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NUCLEAR SCIENCE SERIES

The Radiochemistry of Nickel

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The Radiochemistry of Nickel

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Richland, Washington

November 1961

Subcommittee on Radiochemistry
National Academy of Sciences — National Research Council

Available as NAS-NS-3051 for $9.50 from

National Technical Information Service
U. S. Department of Commerce
Springfield, Virginia 22161

Printed in the United States of America
USDOE Office of Scientific and Technical Information,
Oak Ridge, Tennessee

1961: latest printing May 1985

FOREWORD

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

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

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

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

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

W. Wayne Meinke, Chairman
Subcommittee on Radiochemist

INTRODUCTION

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

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

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Remy, H., "Treatise on Inorganic Chemistry," Tr. by Anderson, J. S., Kleinberg, J., Ed., Volume II, "Sub-groups of the Periodic Table and General Topics," Elsevier Publishing Company, Amsterdam (1956).

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Scott, W.W., "Standard Methods of Chemical Analysis," Furman, N.H., Ed., 5th Ed., Volume I, D. VanNostrand Co., Inc., New York (1939).

II. REVIEWS OF THE RADIOCHEMISTRY OF NICKEL

Brosi, A.R., Ind. Eng. Chem. 44, 955 (1952).

Wahl, A.C., and Bonner, N.A., Eds., "Radioactivity Applied to Chemistry," John Wiley and Sons, Inc., New York (1951).

Finston, H.L., and Miskel, J., Ann. Rev. Nuc. Sci. 5, 269 (1955).

The last two references are not specifically reviews of the radiochemistry of nickel, but contain sufficient information thereon to be of considerable background use.

III. TABLE OF ISOTOPES OF NICKEL[a]

Isotope	Half-life	Decay	Energy, Mev.	Percent Abundance (Stable Isotopes) or Method of Preparation[b]	Thermal Neutron Cross-section, Barns[c]
Ni				100	4.6 ± 0.1
Ni^{56}	6.4 d	EC, no β^+(<1%)		Fe^{54}(α,2n)	
		γ(100)	0.17	Spall Zn	
		γ(30)	0.28		
		γ(40)	0.48		
		γ(80)	0.81		
		γ(10)	0.96		
		γ(5)	1.33		
		γ(15)	1.58		
		γ(2)	1.75		
Ni^{57}	36 h	β^+(87)	0.849	Ni^{58}(γ,n)	
		β^+(11)	0.72	Fe^{54}(α,n)	
		β^+(2)	0.35	Co^{59}(p,3n)	
		β^+(50%)		Ni^{58}(n,2n)	
		EC(50%)		Ni^{58}(He^3,α)	
		γ (14%)	0.1272	Spall Cu	
		γ(0.5%)	0.40		
		γ (86%)	1.368		
		γ (14%)	1.89		
Ni^{58}	Stable			67.76	4.4 ± 0.3
Ni^{59}	8×10^4 y	EC,no β^+	Co K-X-ray	Ni^{58}(n,γ)	
		No γ		Fe^{56}(α,n)	
				Ni^{58}(d,p)	
				Co^{59}(d,2n)	
Ni^{60}	Stable			26.16	2.6 ± 0.2
Ni^{61}	Stable			1.25	2.0 ± 1.0
Ni^{62}	Stable			3.66	15 ± 2
Ni^{63}	125 y	β^-	0.067	Cu^{63}(n,p)[d]	
				Ni^{62}(n,γ)	
Ni^{64}	Stable $t_{\beta\beta}>3\text{x}10^{15}$y			1.16	1.52 ± 0.14
Ni^{65}	2.564h	β^-(57%)	2.10	Ni^{64}(n,γ)	20 ± 2
		β^-(29%)	0.60	Cu^{65}(n,p)	
		β^-(14%)	1.01	Ni^{64}(d,p)	
		γ(29 -x%)	1.49	Cu^{65}(d,2p)	
		γ(14 +x%)	1.12	Cu^{65}(t,He^3)	
		γ (x%)	0.37	Zn^{68}(n,α)	
				Spall Cu,As	
				Spall-fission Ta,Bi,U	

III. TABLE OF ISOTOPES OF NICKEL[a] (Continued)

Isotope	Half-life	Decay	Energy, Mev.	Percent Abundance (Stable Isotopes) or Method of Preparation[b]	Thermal Neutron Cross-section, Barns[c]
Ni^{66}	54.8h	β^- No γ (<1%)	0.20	Spall As Spall-fission Ta,Bi,U	
		β^- (Cu^{66}-91%)	2.63		
		β^- (Cu^{66}-9%)	1.59		
		γ (Cu^{66}-9%)	1.04		

a. All data, except as noted, have been taken from Strominger, D., Hollander, J.M., and Seaborg, G.T., Revs. Modern Phys. 30, 632-3 (1958)

b. Except as noted, all methods of preparation have been taken from Hollander, J.M., Perlman, I., and Seaborg, G.T., Revs. Modern Phys. 25, 496-7 (1953).

c. Hughes, D.J., and Schwartz, R.B., Report No. BNL-325, "Neutron Cross Sections", Second Edition (July 1, 1958).

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d. Preiss, I.L., Fink, R.W., and Robinson, B.L., J. Inorg. Nucl. Chem. 4, 233-6 (1957).

IV. REVIEW OF THOSE FEATURES OF NICKEL CHEMISTRY OF CHIEF INTEREST TO RADIOCHEMISTS*

The ferrous metals, iron, cobalt, and nickel, exist in igneous rocks in the respective abundances 5.0%, 2.3×10^{-3}% and 8.0×10^{-3}%. Nickel is found in nature chiefly in combination with sulfur, arsenic and antimony, and the core of the earth may be composed of iron and nickel.

Nickel, along with iron and cobalt, is a moderately strong reducing agent; all three displace hydrogen from acids, with the formation of bivalent ions. Standard potentials for several couples of these three elements are compared in Table I(1).

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*Except as occasionally referenced, the information in this section has been condensed from the general references in Section I. of this monograph.

TABLE I

Standard Potentials

		E^0_{298}, volts	
Reaction	**Iron**	**Cobalt**	**Nickel**
$M = M^{++} + 2e^-$	0.440	0.277	0.250
$M + 2OH^- = M(OH)_2 + 2e^-$	0.877	0.73	0.72
$M^{++} + 2H_2O = MO_2 + 4H^+ + 2e^-$	---	---	-1.68
$M(OH)_2 + 2OH^- = MO_2 + 2H_2O + 2e^-$	---	---	-0.49
$M(OH)_2 + OH^- = M(OH)_3 + e^-$	0.56	-0.17	---
$M + 6NH_{3(aq)} = M(NH_3)_6^{++} + 2e^-$	---	0.42	0.49
$M + CO_3^= = MCO_3 + 2e^-$	0.756	0.64	0.45
$M + S^= = MS + 2e^-$	0.97(α)	0.90(α) 1.07(β)	0.83(α) 1.04(γ)
$M^{++} = M^{+++} + e^-$	-0.771	-1.842	---

Compounds of the dipositive elements resemble those of chromium (II) and manganese (II), but are somewhat less basic and more strongly hydrolyzed because of their smaller cation radii. The ions resist oxidation in acid solutions, but are reasonably readily oxidized in neutral or alkaline media. The resemblances between cobalt (II) and nickel (II) are close.

Nickel is predominantly electropositively bivalent in its compounds, and all the simple nickel salts are derived from that valence state. Stable compounds are known in the tetravalent state, but the mono- and trivalent states are generally unstable and poorly characterized. Almost all nickel salts can form addition compounds or coordination compounds, both of the type of ammines and of the type of acido-compounds. The coordination compounds of nickel are less strongly complexed than those of cobalt, especially of cobalt (III). The stereochemistry and valence states of nickel have been reviewed by Nyholm(2).

1. Compounds of Nickel

Nickel metal, oxides and hydroxides.

Nickel is a silver-white metal of high luster, density 8.90 (20°), hardness 3.8 (Moh scale), melting point 1453° and boiling point about 2900°. It is ferromagnetic in the cubic lattice, although to a smaller extent than is iron. The electrical conductivity at 18° is 13.8% and 14.9% of that of silver and copper, respectively. Certain nickel alloys, however, have a considerable lower conductivity and are used as electrical resistance wires (e.g., constantan, manganin, nichrome). The thermal conductivity of nickel is about 15% of that of silver.

Compact nickel is very resistant towards water and air at ordinary temperatures, but the finely divided metal may be pyrophoric under certain conditions. Nickel sheet tarnishes like steel when heated in air, and heated nickel catches fire in chlorine or bromine. It also unites with phosphorus, arsenic and antimony. In the molten state, nickel takes up carbon readily. Nickel combines extremely vigorously with aluminum, an equiatomic mixture of the two combining explosively at 1300°. Nickel is completely miscible with cobalt, and its behavior with manganese and chromium is similar at high temperatures. Nickel is also miscible with iron in the solid state.

Metallic nickel decomposes ammonia into hydrogen and nitrogen at moderate temperatures. Hydrogen can be absorbed in fairly large quantities by finely divided nickel, especially at high temperatures, and this ability to take up hydrogen and to convert it to the atomic state is the basis of nickel's action as a hydrogen carrier for unsaturated compounds, and of its use as a catalyst in hydrogenations.

Nickel (II) hydroxide forms as a voluminous apple-green precipitate when alkali hydroxides are added to nickel salt solutions. It is readily soluble in acids and in aqueous ammonia and ammonium salt solutions. An easily filterable form is prepared by the decomposition of the triethanolamine complex in strongly alkaline solution. The active form of nickel (II) hydroxide used in the Edison storage battery is precipitated from sulfate solution with excess sodium hydroxide. The gel is dried slowly with the enclosed salts and alkali, which are subsequently washed out. The excess alkali reduces the porosity of the final product.

A sol of nickel (II) hydroxide results when solutions containing equivalent amounts of nickel tartrate and potassium hydroxide are mixed(3) Precipitation proceeds slowly from solutions as concentrated as normal, yielding a transparent green jelly; however, if the solutions are dilute (about 0.1 N) a sol forms which can be purified by dialysis. Alkali degradation products of albumin act as protecting colloids for this sol.

The hydroxides of nickel are usually obtained by reacting a salt solution with a base (ammonium hydroxide yields precipitates which in most cases ignite better), by hydrolyzing the salts, and through formation on electrolysis. In approximately 0.02 M solutions, hydroxides of various metals begin to precipitate at the pH values which are compared in Table II (4). The hydroxides of nickel, copper, zinc and cadmium are also soluble in excess ammonia. For difficult-to-prepare higher hydroxides such as nickel (III) hydroxide, one first forms the lower oxide and then oxidizes this compound. Thus, nickel (II) hydroxide may be oxidized with chlorine or bromine to higher oxides in which the oxygen to nickel ratio varies from 1.3 to 1.9.

Table II

pH at Beginning of Hydroxide Precipitations

Ion	pH	Ion	pH	Ion	pH
Mg^{++}	10.5	Co^{++}	6.8	Al^{+++}	4.1
Mn^{++}	8.5-8.8	$CdSO_4$	6.7	Th^{++++}	3.5
Lu^{+++}	8.4	Ni^{++}	6.7	In^{+++}	3.4
Ag^{+}	7.5-8.0	Yb^{+++}	6.2	Hg_2^{++}	3.0
$CdCl_2$	7.6	Pb^{++}	6.0	Ce^{++++}	2.7
Ce^{+++}	7.4	Fe^{++}	5.5	Hg^{++}	2
$HgCl_2$	7.3	Cu^{++}	5.3	Sn^{++}	2
Pr^{+++}	7.1	Cr^{+++}	5.3	Sn^{++++}	2
Nd^{+++}	7.0	VO^{++}	4.3	Zr^{++++}	2
Zn^{++}	6.8-7.1	VO_2^{++}	4.2	Fe^{+++}	2
Sm^{++}	6.8			Ti^{++++}	2

Nickel (II) Oxide, NiO, is basic in character and is formed upon ignition of nickel (II) hydroxide, carbonate, or nitrate. Nickel oxide is a green powder, practically insoluble in water but readily soluble in acids. It is reduced to the metal by heating with hydrogen. Nickel (II) oxide may be used for analytical purposes, but one should heat long enough to drive off the last traces of excess oxygen, since Ni_2O_3 forms at 400° and is converted to NiO above 600°(5). It is also possible to precipitate "nickel (III) oxide hydrate" with potassium hydroxide and bromine, and subsequently ignite this to nickel (II) oxide for weighing. Nickel (II) oxide cannot be oxidized to Ni_3O_4 by heating in air, in which case it differs from manganese and cobalt.

Peroxides are often formed when metals are oxidized at the anode; a well-known example is the production of a nickel hydroxide containing more oxygen than Ni_2O_3, which may be a solid solution of hydrated Ni_2O_3 in NiO_2. The higher oxides of nickel have definite, although weak, acidic properties. They exhibit the ability to form double oxides with the more strongly basic oxides, and in so doing simultaneously stabilize the higher oxidation state of nickel (e.g., $Ba_2Ni_2O_5$, $Sr_2Ni_2O_5$, $BaNiO_3$). Distinct phases present in the higher oxides seem to be $NiO_{1.07-1.22} \cdot xH_2O$, $Ni_3O_4 \cdot 2H_2O$, $Ni_2O_3 \cdot xH_2O$ and $NiO_2 \cdot xH_2O$.

Nickel sulfides.

Nickel (II) sulfide is precipitated from nickel salt solutions by ammonium sulfide, initially in an acid-soluble form (α-NiS) which changes rapidly when exposed to air in contact with the solution, into a sulfur-richer compound which is no longer soluble in very dilute hydrochloric acid. Cobalt behaves similarly. Nickel sulfide remains to some extent as a colloidal dispersion when precipitated with ammonium sulfide, and can be coagulated by adding acetic acid and boiling. Stearic acid has also been recommended to retain colloidal nickel sulfide and colloidal sulfur(5). Hydrogen sulfide precipitates a crystalline nickel sulfide (β-NiS) from acetic acid solution, which is sparingly soluble in cold dilute hydrochloric acid. Other sulfides of nickel include γ-NiS, NiS_2, $K_2S.NiS$ and $BaS.4NiS$.

Solubility products of a few of the more common metal sulfides, determined at 18°, are compared in Table III(6). These values should serve primarily as a guide, since in several cases two or more crystalline forms of the sulfides having different solubilities are known to exist.

Table III

Solubility Products of Metal Sulfides

Compound	$K_{s.p.}$	Compound	$K_{s.p.}$
CdS	3.6×10^{-29}	MnS	1.4×10^{-15}
CoS	3×10^{-26}	HgS	4×10^{-53} to 2×10^{-49}
CuS	8.5×10^{-45}		
Cu_2S	2×10^{-47}	NiS	1.4×10^{-24}
FeS	3.7×10^{-19}	Ag_2S	1.6×10^{-49}
PbS	3.4×10^{-28}	ZnS	1.2×10^{-23}

Nickel remains in solution when members of the acid sulfide group are precipitated. Nickel precipitates with other metals of the basic sulfide group, and accompanies zinc and cobalt in the subgroup separation. Zinc may be removed by dissolution of the precipitate and subsequent precipitation of zinc sulfide from a citrate medium buffered at a pH of 4. Nickel and cobalt are reprecipitated as the sulfides after the citrate solution is made basic with ammonia. Nickel can also be separated from other members of the basic sulfide group by precipitation with dimethylglyoxime.

Flaschka (7) has utilized the technique of homogeneous precipitation to form a coarse precipitate of nickel sulfide, which shows [illegible] tendency toward colloid formation. Nickel ions are reacted with [illegible] ammoniacal solution of thioacetamide containing excess ammonium ion. Hydrolysis of the thioacetamide gradually produces the necessary sulfide ion for the precipitation.

Nickel halides.

Nickel (II) chloride is prepared by burning nickel in chlorine, and by heating the compounds $NiCl_2.6H_2O$ and $Ni(NH_3)_4Cl_2$. Nickel chloride is soluble in water and in ethanol, and crystallizes from aqueous solution as the hexahydrate. The hexahydrate converts to the dihydrate on standing over sulfuric acid, and a monohydrate is also known. Nickel chloride will form double salts, e.g., $NH_4Cl.NiCl_2.6H_2O$ and $CsCl.NiCl_2$. Nickel chloride and nickel hydroxide form the compound $NiCl_2.3Ni(OH)_2$, but the hydroxide to chloride ratio may vary between 1.9 to 4.3. The dichloride of nickel, like those of iron, molybdenum and uranium, sublimes direct from the solid state. Nickel (II) bromide and Nickel (II) iodide are prepared in much the same fashion as is nickel (II) chloride, and exhibit similar properties

Nickel (II) fluoride is the sole binary compound of nickel and fluorine, and is prepared by heating the ammonium fluoride double salt, or by reacting fluorine with nickel (II) chloride. Nickel fluoride trihydrate forms upon evaporation of a solution prepared by dissolving nickel (II) hydroxide in hydrofluoric acid. Double salts of the type $KF.NiF_2.H_2O$ are known. Nickel is stabilized in the higher oxidation states through formation of complex fluoro anions (e.g. K_3NiF_6 and K_2NiF_6). $NiF_6^=$ is the only known fluoro complex classified as a "penetration" complex; it is diamagnetic, involving the formation of d^2sp^3 hybrid covalent bonds, whereas other complex fluoro ions are ionic in nature. Only the first mononuclear fluoro complex of nickel (II) exists in appreciable concentrations in dilute aqueous solutions(8).

Because of the use of nickel and high-nickel alloys in equipment for handling fluorine and fluorides, and the presence of nickel (II) fluoride as a frequent impurity in these systems, this compound has received intensive study. A recent review of the literature pertaining to nickel fluoride has summarized important physical and chemical data(9).

Nickel ammines.

Most nickel salts can combine with ammonia, either in the gaseous phase or in the solution phase. The usual coordination number of nickel in the resulting ammines or ammine hydrates is six. Other nitrogen bases, such as aniline, pyridine, quinoline, and ethylenediamine, form similar compounds.

The nickel ammines are mostly soluble in water, either with or without added ammonia. The formation of ammines accounts, for example, for the dissolution of nickel (II) hydroxide and nickel (II) phosphate, both of which are normally insoluble. $Ni(NH_3)_6(ClO_4)_2$ is an exception to this rule of solubility, being very insoluble (contrast with magnesium and barium perchlorates) and utilizable for the quantitative determination of nickel. Ammonia is evolved from this compound only with great difficulty.

Nickel chloride forms ammines with 6, 2, or 1 moles of ammonia. For iodides (hexammines) and sulfates (hexammines; pentammines of copper and zinc) the decomposition temperatures vary in the order nickel > cobalt > iron > copper > manganese > zinc > cadmium > magnesium (4). Nickel forms $Ni(NO_2)_2 \cdot 4NH_3$, but other ammine nitrites are not very readily formed. $Ni(NH_2OH)_6SO_4$ is also known, but compounds of this type generally have less tendency to form than do the ammines.

<u>Nickel cyanides.</u>

When solutions of zinc, nickel, cobalt, manganese, cadmium and iron are treated with potassium cyanide, ill-defined amorphous precipitates are first formed. Long (10) utilized nickel-63 and tagged cyanide ions to elucidate the structure of nickel cyanide, concluding that the structure must contain two "kinds" of nickel, suggesting the formula $NiNi(CN)_4$.

These cyanide compounds dissolve easily in excess potassium cyanide, generally to yield compounds of the type $K_2Ni(CN)_4$. Manganese and iron usually contain six (CN) groupings to the complex, and a similar complex of nickel has also been studied (11). These compounds do not always give the ionic reactions of the elements they contain. Thus potassium ferrocyanide yields no precipitate of ferrous hydroxide, and with an excess of six moles of potassium cyanide to one mole of the complex cyanide, the hydrolysis of the silver, zinc, cadmium, nickel or iron compound is completely suppressed. Such is not the case with the complex cyanides of copper and gold, however.

The complex character of the cyanides is often indicated by the colors of the salts and ions, which differ from those of the simple salts. $K_2Ni(CN)_4$ is a honey-yellow solid, but in solution it undergoes a precipitation reaction with ammonium sulfide, owing to dissociation of the complex. Sodium hydroxide has no effect unless bromine or another oxidizing agent is present, in which case nickel is precipitated and separated from cobalt.

The $Ni(CN)_4^=$ complex may be destroyed by formaldehyde without affecting the similar cobalt complex, and this provides an additional means of separating these two elements. Following the addition of formaldehyde to the complex cyanide solution, nickel may be subsequently separated as nickel dimethylglyoxime.

Reduction of potassium tetracyanonickelate (II) (and of nickel sulfate and nickel acetate) with sodium hypophosphite yields monovalent nickel. $K_2Ni(CN)_4$ reacts with nascent hydrogen to produce the blood-red binuclear compound $K_2Ni(CN)_3$; this compound also forms when double cyanides are reduced electrolytically or with potassium amalgam. Nickel, and its palladium analog, apparently exhibit zero valency in the compounds K_4(Ni or Pd)$(CN)_4$.

Nickel may be determined by titration with potassium cyanide, using silver iodide as indicator(12). The disappearance of the opalescence caused by the silver iodide marks the endpoint of the titration. Nickel may be complexed with citric acid, a known amount of cyanide added, and the excess reagent over that necessary to complex all the nickel is titrated.

Nickel carbonyl.

The carbonyls have received extensive study since Mond, et al(13), first characterized $Ni(CO)_4$. Carbonyls are formed by the group 8 elements, but are less common to the other groups. The metal carbonyls have covalent characteristics, as indicated not only by data on volatility, but also by the fact that these compounds are insoluble in polar solvents but soluble in many non-polar solvents.

Carbonyls are generally formed by the reaction of carbon monoxide on finely divided metals. Nickel carbonyl is also produced by the decomposition of $NiCN(CO)_x$ or $NiSH(CO)_x$, and by the reaction of carbon monoxide with $K_2Ni(CN)_3$. In the laboratory, nickel carbonyl is formed by reacting nickelous salt solutions with carbon monoxide, at the same time providing conditions for the formation of a nickel (IV) compound.

The dipole moment of nickel carbonyl is zero, indicating that the Ni-C-O bonds are linear and that, because of covalency limitations, the C-O bond must be comparable to that in carbon monoxide. Electron diffraction data and Raman spectrographic data support this assumption. In reactions nickel carbonyl has the properties of nickel and of carbon monoxide. The compound reacts with bromine to yield nickel (II) bromide and carbon monoxide. When used in Grignard reactions, the characteristics of carbon monoxide are exhibited. In still other reactions, the characteristics of the compound may predominate. No palladium or platinum analogs of this compound are believed to exist.

Nickel carbonyl is the basis of the Mond process for producing very pure nickel. The carbonyl is formed by the reaction of carbon monoxide on the reduced nickel ore (finely divided nickel obtained by the reduction of nickel oxide with hydrogen below 400°), carried off by the stream of gas at 50-100°, and later brought into contact with nickel at 180-200°, with a resulting decomposition to nickel and carbon monoxide. The gas is returned to the process and nickel is deposited in a very pure form.

The vapor nickel carbonyl is poisonous, paramagnetic, stable in a sealed tube but oxidizes in air. Mixtures of nickel carbonyl and air are explosive. Strong oxidizing agents such as nitric acid and chlorine decompose the carbonyl to nickel (II) salts and carbon dioxide or phosgene. In the presence of alkalis, nickel carbonyl is oxidized by oxygen of the air with the formation of carbon dioxide and nickel (II) oxide. An appropriate gaseous mixture of nickel carbonyl, hydrogen sulfide, hydrogen peroxide or oxygen, and carbon dioxide will stabilize the normally explosive nickel carbonyl for plating nickel on a solid surface by vapor decomposition(14).

Additional nickel compounds.

If sodium hydrogen phosphate solution is added slowly to boiling solutions of the nitrates or chlorides of metals, the solution being kept neutral by the addition of sodium hydroxide, the metals magnesium, barium, cadmium, manganese, iron, cobalt, nickel and copper give normal orthophosphates of the type $M_3(PO_4)_2$. Aluminum, cerium and bismuth form salts of the type MPO_4, and calcium, strontium and zinc form basic salts of the type $3M_3(PO_4)_2 . \underline{M}(OH)_2$. Ammonium phosphate reacts with nickel salt solutions, similarly as with many other metallic ions, to yield insoluble $NiNH_4PO_4$.

Addition of alkali bicarbonates to nickel salt solutions produces $NiCO_3 . 6H_2O$, whereas basic carbonates are formed upon the addition of alkali carbonates. The carbonates of magnesium, zinc, nickel and cobalt almost always separate in the basic form. Conversion to normal carbonates is accomplished by letting the precipitates stand a considerable time, or by heating them in a solution of alkali bicarbonate. All are very insoluble in water. Double carbonates of the types $NH_4HCO_3 . NiCO_3 . 4H_2O$, $K_2CO_3 . NiCO_3 . 4H_2O$ and $Na_2CO_3 . NiCO_3 . 10H_2O$ are known.

Addition of nickel hydroxide or nickel carbonate to an aqueous oxalic acid solution produces $NiC_2O_4 . 2H_2O$. This compound may be dried at 100°, is almost insoluble in water and soluble in strong acids and ammonia solutions. It dissolves in boiling potassium oxalate solution, yielding $K_2C_2O_4 . NiC_2O_4 . 6H_2O$ on cooling. Nickel and cobalt can be precipitated as oxalates, ignited to the oxide and weighed, or the oxalate precipitate may be determined titrimetrically.

Other nickel compounds may be formed by dissolution of nickel metal, hydroxide, or carbonate in the appropriate acid, or by double decomposition reactions with appropriate salts of other metals. Nickel salts formed in one or more of these manners include the acetate, nitrate, nitrite, sulfate, and thiocyanate, to name but a few. These salts are generally crystallized as hydrates, but with nickel the affinity for water is not great and many hydrated salts can lose water even by heating over a steam bath. Many double salts are known, of which $(NH_4)_2SO_4.NiSO_4.6H_2O$ is perhaps best known for its use in electroplating baths.

Solubilities of some compounds are summarized in Table IV[15,16].

Table IV Solubilities of Nickel Compounds

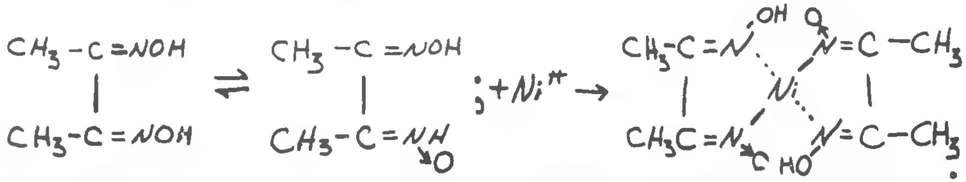
	Solubility in grams per 100 ml of		
Compound	c.H_2O	h.H_2O	Alcohols, acids, etc.
Nickel acetate	16.6	--	i.al.
" acetate, tetrahydrate	s.		s.al.; i.abs.al.
" orthoarsenate	i.		s.a.
" orthoarsenite, acid	i.		s.a., alk.
" benzenesulfonate	14.3^{18}	51.5^{82}	5.9al.; 4.5eth.
" bromate	28	--	s.NH_4OH
" bromide	112.8^{0}	155.1^{100}	s.al.,eth.,NH_4OH
Nickel di-n-butyldithiocarbamate	--	--	i.H_2O,al.;sl.s.bz.,pet.c.
" carbonate	0.0093^{25}	i.	s.a.
" carbonate, basic	i.	d.	s.a.,NH_4salts
" carbonyl	$0.018^{9.8}$	--	s.HNO_3,aq.reg.,al.,eth., chl.,bz.;i.dil.a.,alk.
" chlorate	(?)	v.s.(?)	--
" perchlorate	222.5^{0}	273.7^{45}	s.al.,acet.;i.chl.
" chloride	64.2^{20}	87.6^{100}	s.al.,NH_4OH;i.NH_3
" cyanide	i.	i.	s.KCN
" cyanide, tetrahydrate	i.	i.	s.KCN,NH_4OH,alk.;sl.s. dil.a.
" dimethylgylyoxime	i.	i.	s.abs.al.,a.;i.ac.a., NH_4OH
" ferrocyanide	i.	--	s.NH_4OH,KCN;i.HCl
" fluoride	2.6^{20}	2.6^{90}	i.a.,al.,eth.,NH_3
" formate	s.	--	--
" hydroxide (ous)	0.0013	--	s.a.,NH_4OH
" iodate	1.1^{30}	1.0^{90}	--
" iodide	124.2^{0}	188.2^{100}	s.al.
" nitrate	238.5^{0}	∞	s.al.,NH_4OH;i.abs.al.
" oxalate	i.	--	s.a.,NH_4salts;v.sl.s. oxal.a.
" oxide, mon-	i.	i.	s.a.,NH_4OH
" oxide, sesqui-	i.	i.	s.a.,NH_4OH,KCN
" orthophosphate	i.	i.	s.a.,NH_4salts;i.met. and et.acet.
" pyrophosphate	i.	--	s.a.,NH_4OH
" hypophosphite	s.	--	--
" sulfate	29.3^{0}	83.7^{100}	i.al.,eth.,acet.
" sulfate, hexahydrate	62.5^{0}	340.7^{100}	v.s.al.,NH_4OH;12.5met.al.
" sulfate, heptahydrate	$75.6^{15.5}$	475.8^{100}	s.al.
" sulfide, sub-	i.		s.HNO_3
" sulfide, mono-	0.0036^{18}	d.	s.HNO_3,KHS,aq.reg.,s.s.a.
" sulfide, (ous,ic)	i.		s.HNO_3
" sulfite	i.	--	s.HCl,H_2SO_4
" nitrate, diaquotetrammine	s.	--	i.al
" bromide, hexammine	v.s.	d.	i.c.NH_4OH
" chlorate, hexammine	(gives $Ni(NH_3)_4$)		--
" chloride, hexammine	s.	d.	s.NH_4OH;i.al.
" iodide, hexammine	d.	--	s.NH_4OH
" nitrate, hexammine	4.46	--	--

2. Chelate Complexes and Complex Ions of Nickel

Nickel has a strong tendency to form inner complex salts. These are salts in which the metal ion that replaces hydrogen is, at the same time, coordinatively bound at some other point to the group that functions as the acidic radical. Such compounds are often characterized by extreme insolubility in water, although many are soluble in non-ionizing solvents. In general, the solubility principles for nickel chelates can be illustrated by the following three cases(17): 1. nickel dicyandiamidine, with many amino and imino groups, is very soluble in water, but insoluble in chloroform; 2. nickel dimethylglyoxime is insoluble in water, and only slightly soluble in chloroform, probably because of the polar hydrogen bridges present; 3. the methyl ester of nickel dimethylglyoxime has no hydrogen bonds, is insoluble in water and very soluble in chloroform.

Chelates of nickel with the dioximes

The best known of the nickel chelates is nickel dimethylglyoxime. When dimethylglyoxime (diacetyldioxime) is used as a precipitant one of the acidic hydrogens is replaced by one equivalent of the metal ion. With nickel (II), two molecules of dimethylglyoxime react to give a voluminous bright red precipitate:



The precipitation is carried out in an ammoniacal citrate or tartrate medium, the presence of citrate or tartrate being necessary to prevent the coprecipitation of metal ions which would ordinarily come down as insoluble hydroxides. Palladium partially precipitates from ammoniacal solution, and is therefore removed previously by precipitation with hydrogen sulfide from an acidic medium. The presence of large amounts of oxidizing agents may prevent the precipitation of nickel by providing an avenue for the formation of the soluble oxidized complex of nickel dimethylglyoxime. This latter reaction provides a means for the colorimetric determination of nickel(18).

Using dimethylglyoxime, one may quantitatively separate nickel from cobalt, and a 200-fold excess of cobalt does not prohibit detection of nickel if cobalt is first oxidized to cobalt (III). However, cobalt forms a soluble complex which lessens the sensitivity of determining nickel and increases the solubility of the nickel dimethylglyoxime, cobalt (II) having a greater effect than cobalt (III). Iron (II) also forms a red soluble complex, while palladium and platinum form insoluble yellow complexes which can be volatilized *in vacuo*.

The usual physical form of the nickel dimethylglyoxime precipitate is voluminous and amorphous, and not well suited to the separation of nickel from trace activities of isotopes of other elements. However, it is relatively simple to form dense crystals of this compound by gradually and homogeneously raising the pH of the precipitation medium by the hydrolysis of urea(19). The resulting reddish-brown crystalline precipitate has very little tendency to adsorb extraneous materials and ions from the solution.

Singer and Kurbatov(20) applied the technique of homogeneous precipitation to the preparation of ten-gram quantities of crystalline nickel-63-labeled nickel dimethylglyoxime. After several precipitations, they were able to obtain the crystalline compound essentially free from all impurities. Wilkins and Williams (21) purified nickel-63 in about the same fashion. This author (22) has applied the technique to the preparation of a several-hundred-gram batch of crystalline nickel dimethylglyoxime for calorimetric measurements. The compound was purified by extraction with pyridine in a Soxhlet extractor, the pure nickel dimethylglyoxime collecting gradually in the solvent flask while the impurities remained in the thimble. Crystals averaging 5 mm in length were formed and the last traces of pyridine were removed by prolonged pumping under high vacuum, leaving a compound containing the theoretical quantities of the constituent elements.

The value of homogeneous precipitation techniques in separations of this sort is self-evident. The compound formed is easily filtered and washed, and one need increase the pH of the solution only to the point where precipitation is complete. Similar hydrolysis reactions which have proven useful in other instances include the hydrolysis of acid amides, trichloroacetates, and (at lower pH's) ammonium peroxydisulfate. One can also perform homogeneous oxidations and reductions. The reader is referred to a recent book(23) for additional details on this subject.

Several other α-dioximes have proven effective for the determination of nickel. Taylor(24) determined small amounts of nickel colorimetrically with α-furildioxime. Iron, chromium and alkali metal interferences were studied, and the method was used to measure nickel in plutonium solutions. Whereas the use of dimethylglyoxime had given erratic results in this case, the use of α-furildioxime surmounted these difficulties.

Hooker and Banks (25) and Banks and Hooker(26) studied some substituted alicyclic vic-dioximes and described procedures for gravimetric and spectrophotometric determinations of nickel and palladium using 4-methyl- and 4-isopropyl-1,2-cyclohexanedionedioximes. The 4-methyl-derivative proved to be an excellent reagent for the gravimetric separation of nickel, with precipitation beginning a pH 3. The 4-isopropyl-derivative, although less stable than the 4-methyl- derivative, also proved to be a good reagent. Voter and Banks (27) earlier examined 1,2-cyclopentanedionedioxime and concluded that it had no value as an analytical reagent for nickel and palladium.

With the syn-dioximes, such as dimethylglyoxime, the active part of the molecule with respect to chelate formation is -C(=NOH)-C(=NOH)-. Although these α-dioxime groups mainly determine the selective action of the compounds, the rest of the molecule also plays a part and affects the specificity. For example, benzoquinonedioxime and c-napthoquinonedioxime form precipitates with most metal ions. However, if the double bonds are removed the specificity returns. In general α-dioximes containing saturated R_1 and R_2 groups form chelate compounds, whereas those with unsaturated R_1 and R_2 groups act as dibasic acids.

The uses of the dioximes in analytical chemistry have been reviewed by Diehl(28).

<u>Other nickel chelates.</u>

Nickel may be determined with 8-hydroxyquinoline (oxine), although this reaction does not have the advantages of several other methods. The solubility order of the metal oxinates follows the order nickel > iron > copper > thorium > uranyl(29). The nickel salt, $Ni(C_9H_6ON)_2 \cdot 2H_2O$, precipitates over the pH range 4.3 to 14.6 and can be titrated or dried at 130° and weighed. With oxines, the technique of homogeneous precipitation has been applied to the precipitation of magnesium, aluminum, zinc, uranyl, thorium, iron(III), copper, cobalt, nickel, lead, manganese and cadmium(30), and this may prove useful in a few cases for the radiochemical separation of nickel.

The stability constants of the bivalent metal ion complexes are reported to follow the order Pd > Cu > Ni > Pb > Co > Zn > Cd > Fe > Mn > Mg for complexes of the metal ions with salicylaldehyde, ethylenediamine, glycine, 8-hydroxyquinoline, and to a limited extent EDTA(31). The order for complexes with 4-hydroxybenzothiazole is Cu > Pb, Ni, Co > Zn > Cd > Mn > Mg(32); with 2-hydroxymethylnapth-2,3-imidazole, Cu > Co > La > Mn > Ni > Zn; and the corresponding -1,2-imidazole, Cu > La > Co(33). The order for complexes with acetylacetone is Cu > Be > UO_2^{++} > Ni > Co > Zn > Mn > Cd > Mg > Ce (34).

Copper, nickel and uranyl complexes with hydroxyproline, asparagine, and N,N-dimethylglycine have received recent study(35), as have the complexes of copper, nickel, cobalt (II), zinc and cadmium with 2-picolylamine, 2-picolylmethylamine and 2-(2-amino-ethyl)pyridine(36). The formation constants for manganese (II), cadmium, zinc and nickel with citrate and carballylate are reported by Li,et al(37). Christie and Osteryoung have recently determined polarographically(38) that the chloro-complexes follow the order cadmium > lead > nickel in fused lithium nitrate-potassium nitrate.

Water-soluble chelates of nickel are formed with cupferron, α-nitroso, β-napthol, and EDTA, to name a few. This property is used in colorimetric analysis, titrimetry, and polarography, and is important for its masking action in radiochemical separations. Nickel may be determined in the aqueous solution following an iron cupferrate extraction, and similarly following the removal of cobalt with α-nitroso, β-napthol. Nickel forms a strong complex with EDTA at a pH of 4; the relative strengths of various metal-EDTA complexes at pH 4 are Cr > Cu > Ni > Pb > Co; at pH 6.5 Ni > Cu > Co > Zn,Cd > Ca; at pH 8.65 Ni > Co > Cu > Zn,Cd > Ca>Mg > Sr > Ba; at pH 11.00 Co > Ni > Cu > Zn,Cd > Ca > Mg > Sr > Ba(39).

Biguanidine sulfate may be used to determine nickel in the presence of aluminum, chromium, iron, zinc, titanium, uranium and beryllium. Salicylaldehyde forms insoluble salicylimine complexes with ammoniacal solutions of copper and nickel, and ethylenediamine will precipitate nickel, while cobalt remains in solution. Nickel may be precipitated with dicyandiamide sulfate in solution containing ammonia and excess potassium hydroxide. Recently, diallyldithiocarbamidohydrazine has been suggested for the gravimetric determination of nickel(40).

The reader is referred to Martell and Calvin(41), where detailed information is tabulated on stability constants of various chelates. Additional information is available in books by Mellan(42) and Welcher(43).

3. Chromatography of Nickel

Cernak(44) has compiled a bibliography of the ion exchange behavior of a number of elements, including 25 references to nickel.

Cation exchange.

Bonner and co-workers(45, 46) studied a number of cation exchange equilibria on Dowex-50, including the calcium (II)-Nickel (II) and manganese (II)-nickel (II) systems, with resins of 4, 8 and 16 percent DVB content. They reported a selectivity scale for various divalent ions on Dowex-50 which follows the order uranyl $<$ magnesium $<$ zinc $<$ cobalt $<$ copper $<$ cadmium $<$ nickel $<$ calcium $<$ strontium $<$ lead $<$ barium for systems of ionic strength 0.1 M.

The phenomenon of tailing during elution of cobalt and nickel was investigated by Kadomtzeff.(47) Bench, et al(48) utilized the sodium form of Dowex-50 to separate copper and nickel from uranium, eluting with 5 percent ammonium tartrate first at a pH of 7, than at a pH of 3. Part of the uranium accompanied copper and nickel in the first fraction.

Strelow(49) studied the distribution of various cations on AG 50W-X8 resin in hydrochloric acid. Most cations are strongly adsorbed from 0.5 N hydrochloric acid, whereas cadmium is not, allowing the easy separation of cadmium from uranium, cobalt, nickel, manganese, zinc, copper and titanium. Magnesium, calcium, strontium, barium, iron (II), iron (III), aluminum, zirconyl, thorium, yttrium, lanthanum and the rare earths are also separated, while tin (IV) accompanies cadmium.

Several investigators have reported the use of Amberlite IR-120 to separate various elements, including nickel, from uranium. Cellini and Palomino(50) separated uranyl, copper, nickel, iron(III), cadmium, manganese (II) and chromium from 4 N sulfuric acid solutions. Draganic, Draganic and Dizdar(51) determined various trace impurities in uranium by first eluting iron and copper with 0.5 N sulfuric acid; then cadmium, nickel, cobalt, and manganese with 1 N hydrochloric acid; and finally the rare earths with ammonium citrate at a pH of 4. Determinations of the individual elements were made polarographically, spectrophotometrically or colorimetrically.

Carleson(52) has reported a procedure for separating barium, nickel, manganese, cobalt, copper, zinc and bismuth by partition elution from

Dowex-50 cation exchange resin. Methylisopropylketone and hydrochloric acid (>7.5 M) mixtures are utilized to achieve complete separation, whereas elution with simple hydrochloric acid solutions does not afford this resolution. For example, in the latter case copper is easily separated from cobalt and nickel, but these two cannot readily be separated from each other.

Anion exchange.

Moore and Kraus(53) reported the anion exchange characteristics of cobalt and nickel in hydrochloric acid solutions over the range 0.5 - 12 M hydrochloric acid. The characteristics enable the easy separation of these elements, also including iron, from hydrochloric acid solution on Dowex-1 columns. Whereas cobalt exhibits an adsorption maximum from about 9 M hydrochloric acid and the adsorption of cobalt is negligible only over the range 0.5 - 3 M hydrochloric acid, nickel exhibits negligible adsorption over the entire range studied. Iron (III) exhibits greater adsorption in concentrated hydrochloric acid, but no maximum was observed.

Kraus and Moore(54) later reported conditions for separating the divalent transition elements manganese to zinc in hydrochloric acid. The concentration of hydrochloric acid where noticeable adsorption occurs increases as zinc > copper > cobalt > iron > manganese, while nickel exhibits no noticeable adsorption. It appears that the negatively charged chloride complexes (the adsorption on anion exchange resins is attributed to the singly charged anion chloride complexes) of these elements decrease in the same order. Herber and Irvine(55) have indicated that with nickel, in the system Nickel (II)-hydrochloric acid-Dowex-1, the anionic species $NiCl_3^-$, $NiCl_4^=$, etc., are absent in the resin phase. Optical measurements in aqueous solutions of nickel (II) chloride in hydrochloric acid, perchloric acid and lithium chloride indicate the presence of only Ni^{++} and $NiCl^+$ up to a chloride ion concentration of about 11 M, and no evidence was observed for $NiCl_2$ in these solutions.

With bromide complexes, Herber and Irvine(56) have observed behavior similar to that observed with hydrochloric acid solutions for the complexes of cobalt, copper, zinc, gallium (III) and nickel. The order of decreasing strength of complexes of the type MBr^+ is reported to be zinc > copper > cobalt > nickel. The strength of the related gallium complex lies between copper and cobalt. Nickel is not adsorbed on anion exchange columns from hydrobromic acid solutions.

Dowex-1 columns were utilized by Hague, Maczkowske and Bright(57) to determine nickel, manganese, cobalt and iron in high temperature alloys. Nickel and manganese were eluted with 9 M hydrochloric acid, cobalt with 4 M hydrochloric acid, and iron with 1 M hydrochloric acid. Nickel was subsequently determined as nickel dimethylglyoxime.

Liška and Klůč(58) utilized Anex-L resin and 9-10 M hydrochloric acid to separate small amounts of cobalt from nickel. Mellish(59) utilized anion exchange techniques to separate carrier-free isotopes from target materials, including cobalt-58 from nickel. Kuwada and Yoshikawa(60) precipitated iron on an ion exchanger activated with ammonium hydroxide, while allowing the nickel to pass through the column.

The adsorption of lithium, copper and cobalt (II) chlorides and nickel nitrate from organic solvents by anion exchange resins was reported by Kennedy and Davies(61). Adsorption by the basic form of the resin Deacidite-H takes place through complex formation with resin functional groups and both cation and anion are adsorbed in equivalent proportions. Adsorption is influenced by the nature of the solvent and is much greater from acetone than from dimethylformamide. The effect of an increase in crosslinking was also measured.

Preiss, Fink and Robinson(62) separated nickel-63 from copper, cobalt-60, and zinc-65 in 7 N hydrochloric acid, collecting the nickel essentially residue-free while the other elements remained on the anion exchanger.

Other adsorption columns.

The use of alumina for the chromatographic separation of long-lived radioisotopes and corrosion elements from a mixture of fission products was reported by Nemoda(63). By the proper choice of eluents, the mixture was separated into fractions containing one or more elements. Experiments were carried out with artificial mixtures containing cesium-137, strontium-90-yttrium-90, barium-140-lanthanum-140, cerium-144-praseodymium-144, zirconium-95-niobium-95, ruthenium-103-rhodium-103, tellurium, iron, cobalt, nickel, molybdenum, chromium, aluminum, lead and uranium.

A cellulose column has been utilized to determine impurities in nickel plating baths(64). Nickel remained on top of the column and was gradually converted from the sulfate to the chloride form upon elution with acetone-hydrochloric acid. Dimethylglyoxime columns have been used to separate nickel from large amounts of cobalt, iron, and even palladium, which pass through the column while nickel is retained(65).

Silica gel columns have been utilized to separate the oxinates of copper, tungsten, iron, aluminum, bismuth, nickel and lead from chloroform solution(66). Elution is carried out with chloroform and ethanol. This type of separation, however, suffers the disadvantage that one always finds zones in contact with one another, and the separation is not complete. Wells(67) also cites the use of 8-hydroxyquinoline on columns.

Paper chromatography.

Nickel has usually been included among the cations utilized in various paper chromatographic studies. While this would appear to be a useful technique for separating nickel-59 or nickel-63, there nevertheless seems to have been little radiochemical application of the paper chromatographic method to nickel. However, a brief summary of the solvent systems employed may prove of future use to some investigators. Useful reviews of the paper chromatographic method are included in the list of references(67-70).

Lederer(71) utilized butanol-hydrochloric acid, butanol-nitric acid and butanol-hydrobromic acid developing solutions to study the influence on Rf values by the solvent in those cases where complexes between the cation and acid contained in the solvent were formed. Data are also reported by Lederer(72) for solvents containing hydrochloric acid and ether, isopropyl, butyl, and amyl alcohols. Anderson and Whitley(73) utilized diethyl ether saturated with hydrochloric, hydrobromic, sulfuric, or nitric acid, and Martin(74) reports the use of butanol-thiocyanic acid. The separation of cobalt, copper, iron, manganese and nickel is described by Arden, et al(75); and others(76, 77, 78)have applied paper chromatographic techniques to the separation of elements into groups for qualitative analysis. Pollard, et al(78, 79, 80) have reported a fairly complete picture of the behavior of a large number of cations and anions with various solvent mixtures, alone and with complex-forming reagents. Hartkamp and Specker studied various cations with the tetrahydrofuran-water-hydrochloric acid system(81) and also utilized acetone, methylethylketone and methanol(82).

Papers impregnated with complexing agents have proved useful. Reeves and Crumpler(83) utilized 8-quinolinol-impregnated papers and butanol-hydrochloric acid solvent to achieve a good separation of aluminum, nickel, cobalt, copper, bismuth, zinc, cadmium, mercury and iron in descending chromatography. A similar study is reported by Laskowski and McCrone(84), who also included antimony, barium, calcium, magnesium and lead.

Lederer and Ward(85) utilized alcoholic potassium thiocyanate in electromigration studies on filter paper, and Mukergee(86) studied a number of nickel-containing mixtures by electromigration techniques. Strain and Sullivan(87) utilized a combination of electromigration and chromatography, in which the flow of electrical current is perpendicular to the flow of solvent through the paper sheet. Strain(88) utilized two-way and three-way electrochromatography to study the migration of copper and nickel ions with various solvents and complex-forming reagents. This latter technique is generally versatile and sensitive, and provides a rather widely applicable analytical tool.

4. Electrochemical Behavior of Nickel

One finds in the literature many references to electroplating of nickel. Electrodeposited sources (and those prepared from nickel dimethylglyoxime) have proved very useful as counting sources and as target sources.

In analytical separations, nickel is electrodeposited after the deposition of copper from a sulfuric acid-nitric acid solution(89). After removing nitrate, the solution is made basic with ammonium hydroxide. In excess ammonia plus ammonium sulfate a very satisfactory nickel plate is obtained, but nickel will not separate quantitatively from a weakly acid solution. Chloride solutions may be used, but the results are generally not as satisfactory as those obtained from sulfate solutions. Nitrate ion, as well as those cations which precipitate the hydroxide from ammoniacal solution, should be removed prior to the electrolysis. Silver and zinc, which form ammines similar to that formed by nickel, should also be absent. The electrolysis should not be unduly prolonged.

Nickel may be separated by electrodeposition into a mercury cathode from 0.1 N sulfuric acid solution. For the same acidity, its behavior is comparable to that of cadmium, chromium (III), cobalt, copper, indium, iron, manganese (VII), thallium, and zinc. Sulfuric, phosphoric and perchloric acid solutions have been used. Nickel, along with zinc, cadmium, copper, iron, cobalt, and lead, is recovered by distillation of the mercury. The determination of nickel may be concluded polarographically and provides a separation from the alkali metals, magnesium, alkaline earths, aluminum and uranium.

The electrolytic method has been used for making nickel-58 Van de Graaff targets(90). Satisfactory contamination-free targets are produced in sulfate baths from nickel metal and oxide.

The polarographic behavior of nickel has been reviewed by Kolthoff and Lingane(91). In non-complexing supporting electrolytes, the hexaquonickel ion is reduced at a half-wave potential of about -1.1 v. vs the saturated calomel electrode (S.C.E.). In the presence of thiocyanate and pyridine the potential is much more positive, being -0.7 v. vs S.C.E. in 1 N potassium thiocyanate and -0.78 v. vs S.C.E. in 1 N potassium chloride- 0.5 M pyridine. These media are ideally suited to the determination of small amounts of nickel in the presence of large amounts of cobalt. In 1 M ammoniacal solution containing ammonium chloride the half-wave potential is slightly more negative than -1 v. vs S.C.E. Solutions of $Ni(CN)_4^{=}$ in 1 M potassium chloride or sodium hydroxide produce an extended wave starting at -1.35 v. vs S.C.E. A cyanide supporting electrolyte is useful for the determination of nickel in the presence of excess copper and zinc.

Other useful electroanalytical procedures for nickel have been summarized by Lingane(92). The amperometric titration of nickel in ammoniacal solution may be accomplished with dimethylglyoxime, with the dropping mercury electrode set at -1.85 v. vs S.C.E. Controlled potential deposition at -1.10 v. vs S.C.E. in ammoniacal tartrate solution containing sodium sulfite separates nickel from zinc, aluminum and iron. Nickel and cobalt may be separated by controlled potential deposition at a mercury cathode(93). Nickel is deposited at -0.95 v. vs S.C.E. from pH 6.5 to 7 solution. Cobalt is later deposited at -1.20 v. vs S.C.E.

5. Solvent Extraction Behavior of Nickel

A number of solvent extraction procedures for nickel are indicated in the books by Morrison and Freiser(94) and by Martell and Calvin(95). These procedures for the most part rely on the prior formation of a nickel chelate.

Nickel dimethylglyoxime is extracted into chloroform over the pH range 4-12, in the presence of tartrate; or pH 7-12, in the presence of citrate. In a typical experiment, 20-400 μg of nickel in 100-200 ml of solution is treated with 10 ml of 50 percent ammonium citrate solution, and the solution then made just alkaline with ammonium hydroxide. After cooling and adding about 20 mg of dimethylglyoxime in ammoniacal solution, the solution is shaken with 12 ml of chloroform. Milligram quantities of cobalt do not interfere if sufficient dimethylglyoxime is present. If large amounts of copper are present, the solution is treated prior to the extraction with tartrate, sulfite, and hydroxylamine hydrochloride.

α-Furildioxime forms complexes which are more soluble in chloroform and o-dichlorobenzene, and extracts nickel quantitatively over the pH range 7.5 to 8.3. Nickel has also been extracted following treatment with cyclohexanedionedioxime and salicylaldoxime. 8-hydroxyquinoline complexes with nickel may be extracted over the pH range 4.5 to 9.5, but this is not a very selective method, especially at the lower pH values. Pyridine forms water-insoluble, chloroform-soluble complexes which are more useful for copper than for nickel and cobalt. Sodium diethyldithiocarbamate has been used to extract nickel following a cupferron extraction to remove iron(96). The keto-dithizone complexes are extractable into chloroform, but these extractions are better for Mercury (II), copper (II), etc., than for nickel.

Sharp and Wilkinson(97) utilized the solvent extraction of nickel with thiocyanate to separate nickel-57 from proton-irradiated cobalt, as well as to prepare nickel-free cobalt salts. Irving and Edgington(98) studied the extraction of several chloride complexes from hydrochloric acid into tributyl phosphate. Iron (III), cobalt (II), and zinc were studied as tracers, and nickel, copper and uranyl ion by spectrophotometric procedures. Neither of these systems would be very selective except in a limited number of cases where the solution mixtures were not too complex.

6. Activation Analysis

Activation analysis has proved useful for the determination of nickel in various materials. There are a number of sources which may be consulted for background on the method of activation analysis(99-103).

Nickel has been determined in titanium metal, alloys, and compounds, along with tungsten, chlorine, vanadium, copper, manganese, and silicon(104). Nickel-65 is formed by the reaction $Ni^{64}(n,\gamma)Ni^{65}$, separated as nickel dimethylglyoxime, and measured using an end-window GM counter. Nickel, along with copper, manganese, iron, zinc and tantalum, was determined similarly in NBS aluminum alloys(105).

Whereas most activation analyses rely on a thermal neutron source, this being generally the most sensitive and available, the use of 14.5 Mev neutrons was recently reported by Coleman(106). For nickel, the reactions of interest are $Ni^{61}(n,p)Co^{61}$ and $Ni^{58}(n,2n)Ni^{57}$. Copper is also measured by the reaction $Cu^{65}(n,p)Ni^{65}$. The relative proportions of (n,p) and (n,2n) reactions are reported to be roughly 16:4 for the reaction of 14 Mev neutrons with nickel-58(107); thus, one expects that the $Ni^{58}(n,p)Co^{58}$ reaction would also be of significant, though somewhat less, value for these purposes. Fission neutrons have been used to determine nickel by this last-named reaction(108).

7. The Biological Significance of Nickel

Nickel is not known to be essential to life(109). There is about 0.01 g of nickel in a 70 kg man, or roughly less than 1.4×10^{-5} weight percent.

Nickel carbonyl is considered to have carcinogenic properties. However, rats exposed to sublethal quantities of the compound failed to give good supporting evidence to this thought(110). No significant retention of nickel by dogs six days after ingestion is reported(111), and detailed spectrographic analyses of human tissues for trace elements indicates that the concentration of nickel is extremely small(112).

The biological and related physical constants for nickel isotopes were recently reviewed and revised by Committee II of the International Commission on Radiological Protection, as were the constants of other radioisotopes(113). Their report or Handbook 69(114) should be consulted for further information relating to maximum permissible concentrations, etc.

V. DISSOLUTION OF NICKEL-CONTAINING MATERIALS

The materials in which nickel occurs may generally be dissolved by treatment with acids. Nickel dissolves easily in dilute nitric acid, more slowly in hydrochloric acid, and more slowly still in sulfuric acid. Nickel is passivated by concentrated nitric acid. Nickel is attacked perceptibly slower by dilute acids than is iron. Nickel-containing alloys are generally soluble in mixed hydrochloric and nitric acids. With some refractory ores and alloys, a fusion is required first to make the treatment effective. Potassium bisulfate works well on finely powdered nickel and cobalt oxides, and sodium and potassium carbonates, containing potassium nitrate, are effective in other cases.

VI. COUNTING TECHNIQUES FOR NICKEL NUCLIDES

Nickel-56 decays almost entirely by orbital electron capture. The gamma-ray spectrum is complicated and not readily adaptable to the precise measurement of this isotope, although gross-gamma-counting may be employed. The 72-day cobalt-56 daughter emits positrons and gamma-rays which may be used to measure nickel-56 indirectly by the usual techniques of beta-counting, gamma-counting or coincidence-counting.

Nickel-57 decays half by positron emission and half by orbital electron capture and may be measured by the usual beta-counting techniques(115, 116). Discrete gamma-rays are available for counting at 1.89 Mev (14 percent), 1.368 Mev (86 percent), and 0.127 Mev (14 percent), and use may be made of coincidence-counting of the positron annihilation radiations. The 267-day cobalt-57 daughter emits gamma-rays at

0.122 and 0.136 Mev which must be taken into account after moderate decay of the nickel parent isotope has occurred.

Nickel-59 decays entirely by orbital electron capture. Its measurement may be concluded by utilizing a thin window proportional counter or thin crystal scintillation counter to measure the cobalt k-x-ray. The long half-life suggests, however, that mass spectrometric analysis might be competitive with counting for this isotope.

Nickel-63 is frequently used in tracer experiments and reaction rate and exchange studies(10, 20, 21, 117, 118) being well suited to these purposes. This isotope may be counted by standard beta-counting detectors, including Geiger-Muller tubes(118), 2π(119), and 4π(120, 121) counters. Because of the low maximum beta energy (0.067 Mev) 2π or 4π techniques are preferable. A large gas proportional counter was used to study the beta spectrum, utilizing iron-55 as an internal energy standard(62). Hall and Willeford(122) used a Lauritsen electroscope to follow exchange studies using nickel-63 and electrodeposited sources. Schweitzer, Stein and Nehls(123) used a windowless flow counter to measure self-absorption phenomena in the measurement of nickel-63.

Nickel-63 recently has been used to determine dusts and aerosols by a variation of the "absorption counting" technique(124). The gaseous sample is passed over an ultrafilter which contains nickel-63, positioned under a GM counter. The sample acts as an absorber and the decrease in counting rate of the ultrafilter provides a measure of the concentration of the dust or aerosol.

Nickel-65 was used in exchange studies by Johnson and Hall(125). It has been measured as a by-product of the high energy spallation of copper(116). Standard beta-counting techniques are usually employed(104, 105, 116, 125). Gamma-counting at discrete energies (1.49 Mev, 1.12 Mev, 0.37 Mev) may also be employed, or gross-gamma similarly counted. Miller(126) has recently compared the methods of counting nickel-65.

Nickel-66, or the equilibrium mixture nickel-66-copper-66, may be counted by standard beta-counting techniques. Time must be allowed after the final nickel separation for the 5.1-minute copper-66 to come to equilibrium with its parent nickel isotope. If experiments were conceived whereby one might not wish to wait for equilibrium to be reached, the sample could be counted with and without a suitable absorber to determine the nickel-66 contribution to the counting rate. For gamma-counting, 9 percent of the copper-66 disintegrations produce a 1.04 Mev gamma-ray which may be used to count the equilibrium mixture.

VII. COLLECTION OF DETAILED RADIOCHEMICAL PROCEDURES FOR NICKEL

Procedure 1

Source: L. J. Kirby

Sample type: Water containing mixed activation products and fission products.

Advantages: Separates very low levels of nickel-65 (near the detection limit for counting this isotope) from relatively large amounts (>1000 x Ni^{65}) of Cr^{51}, Cu^{64}, As^{76}, Np^{239}, Mn^{56}, Na^{24}, P^{32} and Zn^{69}. Intermediate quantities of other activation products and fission products are also separated. Time required, including counting, is <5 hours.

Yield: About 100 percent.

Procedure:

1. To a 2-3 gallon water sample (preferably in a jug) add 10 mg each of Ni, Cu, Zn, Fe, Cr, Mn and Co carriers. Add 100 ml of 40 percent ammonium tartrate solution and 50g of ammonium chloride. Add sufficient dimethylglyoxime, slurried in ethanol, to precipitate all nickel and provide a ten-fold excess of reagent.

2. Filter the precipitate by using lab vacuum to siphon the contents of the sample container, and suitable rinses, through a Buchner funnel.

3. Dissolve the nickel dimethylglyoxime precipitate by drawing a minimum of nitric acid (about 8 N) through the filter, collecting the resulting solution in a small tube. Transfer to a 50 ml beaker and evaporate barely to dryness.

Procedure 1 (Continued)

4. Dissolve the residue in 12 ml of $2\underline{M}$ hydrochloric acid. Add 10 mg each of Fe and Mn carriers. Make the solution basic with NH_4OH, centrifuge and discard the precipitate. Evaporate the supernatant liquid barely to dryness.

5. Dissolve the residue in 5 ml of concentrated hydrochloric acid and add 15 ml. of water. Add 10 mg of Cu carrier. Heat the solution to boiling and add Al shavings to precipitate Cu^{0}. Filter and discard the copper precipitate.

6. Add sufficient NaOH solution to precipitate all nickel as the hydroxide. Centrifuge and discard the supernatant solution.

7. Repeat steps 5 and 6 twice on the $Ni(OH)_2$ precipitate.

8. Dissolve the $Ni(OH)_2$ precipitate in a solution of 2.3 ml H_2SO_4 in 7.7 ml H_2O. Filter and add a large excess of NH_4OH (about 10 ml.) to the filtrate. Filter again, if necessary, into an electroplating cell. Electrolyze for one hour at 0.2-0.4 a., collecting the nickel on one side of a 7/8" copper disc (see note).

9. Rinse the plate with water, acetone, and air-dry, in that order. Weigh and determine Ni^{65} by β- or γ-counting.

Note: Add a little conc. NH_4OH from time to time during the electrolysis.

Procedure 2

Source:	Burgus, W. H., in U.S.A.E.C. Report No. LA-1721, Kleinberg, J., Ed., pp. Ni 1-7 (September 10, 1954).
Sample type:	Nickel plus fission products.
Advantages:	Nickel separated from F. P. and determined in a total of about 4-1/2 hours.
Yield:	About 75 percent.
Introduction:	Nickel is separated from fission products by precipitation with dimethylglyoxime (DMG) from an ammoniacal medium in

the presence of a large quantity of citrate ion. Three precipitations in the presence of cobalt as a holdback carrier are carried out. After appropriate scavenging steps, the nickel is again precipitated with dimethylglyoxime and the nickel-dimethylglyoxime complex is extracted into chloroform. The nickel is then back-extracted into dilute hydrochloric acid solution and is finally plated out of strongly ammoniacal solution. The chemical yield is approximately 75 percent. About 2-1/2 hours are required for the decontamination of a single sample, and 2 hours for plating.

Reagents:

Ni carrier: 10 mg Ni/ml (added as $Ni(NO_3)_2 \cdot 6H_2O$ in very dilute HNO_3)--standardized
Co carrier: 10 mg Co/ml (added as $Co(NO_3)_2 \cdot 6H_2O$ in very dilute HNO_3)
Pd carrier: 10 mg Pd/ml (added as $PdCl_2 \cdot 2H_2O$ in very dilute HCl)
Cu carrier: 10 mg Cu/ml (added as $CuCl_2 \cdot 2H_2O$ in H_2O)
Fe carrier: 10 mg Fe/ml (added as $FeCl_3 \cdot 6H_2O$ in very dilute HCl)

HCl: conc.; HCl: 6M; HNO_3: conc.; H_2SO_4: conc.; NH_4OH: conc.; $(NH_4)_2SO_4$: solid; Sodium citrate: 10 percent in H_2O; H_2S: gas; Dimethylglyoxime reagent (DMG): 1 percent in ethanol; Chloroform; Ethanol: 95 percent.

Equipment: Centrifuge, Fisher burner, Block for holding centrifuge tubes, Forceps, Mounting plates, Tongs for Erlenmeyer flasks, Pipets: 2- and 5-ml, 600-ml separatory funnels (one per sample), Wash bottle, 125-ml Erlenmeyer flasks (three per sample; one per standardization), 2", 60° short stem glass funnels (two per sample), 100-ml beaker (one per sample), 40-ml conical centrifuge tubes: Pyrex 8320 (three per sample), Pharmaceutical graduated cylinders: 10-, 30-, and 60-ml, No. 40 Whatman filter paper (9 cm), Stirring rods, Plating cells (one each per sample and standard).

Preparation and Standardization of carrier: Dissolve 49.5 gm of $Ni(NO_3)_2 \cdot 6H_2O$ in H_2O, add 1 ml of HNO_3, and dilute to 1 liter with H_2O.

Pipet 5.0 ml of the carrier solution into a 125-ml Erlenmeyer flask, add 3 ml of conc. H_2SO_4, boil down to SO_3 fumes to remove NO_3^- ion, and cool to room temperature. Dilute to 8 to 10 ml, and cautiously neutralize with conc. NH_4OH, adding 1 ml in excess. Add 1 gm of $(NH_4)_2SO_4$, quantitatively transfer to plating cell, and plate for 3 hours at 0.10 amp and about 3 volts. Add a drop of conc. NH_4OH about every 30 min. When the plating has been completed, wash the cathode several times with distilled H_2O and once with ethanol. Air-dry and weigh.

Four standardizations are carried out with results agreeing within about 0.2 percent.

Procedure:

Step 1. To 5 or 10 ml (or less) of the sample in a 40-ml centrifuge tube, add 2 ml of the standard Ni carrier, 10 drops of Co holdback carrier, and 10 ml of 10 percent Na-citrate solution. Make ammoniacal by addition of conc. NH_4OH. (A color change to deep blue-violet indicates that sufficient NH_4OH has been added.) Dilute to 25 ml. Precipitate Ni by the addition of 15 ml of 1 percent alcoholic DMG reagent. Centrifuge and wash precipitate with 30 ml of H_2O containing a drop of conc. NH_4OH. Discard the supernate and washings.

Step 2. Dissolve the Ni-DMG precipitate in 2 ml of conc. HCl and dilute to 15 ml. (Disregard any DMG which precipitates at this stage.) Add 10 ml of 10 percent Na-citrate, 2 drops of Co carrier, and 5 ml of DMG reagent. Precipitate Ni-DMG by addition of conc. NH_4OH. Centrifuge and wash as before (Step 1).

Step 3. Repeat Step 2.

Step 4. Dissolve the Ni-DMG precipitate in 10 ml of conc. HNO_3, and transfer to 125-ml Erlenmeyer flask. Boil to dryness and heat to destroy all organic matter (Note 1). Dissolve NiO (black) in a few milliliters of conc. HCl by heating. The solution process is aided by the addition of a drop or two of conc. HNO_3. Boil until $NiCl_2$ precipitates and then dilute to 20 ml. (Be certain that the heating is continued for sufficient time to remove HNO_3.)

Step 5. Add 3 drops of conc. HCl and 4 drops each of Cu and Pd carriers. Heat to boiling and pass in H_2S for 5 min. Filter sulfide scavenger precipitate and discard.

Step 6. Boil out H_2S, add 2 drops of conc. HCl, 4 drops each of Cu and Pd carriers, dilute to 20 ml, heat and remove another sulfide scavenger precipitate with H_2S. Boil out H_2S from the filtrate and transfer to a 40-ml centrifuge tube.

Step 7. Dilute to 20 ml. Add 8 drops of Fe carrier and precipitate $Fe(OH)_3$ from hot solution by the addition of conc. NH_4OH (1 ml in excess). Centrifuge and discard $Fe(OH)_3$ scavenger precipitate.

Step 8. Acidify the supernate with HCl or HNO_3. Add 8 drops of Fe carrier and remove a second $Fe(OH)_3$ scavenge. Transfer the supernate to a 100-ml beaker.

Step 9. To the supernate from the $Fe(OH)_3$ scavenge, add 10 ml of 10 percent Na-citrate and 1 drop of Co carrier. Add 15 ml of DMG solution and transfer to a 600-ml separatory funnel. Add 500 ml of $CHCl_3$ and extract Ni-DMG (Note 2).

Step 10. Wash $CHCl_3$ layer twice with 50-ml portions of H_2O containing 1 drop of conc. NH_4OH. Discard washings.

Step 11. Back-extract Ni into 20 ml of 6M HCl. Transfer water layer to a 125-ml Erlenmeyer flask (Note 3), and boil nearly to dryness. Add 4 to 5 ml of conc. HNO_3. Boil nearly to dryness. Add about 3 ml of conc. H_2SO_4 and heat to SO_3 fumes (Note 4). Cool to room temperature.

Step 12. Add 8 ml of H_2O and cautiously neutralize with conc. NH_4OH (1 ml in excess). Add 1 gm of $(NH_4)_2SO_4$, dilute to 20 ml, and transfer to plating cell. Plate Ni on a weighed Pt foil. (For a circular foil of 7/8" diameter, plate for 2 hours at 0.10 amp. Add a drop of conc. NH_4OH about every 30 min.) After plating, wash with H_2O and then with ethanol. Air-dry, weigh, and count (Note 5).

Notes:

1. When boiling down with conc. HNO_3, be certain to take to dryness, and then heat a little longer. All citrate and decomposition products of DMG must be removed, otherwise it is impossible to precipitate $Fe(OH)_3$ in Step 7.

2. Freshly precipitated Ni-DMG ordinarily extracts rapidly into $CHCl_3$. If it does not do so, add an additional 50 ml of $CHCl_3$ and shake the separatory funnel vigorously. The $CHCl_3$ and H_2O layers do not separate quickly, and at least 5 min should be allowed for the emulsion to break and for separation to occur.

3. The complete disappearance of the yellow-orange color of Ni-DMG in the $CHCl_3$ layer indicates that back-extraction is complete.

4. For successful plating, all organic material and nitrates must be removed.

5. If 36h Ni^{57} is being counted, mount the sample and cover with 1 mil Dural in order to absorb the radiations of $2x10^5$y Ni^{59} and of 300y Ni^{63}.

Procedure 3

Source:	Brooksbank, W.A., Jr., U.S.A.E.C. Report No. ORNL-2226, pp. 27-31 (December, 1956).
Sample type:	Nickel impurity in aluminum metal; nickel-65 isolated and measured following neutron activation.
Advantages:	Nickel-65 determined in presence of radioactive isotopes of Cu, Mn, Fe, Zn, Ti, Co, Ag, Zr and Sb.
Yield:	About 62 percent (range 26.3-78.1).

Procedure:

The aluminum samples are allowed to decay for two hours before the samples are dissolved. One milliliter of nickel carrier and all the hold-back carriers except nickel are added. The acidity is adjusted to 1<u>M</u> with hydrochloric acid and cupric sulfide is precipitated by passing a stream of hydrogen sulfide gas through the solution. The precipitate is removed by centrifugation. The supernatant liquid is filtered through 41H filter paper into a clean centrifuge tube. Hydrogen sulfide and colloidal metal sulfides are destroyed by boiling the solution with concentrated nitric acid and bromine water. The hydroxides of iron(III) and aluminum are precipitated with 15<u>M</u> aqueous ammonia, the solution centrifuged, and the precipitates discarded. The nickel in the filtrate is precipitated as nickel dimethylglyoxime. The precipitate is filtered, washed, dissolved and reprecipitated in the presence of cobalt(II), strontium and zinc hold-back carriers. The precipitate of nickel dimethylglyoxime is filtered, washed with water and then with alcohol, and dried at 105° for fifteen minutes. After cooling, the precipitate is weighed to determine the carrier yield, and mounted for beta counting. Mounting entails placing the precipitate on a one-inch diameter watch glass and taping the watch glass to a 3 1/4 by 2 1/2 inch card and below a one-inch hole in the center, covered with a thin plastic film.

Counting is done at usual second shelf geometry on the Geiger-Mueller counter. Decay data is obtained every hour for five hours, and again at thirteen and twenty-three hours. This data is plotted and the contribution of the two and one-half hour component, nickel-65, is determined. The calculations are as follows:

Comparator

$$S = \frac{\dfrac{A}{(Y)(e^{-\lambda t})} \times D}{W}$$

A = Activity at time of first count, in counts per minute,

Y = ratio of nickel dimethylglyoxime recovered to nickel dimethylglyoxime theoretically present,

D = dilution factor,

$e^{-\lambda t}$ = decay correction in time first sample was counted,

W = comparator weight, in grams.

The nickel content of a sample is given by:

$$\frac{\dfrac{A_s}{(Y_s)(e^{-\lambda t})}}{S \times W_s} \times 10^{-4} = \text{percent nickel in sample}$$

A = activity at time of counting taken from the decay curve,

Y_s = chemical yield,

$e^{-\lambda t}$ = decay correction to time first sample was counted,

S = specific activity in counts per minute per gram,

Procedure 3 (Continued)

W_s = weight of sample, in grams.

Note: In all samples analyzed, a long-lived component appeared in the separated nickel-65 fraction. Spectral analysis showed the component to be sodium-24. Its contribution to the total count is readily obtained from the decay curves.

Procedure 4

Source:	Hopkins, H.H., Jr., in U.S.A.E.C. Report No. AECD-2738, Meinke, W.W., Ed., p. 28-1 (August 30, 1949).
Sample type:	Deuteron-irradiated arsenic.
Advantages:	Nickel separated in 45 minutes; D.F. $\sim 10^3$.
Yield:	95 percent.

Procedure:

1. Dissolve As in minimum HNO_3 + HCl, add 2 mg Se, Ge carriers, and 5 mg Ni.

2. Add NH_4OH to alkaline and pass in H_2S rapidly. Centrifuge and wash NiS with H_2O.

3. Dissolve with conc. HCl and reppt from NH_4OH.

4. Dissolve in minimum conc. HCl, boil out H_2S, add carriers below Ge, dilute to 10 ml and adjust pH to ~ 3 with HAc.

5. Add dimethylglyoxime solution until precipitation is complete. Centrifuge, dissolve ppt in conc HNO_3 and boil.

6. Dilute to 10 ml, make alkaline with NH_4OH and reppt with dimethylglyoxime.

Procedure 5

Source: Goeckermann, R.H., in U.S.A.E.C. Report No. AECD-2738, Meinke, W.W., Ed., p. 28-2 (August 30, 1949).

Sample type: Particle-irradiated bismuth (~1g Bi).

Advantages: Nickel separated from fission and spallation products in 1-2 hours; D. F. ~ 10^4.

Yield: About 60 percent.

Procedure:

1. To aliquot of HNO_3 soln of target, add 10 mg Ni, make neutral, add 5 ml 1 percent dimethylglyoxime in alcohol, wash with H_2O and EtOH.
2. Dissolve Ni d-m-g in 1 ml conc. HNO_3, dilute, and scav twice with CuS.
3. Scav three times with PdS.
4. Scav with Sb_2S_3.
5. Boil out H_2S, make basic with NH_3, scav twice with $Fe(OH)_3$.
6. Make 0.5 $\underline{N}$ in HCl and scav with Pd d-m-g.
7. Neutralize supn and ppt Ni d-m-g.
8. Dissolve in conc HNO_3, reppt Ni d-m-g, filter, wash with H_2O and EtOH, dry 10 min at 110°C. Weigh as Ni d-m-g (29.4 mg per 10 mg Ni).

Remarks: Designed to purify a little Ni from a lot of activity spread over the periodic table. A few mg of carrier are used in the scavenges.

Procedure 6

Source: Batzel, R.E., in U.S.A.E.C. Report No. AECD-2738, Meinke, W.W., Ed., p. 28-3 (August 30, 1949).

Sample type: Particle-irradiated copper.

Advantages: Nickel separated in 40 minutes with D.F. of 100 from other activities. Good yield and specific for this region.

Yield: 70 percent.

Procedure:

1. Dissolve copper in minimum amount of concentrated nitric acid. Boil to dryness. Add 5 mg of Ni and 1-2 mg of holdback carriers for other elements Zn and below. Remove copper as sulfide from 1<u>N</u> HCl, and wash precipitate with 1<u>N</u> HCl saturated with H_2S.

2. Boil supernate to remove H_2S. Neutralize with NH_4OH and make slightly acid with acetic acid. Add 1 percent alcoholic solution of dimethylglyoxime (2 ml.). Centrifuge and wash the precipitate twice with 3 cc water containing 2-3 drops of acetic acid.

3. Dissolve the precipitate in concentrated HCl and again add 1-2 mg of holdback carriers for other elements. Add NH_4OH to neutralize; make slightly acid with acetic to reprecipitate.

4. Weigh as the Ni - dmg.

Remarks: Reference: Scott's Standard Methods of Chemical Analysis, Volume I, page 619.

Procedure 7

Source:	Stewart-Softky, in U.S.A.E.C. Report No. AECD-2738, Meinke, W.W., Ed., p. 28-4 (August 30, 1949).
Sample type:	Deuteron-irradiated copper foils (300-500 mg Cu).
Advantages:	Complete separation of Ni from Zn, Cu, Fe, Co, Mn; D.F. $\sim 10^6$; rapid method by which many samples can be run simultaneously (3-4 hours for 12 samples).
Yield:	About 100 percent.

Procedure:

1. Dissolve copper in 6 <u>N</u> HCl + a few drops of 30 percent H_2O_2 and boil off excess peroxide. Add 0.5 mg - 1 mg Ni carrier as chloride.

2. Neutralize with NH_4OH and make slightly acid with HCl. Add

NH_4HSO_3 to reduce Cu^{+2} to Cu^{+1} (only 1 - 2 ml necessary) and boil off excess SO_2.

3. Precipitate CuSCN from the warm solution with a few crystals of NH_4SCN, being careful not to add a large excess of NH_4SCN. Let settle for 10 minutes. Filter through Whatman No. 42 filter paper and wash the precipitate with a 1 percent solution of NH_4SCN containing a little NH_4HSO_3.

4. Add 1 ml 50 percent tartaric acid to the filtrate, make very slightly ammoniacal and warm to near boiling. Add 1-2 ml 1 percent dimethylglyoxime in ethanol to precipitate NiDMG.

5. Filter through Whatman No. 40 filter paper and wash with hot water.

6. Dissolve precipitate in dilute HCl and repeat (4) and (5) to reduce Zn and Co contamination.

Remarks: Step (4): If solution is made too strongly ammoniacal, NiDMG will be incompletely precipitated.

Procedure 8

Source:	Folger, R.L., and Hicks, H., in U.S.A.E.C. Report No. AECD-2738, Meinke, W.W., Ed., p. 28-5 (August 30, 1949).
Sample type:	Particle-irradiated uranium foil (about 4 g U).
Advantages:	Nickel separated from most elements in 1-2 hours; D. F. $\sim 10^4$ from fission and spallation products; D. F. $\sim 10^6$ from elements 38-56.
Yield:	About 60 percent.

Procedure:

1. To aliquot of target containing $\sim$ 10 mg Ni pass in NH_3. Centrifuge and wash twice with sat'd AqNH_3. Combine supernatant and washings.

2. Scavenge with $Fe(OH)_3$, then Sr and Ba carbonates and $Fe(OH)_3$.

3. To supernatant add 1-2 ml 1 percent dimethylglyoxime in alcohol. Centrifuge and wash with H_2O.

4. Dissolve Ni d-m-g in 1 ml conc. HNO_3, dilute to 3 N and scav twice with CuS.

5. Dilute to 1 N and scav three times with PdS.

6. Scav with Sb_2S_3.

7. Boil out H_2S, make basic with NH_3, scav twice with $Fe(OH)_3$.

8. Make 0.5 N in HCl and scav with Pd d-m-g.

9. Neutralize supn and ppt Ni d-m-g, wash with H_2O.

10. Dissolve in conc. HNO_3 dilute and neutralize, reppt Ni d-m-g, filter, wash with H_2O, dry 15 min at 110° C. Weigh as Ni d-m-g (29.4 mg per 10 mg Ni).

Remarks:

(1) Designed to purify a little Ni from a lot of activity spread over the periodic table. A few mg of carrier are used in the scavenges.

(2) Where carrier amounts of Cu and Co are present in the original target soln, it may be necessary to remove these before ppt'ng Ni-dmg since Co and Cu form dmg complexes.

(3) Ni-dmg is somewhat soluble both in alcohol and in excess d.m.g. There is also a slight solubility in conc. NH_4OH.

Procedure 9

Source: Lilly, R.C., in U.S.A.E.C. Report No. AECD-2738, Meinke, W.W., Ed., pp. 28-6 (August 30, 1949).

Sample type: Deuteron- or neutron-irradiated copper and nickel.

Advantages: Nickel separated in 1 hour in high purity.

Yield: About 90 percent.

Procedure: A, B and C have steps 4-7 in common.

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

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

(2) Dilute to 50 ml with H_2O and heat to boiling. Ppt Fe $(OH)_3$ by adding NH_4OH in excess and coagulate the ppt well by heating. Filter the $Fe(OH)_3$ ppt through No. 42 Whatman paper in a glass funnel and wash with a small amount of 1 percent NH_4Cl sol'n. (The ppt is worked up separately as described in the procedure for Fe from Cu targets, No. 26-10). Make the filtrate slightly acidic with HCl. Add conc NH_4HSO_3 sol'n dropwise until all of the Cu is reduced (as shown by the lack of any localized blue color when a few drops of conc NH_4OH are added). Add solid NH_4SCN dissolved in a small amount of H_2O until ppt'n is complete.

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

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

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

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

the $Fe(OH)_3$ ppt through No. 42 Whatman paper in a glass funnel and wash with a small amount of 1 percent NH_4Cl sol'n. (The ppt is worked up separately as described in the procedure for Fe from Cu targets, No. 26-10). Make the filtrate slightly acidic with HCl. Add conc. NH_4HSO_3 sol'n dropwise until all of the Cu is reduced (as shown by the lack of any localized blue color when a few drops of conc NH_4OH are added). Add solid NH_4SCN dissolved in a small amount of H_2O until ppt'n is complete.

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

C. Nickel from Cu (0.1 - 0.5 gms) + n - 60"

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

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

(3) Boil the filtrate to a volume of $\sim$10 ml and then transfer it to a 50 ml separatory funnel.

In all three of the above cases continue as follows:

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

(5) Draw off the H_2O layer from this extraction into a second 50 ml separatory funnel, discarding the few drops of mixed sol'ns which remain in the stopcock. (The Co is contained in the organic fraction

and is worked up separately as described in the procedure for Co from Cu targets, No. 27-5).

(6) Add 2 mg of Co as the chloride sol'n to the H_2O layer in the second funnel and reextract with an equal volume of ethyl ether-amyl alcohol (1:1). Draw off the H_2O layer into a 50 ml beaker, boil to a volume of 5 ml, and transfer to a 15 ml. centrifuge cone. Discard the organic layer.

(7) Make the sol'n slightly ammoniacal and add 1 ml of 1 percent DMG in alcohol to ppt Ni. Centrifuge and discard the supernatant. Wash the ppt with H_2O, centrifuge, and discard the wash. Prepare the ppt for counting as desired.

Remarks: See Sandell (Colorimetric Determination of Traces of Metals) for further information on the extraction of Co from thiocyanate sol'ns with ethyl ether-amyl alcohol.

Procedure 10

Source:	Lilly, R.C., in U.S.A.E.C. Report No. AECD-2738, Meinke, W.W., Ed., p. 28-7 (August 30, 1949).
Sample type:	Neutron-irradiated copper (10 g Cu).
Advantages:	Nickel separated from large amounts of copper in 3 hours; D. F. $\sim$100.
Yield:	About 90 percent.

Procedure:

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

(2) Add conc. NH_4HSO_3 sol'n., 1 ml at a time, until all of the

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

(3) Coagulate the CuSCN ppt by heating and filter it through a double thickness of No. 42 Whatman paper in a large glass funnel. Discard the ppt.

(4) Boil the filtrate to a volume of 200 ml and make the sol'n slightly ammoniacal.

(5) Add 1 percent DMG in alcohol until no further ppt is produced. Add NH_4OH until the sol'n is distinctly basic.

(6) Coagulate the ppt by heating and then filter it through No. 42 Whatman paper in a glass funnel. Wash the ppt thoroughly with warm H_2O. Ignite the ppt until all of the paper is burned off.

(7) Dissolve the NiO in HCl and add 100 mg Cu and 10 mg Ni as the chloride sol'ns. Adjust the acidity as in step (1) and repeat steps (2) and (3).

(8) Boil the sol'n to a low volume and transfer to a centrifuge cone. Make slightly ammoniacal and ppt Ni with DMG as in step (5) above. Coagulate the ppt in a hot H_2O bath, centrifuge, and discard the supernatant. Prepare the ppt for counting as desired.

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

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