ethanol. Interfering complexes and some of the excess reagent are removed from the organic layer with concentrated hydrochloric acid. After proper treatment, the absorbancy of the cobalt complex in the organic phase is determined. This reagent has also been used for the separation of microgram quantities of cobalt in the analysis of biological materials (154). A recovery of 95% for microgram quantities of cobalt added to 25-gram samples of bone was reported.

Diphenylthiocarbazone (dithizone) dissolved in carbon tetrachloride has been used to extract microgram quantities of cobalt from solutions at pH 8 containing citrate (161). Metals which form dithizonates in acid solution may first be removed from a citrate solution at pH 3-4 with a solution of dithizone in chloroform (138). The cobalt is left in the aqueous phase.

Solutions of 8-quinolinol in chloroform may be used to extract up to 10 mg. of cobalt from neutral or basic solutions (135). Several metals may be removed at lower pH with this reagent prior to the extraction of cobalt.

Subsequent to masking of Fe(III) and U(VI) with potassium thiocyanate and ammonium fluoride, cobalt may be extracted with a solution of tetraphenylarsonium chloride in chloroform (138). Cobalt is determined spectrophotometrically in the chloroform layer at 615 m μ after reducing any copper which may be present.

The thiocyanate complex of cobalt has been used as a means for the extraction of microgram quantities of cobalt with a mixture of amyl alcohol and ether. The extraction of Fe(III) is prevented by masking with citrate. Cobalt is back extracted into aqueous solution with 2 M ammonium hydroxide. It is finally determined by the nitroso-R-salt method.

3. Ion exchange

A selective review of the recent literature of ion exchange has been made (108). Reference is made to several books of general interest to the analytical chemist (98, 109, 153). The use of ion exchange and its applications to trace analysis have been reviewed (106) and the analysis of ion exchange materials

has been covered (47).

Cobalt has been isolated and determined as the nitroso-R-salt complex employing chromatographic ion exchange (29). Application is made to the determination of cobalt in steels and copper- and nickel-base alloys where interferences due to copper, chromium, nickel, and iron are eliminated. The red nitroso-R-salt complex of cobalt is formed in the usual manner (128). After acidification the solution is passed through an acid-washed alumina column. The cobalt complex and the excess unreacted nitroso-R-salt are adsorbed while the other metal ions pass through the column. The excess reagent is eluted with hot 1 M nitric acid followed by elution of the cobalt complex with 1 M sulfuric acid. After proper dilution, cobalt is determined colorimetrically in the sulfuric acid solution.

The cyanate complex of cobalt(II) has been used in separating cobalt and nickel on an anion exchange resin (205). Separation is reported for cobalt to nickel ratios of 1:50. Cobalt is determined photometrically. Anion exchange resins in the citrate form have been used to quantitatively separate Fe(III), V(IV), Co(II), Ni(II), and Cu(II) from solutions containing alkali metals (158). An anion exchanger in the chloride form after treatment with a citrate solution may be used for the separation of Mg, Ca, Sr, and Ba from V(IV), Fe(III), Cu(II), Ni(II), and Co(II) (159). The separation of the bromide complexes of Co(II), Cu(II), Zn(II), and Ga(III) is possible by anion exchange in hydrobromic acid solution (75).

A separation of heavy metals as their chloro complexes at elevated temperature has been investigated (17). The column containing the anion exchange resin is surrounded by a thermostat maintained at 80°C. A 20% hydrochloric acid solution containing cobalt and nickel is passed through the column followed by three 40-ml. portions of 20% hydrochloric acid which elutes the nickel. Cobalt is eluted by 300 ml. of water at room temperature. An anion exchange paper has been prepared by impregnating filter paper with a strongly basic anion exchange resin (67). It was used in separating the chloro complexes of Co and Ni by elution with 8 M hydrochloric acid.

In order to increase the selectivity of ion exchange resins, chelating compounds have been incorporated into the resin structure (145). An 8-quinolinol resin has been reported to be very effective in the separation of cobalt from copper.

Anion exchange separations have been applied to the determination of nickel, manganese, cobalt, and iron in high-temperature alloys (66). Niobium, tantalum, tungsten, and silicon are removed after dehydration with hydrochloric acid and molybdenum and copper are precipitated with hydrogen sulfide. After treatment with hydrogen peroxide, the filtrate is loaded onto the anion exchange column. Nickel, manganese, and chromium are eluted with 9 M hydrochloric acid, cobalt with 4 M hydrochloric acid, and iron with 1 M hydrochloric acid. The cobalt was determined by electrolysis.

Separation of the constituents of a permanent magnet material (Al, Ni, Co, Cu, Fe) has been carried out with the

aid of an anion exchange resin in the chloride form (193).

Copper is first determined electrolytically after which the other ions in 9 M hydrochloric acid are added to the column. Aluminum and nickel pass through while cobalt and iron are adsorbed.

Cobalt is eluted with 4 M hydrochloric acid.

Anion exchange resin in the chloride form has been used for the separation of trace elements from neutron- or cyclotron-irradiated biological tissue ash (74). Carrier salts of iron, cobalt, and zinc were prepared to which was added Fe^{59} , Co^{60} , Zn^{65} , and P^{32} . After proper treatment, 2 ml. of a solution of the ions was loaded onto the column. Phosphorus was eluted with 12 M hydrochloric acid and the cobalt, iron, and zinc were eluted with 50 ml. each of 4 M, 0.5 M, and 0.005 M hydrochloric acid, respectively. The recovery of the radioactive components was reportedly better than 98% with no cross contamination of the cobalt, iron, and zinc fractions.

Millimicrogram quantities of cobalt in biological materials have been separated and determined (179). After treatment of the sample to remove the organic material, the hydrochloric acid solution of the ions is extracted with isopropyl ether to remove the iron. The remaining trace elements are then loaded onto an anion exchange column and the cobalt is selectively eluted with 4 M hydrochloric acid. Recovery of Co^{60} present as vitamin B_{12} or as inorganic cobalt was 90-100%. Cobalt was determined spectrographically in a d.c. arc using nickel as an internal standard. The sensitivity limit was reported to be 10^{-9} g. of cobalt with a standard deviation equal to or less than 10% in

the $1-500 \times 10^{-9}$ g. range.

4. Chromatography

Trace amounts of cobalt, nickel, copper, and zinc have been separated by paper chromatography with a final spectrophotometric determination of each element (54). The experimental solutions contained 2.5-10 $\mu\text{g.}$ of cobalt and nickel and 25-100 $\mu\text{g.}$ of copper and zinc in 10-40 microliters of solution. After separation cobalt was determined by measuring the absorbancy of the 2-nitroso-1-naphthol complex in isoamyl alcohol at 550 $\text{m}\mu$. Several solutions containing 0.5-2.0 $\mu\text{g.}$ of the ions gave 96-100% recovery.

A solvent mixture of acetone-hydrochloric acid-water has been used for the separation on paper of several mixtures of ions which included the following: Cd, Pb, Cu, Co, Ni; Zn, Cu, Pb, Co, Ni; Hg, Ag, Cu, Pb, Co, Ni; Zn, Co, Ni (122). The R_f values are recorded and variables which affect the values are discussed.

After extraction from an aqueous solution at pH 5.0, the 8-quinolinolates of Cu(II), Ni(II), Co(II), Fe(II), Al(III), Ga(III), and In(III) were separated by adsorption chromatography of the chloroform solutions (81). Silicic acid columns were used and elution was carried out with chloroform and chloroform-ethanol mixtures. The 8-quinolinolates of Al(III), Bi(III), Cd(II), Co(II), Cu(II), Fe(III), Hg(II), Ni(II), and Zn(II) have been resolved on paper using butyl alcohol containing 20% of concentrated hydrochloric acid (150). The solvent decomposed the organic complexes and the metals moved as chloro complexes.

The 2-thenoyltrifluoroacetone chelates of different mixtures of Fe(III), Co(II), Ni(II), Mn(II), and Cu(II) have

been resolved (14). Separations of Fe, Co, Ni; Fe, Ni, Mn; Co, Ni, Cu; and Ni, Mn, Cu were made with various mixtures of methyl alcohol, benzene, and glacial acetic acid on plain paper or paper impregnated with sodium chloride or aluminum oxide. The iron and copper chelates were visible while a spray of 1% sodium sulfide revealed the cobalt and dimethylglyoxime and benzidine revealed the nickel and manganese, respectively. The chromatography of several inorganic cations including Co(II) has been studied using filter paper impregnated with potassium nitrate, ammonium nitrate, sodium nitrate, or sodium chloride (116). In some cases the R_f values differ from those observed with untreated paper and better separations are possible.

A systematic investigation of the R_f values of 79 elements has been made using ascending development with 1:1 mixtures of butanol and various concentrations of hydrochloric acid (63). The most favorable conditions for the separation of elements of the same periodic group and some of different groups are given. Included are conditions for the separation of cobalt and nickel. An ascending paper chromatographic technique may be used for the separation of mixtures of the 1-nitroso-2-hydroxy-3-naphthoic acid complexes of Co, Pd, and U(VI) (27). The solvent consists of a mixture of acetone, isobutyl alcohol, and concentrated hydrochloric acid.

A rapid separation of many cations prior to detection and estimation has been achieved by application of high-voltage paper electrophoresis (62). The metals, Hg, Mn, Pb, Co, Ni, Fe, and Cu, in a citric acid solution adjusted to pH 5.5 with ammonia

as a buffer and complexing agent, were separated in 45 minutes at 100 volts per cm. The cations were detected by spraying the chromatograph with ammonium sulfide and sodium peroxide solutions. Quaternary mixtures of Co, Cd, Pb, Bi; and Co, Cu, Pb, Cd, have been effectively separated electrochromatographically on a 10-cm. filter paper strip at 150 volts (123). A study of the separation of the ions and their rate of migration in electrolytes of different concentrations was made. Electrochromatographic separations of cations has been investigated using filter paper saturated with ammonium hydroxide and ammonium tartrate (124). A separation of Ni(II), Co(II), Mn(II), Zn(II), Sb(V), Al(III), and Cr(III) was reported.

Methods of separation of fourteen cations including cobalt have been devised using the ring furnace technique (191). A sample drop of approximately 0.0015 ml. was found to be adequate, the ions being separated into four groups.

Complete resolution of a mixture of Tl, Hg, Cd, Bi, Fe, Ni, Cu, and Co was achieved by gradient-elution chromatographic analysis (117). The initial solvent, butyl alcohol saturated with normal hydrochloric acid, was treated with additions of concentrated hydrochloric acid, the rate of addition being related to the speed of development.

An adsorption-precipitation chromatographic method for separation of nickel and cobalt has been described (65). A column was prepared which consisted of a mixture of ten parts of charcoal to one part dimethylglyoxime packed over a layer of pure charcoal. This was used for removing nickel from cobalt salt

solutions.

Cobalt has been determined in ferrous alloys using a chromatographic separation. Methods are described for use in the presence and absence of tungsten (177). Interfering elements are chromatographically separated with ethyl methyl ketone and hydrochloric acid and the cobalt is determined with 1-nitroso-2-naphthol.

The chromatographic separation of several elements in different oxidation states has been studied (147). It is reported that a rapid separation of Co(II) and Co(III) is attained on filter paper with a solvent mixture of hydrochloric acid, water, ether, and methyl alcohol. A separation of cobaltamine complexes is also covered.

V. Detection and identification

A. Spot tests

1. Thiocyanate and acetone

When thiocyanate is added to an acid solution of a cobalt(II) salt, a dark blue color is formed if acetone is also present (102). A drop of slightly acid test solution is placed on a spot plate followed by five drops of acetone which has been saturated with ammonium thiocyanate. Nickel will interfere giving a blue color when it is present in large amounts. However, if the volume of the solution is adjusted so that the nickel concentration is 0.2% or less, nickel produces only a light green color. Under these conditions, 0.5 μg . of cobalt per drop (0.05 ml.) of test solution will produce a definite blue color which is distinguishable from the color produced by the nickel (45). The interference due

to copper(II) ions may be eliminated by reducing copper(II) to copper(I) with sodium sulfite. Copper(I) thiocyanate precipitates as a white solid upon addition of the reagent. Iron(III) ions react with thiocyanate to give a red solution which may obscure the cobalt color. In the presence of fluoride the iron(III) is complexed and no longer reacts with thiocyanate. If the presence of iron is suspected, ammonium fluoride crystals are added prior to the addition of the reagent. In this manner, 1 μ g. of cobalt may be detected in 3 drops of test solution in the presence of 1 mg. of iron.

2. α -Nitroso- β -naphthol

In neutral, ammoniacal, or acetic acid solution, cobalt reacts with α -nitroso- β -naphthol to form a red-brown precipitate which is suitable for the detection of 0.05 μ g. of cobalt with a dilution limit of 1 in 1,000,000 (45, 46). Cobalt(II) is oxidized, at the expense of the reagent, to cobalt(III) which forms the complex.

A drop of the slightly acid or neutral test solution is placed on a filter paper followed by a drop of the reagent (1 g. in 100 ml. of 1:1 acetic acid). If cobalt is present, a brown stain will appear.

In the presence of iron, a drop of the acid test solution is placed on a spot plate followed by a drop of reagent (1% solution in acetone) and a few drops of a 10% solution of

trisodium phosphate. A brown color indicates the presence of cobalt. In this manner 0.5 $\mu\text{g.}$ of cobalt may be detected in the presence of 1000 times this amount of iron with a dilution limit of 1:100,000. Uranyl salts react with the reagent to give a yellow precipitate. This interference is eliminated by the addition of ammonium phosphate before carrying out the test as in the case of iron. The limit of detection is 0.25 $\mu\text{g.}$ in the presence of 1000 times this amount uranium with a limit of dilution of 1 in 200,000.

Copper(II) salts react with the reagent to give a brown precipitate which interferes. This is eliminated by the reduction of copper(II) to copper(I) iodide, the iodine formed in the reaction being removed with sodium sulfite. Equal drops of the test solution, 2 M hydrochloric acid, and 10% potassium iodide solution are mixed on a spot plate and a small amount of sodium sulfite is added. This is followed by a drop of the 1% acetone solution of the reagent and several drops of a saturated solution of sodium acetate. In this manner 0.2 $\mu\text{g.}$ of cobalt will give a brown stain in the presence of 2500 times this amount of copper with a dilution limit of 1 in 250,000.

3. Triphenylsulfonium bromide

A blue, chloroform-soluble substance is precipitated when triphenylsulfonium ion or tetraphenylarsonium ion is added to a solution containing cobalt(II) and an excess of thiocyanate (148).

The blue color imparted to the chloroform layer upon extraction is the basis for a sensitive test for cobalt.

Five or ten drops of the slightly acid test solution is placed in a small test tube. One or two drops of a 5% aqueous solution of triphenylsulfonium bromide or a 1% solution of tetraphenylarsonium bromide and one or two drops of 10% ammonium thiocyanate are added. The solution is extracted with a few drops of chloroform, the chloroform layer becoming blue in the presence of cobalt. The maximum color development is obtained at a pH of 3.5 but the acidity is not critical. The limit of identification is about 0.05 $\mu\text{g.}$ of cobalt per test drop (0.05 ml.), corresponding to a dilution limit of 1 to 1,000,000. A greater sensitivity may be obtained by using a volume of chloroform less than that of the test solution.

The extent of interference due to other ions was studied by performing the test on solutions containing 5 and 500 $\mu\text{g.}$ per ml. of cobalt ion and the foreign ion, respectively. Zinc(II) and tin(IV) prevents the full development of the blue color but this interference is minimized by using a large excess of thiocyanate and "onium" reagent. Interference due to iron(III), bismuth(III), and uranium(VI) is eliminated by the addition of 1 or 2 drops of 10% ammonium fluoride solution to the test solution. The addition of sodium thiosulfate prevents interference from ruthenium(III), palladium(II), and platinum(IV). Interference from copper(II) is eliminated by reducing it to copper(I) with iodide ion, the iodine formed being reduced with sodium thiosulfate.

B. Spectrochemical

Several references are available for the general theory and methods of spectrochemical analysis

(2, 20, 72, 73, 139). The limit of detection for cobalt has been placed at about 0.0002%. The most sensitive lines are at 3453.505 Å and 3405.120 Å, however, cobalt has many sensitive lines providing a wide selection for analysis. The possible interfering lines of other elements within ± 0.4 -0.5 Å of these two sensitive lines of cobalt have been tabulated (2).

VI. Determination of cobalt

A. Gravimetric methods

1. α -Nitroso- β -naphthol

The precipitation of cobalt with α -nitroso- β -naphthol, one of the first methods for determining a metal with an organic reagent (86), is probably the most widely used method for cobalt analysis (3, 80, 169). The reagent is not a selective precipitant and preliminary separations must be made. Copper, palladium, and iron are quantitatively precipitated with cobalt from neutral or slightly acid solution (194) while tin, silver, chromium, uranium, vanadium, and bismuth are partially precipitated. Beryllium, aluminum, manganese, nickel, arsenic, antimony, cadmium, mercury, lead, and the alkaline earths and alkali metals are not precipitated. However, in the presence of large quantities of these metals not normally precipitated by the reagent, the voluminous cobalt precipitate may carry down other ions and a second precipitation is recommended. Most of the more common elements which may interfere except chromium and vanadium are removed with the hydrogen sulfide group or with iron in the phosphate separation. Fifty milligrams has been suggested as a

limit for the amount of cobalt which can be readily precipitated by this method (204). The cobalt precipitate is not weighed directly but is either converted to Co_3O_4 (25), to the sulfate (41), or reduced to metal (82). It should be noted that an abrupt decomposition of the cobalt precipitate occurs at approximately 270°C . in the process of its conversion to the oxide (32). The oxide is only a fairly accurate form in which to weigh cobalt. It is reported that the optimum temperature range for ignition of the sulfate is from 600° to 812°C . and an accuracy better than 1% cannot be expected.

2. Potassium hexanitritocobaltate(III)

The precipitation of cobalt as potassium hexanitritocobaltate(III) is generally described as a method for the separation of cobalt from nickel after most all other elements have been removed (80, 169). A modified form of the method, however, indicates that the presence of tartaric acid as a complexing agent allows the separation of cobalt from most of the elements encountered in metallurgical analysis (91). It is reported that the elements of the hydrogen sulfide group do not interfere and elements such as aluminum, titanium, chromium, iron, zirconium, niobium, molybdenum, tantalum, and tungsten are held in solution while cobalt is quantitatively precipitated.

If large quantities of both iron and arsenic are present the latter must be removed. Soluble salts of barium, calcium, strontium, and lead interfere with the separation of cobalt from nickel. These elements may be filtered off if sulfuric

acid is used in the decomposition of the sample. Magnesium sulfate and the amount of calcium soluble in dilute sulfuric acid do not interfere. Cobalt was finally determined by electrolysis but other methods were suggested.

3. Electrolytic

The electrolytic method of determining cobalt has been described as the most satisfactory and accurate method except for small amounts of cobalt (80, 169, 182). A preliminary separation of cobalt is necessary and the method is not a separation from copper or nickel. Recent evaluations of several existing methods have shown that slightly high results are obtained in almost every case even though traces of cobalt remain in the electrolyte (66, 157). The cobalt remaining in solution may be neglected for large cobalt samples but becomes increasingly important for smaller quantities and is generally determined by colorimetric methods.

In a study of ten generally used procedures, the amount of cobalt remaining in the electrolyte varied from 0.01 to 4.0 mg. with an average of 0.46 mg. for 43 determinations (157). This was shown to be due to losses during removal and washing of the deposits. A modified method of washing the deposit by replacing the electrolyte bath with distilled water before the cathode was removed or the current turned off gave approximately the same results. Some disadvantages of the electrolytic method have been listed as incomplete deposition, an occasional slight anode deposit in the absence of a reducing agent, a contaminated deposit in the presence of a reducing agent, and a tendency for

solution of the platinum anode during prolonged electrolysis (197).

An electrolytic separation of cobalt from nickel by the deposition of cobalt(III) oxide has been described (180). It was found impossible, however, to obtain an adherent deposit of the oxide with amounts of cobalt greater than 40 mg. A recent method of anodic deposition combined with isotope dilution eliminates the necessity for complete electrolysis of the cobalt (155, 156). The adherence difficulties of cobalt oxide deposits are therefore eliminated as a source of error.

4. Anthranilic acid

When sodium anthranilate is added to a slightly acid or neutral solution of a cobalt salt, a red precipitate is obtained (56).

The precipitation is quantitative and the method is capable of detecting 0.006 mg. of cobalt in 5 ml. of solution. The anthranilate of cobalt has been found to be appreciably soluble in acetate buffer solutions (172) and phthalate buffers also tend to inhibit precipitation (83). The procedure for determining cobalt in unbuffered neutral solutions gives good results (56, 192) but separations from other metals is limited under these conditions. Many metals such as iron, nickel, and zinc interfere and must be removed. The cobalt anthranilate is readily filtered and washed and its thermogravimetric characteristics show a constant weight range from 108° to 290°C. (32). Cobalt has also been determined with 5-bromoanthranilic

acid (171). The precipitate is easily filtered and does not adhere to glass-ware. The temperature range within which the precipitate maintains a constant weight is from about 48° to 194°C.

5. Phenylthiohydantoic acid

Phenylthiohydantoic acid quantitatively precipitates cobalt as a red colored complex from ammoniacal solution (195).

It is reported that in one operation cobalt may be completely separated from aluminum, chromium, vanadium, uranium, tungsten, molybdenum, arsenic, titanium, zinc, manganese, calcium, and magnesium. Iron is carried down to a very slight extent, nickel is partially precipitated and most metals of the hydrogen sulfide group precipitate. In the presence of iron, the cobalt precipitate appears to retain approximately 1 to 5 mg. as an impurity regardless of the amount of iron originally present. The nickel precipitate is soluble in sufficient ammonia but this ammonia in too large amounts interferes with the precipitation of cobalt. Upon drying, the cobalt precipitate never attains a constant weight over an appreciable temperature range without decomposition of the complex (32). For a gravimetric determination the compound was ignited to an oxide which, if assumed to be Co_2O_3 , gives fairly good results.

6. Other methods

A method for the separation and determination of cobalt and

nickel has been proposed which is based on the difference in stability of their cyanide complexes in acid solution (140). The hexacyanocobaltate(III), $\text{Co}(\text{CN})_6^{-3}$, complex is stable in acid solution and may be precipitated with silver as $\text{Ag}_3\text{Co}(\text{CN})_6$ which is suitable for gravimetric determinations. The hexacyanonickelate(II) is decomposed by acids and remains in the filtrate to be determined by other means. A temperature of 130°C . was recommended for drying of the cobalt precipitate and falls within the temperature range over which the compound was later shown to be stable (32). For obvious reasons, the decomposition of the nickel complex should be carried out in an adequate hood.

α -Nitroso- β -naphthylamine and β -nitroso- α -naphthylamine have been reported to give accurate results for the determination of cobalt (64).

The reagents also precipitate copper and nickel but separations of cobalt from zinc, aluminum, chromium, and manganese were reported. The former reagent is readily accessible but the latter is reported to be difficult to prepare (32). Both reagents give precipitates with cobalt which have satisfactory temperature ranges of constant weight suitable for drying.

Cobalt has been precipitated with an aqueous solution of isonitrosodimedone with which it is reported to be satisfactorily determined in the presence of nickel, copper, zinc, manganese, aluminum, and chromium (64).

A slight coloration is noted with nickel and copper while a deep blue color is produced with iron. Precipitation is rapid and the cobalt complex quickly settles out. The precipitate may be washed with hot water and is dried at 100°C. prior to weighing. This reagent has also been used for the microgravimetric determination of cobalt (59). It is reported that most of the usual ions encountered do not interfere even if their concentration is more than ten times that of cobalt. Silver, iron(II), and iron(III) interfere.

Cobalt may be precipitated with 8-quinolinol but the complex is reported to be of indefinite composition when dried at 120°C.

Precipitations can be made in the presence of magnesium and molybdenum but separations from zinc, nickel, and copper were not possible in acetate solutions. The determination may be completed by the bromate-bromide titration which is based on the bromination of 8-quinolinol to 5,7-dibromo-8-quinolinol (52, 53). The cobalt precipitate is dissolved in hydrochloric acid and an excess of standard bromate-bromide solution is added. The

bromate and bromide react in the acid solution to produce bromine, two moles of which are required per mole of 8-quinolinol. The excess bromine over that required for the 8-quinolinol is reacted with potassium iodide. The liberated iodine is titrated with a standard solution of sodium thiosulfate using the starch-iodine end-point. The reactions for the determination are given below where H_7Q represents 8-quinolinol.

The equivalent weight of cobalt in this reaction is one eighth the atomic weight.

Hydrazine gives insoluble compounds with the thiocyanates of several bivalent metals (162). The reaction is reported to furnish a rapid and accurate general method for the determination of cobalt, cadmium, and nickel if present alone. The addition of ammonium thiocyanate and hydrazine hydrate to a neutral or slightly acid solution of cobalt(II) produces a flesh colored, silky, crystalline precipitate.

The precipitate was dried in a steam oven although other work has shown that the compound is only stable up to 79°C. (32). The precipitate is very slightly soluble in water but insoluble in alcohol and other organic solvents.

Cobalt(II) forms a stable complex with benzimidazole which is sparingly soluble in water (57).

The precipitation is made at pH 10, therefore, all elements forming insoluble hydroxides must be absent. Common anions not present in large excess were found not to interfere. Decomposition of the compound begins at 100°C. but is very slight until 120°C. is reached. For macro-scale analysis, a temperature of 105°C. was recommended to minimize the drying time. Correct estimations were reported for amounts of cobalt between 12 and 63 mg.

B. Titrimetric methods

1. Iron(II) ammonium sulfate

Methods for the determination of cobalt have been proposed which involve its precipitation as cobalt(III) hydroxide with sodium hydroxide in the presence of sodium perborate (38, 196). After the excess perborate was decomposed by boiling, the determinations were completed by dissolving the cobalt(III) hydroxide with an acidified solution of potassium iodide, tin(II) chloride, or titanium(III) sulfate, and titrating the free iodine, or excess reducing agent by standard methods. Iron(III) interfered with the iodometric method and the cobalt(III) hydroxide was not readily dissolved by potassium iodide. Tin(II) and titanium(III) solutions are sensitive to atmospheric oxidation and require special handling.

The determination may be completed by adding an excess of standard iron(II) ammonium sulfate and titrating the excess with standard potassium dichromate (163).

In order to obtain quantitative results, it is necessary to add the weakly acid iron(II) solution to the alkaline mixture of the cobalt(III) hydroxide in an air-free flask. When the solution is boiled to destroy the excess perborate, the oxygen in the flask is displaced by water vapor. A dropping funnel is fitted to the flask with the stopcock open and the stopcock is closed upon removal of the flask from the source of heat. The excess standard iron(II) solution is then added to the funnel and drawn into the flask by the reduced pressure, care being taken to exclude any air. A sulfuric acid solution is added in the same manner and the cobalt(III) hydroxide readily dissolves. After cooling, the dropping funnel is removed and the excess iron(II) is titrated with standard potassium dichromate using diphenylamine sulfonic acid as an indicator. Nickel and small amounts of iron were found not to interfere with the determination but nitrates and other oxidizing substances which give colorations with diphenylamine sulfonic acid must be absent.

A modified form of this method has been recently described in which the end point is observed potentiometrically by using two platinum electrodes and a polarizing voltage (10). This permits the determination of cobalt in the presence of large amounts of tungsten. Colloidal tungstic acids adsorb diphenylamine sulfonic acid and make the visual end point unsatisfactory.

2. Potassium cyanide

Cobalt may be determined by titration with a standard potassium cyanide solution using silver iodide as an indicator (68). Cyanide reacts with cobalt(III) to form the stable complex, $\text{Co}(\text{CN})_5^-$, and with silver iodide to form $\text{Ag}(\text{CN})_2^-$. To the solution containing the cobalt and some iodide ion, a known amount of standard silver nitrate solution is added. This gives the solution a cloudy appearance due to the formation of the insoluble silver iodide. The titration is carried out with a standard solution of potassium cyanide until the cloudiness disappears. At this point, all of the cobalt and silver have been complexed and the amount of cobalt is found by difference. A better procedure is to add sufficient cyanide to expel the cloudiness and then add a few milliliters in excess. The excess cyanide is titrated with standard silver nitrate to the first appearance of silver iodide. This end point is more readily observed.

The amount of cobalt is determined from the total cyanide used minus that equivalent to the total silver nitrate added.

Copper(II) and mercury(II) interfere but are removed with the hydrogen sulfide group. Iron is complexed with citrate. Zinc reacts with potassium cyanide and gives high results. This interference may be reduced with ammonium citrate but is not completely eliminated if zinc is present in excess of 5 mg.

Good results may be obtained in the presence of manganese if not more than 5 mg. are present. Titanium and nickel also interfere. Fifty milligrams of cobalt is given as the maximum that may be determined by this method. The accuracy of the method is reported to be 1 to 3% of the total cobalt present.

3. Potassium hexacyanoferrate(III)

Cobalt(II) salts are oxidized quantitatively in ammoniacal solution by potassium hexacyanoferrate(III) (8, 23, 68, 200).

The solution containing the cobalt is added to an excess of a standard solution of potassium hexacyanoferrate(III) and the excess is back titrated with a standard solution of cobalt(II). The reaction may be followed potentiometrically with an observed break at the equivalence point of approximately 0.2 volt. The method was found to be satisfactory in the presence of copper, nickel, and iron, the three elements which interfere most with other existing methods. Other elements which reportedly did not interfere were mercury(II), lead, bismuth, cadmium, arsenic(V), antimony, tin(IV), selenium, tellurium, molybdenum, chromium(VI), beryllium, aluminum, zinc, titanium, tungsten, uranium, vanadium(V), and zirconium while manganese gives serious interference (68).

A modification of this titration has been made in which ammonia is replaced by ethylenediamine (30). The cobalt(II)-ethylenediamine complex is a stronger reducing agent than the corresponding cobalt(II)-ammonia complex by approximately 0.5 volt. The potential break of the titration with potassium

hexacyanoferrate(III) is increased by a similar amount at the equivalence point. Oxygen is removed from the solution to be titrated and also from the titrants. This is accomplished by passing oxygen-free nitrogen through the solutions. Machlett burets are used for the titrants to prevent further contact with air. Iron, nickel, and copper did not interfere in the presence of citrate or sulfosalicylate. Manganese did not interfere if sulfosalicylate was present in the solution. The direct titration with hexacyanoferrate(III) was used except for the cases in which cobalt was determined in the presence of silver or a three component mixture of chromate, vanadate, and molybdate. The back titration of excess hexacyanoferrate(III) with standard cobalt(II) sulfate was used in these cases.

4. Iodometric

An iodometric method for cobalt has been developed which involves the oxidation of cobalt(II) with hydrogen peroxide in the presence of potassium bicarbonate (112). A carbonato complex of cobalt(III) is formed which reacts with iodide in acid solution to produce cobalt(II) and free iodine. The determination is then completed by titrating the liberated iodine with sodium thiosulfate.

The iodine-starch end point was used except for very dilute solutions (0.001 M) in which case an amperometric method was employed. Unless rendered inactive by complex formation or other means, any element which under the conditions of the method

oxidizes iodide to iodine will interfere. These interfering elements include iron, chromium, manganese, copper, antimony, molybdenum, tungsten, and vanadium. Moderate amounts of iron may be tolerated if fluoride ion is added. The results of analysis of 0.01 M solutions of cobalt showed positive errors of 0.4% or less in the presence of a 3-fold excess of iron. The error with 0.001 M solutions in the presence of a 20-fold excess of iron was of the order of 4 to 5%. Better accuracy was obtained if the fluoride compound of iron which precipitated under the conditions of the method was filtered off. Nickel also interfered but the presence of fluoride improved these results. The results were still high, 1.5 mg. of cobalt being determined with an accuracy of 3.7% in the presence of 50 mg. of nickel. It was concluded that a preliminary separation of cobalt is necessary if appreciable quantities of nickel are present.

The addition of iodine to an ammoniacal solution of cobalt(II) containing ammonium nitrate, chloride, bromide, or iodide results in the formation of the corresponding salt of iodopentamminecobalt(III). The formation of this complex is the basis of an iodometric determination of cobalt (199). An excess of standard iodine solution and some ammonium nitrate are added to the cobalt solution. Ammonia is added and the precipitation of the green iodopentamminecobalt(III) nitrate occurs which is complete within 5 minutes. The excess iodine is determined potentiometrically by titration with a standard arsenic(III) solution.

Iodopentamminecobalt(III) is stable in the presence of arsenic(III). A starchend point was investigated but the results were found to be less satisfactory. Any substance that will oxidize iodide or cobalt or reduce iodine must be absent. Several metals which interfere in their lower oxidation state but not in the higher oxidation state include arsenate, antimonate, chromate, molybdate, vanadate, and tungstate. Under the conditions of the method, nickel, copper, zinc, and cadmium form ammino complexes and lower the pH of the solution. If the pH became less than 8.5, the rate of formation of the cobalt complex was slow and low results were obtained. Sufficient ammonia is therefore added to bring the pH to 9. Silver, lead, and mercury(I) precipitate as iodides in acid solution and cause a decrease of iodide in the solution. This causes an increase in the hydrolysis of iodine in ammoniacal solution and low results are obtained. These metals are precipitated as the iodides before the iodine solution is added. Mercury(II) forms a complex iodide and more iodide is required in its presence. Tartrate prevents the hydroxides of aluminum, bismuth, chromium, iron, and tin from forming which occlude cobalt. Manganese(II) is oxidized by iodine in ammoniacal solutions and is therefore removed as the dioxide from a strongly acid solution.

The amount of cobalt recommended for the determination ranges from 1 to 250 mg. The error reported amounted to approximately $\pm 0.1\%$ of the amount of cobalt present. For

quantities of cobalt of the order of 10 mg. or less, the errors were slightly higher.

5. Ethylenediaminetetraacetic acid

a. Eriochrome Black T

A convenient method has been developed for the determination of cobalt in mixtures containing varying ratios of cobalt and nickel (71). An excess of a standard solution of disodium dihydrogen ethylenediaminetetraacetate dihydrate (EDTA) over that required to react with the nickel and cobalt is added to the sample solution. The pH is adjusted to about 10 with ammonium hydroxide and the excess EDTA is titrated with a standard zinc solution. Eriochrome Black T, the sodium salt of 1-(~~4~~-hydroxy-2-naphthylazo)-6-nitro-2-naphthol-4-sulfonic acid, is used as an indicator, the end point being observed as a color change from blue to red. These reactions are given below where H_4Y and H_3In represent EDTA and Eriochrome Black T, respectively.

Using a second portion of the sample, the cobalt is precipitated with α -nitroso- β -naphthol and extracted with chloroform. The nickel in the aqueous layer is determined in the same manner as given above, the difference of the two titrations representing the cobalt content. Satisfactory determinations were made for various proportions of cobalt and nickel where the total weight of the two elements was 50 mg. It is proposed that if other ions are present that react with EDTA but not with

α -nitroso- β -naphthol, then the cobalt could still be determined. The difference in the two titrations would still represent the cobalt content. This method overcomes several disadvantages of the gravimetric α -nitroso- β -naphthol method in that the voluminous α -nitroso- β -naphthol precipitate does not have to be filtered and washed. Also the time required for digesting the precipitate and converting it to the proper weighing form is eliminated. Any adsorption of simple salts of nickel on the cobalt precipitate will be released when the cobalt passes into the chloroform. The method is not recommended for samples containing more than 50 mg. of cobalt because the color of the cobalt EDTA complex interferes with the end point. A back titration has also been described using manganese(II) to determine the excess EDTA (96).

Another method for cobalt and nickel involves the addition of excess EDTA followed by oxidation of cobalt to the very stable cobalt(III)-EDTA complex with lead dioxide (149, 168). The unreacted lead dioxide is filtered off and the excess EDTA is back titrated with magnesium sulfate using Eriochrome Black T as the indicator.

This gives the total of cobalt and nickel. Potassium cyanide is now added to the solution which produces an amount of EDTA equivalent to the nickel present. The cobalt(III) complex is not decomposed by cyanide.

The EDTA produced in this reaction is then titrated with magnesium sulfate. The difference of the two titrations gives the amount of cobalt present.

b. Zincon

Zincon, o-(2-[α-(2-hydroxy-5-sulfophenylazo)-benzylidene]-hydrazino)-benzoic acid, a colorimetric reagent for zinc and copper (152) has been investigated as an indicator for titrations with EDTA (95). With this indicator only zinc may be titrated with EDTA in a buffered ammoniacal solution. Cobalt is determined by addition of excess EDTA followed by the titration of the excess with a standard zinc solution.

c. PAN

Microdeterminations of several metals including cobalt have been accomplished using the compound 1-(2-pyridyl-azo)-2-naphthol (PAN) as an indicator (49, 51). Excess EDTA is added to the solution made slightly acid with acetic acid and the excess is titrated with a standard copper solution. At the end point, copper reacts with PAN giving a color change from yellow to violet. Satisfactory determinations were made in the presence of large quantities of calcium and magnesium or several milligrams of manganese. In the presence of aluminum, the end point is sluggish and the true equivalence point is not obtained. This results from the EDTA complex of aluminum in acidic solution being of such stability that the replacement of aluminum with copper during back titration is not complete. With amounts of metals corresponding from 1 to 10 ml. of 0.01 M solution, the

titration error amounted to ± 0.02 to 0.03 ml. The end point error may be reduced by establishing the end point with the copper solution, adding a slight excess of copper, and then re-establishing the end point with EDTA. Three or four readings may be averaged and a more accurate value obtained.

The back-titration method using PAN indicator has been applied to the determination of cobalt in the presence of tungsten, titanium, niobium, tantalum, and iron without prior separations (113). These interfering metals are masked with tartrate and fluoride. Cobalt was satisfactorily determined in several samples of cemented carbides containing the above mentioned metals with the cobalt content varying from 4 to 20%. Nickel and vanadium will not be masked and are quantitatively titrated along with the cobalt.

A more convenient direct method has been developed for macro titrations using this same indicator (50). If a macro determination is attempted by an indirect titration method, a considerable excess of EDTA is normally added to assure chelation of all the metal. The large volume of copper solution required for the back titration produces the blue copper-EDTA complex in such high concentrations that the end point color of the PAN is obscured. However, it has been found that the stability of the copper-PAN complex is so great that in the presence of other metals the following reaction takes place.

Therefore only enough copper-EDTA complex need be present to give a reaction with the PAN indicator and the titration may be

made directly with EDTA. Cobalt may be titrated accurately in acidic media at a pH not lower than 3. After adjustment of the pH, a few drops of a solution of copper-EDTA complex is added followed by enough PAN indicator solution to produce an intense violet color. The solution is heated to boiling and titrated directly with EDTA until the color changes to a clear yellow. The EDTA complex of cobalt is red-colored and can interfere with the copper-PAN indicator color. For this reason it is recommended that the concentration of cobalt be kept below 10 mg. per 100 ml. of solution.

d. Xylenol Orange

Xylenol Orange, 3,3'-bis[N,N-di(carboxymethyl)-aminomethyl]-o-cresolsulfonphthalein, may be used as an indicator for the EDTA titration of several metals in acid solution. The color change is from red to yellow in direct titrations, the hues being affected by the color of the metal ions or their EDTA complexes. The combination of the iodometric method for copper and the complexometric method for cobalt has been used for the determination of these two metals in a single sample of a ferromagnetic alloy (105). One aliquot of the sample is treated with ascorbic acid and potassium iodide which reduces the copper and precipitates it as copper(I) iodide. Without filtering off the copper precipitate, the cobalt is titrated at a pH of 5 to 6 with EDTA using Xylenol Orange. A second aliquot is neutralized and the copper is determined iodometrically in the usual manner. This indicator has also been used for the determination of cobalt using a back titration (97). Excess EDTA is added to an

ammoniacal cobalt(III) solution along with some 30% hydrogen peroxide to form the cobalt-EDTA-peroxide complex. The pH is adjusted to 2 and the back titration is carried out with a standard thorium solution.

e. Pyrocatechol Violet

Dilute solutions of cobalt containing no more than 5 to 6 mg. per 100 ml. have been analyzed by a direct titration with EDTA using Pyrocatechol Violet, 3,3',4'-trihydroxyfuchson-2"-sulfonic acid, as an indicator (178). The titration is carried out in an ammonium acetate-ammonium hydroxide buffered solution, the end point being observed as a color change from greenish-blue to reddish-purple. Higher concentrations of cobalt tend to give turbid solutions.

f. Azoxine

Cobalt in weakly acid solution may be directly titrated with EDTA using Naphthylazoxine, 7-(1-naphthylazo)-8-quinolinol-5-sulfonic acid, as an indicator (55). A fairly sharp end point is observed but it may be improved by the addition of a copper(II) solution. In this case the cobalt is titrated with EDTA until the indicator changes from yellow to its full red color. At this point, a small known amount of a dilute standard copper nitrate solution is added which reacts with the indicator changing it back to its yellow form. The titration is then completed with EDTA taking the sharpest color change from yellow or yellow-orange to red as the end point. The amount of EDTA solution required for complexing the added copper (determined by a separate titration) is subtracted from the buret reading.

At the pH range of 5.5 to 6.5, cadmium, lead, nickel, rare earths, yttrium, and zinc are also titrated. Aluminum, iron(III), thorium, and zirconium react irreversibly with the indicator at this pH. Magnesium and the alkaline earths do not interfere.

C. Colorimetric methods

1. Thiocyanate

The thiocyanate method has been one of the classical colorimetric methods for the determination of cobalt (176). The color intensity is not very high in aqueous solution and methods for intensification of the color have been investigated. The addition of acetone decreases the dissociation of the complex and thus intensifies the color. The cobalt thiocyanate complex may also be extracted with organic solvents which serves as a means of concentrating the complex.

A more complete study of the absorption spectrum of the cobalt thiocyanate complex has revealed a peak of much higher absorption in the ultraviolet region (121). The absorbancy maximum is not observed in aqueous medium and the cobalt complex must be extracted into an organic solvent. The method consists of extracting the cobalt complex from aqueous solution with isoamyl alcohol previously saturated with ammonium thiocyanate. The absorbancy of the alcohol solution is then measured at 312 m μ using the extractant as a reference. The system conforms to Beer's law for concentrations from 0.2 to 10 p.p.m. of cobalt. The absorbancy increases with increasing concentration of ammonium thiocyanate in the aqueous phase, however, no appreciable increase was noted after the concentration had

reached approximately 22%. Maximum absorbancy readings were obtained when the extraction was made from aqueous solutions having a pH range of 1.6 to 1.9. However, the readings were not reproducible and a pH range of 3.0 to 5.3 was recommended. Perchloric acid and ammonium hydroxide were used for adjustment of the pH. Absorbancy readings were shown to be essentially constant over a 24 hour period.

A study of the effect of diverse ions showed negligible interference from 1000 p.p.m. of acetate, arsenate, ammonium, cadmium, chloride, calcium, magnesium, nitrate, potassium, sodium, and sulfate. The permissible amounts of the following ions in p.p.m. were V(V), 10; Mo(VI), 100; Cu(II), 10; Al(III), 100; Mn(II), 75; Pb(II), 25; Ni(II), 5; Zn(II), 100; IO_3^- , 50; and $\text{HC}_4\text{H}_4\text{O}_6^-$, 100. The following ions must be absent: Fe(III), U(VI), Cr(III), Cr(VI), Sn(IV), Ti(IV), $\text{Fe}(\text{CN})_6^{4-}$, and $\text{HC}_6\text{H}_5\text{O}_7^-$.

A study of the thiocyanate-acetone system has produced a spectrophotometric method for the simultaneous determination of cobalt, copper, and iron (99). A single solution containing all three ions is used for the color development with spectrophotometric measurements being made at 380, 480, and 625 m μ .

The solvent in which the absorbancy is measured is 50% by volume of acetone. The presence of acetone increases the absorbancy of iron and permits the formation of the color of the cobalt complex which does not exist in aqueous solution. A similar increase in absorbancy with increasing concentrations of acetone up to 40% also occurs for copper. It is necessary that the final solution be acidic and contain an excess of

thiocyanate. To eliminate fading of the color of the cupric thiocyanate complex, small amounts of potassium peroxydisulfate are added. It was found that the amount must be carefully controlled.

The iron-thiocyanate system conforms to Beer's law with concentrations up to 6 p.p.m. at all three wavelengths. The copper-thiocyanate system is in conformance up to 30 p.p.m. at 380 m μ , 60 p.p.m. at 480 m μ , and 90 p.p.m. at 625 m μ . The cobalt-thiocyanate complex does not absorb at 380 or 480 m μ and obeys Beer's law at 625 m μ with concentrations up to 60 p.p.m.

The following ions interfered and must be absent; barium, calcium, lead, mercury(I), silver, strontium, thiosulfate, tungstate, cerium(IV), chromium(III), dichromate, bismuthyl, molybdate, and titanium.

The concentrations of the three ions are found by setting up three equations involving the absorbancy at each wavelength, the molar absorbancy index for each complex, and the concentration of each complex. The theory of spectrophotometric analysis of colored mixtures has been covered (58).

The procedure recommended is applicable for samples containing more than 50 μ g. of cobalt and/or copper, and more than 5 μ g. of iron. It is not suitable for the determination of traces of any of the three metals in the presence of large amounts of the others without prior separation.

2. α -Nitroso- β -naphthol

The cobalt complex of α -nitroso- β -naphthol is soluble in chloroform and exhibits an absorbancy peak in the ultraviolet region of the spectrum (121). The system conforms to Beer's law at 317 m μ and with concentrations from 0.2 to 2 p.p.m. cobalt. Cobalt is precipitated from an ammoniacal citrate solution with the pH adjusted within the range of 4.0 to 5.5. The precipitate is allowed to stand after which it is extracted with chloroform. The absorbancy of the chloroform extract was found to be dependent upon the time of digestion of the precipitate. No increase in absorbancy was noted if the precipitate was allowed to stand for at least 2 hours before extraction.

A change in absorbancy of 3% or less was noted for 500 p.p.m. of chloride, nitrate, perchlorate, sulfate, and tungsten, and with 200 p.p.m. of aluminum, cadmium, chromium, molybdenum, and zinc. Copper and iron(III) must be absent while the following concentration of other ions in p.p.m. were found to be permissible: Ti(IV), 5; Sn(II), 10; V(V), 20; Pb(II), 50; Ni(II), 50; and Mn(II), 150.

Five p.p.m. of iron(III) produced an error of 45% in the determination of 1 p.p.m. cobalt. This interference was eliminated by extracting the iron with ether which had been previously equilibrated with 6 M hydrochloric acid. With this separation, 1 p.p.m. cobalt was successfully determined in solutions which contained 5, 10, and 20 p.p.m. of iron(III) ions.

3. 3-Nitrososalicylic acid

Separation and codetermination of small amounts of cobalt and nickel may be carried out using 3-nitrososalicylic acid as the reagent for both metals (146). The reagent forms a brown colored complex with cobalt which is soluble in petroleum ether. The red nickel complex formed is water soluble. A method for the preparation of the reagent is given. It is stored as a solution of its calcium salt and the 3-nitrososalicylic acid is extracted into petroleum ether prior to use.

Before extraction, the pH of the aqueous solution containing the cobalt and nickel is adjusted within the range of 5.6 to 6.0 with a sodium acetate-acetic acid buffer. The petroleum ether solution of the reagent is added which extracts the cobalt. The pH of the aqueous solution now containing the nickel is readjusted if necessary and more reagent is added. The nickel complex forms and remains in the aqueous phase. The absorbancy of both solutions was measured at approximately 520 m μ because the reagent does not absorb at this wavelength. Beer's law was obeyed up to concentrations of 0.2 mg. of cobalt and nickel.

Of the ions tested, only iron(II) and copper(II) ions caused interference in a concentration range up to 0.2 mg. Silver, calcium, permanganate, potassium, sodium, dichromate, aluminum, cadmium, chloride, ammonium, sulfate, nitrate, mercury(II), magnesium oxalate, and phosphate caused no interference. Iron(III) in a concentration above 1000 μ g. interfered with the cobalt method. Below this amount, the interference due to iron(II) was eliminated by oxidation to

iron(III). Elimination of the interference of copper(II) is effected by removal of the ion or by its determination. A red water-soluble complex is formed by copper(II) and 3-nitroso-salicylic acid at pH 4. Nickel does not react below pH 5. The copper may therefore be determined at pH 4 and the sum of the nickel and copper determined after adjusting the pH within the range of 5.6 to 6.0.

4. Nitroso-R-salt

In hot solution buffered at pH 5.5 ± 0.5 with sodium acetate and acetic acid, cobalt and nitroso-R-salt, disodium 1-nitroso-2-naphthol-3,6-disulfonate, react to form a soluble red complex. The absorbancy may be measured at 425 m μ or 525 m μ depending upon the concentration of the cobalt chelate (174). At 525 m μ , the absorbancy of a relatively wide range of cobalt concentrations may be measured with moderate sensitivity. For a given concentration the absorbancy of the cobalt-nitroso-R-salt is much larger at 425 m μ than at 525 m μ which provides a narrower concentration range with increased sensitivity. The absorbancy of the nitroso-R-salt is also large at 425 m μ while at 525 m μ it is negligible. Therefore, when making measurements at 425 m μ , the excess reagent must be decolorized, a suitable oxidizing agent being potassium bromate (174).

In a study to establish interfering elements, 40 μ g. of cobalt in 25 ml. of solution was satisfactorily determined with little or no interference from 3 mg. of antimony(III), bismuth(III), cadmium(II), lead(II), mercury(II), tin(IV), zinc(II), cerium(III), manganese(II), molybdenum(VI), uranium(VI),

or vanadium(V) (173). Interfering cations and the minimum amounts which caused interference were as follows in $\mu\text{g.}$ per 25 ml.: Fe(II), 400; Fe(III), 60; cerium(IV), 100; chromium(III), 400; chromium(VI), 40; nickel (II), 2400; tin(II), 1000; vanadium(IV), 1000; copper(II), 300-1000. Interference caused by iron(II) may be eliminated by use of additional nitroso-R-salt, however, this operation enhances the interfering effect of any iron(III) which may be present. Iron interference has been eliminated by treating the solution with bromine, boiling to remove the excess, and adding potassium fluoride (143). This oxidizes the iron to iron(III) which forms a stable colorless complex with the fluoride ion. Interferences due to cerium(IV), chromium(III), chromium(VI), and nickel(II), are also eliminated by addition of potassium fluoride prior to addition of nitroso-R-salt (173). Copper(II) interference is overcome by addition of excess reagent. The interferences of vanadium(IV) and tin(II) are eliminated by oxidation with bromine.

5. Tetraphenylarsonium tetrathiocyanatocobaltate(II)

If ammonium thiocyanate and tetraphenylarsonium chloride are added to a slightly acidic solution of a cobalt(II) salt, tetraphenylarsonium tetrathiocyanatocobaltate(II) will precipitate.

Traces of cobalt may be separated from aqueous solution by extraction of the precipitate with chloroform (1). The determination of the cobalt content of the chloroform layer is made spectrophotometrically at 620 m μ . It is reported that the method is applicable to the determination of cobalt in

cobalt-copper alloys and alloy steels without prior separation of iron, nickel, or copper.

The optimum range of concentration was found to be 5 to 25 μg . of cobalt per milliliter. The chloroform extracts of the cobalt complex are stable with no change in absorbancy over long periods of time. The hydrogen ion concentration is not critical as 90% of the cobalt is removed with one extraction from solutions with a pH in the range from 1.9 to 6.8. The maximum amount was extracted from solutions of pH 5.5.

Iron(II) does not interfere but iron(III) forms the blood-red thiocyanate complex which extracts into the chloroform layer and obscures the color of the cobalt complex. An excess of ammonium fluoride eliminates this interference through the formation of the colorless hexafluoroferrate(III) complex. The amount of ammonium fluoride needed varies with the amount of iron present but in any case, a sufficient quantity should be added to expel the red color of the iron(III) thiocyanate complex.

Copper(II) ions interfere in the same manner as does iron(III). This interference is eliminated by reducing the copper(II) to copper(I) with iodide ion which also reduces iron(III). Copper(I) iodide precipitates and dissolves upon further addition of potassium iodide to form the colorless iodocuprate(II) complex. The iodide treatment is used if the sample contains more than 0.1% copper. In the analysis of steel samples containing less than 0.1% copper, the interference is too small to be detected. The excess iodide present reacts with

the iodine produced in the reduction to form the colored triiodide ion. To prevent this from being extracted into the chloroform as tetraphenylarsonium triiodide, the triiodide is reduced by the addition of an excess of thiosulfate.

If the sample contains a large percentage of copper, it will be necessary to add a large excess of iodide ion. Because iodide is oxidized to iodine in acid solution by oxygen, it is necessary to adjust the pH to 4 or greater before extracting the cobalt. In the presence of a large amount of iodide ion it was found that a large excess of thiocyanate must be present to obtain efficient extraction of the tetraphenylarsonium tetrathiocyanatocobaltate(II).

Interference caused by molybdenum(V) and (VI) was eliminated by addition of ammonium fluoride. Vanadium(V) interferes by oxidizing the thiocyanate giving yellow products which are extracted into the chloroform. To prevent this, vanadium(V) is reduced to vanadium(IV) by iron(II) with subsequent addition of sufficient ammonium fluoride to complex the iron(III) formed. Thiocyanate is also oxidized by high concentrations of nitric acid. Fuming with sulfuric acid is recommended for removal of any nitric acid introduced for dissolution of the sample. Extraction may be made difficult by the presence of large quantities of solid material which tends to emulsify the chloroform.

D. Polarographic methods

The half-wave potential for the hexaquocobalt(II) ion is about -1.4 volts vs. the saturated calomel electrode in

supporting electrolytes which form no complexes with the cobalt ion (103). The reduction of the hexamminecobalt(II) ion to the metal in a solution which is 1 M in ammonium chloride and 1 M in ammonia occurs at -1.3 volts vs. the saturated calomel electrode. Dissolved oxygen oxidizes hexamminecobalt(II) to hexamminecobalt(III) which exhibits a two-step reduction to the metal, the first step being observed at -0.5 volt vs. the saturated calomel electrode.

An investigation of the reduction of complex ions formed by the progressive substitution of the ammonia molecules in the hexamminecobalt(III) ion with other groups has been made (198). Half-wave potentials for the complete series from $[\text{Co}(\text{NH}_3)_6]^{+++}$ to $[\text{Co}(\text{NO}_2)_6]^{---}$ except for $[\text{Co}(\text{NH}_3)(\text{NO}_2)_5]^-$ were determined. A study was also made of some chloro- and aquo-substituted complexes. Two steps were observed for every compound studied except the hexanitrocobaltate(III) and chloropentamminecobalt(III). The step heights indicated and application of the Ilkovic equation confirmed that the first step was a one electron reduction and the second step was a two electron reduction. The half-wave potential of the first reduction varied from compound to compound while that of the second reduction was essentially constant. This is apparently due to the hydrolysis of the cobalt(II) complexes to form the hexaquocobalt(II) ion. The reaction of the second step is then the same for each complex giving the same half-wave potential. One M potassium sulfate, 0.1 M potassium sulfate, and 0.1 M sodium acetate were used as supporting electrolytes.

The variation of the half-wave potential with supporting electrolyte was determined for several cobalt complexes.

1. Cobalt(II)

A polarographic method for the simultaneous determination of cobalt and nickel has been described (118). The method may be used for cobalt and nickel in the presence of iron, copper, chromium, and manganese.

The half-wave potentials of the aquo complexes of cobalt and nickel are very close together. This prevents their simultaneous determination in the presence of a non-complex-forming supporting electrolyte because only a single wave is produced. A double wave is obtained in ammoniacal medium, the nickel being reduced first, but the difference in the half-wave potentials for the ammine complexes of cobalt and nickel is still not sufficient to permit an accurate measurement of the individual diffusion currents.

The half-wave potentials of both cobalt and nickel are shifted to more positive values when pyridine or thiocyanate is used as the supporting electrolyte. The nickel wave is shifted more than the cobalt and the resulting half-wave potentials are separated by 0.3 volt. This separation permits the simultaneous determination of the two metals. For the determination of both metals, pyridine is preferred over thiocyanate as a supporting electrolyte because an irregular diffusion current is obtained for cobalt in solutions of the latter.

In pyridine solutions, maxima were observed for both cobalt and nickel, however, the diffusion currents were still well defined. In 0.5 M pyridine, the nickel maximum was eliminated with 0.01% gelatin but the cobalt maximum remained in the presence of 0.05% gelatin. In the presence of 0.05% gelatin and pyridine concentrations smaller than 0.2 to 0.3 M, the maxima were eliminated.

The diffusion current of iron(III) interferes with the waves of practically all other metals when it is present in large excess. Relatively large quantities of iron may be separated from cobalt, nickel, and copper by precipitation as hydrous iron(III) oxide in pyridine solution. Solution compositions corresponding to 1% of cobalt and nickel in steel were satisfactorily analyzed and it was shown that cobalt and nickel did not coprecipitate with the iron. The chromium(III) ion coprecipitated with the iron and did not interfere if sufficient iron were present. Manganese(II) is reduced at a potential more negative than that of pyridine and does not interfere with the cobalt and nickel waves. Copper in pyridine exhibits two reduction waves whose half-wave potentials are more positive than that of nickel. Copper does not interfere with the cobalt-nickel determination when its concentration is about the same as or smaller than that of cobalt and nickel.

Pyridine has been used as a supporting electrolyte for the simultaneous determination of cobalt, nickel, and copper in titanium alloys (132). Most of the titanium is removed by hydrolysis in acid solution and the remainder is precipitated

by the addition of excess pyridine before a polarogram is run on the solution. It is reported that no appreciable quantity of cobalt, nickel, or copper is coprecipitated with the titanium. With the exception of chromium, none of the elements normally found in commercial titanium alloys interferes with the simultaneous determination of cobalt, nickel, and copper. Chromium interference was removed by the addition of barium chloride. Satisfactory results were obtained for cobalt, nickel, and copper in synthetic titanium samples where the concentration of these three metals varied from 0.2 to 5.0%.

2. Cobalt(III)

a. Sodium perborate oxidation

Because the polarographic wave of nickel(II) precedes that of cobalt(II) in nearly every known supporting electrolyte, it is not possible to determine trace amounts of cobalt in the presence of large amounts of nickel without some modification. This analysis may be accomplished if cobalt is first oxidized to the +3 state because the polarographic reduction wave of cobalt(III) to cobalt(II) precedes that of nickel(II).

Cobalt(II) in ammoniacal solution may be oxidized to an ammine complex of cobalt(III) by boiling with sodium perborate, $\text{NaBO}_3 \cdot \text{H}_2\text{O}$ (189). The oxidation is rapid and quantitative. The excess perborate being decomposed by boiling the solution for 5 or 10 minutes. In order to eliminate excessive loss of ammonia from the solution, it was necessary to provide the oxidation flask with a reflux condenser. The upper opening of the condenser was attached to a trap containing a small amount of

water which was added to the sample after the decomposition of the perborate.

The sample may contain 1 to 120 mg. of cobalt as the nitrate, sulfate, chloride, or perchlorate in 25 ml. of aqueous solution. After the addition of reagents subsequent to the oxidation process, this solution is diluted to 100 ml. for polarographic analysis. Gelatin was used as a maximum suppressor. The wave corresponding to the reduction to the complex cobalt(II) ammine was found to have a half-wave potential of -0.534 volt vs. the saturated calomel electrode and a constant diffusion current between -0.80 and -1.10 volt vs. the saturated calomel electrode.

The effect of the concentration of ammonium hydroxide on the polarographic wave of the cobalt(III) complex was investigated. The diffusion current was found to be constant within experimental error when the final concentration of ammonia was varied from 0.31 to 3.1 M. The oxidation was quantitative in all solutions containing 10 ml. or more of 6.25 M ammonium hydroxide per 100 ml. of final solution.

As much as 1.2 grams of nickel ion could be retained in solution if 40 ml. of 6.25 M ammonium hydroxide per 100 ml. of final solution were used. In the presence of nickel, the diffusion current increased rapidly at -0.9 volt (S.C.E.) but 1.2 grams of nickel ion had no effect on the cobalt(III) wave. In the presence of large amounts of nickel, the diffusion current for cobalt was measured at -0.85 volt (S.C.E.). The reduction wave of zinc, a usual contaminant of nickel salts, occurs at a

more negative potential than the cobalt(III) wave and does not interfere. Large amounts of iron lead to low results due to the coprecipitation of cobalt with the hydrous iron(III) oxide in the course of the procedure. A large excess of iron must be separated but it was found that the separation did not need to be quantitative. For example, 11.2 mg. of iron in a sample containing 29.5 mg. of cobalt did not interfere with the cobalt determination. Coprecipitation of cobalt also occurs in the presence of manganese(II) which is oxidized to manganese dioxide by the sodium perborate. Cobalt was separated from manganese by precipitation with α -nitroso- β -naphthol in 50% acetic acid solution. The precipitate was ignited to the oxide and the cobalt in the oxide was determined polarographically. Copper interferes but may be removed with zinc amalgam where the sample contains 0.1 gram or less of copper. Chromium interferes but may be removed with barium perchlorate. Vanadium and molybdenum do not interfere.

b. Lead dioxide oxidation

Cobalt may be determined polarographically through reduction of trioxalatocobaltate(III) to dioxalatocobaltate(II) (10^4).

The reduction of the cobalt(III) complex occurs at a more positive potential than the oxalato complexes of most other metals. The method is applicable in the presence of a large excess of nickel, copper, and iron as well as most other elements. Vanadate, chromate, cerium(IV), and trioxalatomanganate(III) interfere.

It is recommended that the sample should contain from 2 to 60 mg. of cobalt and not more than 0.6 gram of iron in 25 ml. of aqueous solution. Cobalt may be present as the nitrate, sulfate, or perchlorate. After proper adjustment of the pH of the solution, potassium oxalate is added and the solution is diluted to a known volume. Lead dioxide is added to a portion of the solution which oxidizes the cobalt. After filtering, a maximum suppressor is added and the diffusion current is determined. In the absence of other complex-forming metal ions, the diffusion current is determined at a potential of 0.0 to -0.1 volt vs. a saturated calomel electrode, at -0.1 volt in the presence of much nickel and at -0.04 volt in the presence of much iron. The residual current is determined on a portion of the sample which was not oxidized. If vanadium, cerium, chromium, or manganese are present, they are reduced by the addition of hydroxylammonium chloride. Molybdenum and uranium do not interfere. The oxalate precipitates any calcium which is present and some cobalt is coprecipitated. Iodide interferes as a result of its oxidation to iodine by lead dioxide. The anodic depolarization wave of bromide interferes below -0.1 volt vs. the saturated calomel electrode. Large concentrations of chloride should be avoided as it causes a shift in the cobalt(III) wave to more negative potentials.

c. Potassium permanganate oxidation

A more recent method for traces of cobalt in the presence of nickel involves the oxidation of cobalt(II) in an ammoniacal ammonium chloride solution with an excess of potassium permanganate (129). The excess permanganate is destroyed upon

addition of an excess of hydroxylammonium sulfate. This method has the advantage over the methods using sodium perborate or lead dioxide in that no refluxing or filtering is necessary to eliminate the excess oxidizing agent. The excess hydroxylamine does not reduce the cobalt(III) complex at a measurable rate at room temperature.

Two samples are taken for analysis, both being treated in an identical manner except one is oxidized with permanganate. The wave of the unoxidized solution is used as a base line for the measurement of the diffusion current of the cobalt(III) complex. This procedure eliminates any error which may be caused by the reduction of other metal ions such as copper which exhibits a half-wave potential at about -0.5 volt vs. S.C.E. The vertical distance between the two curves at approximately -0.7 volt vs. S.C.E. is taken as the diffusion current for the cobalt(III) complex. This value is then compared with the diffusion currents obtained from solutions of known cobalt concentrations which have been treated in the same manner.

In this procedure the final solutions are about 0.5 M in ammonium chloride and 1 M in ammonia. When insufficient ammonium ion was present, low diffusion currents were obtained and the ratio of diffusion current to cobalt concentration decreased with increasing cobalt concentration. In the presence of too much ammonium ion, the reduction wave is not well defined. Therefore, if the solution to be analyzed is obtained from the dissolution of a metal sample with acid, it

should be nearly neutralized with sodium hydroxide before beginning the analysis. The concentration of ammonia is not as critical but a sufficient amount should be present to complex the nickel and prevent its precipitation.

Arsenic, cadmium, antimony, tin, and zinc do not interfere with the method. Bismuth, copper, iron, manganese, and molybdenum may be tolerated in moderate amounts. Large amounts of chromium may be removed with barium chloride and lead with sodium sulfate. Tungsten and vanadium must be absent.

E. Spectrochemical methods

1. Nickel alloys

Cobalt along with aluminum, chromium, copper, iron, magnesium, manganese, silicon, and titanium have been spectrographically determined in thermionic cathode nickel alloys (88). The sample was obtained by filing, drilling, or milling of the materials to be analyzed. In this manner a sample of a more or less common form could be obtained from a variety of materials of different sizes and forms.

Nickel samples analyzed by other procedures were used as standards. The standards were selected to contain each of the elements to be determined over a concentration range from 0.003 to 0.2% except for cobalt, where the range extended to 0.70%. A charge of 10 mg. of sample was placed in an undercut crater of a 3/16-inch diameter graphite electrode and excited in a 250-volt direct current arc at 16.5 amperes for 55 seconds. The nickel line at 2834.55 Å. was used as the internal standard line and the line at 3044.01 Å. was used as the analytical line for

cobalt. A filter band of 7.4% transmittance was used for the nickel line and one of 22% transmittance for the cobalt line. Approximately 0.1% cobalt was determined in a standard alloy with a standard deviation of $\pm 3.8\%$. It is reported that this method gives results comparable to dry powdered oxide technique which has previously been described (89).

2. Stainless steel

A spectrographic method for the determination of cobalt, manganese, niobium, titanium, tantalum, and molybdenum in 18-8 stainless steel has been reported (60). Due to the varied metallurgical history of the samples, a solution or salt technique was chosen as the best approach. Samples were prepared by dissolving metal drillings in aqua regia, adding a small amount of sulfuric acid, and evaporating to dryness. The metal sulfates were baked at 350°C. until all fuming had ceased. After scraping from the beaker, the salt was mixed with an equal volume of graphite powder and this mixture was used for the analysis.

Standards were prepared by dissolving standard steel of known composition in aqua regia. Before evaporating to dryness, known amounts of solutions of pure elements were added to give the desired concentration. The solution was then evaporated and the metal sulfates were treated as above.

The salt-graphite mixtures were loaded into a cup type graphite electrode and excited in an alternating current arc (2400 volts, 4.8 amperes) with no prearc time and 50 seconds exposure time. The iron line at 2886.32 Å. was used as the

internal standard line and the line at 3044.00 A. was used as the analytical line for cobalt. This method was used for cobalt concentrations ranging from 0.02 to 0.2%. Results showed that a precision of approximately $\pm 10\%$ of the amount present could be expected.

3. Low alloy steel

The cobalt content of low alloy steels ranging from 0.007 to 0.03% may be determined by a point-to-plane a-c arc technique (6). The method is applicable to steel samples on which a flat area of 1/2-in. diameter or greater can be prepared. The arc discharge is directed to the flat portion from a graphite counter electrode. Samples which weigh at least 20 g. and have a thickness of at least 1/8 in. are of sufficient mass to prevent overheating. Smaller samples may be used if adequate cooling is provided. The excitation conditions were 4700 volts and 2.3 amperes with 120 discharges per second. The spectra were recorded photographically using a 5 second preburn and a 30 second exposure. The iron line at 3457.09 A. and the cobalt line at 3453.51 A. were used as the internal standard line and the analytical line, respectively. The chromium line at 3453.33 A. interferes with the cobalt line. Analytical curves are established using alloys of known cobalt concentrations which cover the range of interest.

4. Animal tissue

Two spectrographic methods for the determination of trace quantities of cobalt in animal tissues have been developed (92). One method is directly applicable to the ash of tissues of

animals containing at least 0.025 $\mu\text{g.}$ of cobalt per gram of fresh tissue, in excess of that present in normal tissue. This method was applied only to the soft tissue of animals which had been exposed to known concentrations of cobalt metal fume for specific periods of time. The second method is applicable to the determination of cobalt deposited in the bones of exposed animals or to that present normally in the bone and soft tissues of unexposed animals.

In the first method, the tissue is ashed, extracted with dilute hydrochloric acid, the solution is filtered, and the filter is dried and re-ashed. The ash is re-extracted, and treated as above. The filtrates are combined and evaporated to a predetermined volume which will contain approximately 2 mg. of tissue ash per 0.05 ml. A crater type electrode is waterproofed with a paraffin wax solution and the cone-shaped bottom of the crater is slightly more than filled with 10 mg. of a ground and desiccated lithium chloride spectroscopic buffer mixture. A volume of 0.05 ml. of the sample solution is added to the electrode and the electrode is dried at 85°C. After cooling, 0.05 ml. of an internal standard solution of palladium is added and the electrode is dried at 105°C. and reserved for spectrographic exposure. The electrodes containing the samples are burned as anodes in a 220-volt direct current arc operating at 9 amperes. The palladium line at 3460.8 A. was used as the internal standard line and the analytical line of cobalt was 3453.5 A. For the preparation of standard curves, known amounts of cobalt were added to solutions of ash obtained from normal

tissue. The amount of cobalt in normal tissue was considered as negligible since it could not be detected by this method.

Analytical curves were prepared to cover the range from 0.005 to 1.25 $\mu\text{g.}$ of cobalt in 2 mg. of tissue ash. The upper limit was extended to 50 $\mu\text{g.}$ by using the cobalt line at 3455.2 A. for the higher concentrations. A check on the accuracy of the method showed that the amount present could be determined within $\pm 10\%$.

In the second method, the tissue was prepared in the same manner except that the cobalt was extracted from the combined filtrate with chloroform as the α -nitroso- β -naphthol complex. The chloroform solution was added to an alcoholic solution of aluminum nitrate which acts as a carrier element to provide bulk. After evaporation to dryness, the mixture was subjected to alternate dry ashing in a muffle furnace and wet ashing with concentrated nitric acid. Weighed portions of the aluminum and cobalt oxides from the ashing procedure are mixed with appropriate amounts of the spectroscopic buffer and added to the electrode. Palladium, the internal standard, is added and the electrode is dried. The excitation conditions are the same as in the first method and the same palladium and cobalt lines are used. The method was applied to known amounts of cobalt varying from 0.03 to 0.4 $\mu\text{g.}$ The recovery was shown to be within the range of 90 to 98%. The method is reported to possess a sensitivity of about 0.001 p.p.m. for a 30-gram sample of fresh tissue. It also provides greater accuracy in individual sample analysis than does the direct method.

5. Unknown materials

A powder d-c arc semiquantitative technique has been described which provides for the determination of cobalt and several other elements in unknown materials (6). The method covers the concentration ranges from 0.1 to 100% for each element.

If the sample is not already in the form of a salt or oxide, it must be converted to this form for the analysis. Metallic solids are dissolved in a suitable acid and evaporated to dryness. The sample is then ground in a boron carbide mortar until the powder will pass a No. 325 sieve. A 50-mg. portion of the sample is mixed thoroughly with 250 mg. of lithium carbonate and 900 mg. of graphite powder, lithium serving as the internal standard. This mixture is packed into a cup-type electrode and excited in a 250 volt-10 ampere d-c arc for 45 seconds.

The external optics of the spectrograph includes a two-step, absorption type filter which produces a horizontally filtered spectrum of 10 and 100% transmittance. The exposure conditions are adjusted so that the relative transmittance of the filtered half of the 3232.61 Å. lithium internal standard line is between 50 and 60%. The unfiltered portion of the cobalt line at 3044.01 Å. is used for the concentration range from 0.1 to 50.0% cobalt and the filtered portion for the range from 50.0 to 100%.

Several standard samples are prepared from reagent-grade carbonates or oxides to give a fairly wide concentration range of the elements of interest. A 50 mg. portion of each standard is mixed thoroughly with lithium carbonate and graphite and excited under the same conditions as the unknown. Data on the

precision of the method may be found in the reference.

VII. Specific methods for determining cobalt

A. Gravimetric (91)

1. Dissolution of sample

a. Alloys

Dissolve approximately 1 gram of the sample in 20 to 40 ml. of aqua regia with gentle heating. Some high heat resisting alloys dissolve more readily in cold aqua regia. If the sample contains titanium, niobium, molybdenum, tantalum, or tungsten, add 3 grams of tartaric acid when the decomposition of the sample is complete. Evaporate the solution to dryness on a steam bath. Add 5 grams of tartaric acid, 75 ml. of water, and heat until the salts are in solution.

b. Carbides and refractory metal alloys

Treat approximately 1 gram of sample in a platinum dish with 20 ml. of hydrofluoric acid followed by the occasional addition of 5-ml. portions of nitric acid until the decomposition is complete. Gentle heating may be required for complete dissolution of the sample, however, the reaction may be vigorous without heating in which case the dish is covered with a platinum cover. Some carbides yield more readily to decomposition by treating the sample with nitric acid followed by small additions of hydrofluoric acid or by igniting the sample prior to the acid treatment. In any case, when the decomposition is complete, evaporate the solution to dryness on a steam bath and then add 20 ml. of 40% tartaric acid solution. Heat until all of the salts dissolve, disregarding any undissolved graphitic carbon or

tungsten trioxide, transfer to a 600-ml. beaker, and dilute the solution to 75 ml.

c. Ores

Dissolve 1 or 2 grams of sample in nitric and hydrochloric acids. When the action ceases, add 20 ml. of sulfuric acid, evaporate slowly to strong fumes of sulfur trioxide and cool. If both iron and arsenic are present, add 25 ml. of hydrobromic acid and again evaporate slowly to fumes of sulfur trioxide and cool. Repeat the hydrobromic acid treatment and cool. Add approximately 150 ml. of water and a drop of hydrochloric acid to precipitate any silver. Heat the solution to boiling, cool, and filter off any precipitate, Evaporate the filtrate to fumes of sulfur trioxide and then to dryness. When the dry salts have cooled, add 5 grams of tartaric acid and 75 ml. of water and heat until solution is complete.

Some samples are not readily attacked by acids. If this is the case and the sample is low in chromium, fuse the sample in a quartz or porcelain crucible with potassium bisulfate. Dissolve the melt in dilute hydrochloric acid and precipitate cobalt with sodium hydroxide and sodium peroxide. Filter the solution and wash the precipitate thoroughly with hot water. Dissolve the precipitate in dilute hydrochloric acid and evaporate to dryness or fume the paper and the precipitate with nitric and sulfuric acids and evaporate to dryness. Add 5 grams of tartaric acid and 75 ml. of water to the dry salts and heat until the salts are in solution.

Some samples yield to decomposition by perchloric acid. After dissolution, remove the perchloric acid by evaporating the solution to dryness or by fuming with sulfuric acid. If chromium is present, it is expelled as chromyl chloride before the evaporation. To the dry salts, add 5 grams of tartaric acid and 75 ml. of water and heat until the solution is complete.

2. Separation

To the tartaric acid solution containing the cobalt, slowly add a saturated solution of potassium hydroxide until the solution tests alkaline to litmus. If a precipitate forms at the neutral point or if insoluble tungstic or rare earth acids are present, add an excess of potassium hydroxide. The solution should have a volume of less than 100 ml. at this point. Acidify with glacial acetic acid and add 4 ml. in excess. The solution should be clear, however, any cloudiness or small precipitate may be disregarded as reprecipitation will eliminate the contaminating impurity while precipitation of cobalt is complete.

Warm the solution and add 200 ml. of hot potassium nitrite solution with vigorous stirring. Potassium hexanitrito-cobaltate(III) precipitates immediately if the cobalt content of the sample is high. If the amount of cobalt present is less than 50 mg., a slightly longer time is required for initial precipitation. Heat the solution and hold the temperature near the boiling point for 5 to 10 minutes or until brown fumes of nitrous oxides cease to escape. Allow the solution to stand cold for 4 hours or preferably overnight. Filter the solution

through a filter paper which is applicable to moderately fine crystalline precipitates, using some filter pulp. Wash the paper and precipitate eight times with a cold 3% solution of potassium nitrite and once with cold water. One separation is sufficient to remove iron, chromium, and other elements which hydrolyze in an alkaline solution. Two separations are necessary in the presence of large amounts of tungsten. Large amounts of nickel or large amounts of cobalt with medium quantities of nickel usually require reprecipitation of the potassium hexanitrito-cobaltate(III).

For reprecipitation, place the paper containing the precipitate in the original beaker and add 15 ml. of nitric acid and 15 ml. of sulfuric acid. After completion of the initial reaction, slowly evaporate the solution to fumes of sulfuric acid. Elevate the cover of the beaker with glass hooks, increase the heat, and evaporate the solution to dryness or until fumes of sulfuric acid cease to escape. The precipitate may be dissolved in hot dilute hydrochloric acid in which case the solution is evaporated to dryness. Add 3 to 5 grams of tartaric acid and 75 ml. of water to the dry salts and heat until solution is complete. Neutralize the solution with potassium hydroxide solution, add 4 ml. of glacial acetic acid, and precipitate the cobalt as described above.

3. Electrolytic determination

Place the paper containing the potassium hexanitrito-cobaltate(III) in the original beaker and add 20 ml. of nitric acid and 20 ml. of sulfuric acid. After the vigorous reaction

ceases, evaporate the solution to fumes of sulfuric acid. It may be necessary to add more nitric acid to destroy any organic matter. Dissolve the salts in a small amount of water and again evaporate to fumes of sulfuric acid. Repeat this fuming to expel all of the nitric acid. Cool, add 50 ml. of cold water, stir, add 150 ml. of hot water to dissolve the cobalt sulfate, and cool to room temperature. Neutralize the solution with ammonium hydroxide and add an excess of 60 to 70 ml. Add about 2 grams of sodium bisulfite and electrolyze on a tared platinum gauze electrode in a stirred solution at 2 amperes for 1 hour. Withdraw a few drops of solution and test for complete deposition by one of the methods given in section V-A. When deposition is complete, wash the cathode, rinse in alcohol, dry, and weigh.

Dissolve the weighed deposit in concentrated nitric acid. Evaporate to dryness several times with hydrochloric acid and determine the sulfur as barium sulfate. Subtract the weight of sulfur found from the weight of cobalt. For most routine work, it is sufficient to subtract 0.5 mg. from the weight of the cobalt deposit.

B. Titrimetric (30)

1. Reagents

a. Ethylenediamine

Distill commercial ethylenediamine over sodium hydroxide and collect the fraction boiling at 115 to 116°C.

b. Cobalt(II) sulfate

Add 240 grams of reagent-grade cobalt(II) chloride hexahydrate and 160 grams of ammonium chloride to 200 ml. of water and stir until most of the salts are dissolved. Add 4 to 5 grams of activated decolorizing charcoal and 500 ml. of concentrated aqueous ammonia to the solution. Pass a stream of air through the solution for about 4 hours or until the solution changes to a yellowish-brown color and filter off the crystals and carbon. Add the crystals to 1500 ml. of water containing enough hydrochloric acid to make the solution acid (20 to 30 ml. of concentrated acid). Heat until solution is complete and filter off the carbon from the hot solution. Add 400 ml. of concentrated hydrochloric acid to the filtrate and cool in an ice bath. Filter the crystals of hexamminecobalt(III) chloride and wash with 60% alcohol followed by 95% alcohol. Dry the crystals at 80 to 100°C. (16). Add sufficient water to completely dissolve the crystals. Then add a sufficient amount of a sodium oxalate solution to completely precipitate the hexamminecobalt(III) ion. Filter the hexamminecobalt(III) oxalate, wash with cold water and dry at 96°C. Ignite the oxalate at a dull red heat to cobalt(III) oxide. Dissolve the oxide in a sulfuric acid solution, filter the solution, and concentrate the filtrate. Allow the hydrated cobalt(II) to crystallize, filter it off, dry, and finally heat it to 555°C. Prepare a 0.1 M master solution of the anhydrous cobalt(II) sulfate; dilute aliquots of this solution as required. Prepare an approximately 0.01 M solution for use in back

titrations. Put the 0.01 M solution in a Machlett buret and free it of oxygen by the passage of oxygen-free nitrogen for 4 hours. (Oxygen-free nitrogen may be obtained by passing tank nitrogen through three wash bottles. Charge the first two with 100 grams each of lightly amalgamated zinc and 100 ml. of 0.1 M vanadyl sulfate containing some free sulfuric acid. Add 100 ml. of water to the third wash bottle (130).)

c. Potassium hexacyanoferrate(III)

Prepare an approximately 0.01 M solution by dissolving 6.6 grams of reagent-grade potassium hexacyanoferrate in 2 liters of water. Place the solution in a Machlett buret and pass oxygen-free nitrogen through it for 4 hours. Standardize the solution against the standard cobalt(II) sulfate solution. Solutions of hexacyanoferrate(III) ion decompose slowly on standing. (A decrease in normality of 12% was observed after storage for 46 days without exposure to air for the 0.01 M solution.) Therefore, standardize the hexacyanoferrate(III) solution just prior to the titration of the unknown sample.

2. Standardization

Pipet an aliquot of the standard solution of cobalt(II) sulfate containing 20 to 30 mg. of cobalt into the titration cell. (A three-necked vessel having a gas inlet tube sealed near the bottom is a convenient container in which to carry out the titration.) Add 2 ml. of 1:1 sulfuric acid and dilute to approximately 35 ml. Pass oxygen-free nitrogen through the solution for 10 minutes. Add 2.0 ml. of ethylenediamine and titrate with 0.01 M potassium hexacyanoferrate(III). Follow the

titration potentiometrically using a platinum working electrode and a saturated calomel reference electrode.

3. Bronze (silver absent)

Weigh out a sample of not more than 1 gram which contains 5 to 30 mg. of cobalt. Dissolve in a minimum amount of nitric acid (4 ml. for a 0.3-gram sample) and then add 5 ml. of perchloric acid. Evaporate the solution over a burner to strong fumes of perchloric acid. Cool the mixture, dilute to 30 ml., and boil for 5 minutes. Cool again, transfer to the titration vessel, and bubble oxygen-free nitrogen through the solution for 10 minutes. Add 2.5 ml. of ethylenediamine for a 0.3-gram sample or 5.0 ml. for a 1-gram sample and titrate with 0.01 M hexacyanoferrate(III).

4. Bronze (silver present)

Weigh out a sample of 0.5 gram or of such size as to contain 5 to 30 mg. of cobalt. Dissolve in a mixture of 5 ml. of nitric acid and 5 ml. of perchloric acid. Evaporate the solution to strong fumes of perchloric acid, cool, and dilute to 30 ml. Boil the solution for 10 minutes. (If a precipitate of silver chloride appears, discard the sample.) Cool the solution, transfer to the titration vessel, and bubble oxygen-free nitrogen through the solution for 10 minutes. Add concentrated sodium hydroxide solution dropwise to the point of incipient precipitation, and then add 5 grams of sodium citrate. In rapid succession, add an excess of standard hexacyanoferrate(III) and 2 ml. of ethylenediamine. Titrate the solution with a standard cobalt(II) sulfate solution. Standardize the hexacyanoferrate(III) solution

against cobalt(II) sulfate under these same conditions.

5. Stainless steel

Weigh out a sample of less than 1 gram which contains 5 to 30 mg. of cobalt. Dissolve in a mixture of 5 ml. of nitric acid and 10 ml. of hydrochloric acid, heating gently if necessary. Add 6 ml. of perchloric acid and evaporate to strong fumes of perchloric acid. Cool and dilute to 30 ml. with water. Add 4 ml. of 15% hydrogen peroxide and boil the solution for 10 minutes to reduce the volume and destroy the excess peroxide. Transfer the resulting blue solution to the titration vessel and add 3 grams of sulfosalicylic acid. Bubble oxygen-free nitrogen through the solution for 15 minutes to remove dissolved oxygen. Add 5 ml. of ethylenediamine and titrate the sample with 0.01 M hexacyanoferrate(III).

6. Chrome-vanadium-molybdenum steel

Weigh out a sample of 0.1 to 0.2 gram and dissolve in a mixture of 5 ml. of nitric acid and 5 ml. of hydrochloric acid. Add 5 ml. of perchloric acid and evaporate the solution to strong fumes of perchloric acid. Cool the mixture, dilute to 30 ml., and boil for 10 minutes. Cool again and transfer the solution to the titration vessel. Add concentrated sodium hydroxide dropwise until a pH of 2.0 to 2.5 is reached, and bubble oxygen-free nitrogen through the solution for 10 minutes. Add in rapid succession 5 ml. of a saturated solution of sodium citrate, an excess of hexacyanoferrate(III), and 2.5 ml. of ethylenediamine. Titrate the solution with the standard cobalt(II) sulfate.

7. Stellite

Weigh out a sample of about 2 grams and dissolve in 60 ml. of hydrochloric acid over a low heat. Add 50 ml. of perchloric acid and heat over a burner to strong fumes of perchloric acid. Cool the mixture, dilute to 150 ml., and add 10 ml. of 15% hydrogen peroxide. Boil the solution to destroy excess peroxide, cool, and dilute to 1 liter in a volumetric flask. Withdraw an aliquot containing 5 to 30 mg. of cobalt and transfer to the titration vessel. Bubble oxygen-free nitrogen through the solution for 15 minutes, add 2 grams of sulfosalicylic acid and 2.5 ml. of ethylenediamine, in that order. Titrate the solution with hexacyanoferrate(III).

C. Colorimetric (29)

1. Reagents

a. Cobalt(II) sulfate

Prepare a standard solution of cobalt, 1.00 ml. = 1.00 mg., by dissolving 2.630 grams of reagent-grade cobalt(II) sulfate (previously dried at 500°C.) in distilled water. Add 8 ml. of 72% perchloric acid and dilute to 1 liter. Prepare a weaker standard, 1.00 ml. = 0.0100 mg., by pipetting 10 ml. of this solution into a 1-liter volumetric flask. Add 7 ml. of 72% perchloric acid and dilute to 1 liter.

b. Nitroso-R-salt

Prepare a 1% aqueous solution by dissolving 10 grams of the commercial-grade salt in 200 ml. of warm water. If a golden yellow solution is not obtained, pass the solution through a perchloric acid-washed alumina column at the rate of 2 to 3 ml.

per minute. This removes the dark green iron(II) complex which is often present as an impurity. Discontinue the passage of solution when the effluent shows a greenish tint. Dilute the chromatographed liquid five-fold. The column is recharged as described below.

2. Alumina column

Repeatedly wash adsorption alumina with water, decanting and discarding the finely divided portions, until only a rapidly settling product is obtained. Add a water slurry of the alumina to an adsorption column until the packed solids extend to a depth of 5 to 6 cm. Treat the alumina column with a 1 M solution of perchloric acid until the effluent liquid shows a distinct acid reaction. Wash the column with several portions of distilled water to remove the excess acid.

To recharge the column, treat with a 1 M solution of sodium hydroxide until the effluent liquid is distinctly basic. Wash with several portions of distilled water and treat with perchloric acid as described above. Ignore any yellowish material which may be eluted by the sodium hydroxide solution during the recharging operation.

3. Dissolution of sample

a. Cast irons and plain carbon steels

Dissolve about 0.5 gram of sample in 5 ml. of 72% perchloric acid plus 10 ml. of distilled water. When dissolution is complete, add 1 ml. of concentrated nitric acid and boil the solution several minutes to oxidize all iron salts.

b. Stainless steels

Dissolve about 0.5 gram of sample in a minimum amount of concentrated hydrochloric acid sufficient to bring about complete dissolution. Filter off any free carbon and wash well with hot 1% perchloric acid solution.

c. Nonferrous alloys

Dissolve about 0.5 gram of sample in 12 ml. of 5 M nitric acid. If large quantities of chloride or nitrate ions are introduced during the dissolution of any type of sample, the entire solution should be evaporated to fumes of perchloric acid after any carbon has been filtered off; 5 ml. of 12 M perchloric acid is adequate for this purpose. After fuming, dilute the solution with 20 ml. of distilled water, add 5 ml. of 3% hydrogen peroxide, and boil several minutes to reduce any dichromate or permanganate ions which may have been formed and to expel excess peroxide.

4. Determination

To the entire sample, or to a suitable aliquot portion, add 5 ml. of 1% solution of nitroso-R-salt and sufficient 4 M ammonium acetate solution to adjust the pH between 5.0 and 5.5. Heat the solution to boiling and add 0.5 ml. of 72% perchloric acid for each milliliter of 4 M ammonium acetate used. Swirl the solution to dissolve any hydrated oxide precipitate, and cool to room temperature. Sufficient perchloric acid must be added to ensure the presence of all acetate ions in the form of nonionized acetic acid and to destroy the nitroso-R-salt complexes of other metal ions.

Pass the sample solution through the perchloric acid-washed alumina column at the rate of 15 to 20 ml. per minute, rapidly enough so that the individual drops of effluent can barely be discerned. The cobalt-nitroso-R-salt complex forms a brilliant red band at the top of the alumina column, while immediately below will be a diffuse yellow band formed from the excess nitroso-R-salt. Wash the column with hot (70° to 80°C.) 1 M nitric acid (free from nitrite ions) until the effluent is colorless when a 25-ml. portion is observed against a white background. This operation elutes the excess nitroso-R-salt and may cause a "bleeding" or several millimeters of the red cobalt band. Too rapid a passage, too hot a solution, or the presence of nitrite ions will cause severe "bleeding" and possible elution of some of the cobalt complex. Usually 200 ml. of wash solution is sufficient.

Elute the cobalt complex with 1 M sulfuric acid at a rate of 5 to 10 ml. per minute until the effluent appears colorless, then pass an additional 10-ml. portion. Usually 50 ml. will be required. Transfer the eluant to a 100-ml. volumetric flask and dilute to the mark. Determine the absorbancy at a wavelength of 500 to 520 mμ. and obtain the concentration from a calibration curve.

Prepare the standard calibration curve from known amounts of cobalt and reagent which have been similarly developed but not necessarily chromatographed. If the standards are not chromatographed, make a correction for the absorbancy of the excess nitroso-R-salt reagent. The cobalt complex is stable for

48 hours in the absence of excess dye.

D. Polarographic (104)

1. Reagents

a. Cobalt(II) solution, 0.1 M

Pure anhydrous cobalt(II) sulfate may be prepared according to the procedure given in this section, part B-1. Dissolve 15.501 grams of anhydrous cobalt(II) sulfate in water containing 10 ml. of 0.5 M sulfuric acid and dilute to 1 liter.

b. Hydroxylammonium chloride, 20%

Dissolve 1 gram of analytical reagent in 5 ml. of water. The solution, which is stable for several days, can be added to the cell by a medicine dropper.

c. Gum Arabic, 5%

Dissolve 1 gram of gum arabic in 19 grams of hot water. The solution is stable for several days.

2. Determination

The sample to be determined should contain 2 to 60 mg. of cobalt and no more than about 0.6 gram of iron in an aqueous solution of not more than 25-ml. volume. The cobalt may be in the form of nitrate, sulfate, or perchlorate. Neutralize the solution by adding dilute sodium hydroxide until a permanent turbidity or precipitate is just observed. Add 4 ml. of 1:1 acetic acid, 10 ml. of 2 M ammonium acetate, and 50 ml. of 2 M potassium oxalate. Dilute to 100 ml. and mix well.

Transfer approximately 75 ml. of the solution to a 125-ml. Erlenmeyer flask, add 1 gram of lead dioxide (manganese-free), and shake at frequent intervals for 5 minutes. If the green

color is very intense, add 0.5 gram more of lead dioxide. Filter through a quantitative filter paper (suitable for fine crystals or turbid solutions) and return the first portion to the unfiltered solution. The funnel stem should be filled with liquid to ensure rapid filtration.

In the absence of vanadate, chromate, cerium(IV), or trioxalatomanganate(III), which interfere, collect a suitable volume of the filtrate in a dry polarograph cell or one previously rinsed with small volumes of the filtrate. Add 3 drops (0.10 ml.) of 5% gum arabic for each 25 ml. of solution and rapidly pass oxygen-free nitrogen (see this section, part B-1) through the solution for 3 minutes. Insert the saturated calomel anode and the dropping mercury electrode and measure the diffusion current at 0.0 to -0.1 volt versus the saturated calomel electrode in the absence of other complex-forming metal ions, at -0.1 volt versus the saturated calomel electrode in the presence of much nickel, or at -0.04 volt versus the saturated calomel electrode in the presence of much iron. To determine the residual current, transfer the 25-ml. portion of the solution which was not oxidized to a polarograph cell and proceed in the same manner.

In the presence of vanadium, cerium, chromium, and/or manganese, add the maximum suppressor and reducing agent to the dry cell in which the filtrate is to be collected. Add 3 drops of 5% gum arabic, and for each 20 mg. of total content of manganese, chromium, and cerium, or for each 6 mg. of vanadium in the sample add 1 drop of hydroxylammonium chloride solution,

allowing 0.5 to 1 drop in excess. Bubble oxygen-free nitrogen through the filtrate in the cell during the filtration process to hasten mixing. Collect approximately 25 ml. of the filtrate. Pass oxygen-free nitrogen through the cell an additional 3 minutes. Without interruption, insert the saturated calomel anode and the dropping mercury electrode, and continue as indicated in the previous paragraph. If the contents of chromium, vanadium, and manganese are not known, no appreciable error will result from adding an amount of hydroxylammonium chloride known to be an excess.

In the presence of much iron, there is a slight decomposition of trioxalatocobaltate(III) by hydroxylammonium chloride. This can be corrected for by making a second current measurement after an equal interval of time. Add the difference between this and the first measurement to the first measurement.

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