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ANALYTICAL CHEMISTRY OF NICKEL

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Translated by J. SCHMORAK



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ANALYTICAL CHEMISTRY OF THE ELEMENTS

ANALYTICAL CHEMISTRY OF NICKEL

Analytical Chemistry of the Elements

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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 the 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 nickel has been the subject of numerous studies. Many of these deal with the reactions between nickel and α -dioximes, which were first introduced into analytical chemistry by L. A. Chugaev. For this reason, the use of α -dioximes as reagents for nickel has been described in detail in the present volume.

The arrangement of this book follows the general outline of the series *Analytical Chemistry of the Elements*. Due to the large amount of material available, the authors did not consider it advisable to give an exhaustive bibliography of the methods for the determination of nickel; preference has been given to general reviews and to summaries of results.

The authors wish to express their gratitude to A. A. Fedorov, Senior Scientific Worker at the Central Ferrous Metals Research Institute, for putting at our disposal a number of new GOST draft specifications for the determination of nickel in steels which have been developed in the Institute by the team led by Dr. P. Ya. Yakovlev.

V. Peshkova
V. Savostina

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CHAPTER I

Chemical and Analytical Properties of Nickel

Nickel was discovered in 1751 by the Swedish chemist Cronstedt, but was not obtained in the pure state until 1804. Richter, Proust, Thénard and other chemists proved its elemental nature [951].

Nickel belongs to Group VIII of the Periodic Table. Its atomic number is 28; its atomic weight on the carbon scale is 58.71. The natural and artificial isotopes of nickel are listed in Table 1. The isotopic composition of nickel explains the fact that the atomic weight of naturally occurring nickel is lower than that of cobalt, which has the atomic number 27 [9, 58, 332]. The nickel atom has the following electron structure:

<i>K</i>	<i>L</i>	<i>M</i>	<i>N</i>
2	2, 2, 4	2, 2, 4, 3, 5	2

The radius of Ni^{2+} ion is 0.78 \AA ; the ionic potential $Z/R = 2.6$.

The elements of the first transitional period can be arranged in the order of increasing third ionization potential [233]: Sc, Ti, V, Fe, Co, Mn, Ni, Cu, Zn, Ca. The difficulty encountered in oxidizing Cu^{2+} and Ni^{2+} ions is due to the high values of their third ionization potentials.

Nickel is positively bivalent in most of its compounds, but in certain compounds, mainly complexes, it may have the valency +3 or +4.

The abundance of nickel in nature is somewhat higher than that of copper and somewhat less than that of zinc. Its average content in the Earth is 0.018 wt. %.

Table 1
ISOTOPES OF NICKEL [1199]

Atomic weight	Type of radiation	Half-life	Origin of isotope	Content in naturally occurring nickel, %
56	γ	6.4 days	Artificial	—
57	β^+	36 hours	Artificial	—
58	—	Stable	Natural	67.76
59	K, no β^+	$5 \cdot 10^4$ years	Artificial	—
60	—	Stable	Natural	26.16
61	—	Stable	Natural	1.25
62	—	Stable	Natural	3.66
63	β^-	125 years	Artificial	—
64	β^-	More than $3 \cdot 10^{15}$ years	Natural	1.16
65	β^-, γ	2.6 hours	Artificial	—
66	β^-	54.8 hours	Artificial	—

Its content in the crust is $2 \cdot 10^{-2} \%$, in the lithosphere $8 \cdot 10^{-3} \%$, in stony meteorites 0.14% and in iron meteorites 8.6% by weight [299].

It is assumed that the Earth's core contains 6–8% nickel. The average content of nickel in plants is $10^{-6} \%$.

Sulfide, silicate and oxide nickel ores are of industrial importance.

Nickel is a silvery white metal with a hardly noticeable brownish tinge, very malleable and ductile, easily rolled; it is ferromagnetic, but less so than iron. The density of nickel is 8.85–8.9 g/cm³. Nickel of high purity (99.94%) melts at 1455°.

In the electrochemical series nickel is situated to the right of cobalt, with a standard electrode potential of -0.250 v.

At room temperature and in the absence of moisture metallic nickel is stable to the action of oxygen and halogens; when heated to 500° in the air, it becomes oxidized to a certain extent and decomposes water with evolution of hydrogen. Nickel powder obtained by distillation from amalgams or by electrolysis is to a certain extent pyrophoric. Nickel is not very reactive and is unaffected by water at room temperature. In dilute mineral acids (HCl, H₂SO₄) it dissolves slowly; nitric acid dissolves it more readily. Concentrated nitric acid passivates nickel, as it does iron. Alkali hydroxides and sodium and potassium carbonates do not react with nickel either in aqueous solutions or in the melt.

Nickel is a constituent of numerous alloys with iron, and also with copper, aluminum and many other elements.

Finely powdered metallic nickel absorbs hydrogen at elevated temperatures and is used as catalyst in the hydrogenation of organic compounds. The existence of the hydride NiH has been demonstrated [296]. NiH₂ and NiH₄ are also known.

Nickel reacts with carbon monoxide with the formation of carbonyls.

As for other doubly charged ions, the coordination number of nickel for water molecules is six [210, 823]. The first hydrolysis constant of hydrated nickel ion, in accordance with the equation



found by pH-metric titration of nickel nitrate in 10^{-2} M potassium sulfate or chlorate at 25° is $\text{pK} = 10.92$ [400].* According to another study [701] $\text{pK} = 10.64$.

It was found by spectrophotometric studies that the hydrated nickel ion contains six water molecules; the total addition constant $\log \beta_6/6 = 0.09$ [813].

Nickel oxides and hydroxides

A number of nickel oxides are known [496]. The oxide of bivalent nickel, NiO, is a light greenish yellow powder, soluble in hot nitric acid and in solutions of ammonia. After ignition at high temperatures NiO becomes insoluble in alkalis, ammonia and mineral acids. It may be used as a weighing form; it may be obtained, for example, by ignition of nickel dimethylglyoximate.

Nickelic oxide (III) and nickelic-nickelous (II and III) oxide Ni_3O_4 are, respectively, dark gray and brownish black powders. They are soluble in sulfuric and nitric acids with the evolution of oxygen and in hydrochloric acid with the evolution of chlorine.

Nickel dioxide NiO_2 is a black, amorphous substance. This is the least stable nickel oxide. It dissolves sluggishly in mineral acids with the evolution of oxygen or chlorine.

Depending on the experimental conditions [496], nickel ion with hydroxyl ions forms a number of different compounds, which display a tendency to form basic salts [52a, 501].

Nickel (II) hydroxide $\text{Ni}(\text{OH})_2$ is a light green powder, which decomposes into NiO and H_2O at 230° . It is soluble in acids and in ammonia. Data on the solubility product of $\text{Ni}(\text{OH})_2$ are contradictory (Table 2).

Nickel (II) hydroxide is converted in the presence of strong oxidants (Cl_2 , Br_2) in alkaline medium into nickel (III) hydroxide $\text{Ni}(\text{OH})_3$.

Nickel (III) hydroxides of other compositions, e.g., $\text{Ni}_x\text{O}_y(\text{OH})_z$ are also known [496]. Nickel (III) hydroxide can be obtained in two modifications: 1) the β -modification, which does not appear to be crystalline and is converted into $\text{Ni}_3\text{O}_2(\text{OH})_4$

* The following notation will be used in what follows:

β_n —total stability constant for the reaction $\text{Ni}^{2+} + n\text{A}^{-m} \rightleftharpoons \text{NiA}_n^{2-mn}$;

K_m —stepwise stability constant $\text{NiA}_{n-1}^{2-(n-1)m} + \text{A}^{-m} \rightleftharpoons \text{NiA}_n^{2-mn}$;

S—solubility of compound.

4 ANALYTICAL PROPERTIES OF NICKEL

Table 2
SOLUBILITY PRODUCT OF $\text{Ni}(\text{OH})_2$

Temperature, °C	pL_p	References	Temperature, °C	pL_p	References
17	18.06	[501]	25	18.06	[219a]
18	14.87	[3]	25	17.19	[700]
20	15.0	[581]	25	15.5	[1119]
25	13.81	[598]	28–30	16.0	[795]
25	14.5	[1009]	75	16.2	[93]
25	15.21	[993]			

on standing in the air; 2) the γ -modification, which is crystalline (hexagonal crystals or platelets). Both modifications are soluble in H_2SO_4 with the evolution of oxygen and decompose when heated to 138–140°.

The nickel (II, III) compound $\text{Ni}_3\text{O}_2(\text{OH})_4$ separates out as fine black hexagonal crystals; when heated to 140°, it is converted to NiO with the evolution of water and oxygen.

Nickel hydroxides are prepared by indirect methods: $\text{Ni}(\text{OH})_2$ by the action of dilute alkali solutions on nickel salts (the hydroxide is basic); nickel (III) and nickel (II, III) hydroxides are prepared by the action of oxidizing agents in alkaline media. $\text{Ni}(\text{OH})_3$ may also be prepared by the action of hydrogen peroxide in weakly acetic acid medium on nickel salts. This method is often employed in qualitative analysis for the detection and separation of nickel.

Chugaev and Khlopin [362] reported the preparation of nickel (I) hydroxide NiOH .

Complex nickel compounds with OH^- as ligand have been studied mainly with a view to determining the values of K_1 (Table 3). A number of workers [549, 701, 873] calculated the hydrolysis constants of nickel ion.

Table 3
STABILITY OF THE COMPLEX COMPOUND
OF NICKEL $[\text{NiOH}]^+$ WITH HYDROXYL ION

Temperature, °C	$\log K_1$	$\log \beta_1$	References
20	4.70	—	[906]
25	—	12.96	[590]
25	5.0	—	[1119]
100	3.77	—	[876]

Nickel sulfides

The separation of nickel as sulfide is widely employed in chemical analysis. Three modifications of nickel sulfide NiS (α , β and γ) are known [223], which have different solubilities in aqueous solutions and in acids [604]. Whatever the modification in which it is isolated, nickel sulfide after isolation and drying is a black powder. If kept moist in the air, NiS_α passes into NiOHS . Table 4 gives the values of the solubility products pL_p and solubilities in acids.

The sulfide NiS_α readily forms colloidal solutions (sols), which pass through the filter paper; the compound is difficult to coagulate.

Nickel is often separated (usually together with cobalt) from other elements as sulfide. It is therefore important to work under conditions ensuring the formation of an easily filterable NiS_α precipitate.

To obtain such a precipitate [46], $\frac{1}{10}$ volume of 25% ammonia solution is added to one volume of hot neutral solution containing nickel and other cations of the first three analytical groups, and the mixture is saturated with H_2S . The solution is left to stand for 20–25 minutes, and the precipitate is filtered and washed first with hot water containing ammonium sulfide and ammonium chloride, and then with 2 N HCl.

High-quality nickel sulfide can also be obtained by precipitating with a freshly prepared solution of ammonium sulfide (free from ammonium carbonate).

Nickel and cobalt sulfides are precipitated in the crystalline state by hydrogen sulfide in the presence of pyridine [234].

Table 4
PROPERTIES OF NICKEL SULFIDES

Compound	Temperature, °C	pL_p	References	Acids in which the sulfide is soluble	References
NiS_α	—	20.5	[1183]	1–2 N HCl in the cold	[6]
	25	20.5	[219a]		
	18–25	20.5	[1085]		
NiS_β	25	18.5	[46]	6 N HCl + H_2O_2	[6]
	—	26.0	[1183]		
	18–25	26.0	[1085]		
NiS_γ	25	24.0	[46]	2 N HCl + H_2O_2	[46]
	—	27.7	[1183]		
	18	23.85	[1085]	2 N HCl + KClO_3	
	18	24.16	[46]	$\text{CH}_3\text{CO}_3\text{OH} + \text{H}_2\text{O}_2$	[171, 139]
	18–28	27.7	[512]	Hot concentrated HNO_3	[6, 46]
	20	29.96	[513]	Mixture of HNO_3 and HCl	
	25	20.7	[1091]		
			[984]		

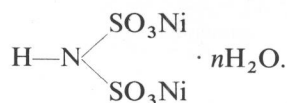
Moser and Behr [984] studied the precipitate of nickel sulfide by X-ray diffraction method and failed to detect the α , β , and γ -forms; the precipitate of nickel sulfide ages to form Ni_{1-x}S , with an increasing value of x .

The compound NiS_2 was obtained as a crystalline, grayish black powder; the greenish black polysulfide Ni_3S_4 is known to occur in nature.

Cobalt sulfides are similar to nickel sulfides. $pL_p\text{CoS}_\alpha = 22.5$; $pL_p\text{CoS}_\beta = 26.7$.

Complex salts of nickel with inorganic ligands

Nickel is bivalent in most of its compounds. In certain complex compounds it is monovalent; it may also appear in valencies higher than two. The compound $\text{K}_4[\text{Ni}(\text{CN})_4]$, with a formal valency of zero, is formed when metallic nickel is made to act on $\text{K}_2[\text{Ni}(\text{CN})_4]$ in liquid ammonia. The compound of monovalent nickel $\text{K}_2[\text{Ni}(\text{CN})_3]$ has also been obtained [453, 1024]. Chugaev and Khlopin [362] described the crystalline violet compound of nickel (I) with the probable formula



If alkali is added to the compound, the blue hydroxide NiOH is obtained. The following compounds of nickel (I) are also known: $\text{K}_3[\text{Ni}(\text{NO})_2(\text{S}_2\text{O}_3)_2]$, $\text{K}_2[\text{Ni}(\text{CN})_3\text{NO}]$, $\text{Ni}(\text{NO})\text{Cl}$, $\text{Ni}(\text{NO})\text{Br}$, $\text{Ni}(\text{NO})\text{I}$.

Nickel sulfate forms a number of hydrates: $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{NiSO}_4 \cdot 4\text{H}_2\text{O}$ [138]. Table 5 gives the values of the stability constants obtained for the compound of nickel with sulfate ions.

Double salts $\text{Me}_2^+\text{SO}_4 \cdot \text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, where $\text{Me} = \text{NH}_4^+$, are used in nickel-plating baths.

Nickel nitrate forms several hygroscopic hydrates, depending on the temperature: $\text{Ni}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$.

Table 5
STABILITY OF THE COMPOUND OF NICKEL
WITH SULFATE IONS

Temperature, °C	Determination method	$\log K_1$	References
0	Cryoscopic	2.06	[497]
0	Cryoscopic	2.34	[832]
25	Conductometric	2.40	[679]