

ANALYTICAL CHEMISTRY OF COBALT

I. V. PYATNITSKII

Translated by N. KANER



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ANALYTICAL CHEMISTRY OF ELEMENTS

ANALYTICAL CHEMISTRY OF COBALT

Analytical Chemistry of Elements

Series prepared by the Vernadskii Institute of Geochemistry and Analytical Chemistry
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ANALYTICAL CHEMISTRY OF BERYLLIUM

ANALYTICAL CHEMISTRY OF BORON

ANALYTICAL CHEMISTRY OF COBALT

ANALYTICAL CHEMISTRY OF GALLIUM

ANALYTICAL CHEMISTRY OF MOLYBDENUM

ANALYTICAL CHEMISTRY OF NICKEL

ANALYTICAL CHEMISTRY OF NIOBIUM AND TANTALUM

ANALYTICAL CHEMISTRY OF PLUTONIUM

ANALYTICAL CHEMISTRY OF POTASSIUM

ANALYTICAL CHEMISTRY OF PROTACTINIUM

ANALYTICAL CHEMISTRY OF RUTHENIUM

ANALYTICAL CHEMISTRY OF TECHNETIUM, PROMETHIUM, ASTATINE
AND FRANCIUM

ANALYTICAL CHEMISTRY OF THALLIUM

ANALYTICAL CHEMISTRY OF THORIUM

ANALYTICAL CHEMISTRY OF URANIUM

ANALYTICAL CHEMISTRY OF YTTRIUM AND THE LANTHANIDE ELEMENTS

ANALYTICAL CHEMISTRY OF ZIRCONIUM AND HAFNIUM

FOREWORD

The Vernadskii Institute of Geochemistry and Analytical Chemistry of the USSR Academy of Sciences has begun the publication of a series of monographs on the analytical chemistry of individual elements. This series, *Analytical Chemistry of Elements*, will include about fifty volumes, and it is planned to complete the publication during the coming five years. The necessity for such a project has been felt for a long time. We also have at our disposal the accumulated experience of numerous laboratories which now can (and should) be summarized. In this way the present series originated, the first of its kind. The analytical chemistry of any element with its different compounds is at present extremely varied; this is due to the complexity of the modern materials investigated and the wide range of concentrations determined, as well as to the variety of the methods employed.

With this in mind, a general plan has been worked out for the present series, both with respect to the contents and to the presentation of the material.

The monographs contain general information on the properties of the elements and their compounds, followed by a discussion of the chemical reactions which are the basis of the analytical work. The physical, physicochemical, and chemical methods for the quantitative determination of the element are given in the following order: first, the analysis of raw materials, next the analysis of the typical semi-manufactured products, and last, that of the finished products—metals or alloys, oxides, salts, and other compounds and materials. The underlying principles are always explained; whenever necessary, the exhaustive description of the entire analytical procedure is given. Due attention is paid to rapid analytical methods. A separate place is allotted to techniques for the determination of impurities in high purity materials.

Particular stress is placed on the accuracy and the sensitivity of the various methods, in view of the general tendency toward increased sensitivity of determination of traces of impurity elements.

The monographs contain an exhaustive and up-to-date bibliography. They are intended for a wide circle of chemists: in the first place, for the analysts of research institutes and industrial laboratories of various branches of the national economy, and also for teachers and students of chemistry in institutions of higher education.

Our most prominent experts participated in the preparation of the monographs, drawing upon their own extensive experience in the analytical chemistry of the element in question.

Each volume of the series will be published separately as soon as it has been made ready for publication. [A list of currently available volumes will be found facing the title page. Further titles are in preparation.]

We invite all our readers to send us their comments and criticisms on the monographs.

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PREFACE

The analytical chemistry of cobalt has received considerable attention, owing to the many new applications of the element and its compounds. Cobalt is an indispensable component in special-purpose alloys of high hardness and great thermal stability. Many cobalt compounds have high catalytic activity and are used as catalysts in the synthesis of various chemical compounds. Radioactive cobalt isotopes are widely used in medicine. Some complex organic compounds of this element affect the metabolism in plants and animals. With the growing uses of cobalt, it thus became necessary to find new methods for the detection and determination of this element both as a main component and as an impurity in industrial and biological materials of widely diverse composition. Special attention has lately been paid to the development of methods for the determination of trace amounts of cobalt. At present, these methods mainly include spectrophotometric, kinetic, and electrochemical analytical techniques. Numerous authors have worked on the synthesis of new organic reagents for the determination of cobalt and studied the optimum conditions for their application.

In the preparation of the present monograph, the author consulted all the available literature on the analytical chemistry of cobalt published up to 1963. Attention was paid mainly to papers published in the last decade, as they reflect the present-day level of analytical chemistry and to a considerable extent are based on the application of new organic reagents and new instrumental methods. An attempt was made to evaluate critically the efficiency of individual techniques, using published reports on comparative experimental investigations. Yet, in many cases, this evaluation is very difficult because of the absence of objective chemical analytical characteristics of the reagents and techniques.

The book does not include spectroscopic and X-ray analytical methods.

The author is deeply indebted to Professor A. I. Busev for making available offprints of many papers and for his valuable critical remarks and advice in the editing of the manuscript. The author wishes to express his sincere gratitude to Candidate of Chemical Sciences T.E. Get'man for his invaluable assistance in the selection of references and in the final shaping of the monograph.

I. V. Pyatnitskii

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CHAPTER I

Analytical Characteristics of Cobalt. Cobalt Compounds of Importance in Analytical Chemistry

General remarks

Cobalt compounds were used in ancient Egypt and China as blue pigments for china and glassware. Cobalt was first obtained as an element in 1742 by Brandt, who also described some of its physical and chemical properties.

The atomic number of cobalt is 27, its atomic weight is 58.9332 on the carbon scale [289]. Cobalt belongs to the first triad of Group VIII of the periodic system and is composed of one stable isotope with mass number 59. A large number of radioactive cobalt isotopes have been obtained artificially (Table 1).

The most important isotope in practice is the cobalt radioisotope Co^{60} , which is used in medicine, analytical chemistry, research on the precipitation and extraction of various cobalt compounds, etc.

The atomic radius of cobalt is 1.15\AA , the ionic radius of Co(II) is 0.82\AA (according to Goldschmidt) or 0.72\AA (according to Pauling), and that of Co(III) is 0.64\AA [289].

The cobalt content in the Earth's crust is about 0.003% [289]. However, most of the cobalt is concentrated in the central core of the Earth, where elements of the iron group predominate. Cobalt is present in iron meteorites ($\sim 0.6\%$) and also in stony meteorites (0.08%). Trace amounts of cobalt are found in sea water ($10^{-7}\%$) and in mineral spring water. The average content of this element in the U.S.S.R. soils is about 0.001%, with considerable fluctuations depending on the nature of the soil. According to Young [1523], the cobalt content in different materials varies over a fairly broad range. For instance, it is $2 \cdot 10^{-3}$ – $2.5 \cdot 10^{-2}\%$ in rocks, 10^{-3} –8% in

2 ANALYTICAL CHARACTERISTICS OF COBALT

minerals, up to $10^{-3}\%$ in soils, 10^{-2} – $1.4 \cdot 10^{-3}\%$ in waters, and $5 \cdot 10^{-3}$ – 1.6% in meteorites.

Cobalt is always present in animal and plant organisms. Seaweeds are able to concentrate cobalt from water. The content of cobalt in plants and animals fluctuates from 10^{-5} – $10^{-3}\%$. Cobalt affects the metabolism and activity of enzymes. Vitamin B₁₂ is an organocobalt compound.

Until the end of the 19th and beginning of the 20th century, the industrial application of cobalt was limited by the high cost of the metal and by the inadequate knowledge of its properties and its alloys. At that time, cobalt was mainly used for the production of very fast pigments of various colors.

Cobalt is widely used in metallurgy for special steels and alloys; these steels have high hardness and thermal stability, and are resistant to acids. Steels for high-speed cutting tools contain cobalt in addition to chromium and tungsten. For the composition of some hard cobalt alloys, see [97]. Cobalt-base heat-resisting alloys are used in components of internal combustion engines, turbines, jet engines, atomic power plants, etc. Cobalt is a component of several magnetic alloys [97]. Steels

Table 1
RADIOACTIVE ISOTOPES OF COBALT [283, 289]

Mass number	Radiation	Half-life	Energy of particles, MeV
54	β^+	0.2 sec	> 7.4
55	β^+ (~60%), E.c. (~40%); γ	18 hrs	1.5 (53.3%) 1.03 (39.5%) 0.53 (4.9%) 0.26 (2.3%)
56	β^+ (20%), γ E.c. (80%)	77 days	1.5 (96%) 0.44 (4%)
57	E.c.; γ	270 days	—
58 ^m	I.t.	9.2 hrs	—
58	β^+ (15%); E.c. (85%); γ	71 days	0.485
59	—	—	—
60 ^m	I.t. (99%); β^- (0.28%)	10.1 min	1.56
60	β^- ; γ	5.2 years	0.309
61	β^-	1.7 hrs	1.22
62 ^m	I.t.; β^-	1.6 min	—
62	β^- ; γ	13.9 min	2.88 (75%) 0.88 (25%)

Note: β^+ —positron; β^- —electron; E.c.—electron capture of an orbital electron; I.t.—isomeric transition (transition of nucleus from an upper to a lower isomeric state); the superscript *m* near the mass number indicates metastable excited state.

alloyed with cobalt together with chromium, nickel, tungsten, and molybdenum are used in industrial chemical apparatus which is resistant to acids, alkalis, and other chemicals.

Cobalt and its compounds are used as catalysts in various chemical processes.

For a description of the most important cobalt-containing minerals, see [60, 97, 185, 362].

The world's reserves of cobalt are 800,000 tons (computed as the metal). The principal ore deposits containing about $\frac{2}{3}$ of the world's resources are in Congo and Zambia, as well as in New Caledonia, Canada, U.S.A., Uganda, Brazil, Morocco, Turkey, Japan, Burma, Sweden [212, 362].

In the U.S.S.R., cobalt deposits occur in the Azerbaidzhan S.S.R. (the Dashkesan deposit), in the Tuva A.S.S.R., in the Northern Urals, and in the Krasnoyarsk Territory [60, 212].

The world production of cobalt metal in 1956 was 14,500 tons (excluding the U.S.S.R.) [212].

Metallic cobalt is slowly dissolved by dilute hydrochloric and sulfuric acids, with the formation of salts of bivalent cobalt and liberation of gaseous hydrogen. Cobalt is slowly oxidized by dilute nitric acid, which is thus reduced to nitrogen, nitrogen dioxide, nitric oxide, and ammonia. Concentrated nitric acid reacts much more vigorously, but fuming nitric acid passivates cobalt, so that the dissolving stops. Concentrated acetic and oxalic acids dissolve cobalt metal very slowly, while hydrofluoric acid has practically no action.

Cobalt readily dissolves at ordinary temperatures in a mixture of hydrochloric and nitric acids. Alkali hydroxides do not attack cobalt at ordinary temperatures, but at 500–600° a reaction takes place.

In the electromotive series, cobalt stands left of hydrogen. The values of the normal potentials of $\text{Co}^{2+}-\text{Co}^0$ found by different investigators are listed in Table 2.

Table 2
 $\text{Co}^{2+}-\text{Co}^0$ OXIDATION POTENTIALS
(with respect to normal hydrogen electrode)

Potential, V	References	Potential, V	References
–0.153	[1137]	–0.283	[1271]
–0.298	[958]	–0.246	[973]
–0.292	[583]	–0.278	[808]
		–0.277	[824]

Oxidation potentials for $\text{Co}^{2+}-\text{Co}^0$ in alkaline and ammoniacal solutions have also been measured or calculated, as well as in solutions containing sulfide and carbonate ions (Table 3).

Table 3
Co(II)–Co REDOX POTENTIALS [198, 902]
(with respect to normal hydrogen electrode)

Reaction	Potential, V
$\text{Co(OH)}_2 + 2e = \text{Co} + 2\text{OH}^-$	–0.73
$\text{Co(NH}_3)_6^{2+} + 2e = \text{Co} + 6\text{NH}_{3\text{aq}}$	–0.42
$\text{CoS}_a + 2e = \text{Co} + \text{S}^{2-}$	–0.90
$\text{CoS}_\beta + 2e = \text{Co} + \text{S}^{2-}$	–1.07
$\text{CoCO}_3 + 2e = \text{Co} + \text{CO}_3^{2-}$	–0.64

Ions of trivalent cobalt possess strong oxidative properties and are capable of decomposing water. The potential Co(III)–Co(II) in 3M HNO₃ is 1.842V [972, 1150]; another value of 1.3V has recently [273] been calculated from the solubility product of Co(III) hydroxide ($K_s = 3 \cdot 10^{-41}$).

The potentials of some reactions corresponding to the valence transition Co(III)–Co(II) are listed in Table 4.

The potential for the conversion of Co(IV) oxide (formed in alkali solutions by strong oxidants) to Co(III) hydroxide is 0.7V [781]: $\text{CoO}_2 + 2\text{H}_2\text{O} + e = \text{Co(OH)}_3 + \text{OH}^-$.

Aqueous solutions of highly dissociated cobalt salts contain hydrated ions of Co(II), which are pink.

From the elevation of the boiling point of aqueous solutions of cobalt salts [1244], it was established that the number of water molecules in the hydrated hull of the cobalt ion is 26. Studies of absorption spectra of ethanol-water solutions of cobalt chloride showed that the number of water molecules in the mixed ethanol-water hull of the ion increases at higher concentrations of the salt; the limiting number of water molecules after complete replacement of the ethanol molecules in the solvate hull

Table 4
Co(III)–Co(II) REDOX POTENTIALS [198, 1163]
(with respect to normal hydrogen electrode)

Reaction	Potential, V
$\text{Co(OH)}_3 + e = \text{Co(OH)}_2 + \text{OH}^-$	0.17
$\text{Co(NH}_3)_6^{3+} + e = \text{Co(NH}_3)_6^{2+}$	0.1
$\text{Co(Phen)}_3\text{Cl}_3 + e = \text{Co(Phen)}_3\text{Cl}_2 + \text{Cl}^-$	0.37
$\text{Co(Dipy)}_3\text{Cl}_3 + e = \text{Co(Dipy)}_3\text{Cl}_2 + \text{Cl}^-$	0.31
$\text{Co(Phen)}_3(\text{ClO}_4)_3 + e = \text{Co(Phen)}_3(\text{ClO}_4)_2 + \text{ClO}_4^-$	0.42
$\text{Co(Dipy)}_3(\text{ClO}_4)_3 + e = \text{Co(Dipy)}_3(\text{ClO}_4)_2 + \text{ClO}_4^-$	0.37

Note: Phen—phenanthroline; Dipy— α, α' -dipyridyl.

was found to be 4 [220]. Simple (noncomplex) ions of trivalent cobalt are unstable in aqueous solutions. They may appear as an intermediate form during the oxidation in weakly acid aqueous solutions of Co(II) salts by strong oxidants [285], for example, sodium hypochlorite, ozone [182], etc., but they are readily hydrolyzed even at pH 1.8–2.5, with the immediate precipitation of the hydroxide of Co(III). For the hydrolysis rate of complex ions of trivalent cobalt, see [1169].

Oxides and hydroxides

Oxides and hydroxides are known for bi-, tri-, and tetravalent cobalt.

Oxides and hydroxides of bivalent cobalt

Cobalt(II) oxide, CoO , is formed when cobalt metal is oxidized by water vapor at red heat, as well as when carbonates, sulfates, and the hydroxide of bivalent cobalt are heated in an inert gas atmosphere or in vacuo. Cobalt(II) oxide is gray-green in color; the shade depends on the manner of preparation and varies between green, brown, gray, and black. Cobalt (II) oxide is stable above $900\text{--}930^\circ$ [980]. If the precipitate of Co(II) hydroxide is dried for a long time at 110° , it is converted to HCoO_2 [238]. The thermogram of Co(OH)_2 displays four endothermal effects with temperature ranges of $140\text{--}230$, $270\text{--}310$, $750\text{--}850$, and $910\text{--}960^\circ$. It is assumed that moderate heating causes the transition from Co(OH)_2 to HCoO_2 , then to Co_3O_4 ; at higher temperatures, Co_3O_4 is converted to CoO , which is stable above 920° ; see also [201].

Cobalt(II) oxide is readily soluble in hydrochloric, sulfuric, nitric, and other strong acids, and less readily in acetic, oxalic, tartaric, and hydrofluoric acids, with the formation of the corresponding salts of Co(II), which are pink.

The hydroxide of Co(II) is formed when sodium hydroxide or ammonium hydroxide solution is added to solutions of salts of bivalent cobalt. At ordinary temperatures, especially in the absence of air, if the precipitation is carried out with a small excess of sodium hydroxide solution, a blue precipitate is first formed, which gradually turns violet and, finally, pink. This transformation of the precipitate into the stable pink form is accelerated by heating. X-ray studies have established the crystalline structure of both modifications and the higher dispersity of the blue precipitate [851]. The blue modification is ascribed the formula of the basic salt Co(OH)Cl or hydrated cobalt(II) oxide $\text{CoO} \cdot \text{H}_2\text{O}$, while the pink precipitate is cobalt hydroxide Co(OH)_2 . The latter is slowly oxidized by atmospheric oxygen and converted to Co(OH)_3 , which is brown. The oxidation is accelerated by the addition of chlorine, bromine, hydrogen peroxide, or other oxidants.

Precipitation of cobalt(II) hydroxide begins at pH 7.8. Cobalt is completely precipitated at pH ~ 10 [760]. However, the data of different workers do not always agree. Hillebrand reported the value pH 6.8 in the papers [63, 509]. Apparently,

the discrepancies are explained by the different experimental conditions. It has been proposed [324] that the pH values at the beginning of precipitation be standardized by referring them to the initial activity of the metal ions in solution, taken as unity. In this case, the value of the pH at the beginning of precipitation of Co(OH)_2 was found to be 6.8.

Table 5
SOLUBILITY PRODUCT OF
 Co(OH)_2

K_s	$-\log K_s$	References
$1.3 \cdot 10^{-15}$	14.89	[151]
$2.5 \cdot 10^{-12}$	11.60	[145]
$2.5 \cdot 10^{-16}$	15.60	[751]

If a solution of cobalt chloride is titrated by solutions of NaOH and Na_2CO_3 , hydroxides and basic carbonates are formed [344]. The pH value for the beginning of precipitation depends on the initial logarithmic concentration of cobalt, and varies between 3.8 and 5.6.

The hydrolysis of Co(II) salts proceeds in stages with the intermediate formation of Co(OH)^+ ions. The instability constant for this ion was determined as $4 \cdot 10^{-5}$ [367, 557, 752]. The corresponding equilibrium constant of the hydrolysis reaction $\text{Co}^{2+} + \text{H}_2\text{O} = \text{Co(OH)}^+ + \text{H}^+$ was calculated as 10^{-7} [1184]. The acid dissociation constant, $\text{Co(OH)}_2 = \text{HCoO}_2^- + \text{H}^+$, is $8 \cdot 10^{-20}$ [751].

The values of the solubility product of Co(OH)_2 are listed in Table 5.

For other data, see [210, 254, 315, 141, 61].

Mixed oxide Co_3O_4

This compound is formed when cobalt (II) oxide, CoO , is heated in the temperature range $400\text{--}900^\circ$, or when pyrophoric cobalt burns in air. It is also obtained by heating cobalt hydroxide. It was established thermogravimetrically [238] that in the temperature range $120\text{--}190^\circ$ Co(OH)_3 first forms HCoO_2 , which is converted to Co_3O_4 at $240\text{--}300^\circ$. This oxide is stable between 300 and 770° , but further rise in temperature ($770\text{--}920^\circ$) causes thermal dissociation:



The mixed oxide is readily reduced to CoO and then to the metal when heated in a stream of hydrogen to $300\text{--}350^\circ$. Reduction to metal can also be carried out by heating with carbon, carbon monoxide, etc. [201].

The mixed oxide Co_3O_4 dissolves slowly in acids to give salts of bivalent cobalt and free hydrogen. The dissolution in hydrochloric acid is accompanied by liberation of chlorine.

Cobalt(III) oxide Co_2O_3 and cobalt(III) hydroxide $\text{Co}(\text{OH})_3$

Cobalt(III) oxide Co_2O_3 is a brown or dark brown powder. Some authors doubt its existence in the anhydrous state [851, 1008, 1136]. The known hydrates $\text{Co}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$, $\text{Co}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, and $\text{Co}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ are formed in humid air. According to thermogravimetric data, the hydrate $\text{Co}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (or HCoO_2) exists up to about 240° , above which it dissociates and is converted to the mixed oxide Co_3O_4 .

Cobalt(III) hydroxide, $\text{Co}(\text{OH})_3$, is brown and is formed when $\text{Co}(\text{II})$ salts are oxidized in alkali solutions by chlorine, bromine, sodium hypochlorite, chlorate or persulfate, or other oxidants. The resulting hydrates often contain more oxygen than corresponds to the formula Co_2O_3 [846]. The composition of the hydroxide is best expressed by the formula $\text{Co}_2\text{O}_3 \cdot x\text{H}_2\text{O}$. When it is dried over sulfuric acid or heated, it gradually loses water, yielding hydrates with lower water contents, for example, $2\text{Co}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, $\text{Co}_2\text{O}_3 \cdot \text{H}_2\text{O}$, $3\text{Co}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$. When the compounds $\text{Co}(\text{OH})_3 \cdot x\text{H}_2\text{O}$ are precipitated by hypochlorite from chloride or sulfate solutions, they have no crystalline structure [286], but are gels. When dried at 110° , the preparation $\text{Co}(\text{OH})_3$ is also amorphous to X rays. If it is heated to 200° , it displays a crystalline structure characteristic of the hydrate $\text{Co}_2\text{O}_3 \cdot \text{H}_2\text{O}$.

The oxide and hydroxide of trivalent cobalt dissolve in acids to give salts of bivalent cobalt and oxygen is evolved.

Simple ions of trivalent cobalt are unstable in aqueous solutions and are readily reduced to ions of bivalent cobalt.

The precipitation of the hydroxide of trivalent cobalt by the action of an alkali and an oxidant on a solution of a salt of bivalent cobalt starts at $\text{pH} \sim 6$ and is complete at $\text{pH} 8-10$. The solubility of the precipitate in hot water is $3.2 \cdot 10^{-4}$ mg/liter [390]. The solubility product is $2.5 \cdot 10^{-43}$ [155]; according to other sources [286], the following values were obtained by thermodynamic calculations for the solubility product of $\text{Co}(\text{OH})_3$: $3.2 \cdot 10^{-45}$ at 19° and $3.2 \cdot 10^{-44}$ at 81° . Another reported value was $1 \cdot 10^{-43}$ [198]. The solubility of cobalt hydroxide was determined by means of radioactive cobalt isotopes as $5.6 \cdot 10^{-3}$ mg/liter.

Oxide of tetravalent cobalt CoO_2

This is partially formed during the preparation of Co_2O_3 [852, 1065]. It is unstable, and readily decomposes with liberation of oxygen.

Sulfides

In analytical chemistry, an important part is played by the sulfides of bivalent cobalt, CoS , formed when ammonium sulfide (or hydrogen sulfide) reacts with aqueous solutions of cobalt salts. The sulfide Co_5S_4 and other sulfides can be prepared by direct elemental synthesis at high temperatures [254]. Co_3S_4 occurs as the mineral linnaeite, but can also be prepared artificially [883].