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THE SEPARATION AND MICRODETERMINATION OF COBALT  
IN HIGH PURITY NICKEL

by  
JOHN RICHARD KNAPP, Jr.

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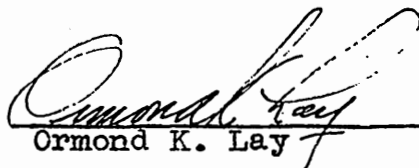
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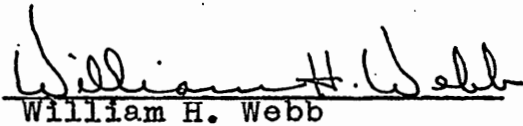
submitted to the faculty of the  
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in partial fulfillment of the work required for the  
Degree of  
MASTER OF SCIENCE in CHEMICAL ENGINEERING  
Rolla, Missouri  
1960

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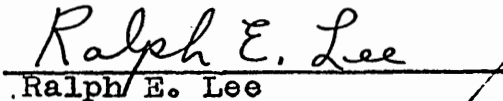
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## I. INTRODUCTION

It has been found that many substances in an extremely pure form or containing certain trace impurities, exhibit many unique physical and chemical properties. Investigators studying these properties have encountered many difficulties, especially in preparing the extremely pure substance and/or in accurately determining the quantity of impurities present. These problems arise chiefly from the very similar chemical properties of the constituents being separated and the possibility of contamination during the necessary processing of the substance for purification or analysis.

Trace analysis, therefore, has become very important in recent years. Where previously analyses based upon parts per hundred were adequate, now the analyst is being required to determine parts per million and in some cases parts per billion of minor constituents. These analyses have been made possible only by the development of specific methods, which either extend the reliable lower limits of standard analytical procedures or apply new principles or reagents.

The United States Bureau of Mines has recently been interested in the production of extremely high purity nickel. They found the standard analytical procedures for

the quantitative determination of residual cobalt, necessary to establish the purity of nickel produced, inadequate. The results obtained for a given sample by application of different methods of analysis and by different analysts, both staff and independent, varied widely. Because of this, it was decided to initiate an investigation on the analysis of trace amounts of cobalt in high purity nickel, which would give reproducible results.

The purpose of this investigation was to develop a method employing ion exchange techniques, for the quantitative separation and concentration of residual amounts of cobalt contained in high purity nickel; so standard analytical procedures could be reliably applied for the quantitative determination of cobalt.

## II. LITERATURE REVIEW

This review is presented in three parts: (1) Ion-exchange, (2) Separation of cobalt and nickel, and (3) Thiocyanate complexes.

### Ion-Exchange

Ion-exchange is not a recent development but has been familiar to man as a phenomena for centuries. The early researchers worked only with naturally occurring materials which exhibited ion-exchange properties. As the theoretical aspects of this phenomena were more clearly understood, synthetic exchangers were developed which would exchange only cations, only anions, or only a few specific cations. The preparation, theory, and uses of these resins have been investigated continuously for the past fifty years, but only in the last ten years have they attained wide spread application. (11,20,24,28,34,40)<sup>1</sup>

Analytical separations incorporating ion-exchange resins can be classified according to the amount of the material in the influent which is adsorbed by the exchanger. When the greater part of the material in the influent is adsorbed and selective fractions removed by elution, the method is one of selective elution. When only the material

1. All references are in bibliography

desired, in the influent, is adsorbed by the resin the method is one of selective adsorption. When small amounts of material are to be concentrated or removed from a relatively large amount of total material, the latter method is usually preferred. (30,36)

### Separation of Cobalt and Nickel

Many methods for separating cobalt and nickel have been investigated, but relatively few of them have incorporated ion-exchange methods. (5) Jacobs and Thompkins (21) reported the elution characteristics of cobalt and nickel from an alumina exchanger. It was concluded from their work that alumina was unsuitable as an adsorbant for quantitative separation of the two. (22) Kamdomitzeff reported that a good separation of cobalt and nickel could be obtained by the selective elution of their cations from Amberlite IR-100. 1000 milliliters of eluent, flowing at a rate of nine milliliters per hour, were required to separate the cobalt from an eight milligram sample of a mixture of cobalt and nickel chlorides. (26) Krause and Nelson reported that cobalt could be separated from nickel with Dowex-1. The cobalt complex formed in 12 molar hydrochloric acid solution was selectively adsorbed by the resin, while nickel passed into the effluent. (15) Herber and Irving reported that the bromide complex of cobalt parallels that of the chloride complex.

(9)  
Dean developed a method using an alumina exchanger and the Nitroso-R-Salt complex of cobalt. The cobalt complex was selectively adsorbed by the exchanger while the nickel passed into the effluent. The Dow Chemical Company (10) has developed a special chelating resin whereby cobalt and nickel amines can be separated. The two amines are first adsorbed on the resin and then the cobalt ammine is eluted with dilute hydrochloric acid. The fractions obtained are not pure because cross contamination of cobalt and nickel occurs. Fujimoto (14) reported that the color produced by the cobalt thiocyanate complex, adsorbed on an anion exchanger, could be used as a spot test for cobalt in the presence of nickel.

### Thiocyanate Complexes

The thiocyanate complex of cobalt was first reported in 1879 by Vogel (39); since that time a number of papers have appeared on this subject. The exact formula for this complex has been found to be dependent on the medium in which it is formed. West and de Vries (41) reported that the complex formed in methyl, ethyl, propyl, or butyl alcohol is a mixture of  $[\text{Co}(\text{CNS})]^+$  and  $[\text{Co}(\text{CNS})_6]^{-4}$ . Katzin and Gebert (23) and Drako and Babko (4) reported that a stepwise reaction occurs and complexes ranging from  $[\text{Co}(\text{CNS})]^+$  to  $[\text{Co}(\text{CNS})_4]^{-2}$  are formed when the solution contains some acetone.

(31)  
Lehne also reported that a stepwise reaction occurs in an aqueous medium and that complexes ranging from  $[\text{Co}(\text{CNS})]^+$  to  $[\text{Co}(\text{CNS})_4]^{-2}$  are formed. He stated that the complex obtained was dependent upon the thiocyanate concentration and that the coordination number of cobalt changed from six to four when the  $[\text{Co}(\text{CNS})_4]^{-2}$  was formed.

Many other thiocyanate complexes have been studied and are reported in the literature. (12,38,33)

### III. EXPERIMENTAL

#### Purpose of Investigation

The purpose of this investigation was to develop a method employing ion exchange techniques, for the quantitative separation and concentration of residual amounts of cobalt contained in high purity nickel: so standard analytical procedures could be reliably applied for the quantitative determination of cobalt.

#### Plan of Experimentation

Adsorption Techniques. The types of ionic medium and ion exchange resin to be used in the separation were studied. The work consisted of qualitative tests to determine which complexes were adsorbed by a particular resin, and quantitative determinations of the degree of adsorption. The qualitative tests were conducted under batch conditions and the results were interpreted by color comparisons and spot-tests. The quantitative determinations for the distribution coefficients of a particular complex involved batch-wise equilibria studies, and the actual separations involved ion-exchange column techniques.

Elution Technique. The ionic medium used for the elution of the cobalt complex from the resin was studied.

The work consisted of qualitative tests to determine a possible eluent and quantitative determinations for the degree of elution. The procedures involved were the same as those for the adsorption techniques, only the reverse effects, those of desorption, studied.

Cobalt Analysis. Existing methods for quantitative analysis of cobalt were studied to establish their applicability for the determination of cobalt after separation. The concentration range to which the method was applicable and the interferences of other ions possibly present were investigated, and appropriate modifications made when required.



### Materials

The following materials were used in this investigation. The specifications, supplier, and use of each material are listed.

Acetone (CH<sub>3</sub>COCH<sub>3</sub>). Analytical reagent, A.C.S., lot No. 791377. Obtained from Fisher Scientific Co., St. Louis, Mo. Used for cleaning organics from glassware.

Acid-Hydrochloric (HCl). Analytical reagent, A.C.S. Obtained from Mallinckrodt Chemical Co., St. Louis, Mo. Used for pH adjustments and for elution studies.

Acid-Sulfuric (H<sub>2</sub>SO<sub>4</sub>). Analytical reagent, A.C.S. Obtained from Fisher Scientific Co., St. Louis, Mo. Used in analytical schemes.

Acid Nitric (HNO<sub>3</sub>). Analytical reagent, A.C.S. Obtained from Mallinckrodt Chemical Co., St. Louis, Mo. Used in analytical schemes.

Ammonium Hydroxide (NH<sub>4</sub>OH). Analytical reagent, A.C.S. Obtained from Fisher Scientific Co. Used as a complexing agent and to adjust pH.

Ammonium Thiocyanate (NH<sub>4</sub>CNS). Analytical reagent, A.C.S., lot No. 754722 and lot No. 782686. Obtained from Fisher Scientific Co., St. Louis, Mo. Used as a complexing agent.

Cobalt (Co). "Matthey" Sponge, Lab. 3900, Spectrographic Standardized Substance. Manufactured by Johnson Matthey and Co., London, England. Obtained from Jarrell-Ash Co., Boston, Mass. Used for preparing standard cobalt solutions for spectrophotometric determinations.

Cobalt-60 (Co<sup>60</sup>). One micro curie per two milliliters, chloride solution, serial No. 10-C, lot No. 4-21-59, uncalibrated. Obtained from Tracerlab, Inc., Waltham, Mass. Used for checking cobalt separations.

Cobalt Chloride (CoCl<sub>2</sub>·6H<sub>2</sub>O). Analytical reagent, A.C.S., lot No. 762873. Obtained from Fisher Scientific Co., St. Louis, Mo. Used in qualitative preliminary tests.

Copper (Cu). Analytical reagent, lot No. 4648. Obtained from Mallinckrodt Chemical Co., St. Louis, Mo. Used for determining the distribution coefficient of the thiocyanate complex.

Iron (Fe). Analytical reagent, lot No. 41915. Obtained from Merck and Co., Inc. Used for determining the absorbance curve and the distribution coefficient of the thiocyanate complex.

Manganese Dioxide (MnO<sub>2</sub>). Analytical reagent. Obtained from Mallinckrodt Chemical Co., St. Louis, Mo. Used for determining the absorbance curve, and the distribution coefficient of the thiocyanate complex.

Nickel (Ni). Obtained from Hydrometallurgy Section of the United States Bureau of Mines, Rolla, Mo. Used for comparative analysis of cobalt.

Nickel (Alloys).<sup>\*a</sup> Standard samples No. 162 and 167. Obtained from United States Bureau of Standards, Washington, D. C. Used for preparing an artificial nickel sample.

Nickel Oxide (NiO).<sup>\*b</sup> Standard Samples No. 671, 672, and 673. Obtained from U. S. Bureau of Standards, Washington, D. C. Used for comparative analysis of cobalt.

Nickel Oxide (NiO). Contains less than 0.003 per cent total impurities. Obtained from International Nickel Co., Inc., Huntington, West Va. Used in the preparation of an artificial nickel sample.

Nickel Sulfate (NiSO<sub>4</sub>·6H<sub>2</sub>O). Analytical reagent, A.C.S., lot No. 782981. Obtained from Fisher Scientific Chemical Co., St. Louis, Mo. Used for comparative analysis of cobalt and for preparing nickel solutions.

Nitroso-R-Salt (ONC<sub>10</sub>H<sub>4</sub>(SO<sub>3</sub>Na)<sub>2</sub>OH). Reagent Chemical. Lot No. 549103. Obtained from Fisher Scientific Chemical Co., St. Louis, Mo. Used for cobalt analysis.

Nickel Chloride (NiCl<sub>2</sub>·6H<sub>2</sub>O). Analytical reagent, lot No. 762784. Obtained from Fisher Scientific Chemical Co., St. Louis, Mo. Used for comparative analysis of cobalt and for preparing nickel solutions.

\*a Analysis in appendix C.

\*b Analysis in appendix D, E, and F.

Potassium Thiocyanate (KCNS). Analytical reagent, A.C.S., lot No. 521299. Obtained from Fisher Scientific Chemical Co., St. Louis, Mo. Used as a complexing agent.

Resins, Ion-Exchange:

Dowex-1 (- $\phi$ -N-(CH<sub>3</sub>)<sub>3</sub>). Strongly basic anion exchanger, solid, 2, 8, and 10% Divinylbenzene (DVB) crosslinkage, chloride form, 50-100 mesh. Obtained from Microchemical Specialties Co., Berkley, Calif. Used in separation procedures and in determining distribution coefficients.

Dowex-2 (- $\phi$ -N-(CH<sub>3</sub>)<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>OH). Strongly basic anion exchanger, solid, 10% DVB crosslinkage, chloride form, 50-100 mesh. Obtained from Microchemical Specialties Co., Berkley, Calif. Used in separation procedures and in determining distribution coefficients.

Dowex-3 (Polyamine). Weakly basic anion exchanger, solid, free base form, 20-50 mesh. Obtained from Microchemical Specialties Co., Berkley, Calif. Used in separation procedures.

Amberlite IR-120 (- $\phi$ -SO<sub>3</sub>H). Analytical grade, strongly acidic cation exchange resin, solid, lot No. 772358, 8% DVB crosslinkage. Hydrogen form. 16-50 mesh. Obtained from Fisher Scientific Chemical Co., St. Louis, Mo. Used in separation procedures.

Amberlite IA-1. Anion exchanger, lot No. 12-7116 highly branched, unsaturated, secondary aliphatic amines, containing 24-27 carbon atoms, liquid, free base form. Obtained from Rhom and Haas Co., Philadelphia, Penn. Used in separation procedures and spectrophotometric method for cobalt analysis.

Amberlite IA-2. Liquid anion exchange, lot No. 12-7208, highly branched, unsaturated, secondary aliphatic amines, containing 24-27 carbon atoms, liquid, free base form. Obtained from Rhom and Haas Co., Philadelphia, Penn. Used for separation procedures and spectrophotometric method for cobalt analysis.

Sodium Hypochlorite (NaOCl). "Clorox," 5.25 weight percent NaOCl. Obtained from A & P Supermarket, Rolla, Mo. Used for elution study of thiocyanate complexes from resins.

Sodium Carbonate (Na<sub>2</sub>CO<sub>3</sub>). Analytical reagent, A.C.S., lot No. 773459. Obtained from Fisher Scientific Chemical Co., St. Louis, Mo. Used for elution study of thiocyanate complexes from resins.

Sodium Nitrite (NaNO<sub>2</sub>). Analytical reagent. Obtained from Fisher Scientific Chemical Co., St. Louis, Mo. Used as a complexing agent for cobalt.

Xylene (C<sub>6</sub>H<sub>4</sub>(CH<sub>3</sub>)<sub>2</sub>). Neutral histological, analytical reagent, A.C.S., lot No. 790637. Obtained from Fisher Scientific Chemical Co., St. Louis, Mo. Used as a diluent for liquid resins.

Apparatus

The following apparatus was used in this investigation. The working specifications, the supplier, and the use of the apparatus are listed.

Balance. Analytical, keyboard, serial No. 11759, Type T-C, United States Bureau of Mines (U.S.B.M.) property No. 1566. Obtained from Fisher Scientific Co., St. Louis, Mo. Used for weighing materials in the preparation of standard solutions.

Balance. Gram-atic, single pan, model No. 1-910, U.S.B.M. property No. 1290. Obtained from Fisher Scientific Co., Eimer and Amend. Used for weighing materials in the preparation of standard solutions and for weighing samples to be analyzed.

Balance. Gent-0-Gram, triple beam, model GG 311, U.S.B.M. property No. 5081. Obtained from Ohaus Scale Corp., Union, N. J. Used for weighing Ammonium Thiocyanate.

Centrifuge. Safe-guard, serial No. A-102862, U.S.B.M. property No. 2704. Obtained from Clay Adams Co., Inc., New York, N. Y. Used for phase separation in extraction work.

Electroanalyzer. Sargent Slomin, U.S.B.M. property No. 2515. Obtained from E. H. Sargent Co., Chicago, Ill. Used for nickel analysis.

GM Tube. Model 10306, serial No. 9223. Obtained from Radiation Counter Laboratories, Skokie, Ill. Used for radiation counting.

pH-Meter. Zeromatic, serial No. 63113. Obtained from Fisher Scientific Co., St. Louis, Mo. Used for pH adjustments.

Polarograph. Cathode Ray recording, model K-1000, serial No. 12, U.S.B.M. property No. 5385. Obtained from Southern Instruments, Ltd., Camberley, England. Used for cobalt Analysis.

Polarograph. Pen recording, model 21. Obtained from E. H. Sargent and Co., Chicago, Ill. Used for cobalt and nickel analysis.

Scaler. Binary, model 163, with a model No. TI dual timer, U.S.B.M. property No. 1822. Obtained from Nuclear Chicago Instrument and Chemical Corp., Chicago, Ill. Used in radiation counting.

Spectrograph. 3-meter grating, 5.6 angstroms per millimeter. Obtained from Baird-Atomics, Inc., Cambridge, Mass.

Source. National Spectrographic Laboratory, rectified dc arc, 10 amps across the arc, 3 millimeter arc.

Plates. Eastman S. A. No. 1. Developed with Eastman D-10. Fixed with Eastman F-5.

Electrodes. Class S. National Carbon Co., special carbon.

Densitometer. National Spectrographic Laboratory.

Spectrophotometer. Linear recording, model DK-2, serial No. 142744, U.S.B.M. property No. 6063. Obtained from Beckman Instruments, Inc., Fullerton, Calif. Used for determining absorption curves of metal thiocyanate complexes and for cobalt analysis.

Spectrophotometer. Model B, serial No. 93945, U.S.B.M. property No. 4805. Obtained from Beckman Instruments, Inc., Fullerton, Calif. Used for cobalt analysis.



### Method of Procedure

The method of procedure for this investigation has been divided into six sections. They are: (1) Determination of distribution coefficients, (2) ion exchange column operation, (3) liquid-liquid extraction procedure, (4) radioisotope tracer technique, (5) chemical analysis, and (6) analytical working curves for spectrophotometers. Sections (2) and (5) are further divided into parts for clarity.

#### Determination of Distribution Coefficients. (6,25,27) The

distribution coefficients for the various complexes were determined by the batch equilibrium method. The method consisted of placing small known amounts of resin and solution in an Erlenmeyer flask and letting it stand, with periodic shaking, for seventy-two hours.

The phases were then separated by filtration and the resin thoroughly washed with fifty milliliters of distilled water. The washings being added to the filtrate. The resulting filtrate was then analyzed for the metal being studied and the distribution coefficient calculated. The distribution coefficient ( $K_d$ ) may be expressed as:

$$K_d = \frac{M_R \times V_S}{M_S \times M_T} \left( \frac{\text{gm}}{\text{ml}} \right)$$

where:  $M_R$  = weight of solute on resin (mg)  
 $M_S$  = weight of solute in solution (mg)  
 $M_r$  = weight of resin (gm)  
 $V_S$  = volume of solution (ml)

Each series of experiments were conducted using constant amounts of resin and metal-ion. Optimum conditions were determined by varying the concentration of the complexing agent and the pH of the aqueous phase.

(29)  
Column Operation. A fixed bed ion exchange column with down-flow operation was used to study the exchange of the various metal ions and metal complexes with the various ion exchange resins.

The columns used in the exchange studies were made from either fifty or one-hundred milliliter burettes. Each burette was converted into an ion exchange column by the insertion of a glass-wool resin support in the bottom of the burette.

The desired bed depth was obtained by introducing the resin beads into the column in the form of a slurry and allowing them to settle by gravity. The excess solution was then removed, leaving only the interstitial volume filled with solution. The resin used in each test was water swollen and new.

Adsorption Tests. The ion exchange column was prepared as previously stated. Each test was then

conducted as follows: (1) The resin was conditioned with a solution identical in composition to that of the test solution, except the metal ions being studied were absent, (2) the test solution was passed through the column at a constant flow rate, maintaining a constant liquid level above the resin bed, and (3) the test solution remaining in the interstitial volume was removed by rinsing with fifty to one-hundred milliliters of conditioning solution.

The samples taken for analysis from each test included the interstitial conditioning solution, the complete test solution, and the rinse solution.

Elution Tests. For the elution tests the material desired to be eluted was put on the resin as explained in the adsorption tests. The eluting solution was then passed through the column and the total or fractional parts of the effluent taken for analysis.

Liquid-Liquid Extraction Procedure. <sup>(35)</sup> The extraction procedure used in studying the liquid ion exchange resins was that of single batch equilibrations. The liquid resins were diluted with known volumes of xylene to minimize emulsion formation and to reduce the viscosity of the extractant.

The tests consisted of contacting a known volume of diluted resin and aqueous solution of the metal complex in a separatory funnel. The two phases were mixed by shaking

the separatory funnel while turning it end over end twenty-five times. The two phases were then allowed to separate and the heavier aqueous phase drained off.

Adsorption studies were conducted by contacting known amounts of the diluted resin with solutions containing known amounts of the complexed metal under examination. After contact, the aqueous phase was separated and taken for analysis to determine the efficiency of extraction.

Elution studies were conducted in the same manner as the adsorption studies; except that diluted liquid resin, containing known amounts of the complexed metal under examination, was contacted with a solution containing an eluting agent.

(13)

Radioisotope Tracer Technique. Cobalt-60 was added as a tracer to solutions containing known amounts of cobalt to determine the efficiencies of both the adsorption and elution steps of the liquid ion exchange separations. Relative counting techniques were employed since the one micro-curie sources of cobalt-60 used for this work were uncalibrated. The cobalt-60 sources were calibrated by diluting to a graduate series of known concentrations and the activities (counts/minute/milliliter) of the series of standards determined. The same equipment used for calibration was used for the test sample counting.

The working equation in determining the degree of separation being:

$$E = \frac{A_s}{A_o} \times 100$$

where for adsorption:

E = per cent adsorbed

A<sub>s</sub> = activity of resin (counts/min.)

A<sub>o</sub> = initial activity of the solution  
(counts/min.)

where for elution:

E = per cent eluted

A<sub>s</sub> = activity of eluent (counts/min.)

A<sub>o</sub> = initial activity of resin  
(counts/min.)

Chemical Analysis. The analytical procedures used to obtain the data for this report are presented under the appropriate heading.

Nitroso-R-Salt Procedure. (2,37,44) A standard spectrophotometric method was used in determining microgram amounts of cobalt. The determination depends on the red color produced by the cobalt complex in a hot solution buffered with sodium acetate. The detailed procedure used is presented in appendix A.

Pyridine Procedure. (42,46) A standard polarographic method used for cobalt and nickel analysis. The determination of the concentration depends on the measurement of the current-voltage curves arising at a

micro-electrode when diffusion is the rate-determining stage in the discharge of the pyridine complexes of the metals. The detailed procedure used is presented in appendix A.

(3,16,45)

Dimethylglyoxime Procedure. A standard gravimetric method was used for nickel analysis. The determination depends on the insoluble precipitate formed by the nickel complex in an alkaline medium. The detailed procedure used is presented in appendix A.

(7,17)

Ceric Ammonium Sulfate Procedure. A standard volumetric method was used for iron analysis. The determination is based on the oxidation-reduction reaction of iron (II) and cerium (IV). The detailed procedure used is presented in appendix A.

(8,18)

Thiosulfate-Iodide Procedure. A standard iodometric method was used for copper analysis. The determination is based on the iodine released when copper (II) salts react with potassium iodide in an acidified solution. The detailed procedure used is presented in appendix A.

(19,47)

Bismuthate Procedure. A standard volumetric method was used for manganese analysis. The determination is based on the oxidation-reduction titration of permanganate by iron (II) after the oxidation of manganese to permanganate by sodium bismuthate. The detailed procedure used is presented in appendix A.

(43)

Analytical Working Curves for Spectrophotometers.

The analytical working curve for spectrophotometric methods of analysis are usually prepared in the following manner:

(1) Weigh an exact amount of the primary standard of the material to be analyzed.

(2) Dissolve the primary standard and prepare a standard solution by dilution to a known volume.

(3) Known amounts of the standard solution are processed by a standard colorimetric procedure.

(4) The absorbances or transmittances, after color development, are then determined with a spectrophotometer.

(5) The analytical working curve is prepared by plotting absorbances versus concentrations on rectangular coordinate paper.

## Data and Results

The data obtained by this investigation have been grouped according to the physical form of the ion-exchange resin employed. Each test is then presented under the appropriate heading.

### Solid Ion-Exchangers

Distribution Coefficients. The data for these determinations are presented in Figures 1 to 7, and Tables I to VII, pages 25 to 38.

For each of the metal complexes studied, 5.00 grams of new resin were used in the equilibration. Hydrochloric acid was used to obtain the pH values 1, 3, and 5 and ammonium hydroxide was used to obtain the pH values 7 and 9.

In each test the distribution coefficient was calculated and its logarithm plotted against the concentration of ammonium thiocyanate.

Column Separations. The data for these separations are presented in Table VIII, page 39.

The ion-exchange column used for each test was a converted fifty milliliter burette. The desired bed depth was obtained by the method stated on page 18.

The flow rates given in the table are average values for the testing period.



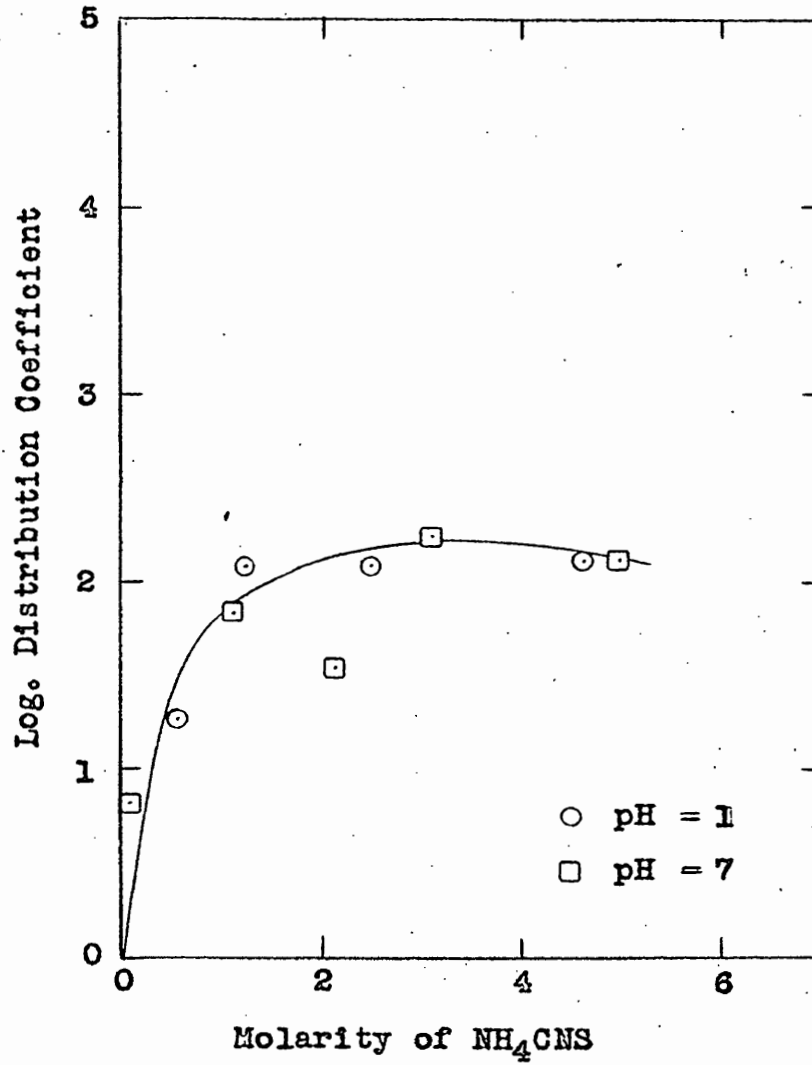


Figure 1. Adsorption of Manganese (II) from Thiocyanate Solutions by Dowex-1x10%

TABLE I

Adsorption of Manganese (II) from Thiocyanate Solutions by Dowex-1<sup>a</sup>

pH	Molarity of NH <sub>4</sub> CNS	Volume of Solution ml	Manganese in Solution mg	Manganese on Resin <sup>d</sup> mg	Distr. Coeff. ml/gm	Log Distr. Coeff.
1.0 <sup>b</sup>	0.12	43.0	29.57	0.53	0.154	-0.823
1.0	0.58	43.0	9.84	20.26	17.7	1.248
1.0	1.25	40.0	1.84	28.26	123	2.090
1.0	2.50	40.0	1.81	28.29	125	2.097
1.0	4.65	43.0	1.84	28.26	132	2.121
7.0 <sup>c</sup>	0.11	46.0	15.67	10.63	6.24	0.795
7.0	1.14	44.0	3.00	23.30	68.4	1.835
7.0	2.13	47.0	5.51	20.79	31.7	1.501
7.0	3.13	64.0	1.79	24.51	171	2.233
7.0	5.00	60.0	2.28	24.02	127	2.104

<sup>a</sup>Dowex-1: 10% crosslinkage, 50-100 mesh, Cl<sup>-</sup>form. 5.00 gm used in each test.

<sup>b</sup>Obtained with HCl.

<sup>c</sup>Obtained with NH<sub>4</sub>OH.

<sup>d</sup>Obtained by differences.

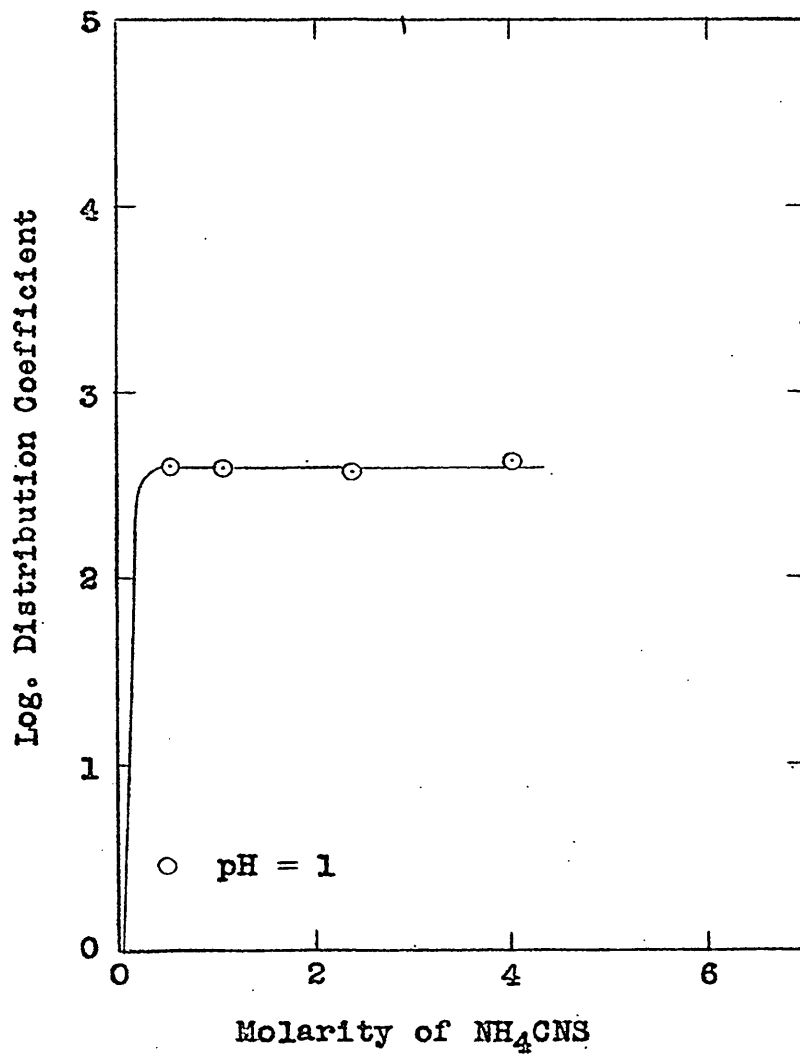


Figure 2. Adsorption of Iron (III) from Thiocyanate Solutions by Dowex-1x10%

TABLE II

Adsorption of Iron (III) from Thiocyanate Solutions by Dowex-1<sup>a</sup>

pH	Molarity of NH <sub>4</sub> CNS	Volume of Solution	Iron in Solution	Iron on Resin <sup>d</sup>	Distr. Coeff.	Log Distr. Coeff.
		ml	mg	mg	ml/gm	
1.0 <sup>b</sup>	0.10	49.0	30.00	1.10	0.360	-0.444
1.0	0.55	46.0	0.54	30.57	520	2.716
1.0	1.09	46.0	0.54	30.57	520	2.716
1.0	2.32	43.0	0.54	30.57	486	2.687
1.0	4.00	50.0	0.54	30.57	565	2.752
7.0 <sup>c</sup>	0.1-4.0	--	pptd. <sup>e</sup>	---	---	---

<sup>a</sup>Dowex-1: 10% crosslinkage, 50-100 mesh, Cl<sup>-</sup> form. 5.00 gm used in each test.

<sup>b</sup>Obtained with HCl.

<sup>c</sup>Obtained with NH<sub>4</sub>OH.

<sup>d</sup>Obtained by differences.

<sup>e</sup>Ppt. occurred before addition of resin; solutions discarded.

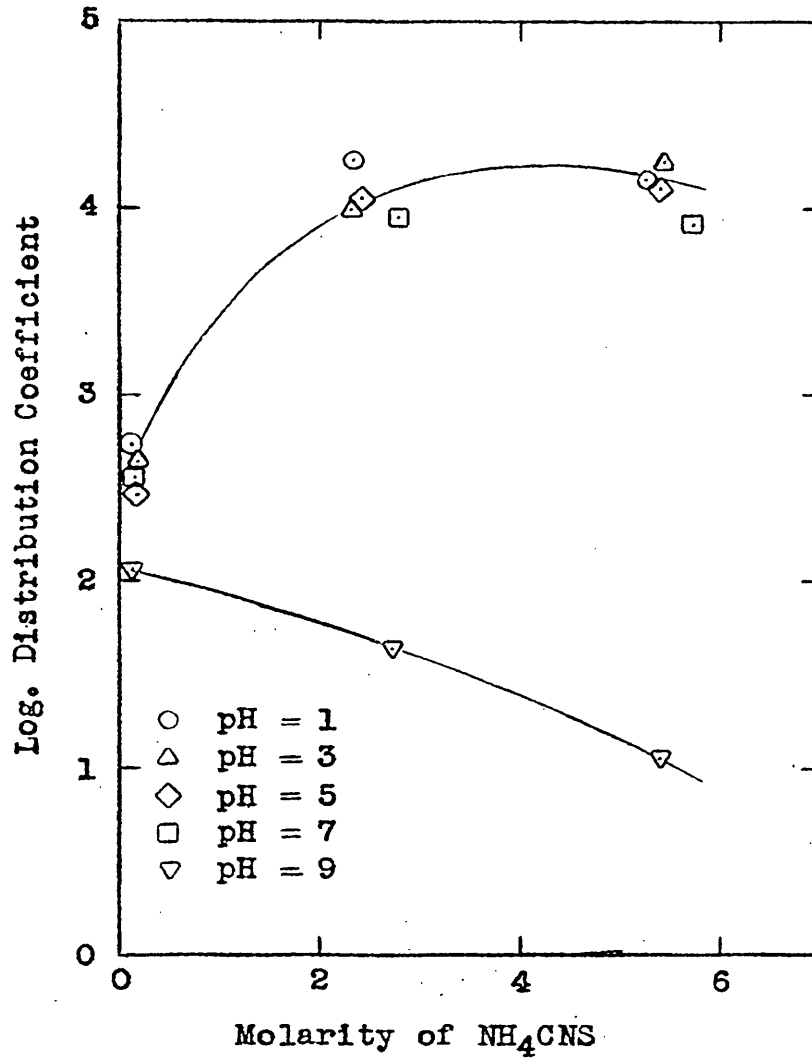


Figure 3. Adsorption of Cobalt (II) from Thiocyanate Solutions by Dowex-1x10%

TABLE III

Adsorption of Cobalt (II) from Thiocyanate Solutions by Dowex-1<sup>a</sup>

pH	Molarity of NH <sub>4</sub> CNS	Volume of Solution ml	Cobalt in Solution mg	Cobalt on Resin <sup>d</sup> mg	Distr. Coeff. ml/gm	Log Distr. Coeff.
1.0 <sup>b</sup>	0.12	42.0	0.436	27.964	583	2.731
1.0	2.31	43.0	0.013	28.387	18,500	4.267
1.0	5.26	38.0	0.015	28.385	14,400	4.158
3.0 <sup>b</sup>	0.16	32.0	0.568	27.832	314	2.497
3.0	2.28	44.0	0.025	28.375	10,200	4.009
3.00	5.40	37.0	0.011	28.389	18,500	4.267
5.0 <sup>b</sup>	0.17	29.0	0.368	28.032	441	2.644
5.0	2.38	42.0	0.020	28.380	11,400	4.057
5.0	5.40	37.0	0.016	28.384	13,200	4.121
7.0 <sup>c</sup>	0.14	35.0	0.614	27.786	317	2.501
7.0	2.78	36.0	0.023	28.377	8,990	3.954
7.0	5.71	35.0	0.023	28.377	8,570	3.933
9.0 <sup>c</sup>	0.16	29.0	1.455	26.945	107	2.029
9.0	2.70	37.0	4.046	24.354	44.4	1.647
9.0	5.40	37.0	11.73	16.63	10.5	1.021

<sup>a</sup>Dowex-1: 10% crosslinkage, 50-100 mesh, Cl<sup>-</sup> form. 5.00 gm used in each test.

<sup>b</sup>Obtained with HCl. <sup>c</sup>Obtained with NH<sub>4</sub>OH. <sup>d</sup>Obtained by differences.

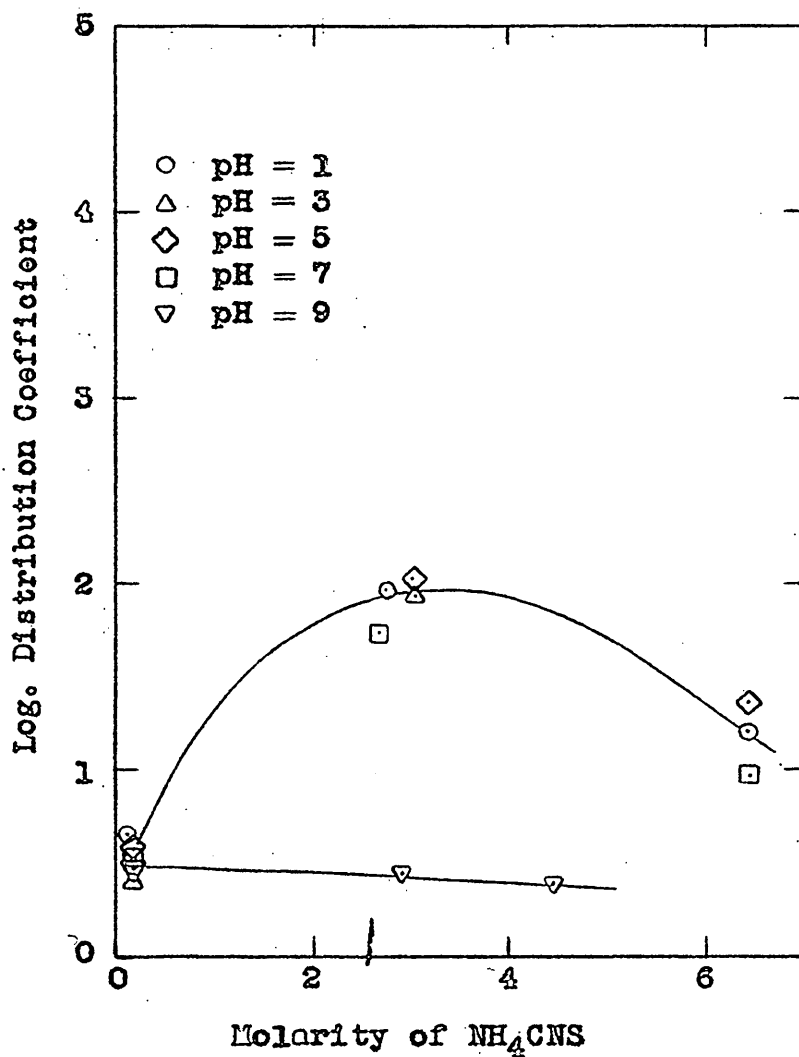


Figure 4. Adsorption of Nickel (II) from Thiocyanate Solutions by Dowex-1x10%

TABLE IV

Adsorption of Nickel (II) from Thiocyanate Solutions by Dowex-1a

pH	Molarity of NH <sub>4</sub> CNS	Volume of Solutions	Nickel in Solutions	Nickel on Resin <sup>d</sup>	Distr. Coeff.	Log Distr. Coeff.
		ml	mg	mg	ml/gm	
1.0 <sup>b</sup>	0.12	41.0	18.07	9.86	4.48	0.651
1.0	2.78	36.0	2.012	25.918	9.27	1.967
1.0	6.45	31.0	8.087	19.843	15.2	1.182
3.0 <sup>b</sup>	0.17	30.0	19.58	8.35	2.56	0.408
3.0	3.03	33.0	1.951	25.979	8.79	1.944
3.0	6.45	31.0	---	---	---	---
5.0 <sup>b</sup>	0.14	36.0	18.31	9.62	3.78	0.577
5.0	3.03	33.0	1.605	26.325	10.8	2.033
5.0	6.45	31.0	5.893	22.037	23.2	1.365
7.0 <sup>c</sup>	0.14	36.0	18.57	9.36	3.63	0.560
7.0	2.70	37.0	3.332	24.598	5.46	1.737
7.0	6.45	31.0	11.46	16.47	8.91	0.950
9.0 <sup>c</sup>	0.16	32.0	20.05	7.88	2.52	0.401
9.0	2.94	34.0	20.38	7.55	2.52	0.401
9.0	4.55	44.0	22.01	5.92	2.37	0.375

<sup>a</sup> Dowex-1: 10% crosslinkage, 50-100 mesh, Cl<sup>-</sup> form. 5.00 gm used in each test.

<sup>b</sup> Obtained with HCl. <sup>c</sup> Obtained with NH<sub>4</sub>OH. <sup>d</sup> Obtained by differences.



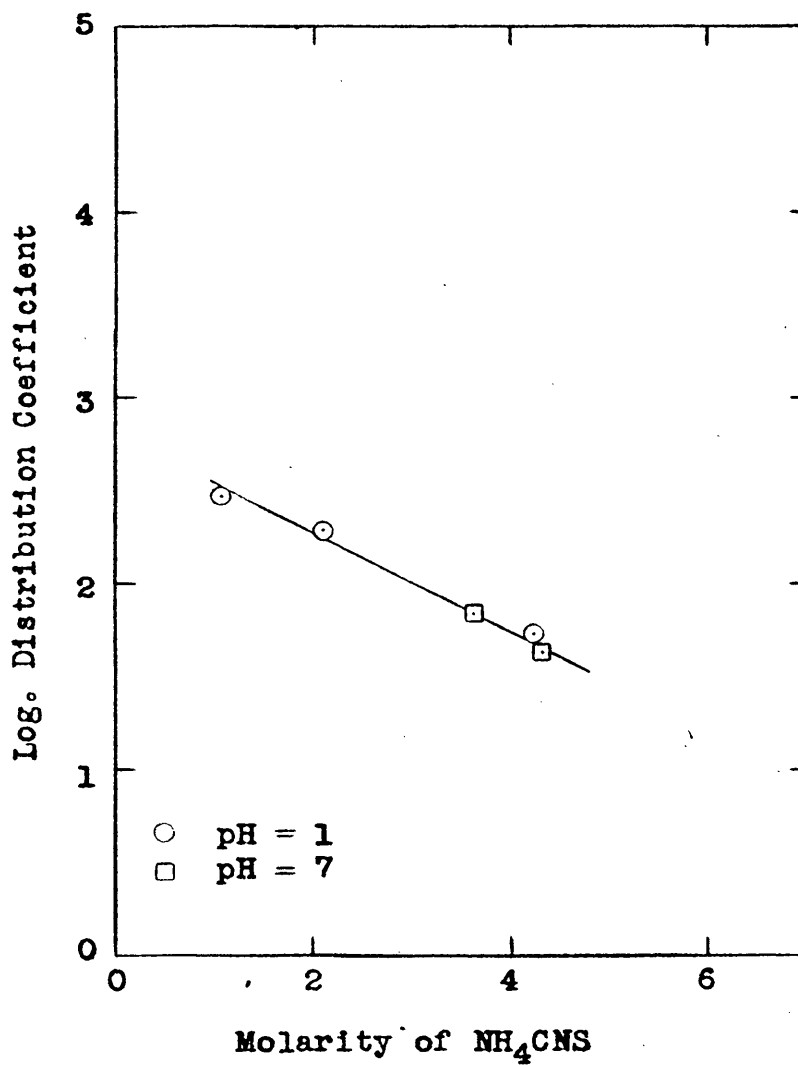


Figure 5. Adsorption of Copper (II) from Thiocyanate Solutions by Dowex-1x10%

TABLE V

Adsorption of Copper (II) from Thiocyanate Solutions by Dowex-1<sup>a</sup>

pH	Molarity of NH <sub>4</sub> CNS	Volume of Solution	Copper in Solution	Copper on Resin <sup>e</sup>	Distr. Coeff.	Log Distr. Coeff.
		ml	mg	mg	ml/gm	
1.0 <sup>b</sup>	0.1	---	pptd. <sup>d</sup>	---	--	---
1.0	0.5	---	pptd.	---	--	---
1.0	1.04	48.0	0.93	28.57	300	2.477
1.0	2.04	49.0	1.39	28.11	198	2.297
1.0	4.16	48.0	4.65	24.85	51.3	1.710
7.0 <sup>c</sup>	0.1	---	pptd. <sup>d</sup>	---	--	---
7.0	0.5	---	pptd.	---	--	---
7.0	1.0	---	pptd.	---	--	---
7.0	3.57	56.0	3.95	23.95	67.9	1.832
7.0	4.28	70.0	7.20	20.70	40.2	1.604

<sup>a</sup>Dowex-1: 10% crosslinkage, 50-100 mesh, Cl<sup>-</sup> form. 5.00 gm used in each test.

<sup>b</sup>Obtained with HCl.

<sup>c</sup>Obtained with NH<sub>4</sub>OH.

<sup>d</sup>Black ppt. occurred before addition of resin; solution discarded.

<sup>e</sup>Obtained by differences.

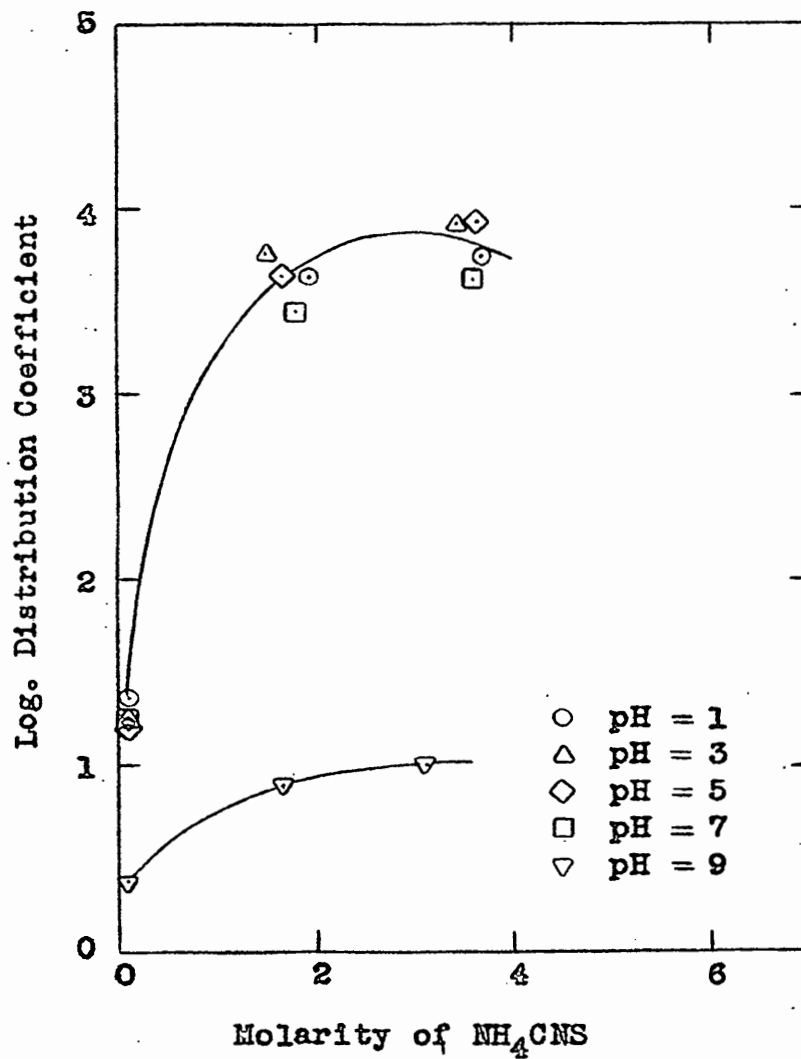


Figure 6. Adsorption of Cobalt (II) from Thiocyanate Solutions by Dowex-2x10%

TABLE VI

Adsorption of Cobalt (II) from Thiocyanate Solutions by Dowex-2<sup>a</sup>

pH	Molarity of NH <sub>4</sub> CNS	Volume of Solution	Cobalt in Solution	Cobalt on Resin <sup>d</sup>	Distr. Coeff.	Log. Distr. Coeff.
		ml	mg	mg	ml/gm	
1.0 <sup>b</sup>	0.09	56.0	8.817	19.583	24.8	1.394
1.0	1.89	53.0	0.063	28.337	4,790	3.680
1.0	3.64	55.0	0.051	28.349	6,070	3.783
3.0 <sup>b</sup>	0.10	50.0	10.09	18.31	18.2	1.259
3.0	1.62	62.0	0.074	28.326	4,770	3.679
3.0	3.64	55.0	0.034	28.366	9,150	3.961
5.0 <sup>b</sup>	0.11	46.0	10.27	18.13	16.2	1.210
5.0	1.49	67.0	0.061	28.340	6,280	3.798
5.0	3.39	59.0	0.036	28.364	9,320	3.969
7.0 <sup>c</sup>	0.10	52.0	10.45	17.95	17.9	1.252
7.0	1.79	56.0	0.105	28.296	3,030	3.481
7.0	3.57	56.0	0.072	28.328	4,420	3.645
9.0 <sup>c</sup>	0.11	47.0	22.64	5.76	2.39	0.378
9.0	1.69	60.0	17.27	11.13	7.74	0.889
9.0	3.13	64.0	15.91	12.49	10.0	1.000

<sup>a</sup>Dowex-2: 10% crosslinkage, 50-100 mesh, Cl<sup>-</sup> form. 5.00 gm used in each test.

<sup>b</sup>Obtained with HCl. <sup>c</sup>Obtained with NH<sub>4</sub>OH. <sup>d</sup>Obtained by differences.

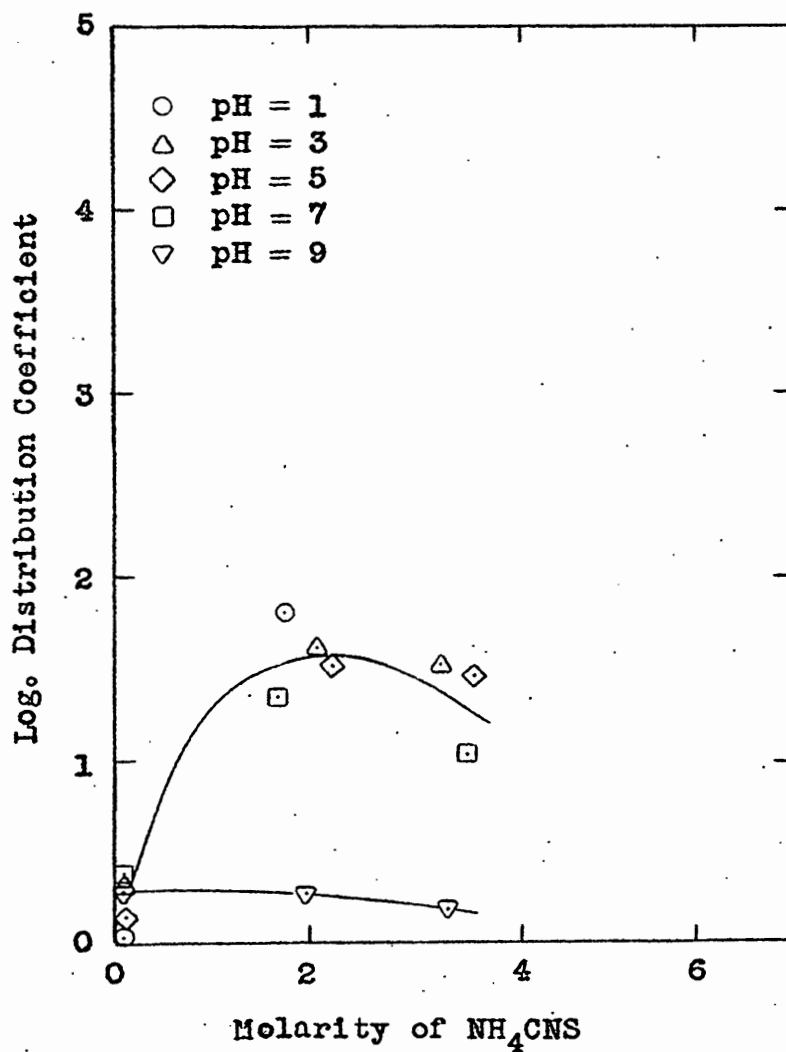


Figure 7. Adsorption of Nickel (II) from Thiocyanate Solutions by Dowex-2x10%

TABLE VII

Adsorption of Nickel (II) from Thiocyanate Solutions by Dowex-2<sup>a</sup>

pH	Molarity of NH <sub>4</sub> CNS	Volume of Solution	Nickel in Solution	Nickel on Resin <sup>d</sup>	Distr. Coeff.	Log Distr. Coeff.
		ml	mg	mg	ml/gm	
1.0 <sup>b</sup>	0.09	55.0	25.42	2.51	1.09	0.037
1.0	1.75	57.0	4.25	23.68	63.5	1.803
1.0	3.64	55.0	---	---	---	---
3.0 <sup>b</sup>	0.10	50.0	22.98	4.95	2.15	0.332
3.0	2.08	48.0	5.21	22.72	41.9	1.621
3.0	3.38	59.0	7.28	20.65	33.5	1.525
5.0 <sup>b</sup>	0.09	53.0	24.65	3.28	1.40	0.146
5.0	2.22	45.0	6.12	21.81	32.1	1.507
5.0	3.70	54.0	7.36	20.57	30.2	1.480
7.0 <sup>c</sup>	0.11	46.0	22.25	5.68	2.35	0.371
7.0	1.67	60.0	9.65	18.28	22.7	1.356
7.0	3.64	55.0	13.92	14.01	11.1	1.045
9.0 <sup>c</sup>	0.09	55.0	23.59	4.34	2.02	0.305
9.0	1.96	51.0	23.69	4.24	1.83	0.262
9.0	3.38	59.0	24.71	3.22	1.53	0.185

<sup>a</sup>Dowex-2: 10% crosslinkage, 50-100 mesh, Cl<sup>-</sup> form. 5.00 gm used in each test.

<sup>b</sup>Obtained with HCl. <sup>c</sup>Obtained with NH<sub>4</sub>OH. <sup>d</sup>Obtained by differences.

TABLE VIII

Column Separations

Resin	Form	Column <sup>a</sup>	Complexing Medium	pH	Flow Rate	Cobalt Added	Cobalt in Effluent	Nickel Added	Nickel in Effluent
		cm x cm			ml/cm sec	mg	mg	gm	gm
Dowex-1x10% (50-100 mesh)	Cl <sup>-</sup>	18 x 1	4.0M NH <sub>4</sub> CNS	3.0	0.127	10.00	0.005	--	--
	Cl <sup>-</sup>	"	4.0M NH <sub>4</sub> CNS	9.5	"	"	C.B. <sup>b</sup>	--	--
	Cl <sup>-</sup>	"	1.0M NH <sub>4</sub> CNS	3.0	"	"	0.007	--	--
	Cl <sup>-</sup>	"	1.0M NH <sub>4</sub> CNS	9.5	"	"	C.B.	--	--
	Cl <sup>-</sup>	"	0.1M NH <sub>4</sub> CNS	3.0	"	"	0.006	--	--
	Cl <sup>-</sup>	"	0.1M NH <sub>4</sub> CNS	9.5	"	"	C.B.	--	--
	CNS <sup>-</sup>	"	4.0M NH <sub>4</sub> CNS	3.0	"	"	0.045	--	--
	CNS <sup>-</sup>	"	4.0M NH <sub>4</sub> CNS	9.5	"	"	C.B.	--	--
	CNS <sup>-</sup>	"	1.0M NH <sub>4</sub> CNS	3.0	"	"	0.005	--	--
	CNS <sup>-</sup>	"	1.0M NH <sub>4</sub> CNS	9.5	"	"	C.B.	--	--
	CNS <sup>-</sup>	"	0.1M NH <sub>4</sub> CNS	3.0	"	"	0.005	--	--
	CNS <sup>-</sup>	"	0.1M NH <sub>4</sub> CNS	9.5	"	"	C.B.	--	--
	CNS <sup>-</sup>	"	0.0M NH <sub>4</sub> CNS	3.0	"	"	1.7	--	--
	CNS <sup>-</sup>	"	0.0M NH <sub>4</sub> CNS	9.5	"	"	C.B.	--	--
	CNS <sup>-</sup>	24 x 1	2.0M NH <sub>4</sub> CNS	5.0	0.118	1.00	N.F. <sup>c</sup>	1.717	1.544 <sup>d</sup>
Cl <sup>-</sup>	25 x 1	1.0M NH <sub>4</sub> CNS	5.0	--	14.00	N.F.	1.022	N.A. <sup>d</sup>	
CNS <sup>-</sup>	24 x 1	2.0M KCNS	5.0	0.142	1.00	N.F.	1.717	1.531	
Dowex-1x8% (50-100 mesh)	Cl <sup>-</sup>	13 x 1	0.8M NaNO <sub>2</sub>	Basic	0.212	10.00	<0.4 <sup>e</sup>	--	--
	OH <sup>-</sup>	13 x 1	0.8M NaNO <sub>2</sub>	Basic	0.212	10.00	<0.4	--	--
	Cl <sup>-</sup>	10 x 1	0.001M R-Salt <sup>f</sup>	--	--	5.00	1.09	--	--
	Cl <sup>-</sup>	10 x 1	0.001M R-Salt	--	--	5.00	2.8	0.750	N.A.
	Acetate <sup>-</sup>	10 x 1	0.001M R-Salt	--	--	2.00	0.057	--	--
Dowex-1x2% (50-100 mesh)	CNS <sup>-</sup>	10 x 1	1.0M NH <sub>4</sub> CNS	3.0	0.127	10.00	0.005	--	--
	OH <sup>-</sup>	10 x 1	0.001M R-Salt	--	0.127	2.00	0.136	--	--
Dowex-3 (20-50 mesh)	CNS <sup>-</sup>	18 x 1	1.0M NH <sub>4</sub> CNS	3.0	0.127	10.00	C.B.	--	--

<sup>a</sup>Expressed as length by diameter. <sup>b</sup>Visual cobalt breakthrough. <sup>c</sup>None found. <sup>d</sup>Not Analyzed. <sup>e</sup>By spot test.  
<sup>f</sup>Nitroso-R-Salt.

Column Elution. The data for these elutions are presented in Table IX, page 42.

The ion exchange column used for each test was a converted fifty milliliter burette unless otherwise stated. The desired bed depth was obtained by the method stated on page 19.

#### Liquid Ion-Exchangers

Absorption Test. The data for these tests are presented in Figures 8 to 10, pages 43 to 45.

These are copies of graphs obtained from a Beckman DK-2, Ratio Recording Spectrophotometer. In each case the value given for the metal concentration is that present in the aqueous phase before extraction. The extractant used in each test was ten milliliters of a 1:1 liquid resin: xylene mixture. The absorbancies listed are those for the complex blanked against a reagent blank. Matched 1.00 centimeter quartz cells were used for each test.

Figure 8 shows the absorption curves obtained for the cobalt, iron, manganese and nickel thiocyanate from 450 to 700 millimicrons. The aqueous phase in each case was 2.5 molar with ammonium thiocyanate. The resin used in the extractant phase was Amberlite LA-2.

Figure 9 shows the absorption curves for the cobalt thiocyanate complex when Amberlite LA-1 was used in the



TABLE IX

Column Elution

Resin	Cobalt on Resin	Nickel on Resin	Form of Ions on Resin	Column	Eluent	Volume of Eluent	Cobalt Eluted	Nickel Eluted
	mg	gm		cm		ml	mg	gm
Dowex-1 x 10% (50-100 mesh)	1.00	0.1730	Co (II) & Ni (II) Thiocyanates	24 x 1	H <sub>2</sub> O	100	N.F. <sup>c</sup>	0.0868
	1.00	0.1862		"	H <sub>2</sub> O	"	N.F.	0.0974
	14.0	---		"	10% Clorox <sup>b</sup>	"	6.7	---
	1.00	0.87		"	10% Clorox <sup>b</sup>	"	0.75	0.086
	1.00	0.89		25 x 1	1.6M HNO <sub>3</sub>	"	0.75	0.088
Amberlite IR-120	3.09	0.61 <sup>a</sup>	Co (II) & Ni (II) Ions	17 x 1 <sup>d</sup>	0.4M NH <sub>4</sub> CNS	"	3.00	0.61 <sup>a</sup>
	3.23	0.61 <sup>a</sup>		"	0.2M NH <sub>4</sub> CNS	"	1.59	0.45 <sup>a</sup>
	3.47	0.46 <sup>a</sup>		"	0.1M NH <sub>4</sub> CNS	"	0.49	0.10 <sup>a</sup>
	3.07	0.46 <sup>a</sup>		"	0.08M NH <sub>4</sub> CNS	"	0.275	0.09 <sup>a</sup>
	3.32	0.31 <sup>a</sup>		"	0.06M NH <sub>4</sub> CNS	"	0.159	0.05 <sup>a</sup>
	2.05	0.31 <sup>a</sup>		"	0.04M NH <sub>4</sub> CNS	"	0.0455	0.02 <sup>a</sup>
	1.46	0.31 <sup>a</sup>		"	0.02M NH <sub>4</sub> CNS	"	0.0023	0.01 <sup>a</sup>
	1.987	0.2999		20 x 1	1.0M HCl	"	0.795	0.107
	1.986	0.2999		"	2.0M HCl	"	1.40	0.267
	1.991	0.2992		"	4.0M HCl	"	1.57	0.296
	Amberlite IR-120 (16-50 mesh)	1.988		0.299	Co (III) & Ni (II) Ammines	17 x 1	H <sub>2</sub> O	"
1.999		0.2993	"	0.68M NaCl		"	0.159	0.0030
1.980		0.2987	"	3.4M NaCl		"	0.496	0.163
1.999		0.2994	"	0.52M Amm. Acetate		"	0.909	0.277
Amberlite IR-120 (16-50 mesh)	2.00	0.28	Co (II) & Ni (II) Ammines	20 x 1	8.0M NH <sub>4</sub> OH	"	None	None
	2.00	0.28		"	4.0M NH <sub>4</sub> OH	"	"	"
	2.00	0.28		"	2.0M NH <sub>4</sub> OH	"	"	"
	2.00	0.28		"	0.8M NH <sub>4</sub> OH	"	"	"
	2.00	0.28		"	0.2M NH <sub>4</sub> OH	"	"	"
	2.00	0.28		"	0.08M NH <sub>4</sub> OH	"	"	"

<sup>a</sup>Analyzed with Nessler tubes. <sup>b</sup>Volume per cent. <sup>c</sup>None found. <sup>d</sup>Column consisted of twenty-five milliliter burette.

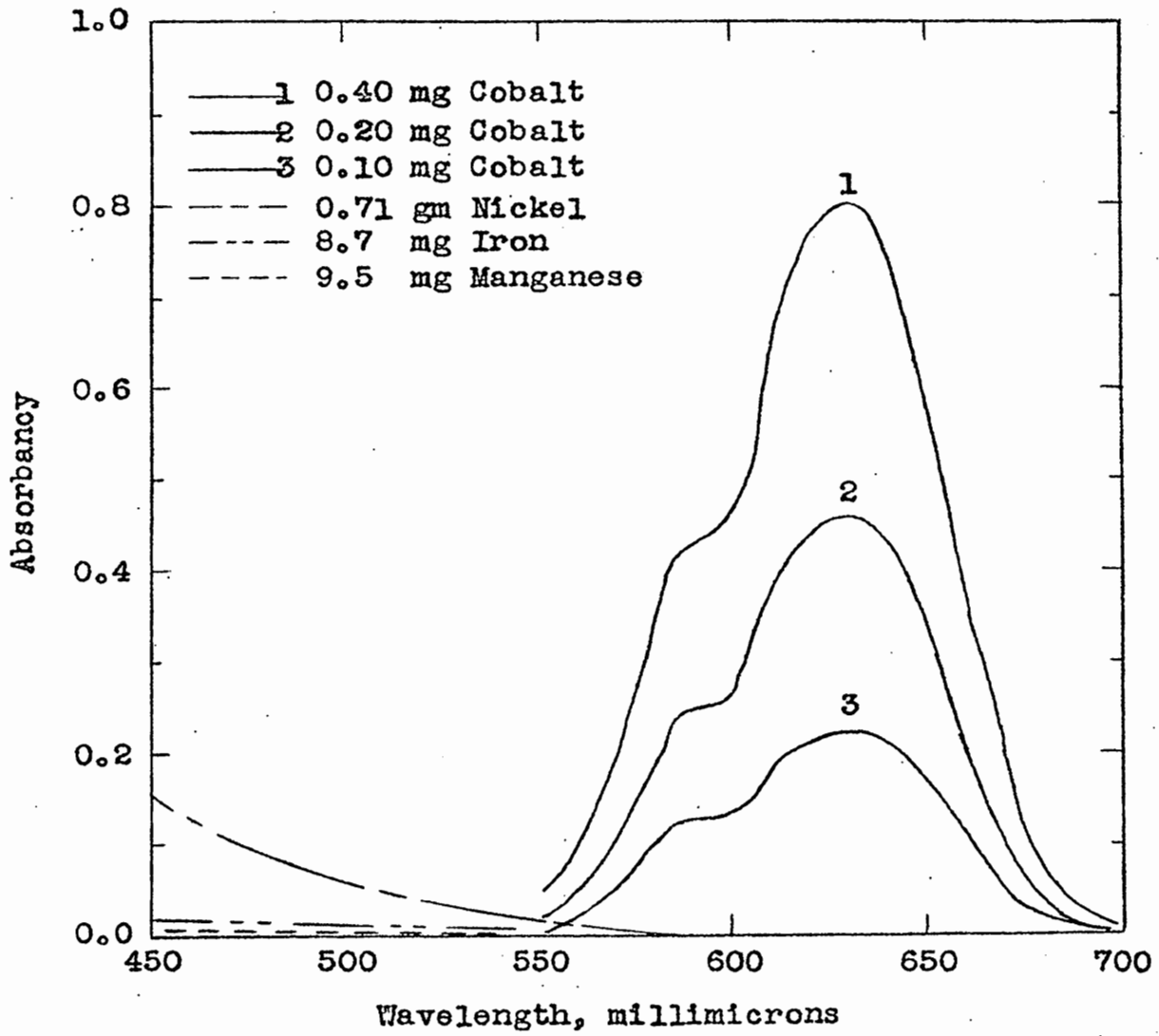


Figure 8. Absorbance Curves for Metal Thiocyanates Adsorbed on Amberlite LA-2

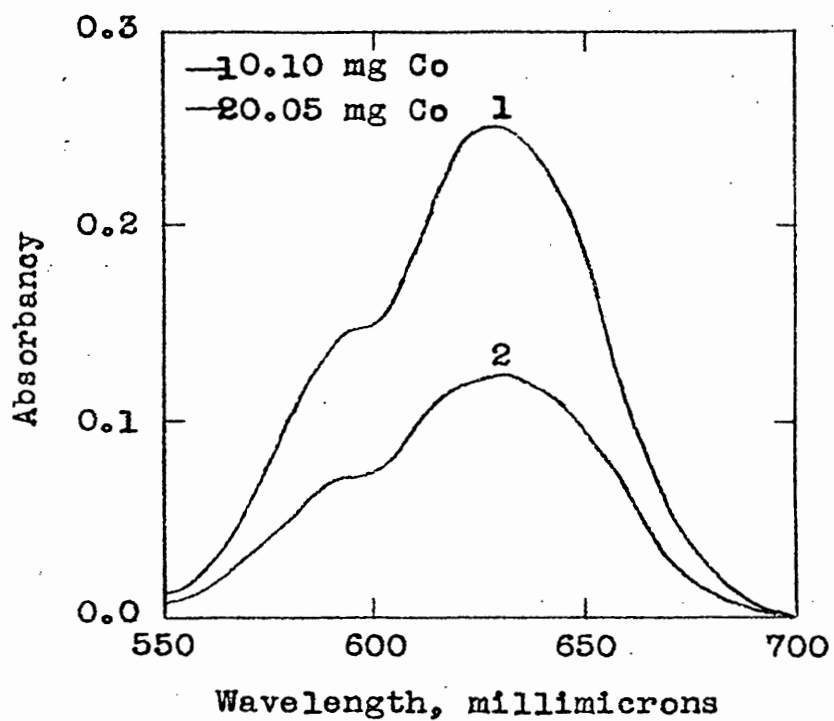


Figure 9. Absorbance Curves for Cobalt (II) Thiocyanate Adsorbed on Amberlite LA-1

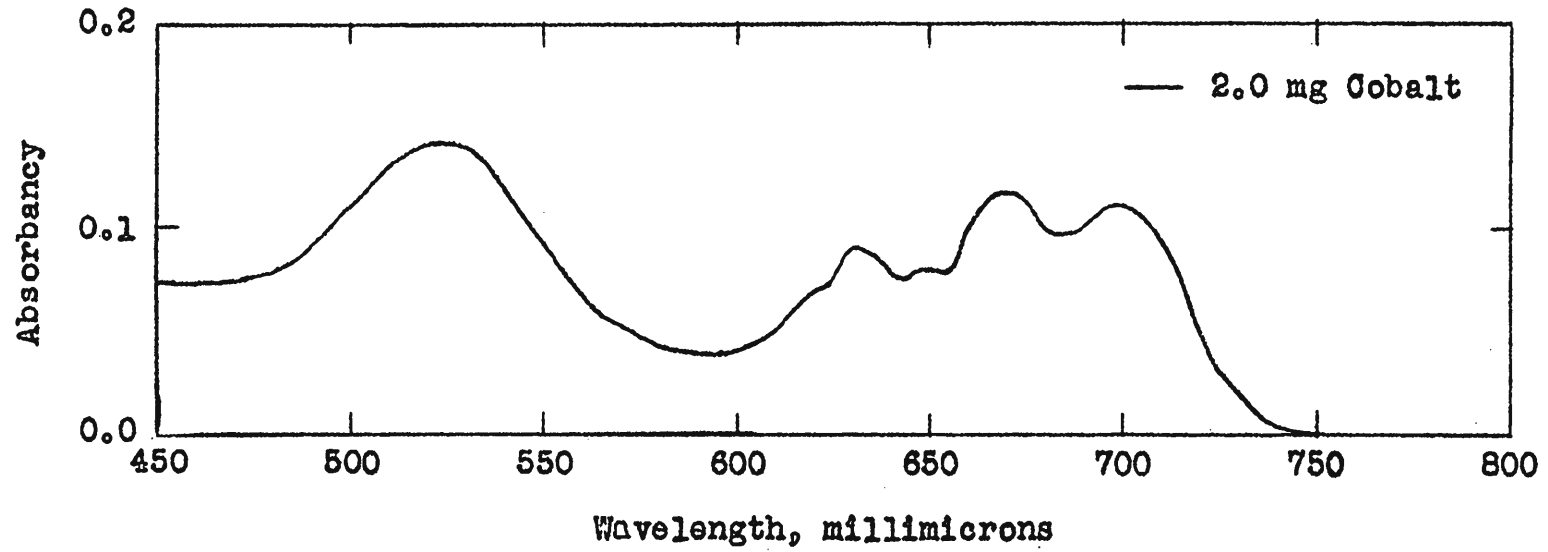


Figure 10. Absorbance Curve for Cobalt (II) Chloride Adsorbed on Amberlite LA-2

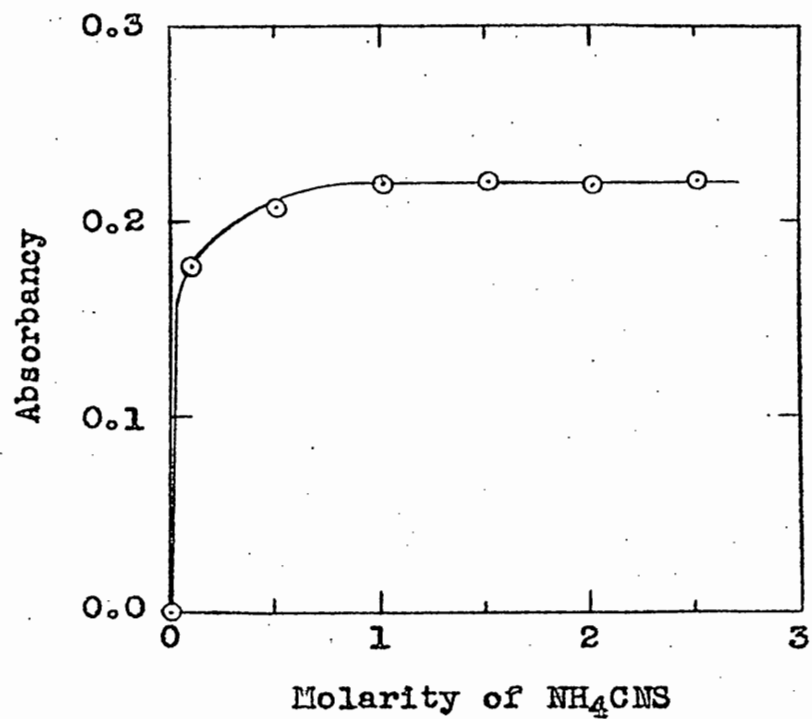


Figure 11. Effect of Ammonium Thiocyanate Concentration on the Adsorbed Cobalt Complex

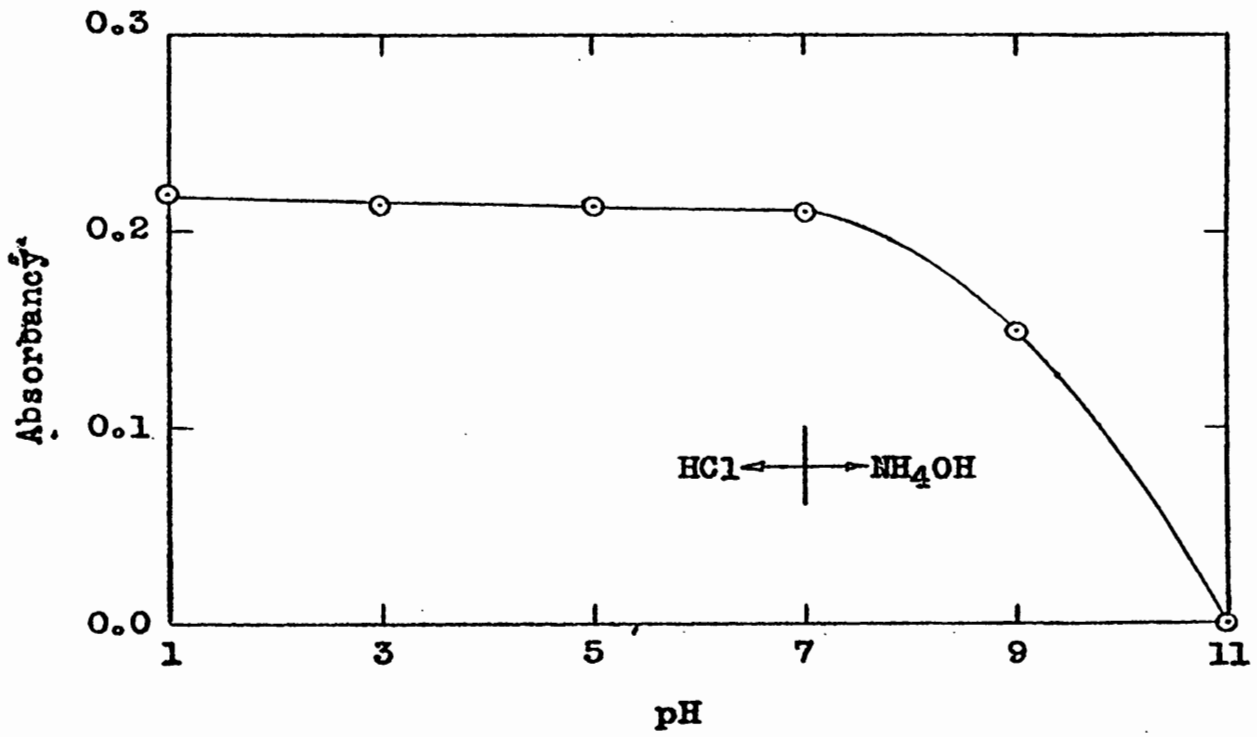


Figure 12. Effect of pH on the Adsorbed Cobalt Complex

TABLE X

Effect of Ammonium Thiocyanate Concentration  
and  
pH on the Adsorbed Cobalt Complex

pH	Molarity of NH <sub>4</sub> CNS	Absorbance for 0.1 mg Cobalt <sup>a</sup>
1.0	0.10	0.177
1.0	0.50	0.208
1.0	1.0	0.220
1.0	1.5	0.220
1.0	2.0	0.218
1.0	2.5	0.220
3.0	2.5	0.216
5.0	2.5	0.215
7.0	2.5	0.212
9.0	2.5	0.150
11.0	2.5	0.000

<sup>a</sup>10 ml of 1:1 Amberlite LA-2:xylene extractant;  
one centimeter cell.

Effect of Time on the Adsorbed Cobalt Complex. The data for this test is presented in Figure 13 and Table XI, pages 51 and 52.

The effect of time on the color produced by the adsorbed cobalt complex was determined by taking periodic readings of a sample containing 0.1 milligrams of cobalt. The top of the absorption cell was sealed with cellophane tape to eliminate evaporation. Periodic readings for the absorbance of the sample were taken until the seal was destroyed by the solvent action of the extractant.

The absorbancies were obtained using one-centimeter cells and a Beckman Model-B Spectrophotometer.

Effect of Resin Concentration on the Adsorbed Cobalt Complex. The data for these determinations are presented in Figure 14 and Table XII, pages 53 and 54.

The cobalt concentration, pH, and ammonium thiocyanate concentration were kept constant for each of these tests.

The effect of the resin concentration in the extractant phase was measured by the change in the absorbance occurring in the resultant sample after extraction. The absorbancies were obtained using one-centimeter cells and a Beckman Model-B Spectrophotometer.

Calibration Curve for Cobalt Analysis. The data for these determinations are presented in Figure 15 and Table XIII, pages 55 and 56.



In each test the aqueous solution was 2.5 molar with ammonium thiocyanate and had a pH equal to 1.0. The extractant in each case consisted of a 1:1 ratio of xylene to resin.

The calibration curves were obtained by extracting known amounts of cobalt and measuring the resulting absorbance. The absorbancies obtained were for a sample contained in a one-centimeter cell and was measured with a Beckman Model-B Spectrophotometer.

Effect of Nickel Concentration on the Adsorbed Cobalt Complex. The data for these tests are presented in Figure 16 Table XIV, pages 57 and 58.

Each test consisted of: (1) adding a known amount of cobalt to a nickel sample, (2) extracting the cobalt in the sample with a resin-xylene mixture and, (3) determining the absorbance of the extracted cobalt.

The resulting data was then plotted as shown in Figure 16. Because of the residual cobalt in nickel used, these plots should be parallel lines with increasing absorbance intercepts. A divergence or convergence in the curves obtained, to the calibration curve, would be an indication of nickel interference.

The absorbancies reported are for a sample contained in one-centimeter cell. The absorbancies were measured with a Beckman Model-B Spectrophotometer.

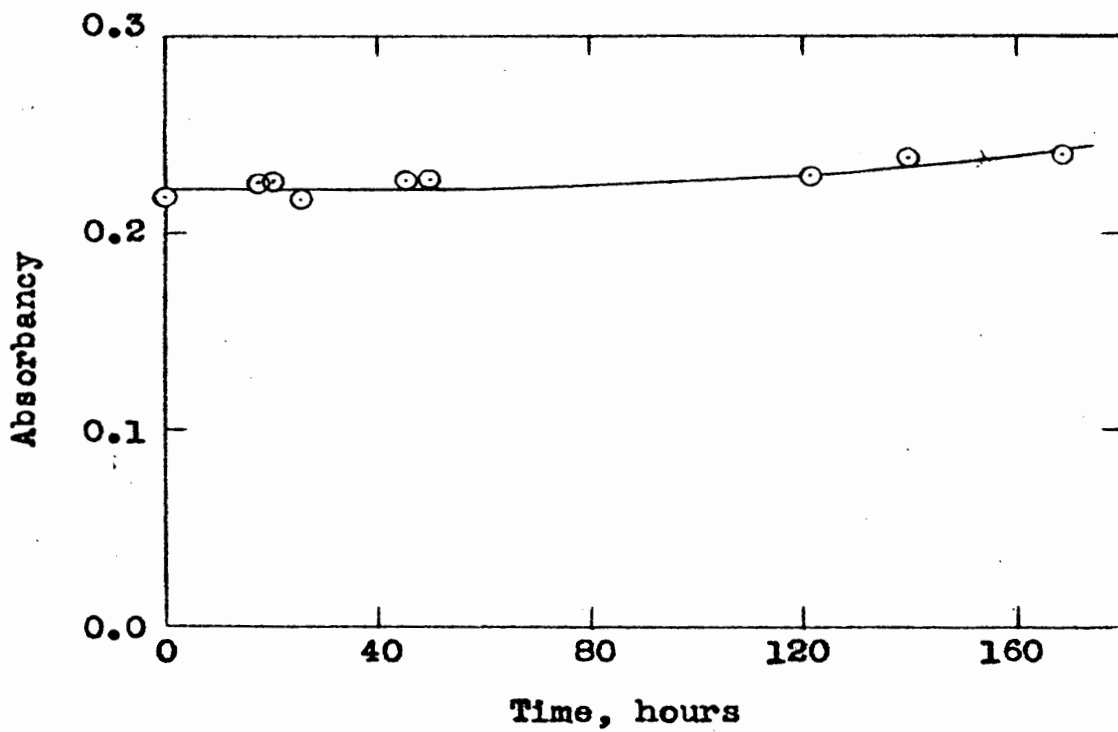


Figure 13. Effect of Time on the Adsorbed Cobalt Complex

TABLE XI

Effect of Time on the Adsorbed  
Cobalt Complex

Time	Absorbance for 0.1 mg Cobalt <sup>a</sup>
Hours	
0.0	0.220
17.0	0.230
19.5	0.230
25.0	0.220
45.0	0.230
49.0	0.230
121.0	0.234
139.0	0.242
168.0	0.244

<sup>a</sup>10 ml of 1:1 Amberlite LA-2:  
xylene extractant. One-  
centimeter cells.

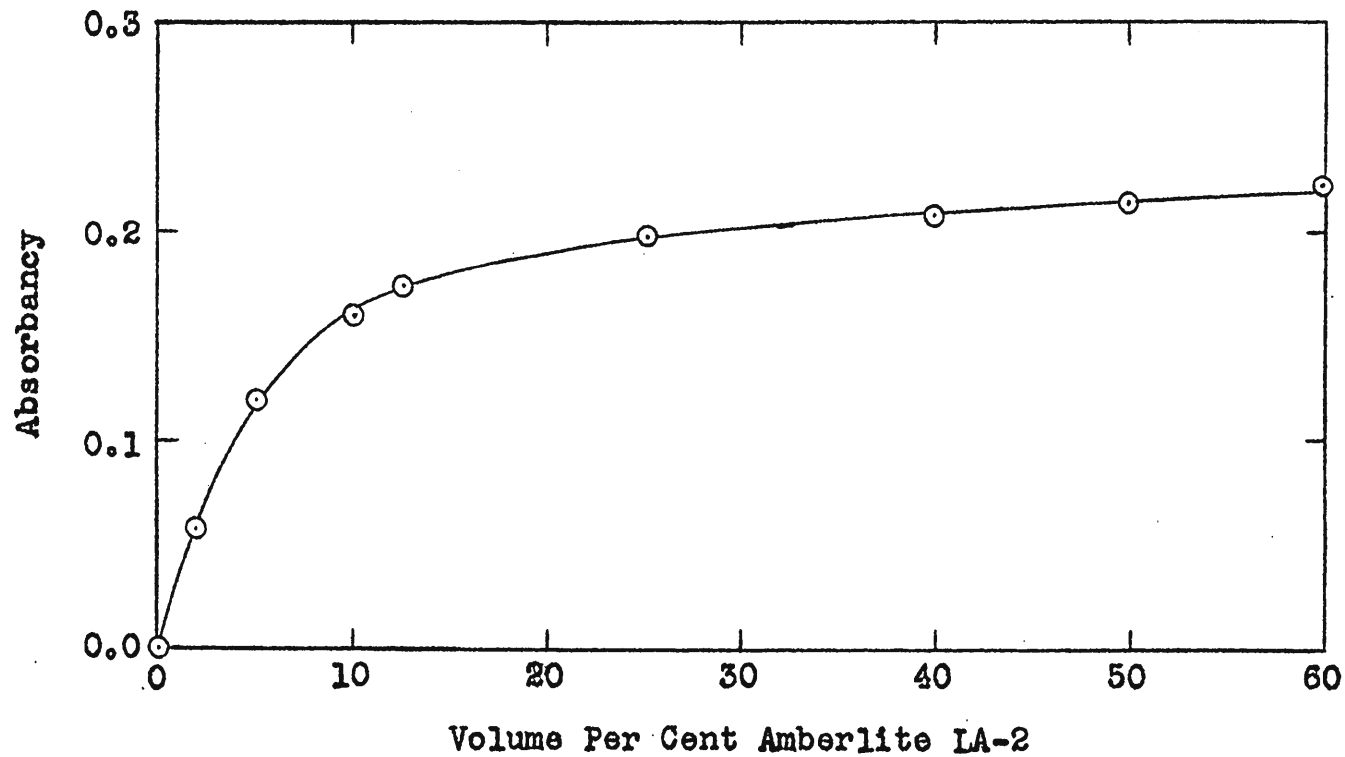


Figure 14. Effect of Amberlite LA-2 Concentration on the Adsorbed Cobalt Complex

TABLE XII

Effect of Amberlite LA-2 Concentration  
on the Adsorbed Cobalt Complex

Volume Per Cent Amberlite LA-2 <sup>a</sup>	Absorbance for 0.1 mg Cobalt <sup>b</sup>
0.0	0.000
2.0	0.058
5.0	0.120
10.0	0.160
12.5	0.175
25.0	0.198
40.0	0.210
50.0	0.215
60.0	0.225

<sup>a</sup>Extractant: Amberlite LA-2 and xylene  
10 ml total volume.

<sup>b</sup>Aqueous Phase: Initially 2.5M NH<sub>4</sub>CNS,  
pH = 1.

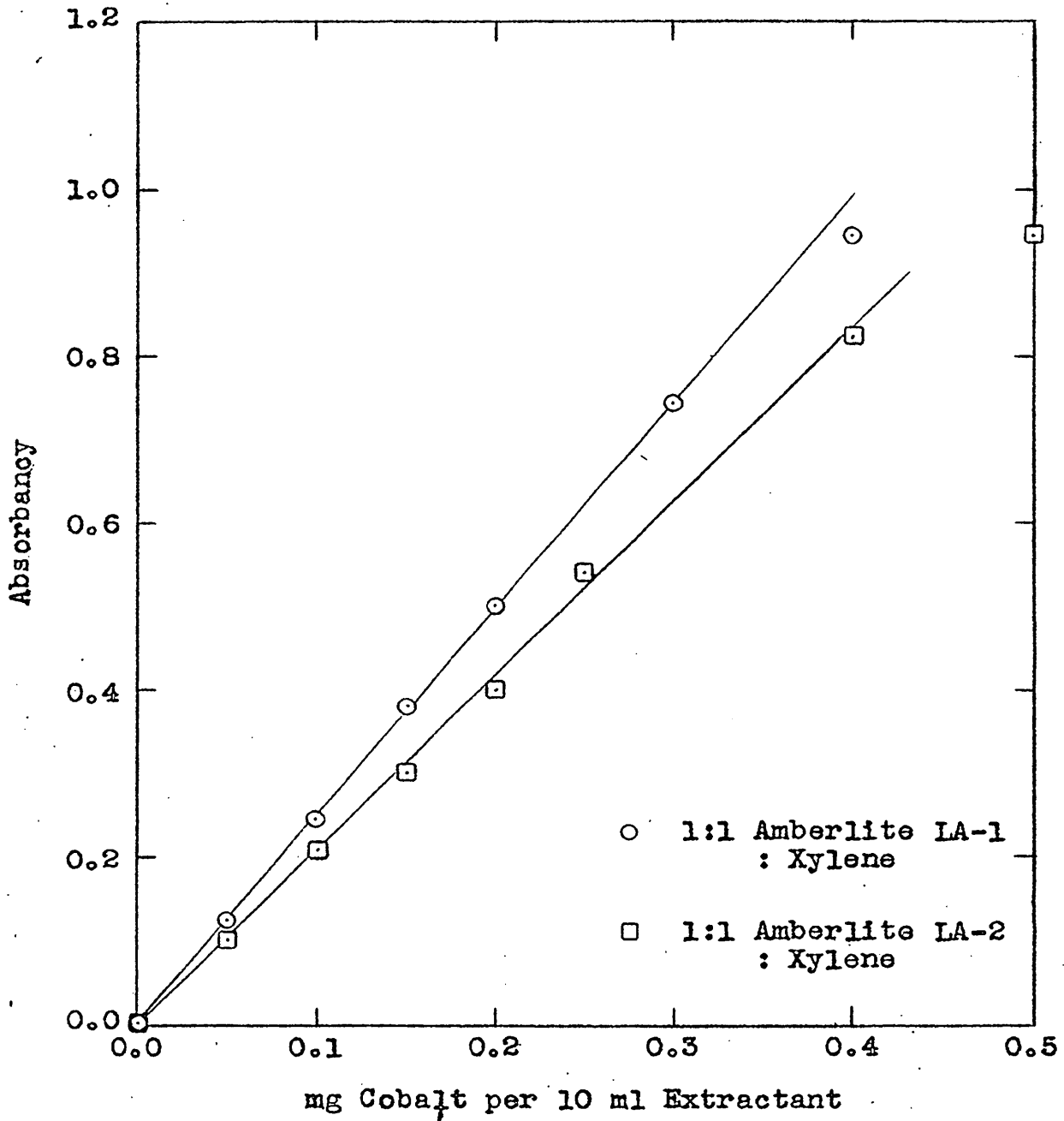


Figure 15. Calibration Curves for Cobalt Analysis

TABLE XIII

Calibration Curves for Cobalt Analysis

Extractant	Cobalt added <sup>a</sup>	Absorbance <sup>b</sup>
	mg	
10 ml of 1:1 Amberlite LA-2:xylene	0.01	0.020
	0.05	0.105
	0.10	0.206
	0.15	0.301
	0.20	0.400
	0.25	0.54
	0.40	0.83
10 ml of 1:1 Amberlite LA-1:xylene	0.50	0.96
	0.05	0.125
	0.10	0.250
	0.15	0.378
	0.20	0.500
	0.30	0.742
	0.40	0.95

<sup>a</sup> 50 ml sample, 2.5M NH<sub>4</sub>CNS, pH = 1.  
<sup>b</sup> one centimeter cells.

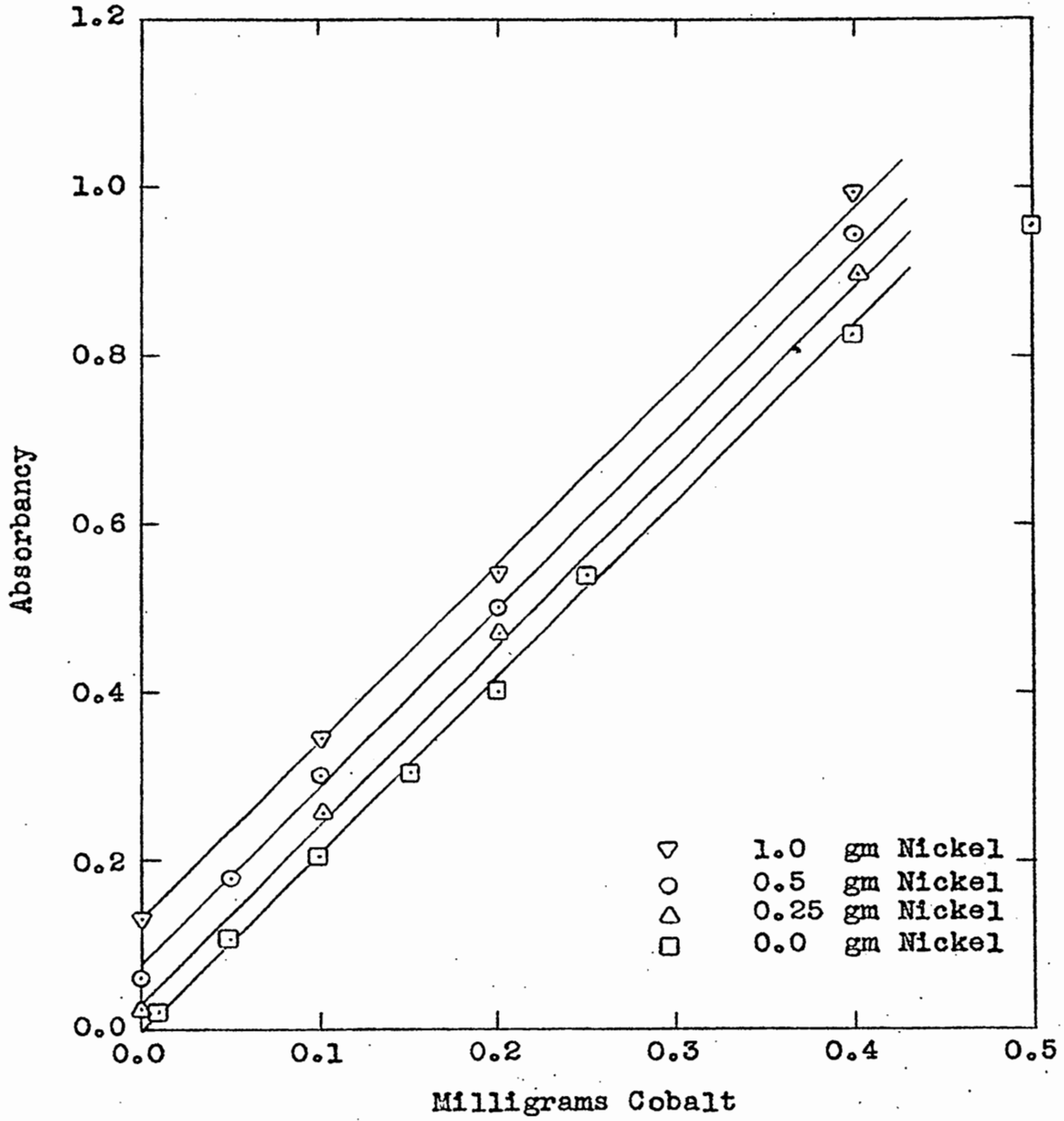


Figure 16. Effect of Nickel Concentration on the Adsorbed Cobalt Complex



TABLE XIV

Effect of Nickel Concentration  
on the  
Adsorbed Cobalt Complex

Nickel Added	Cobalt Added	Absorbance <sup>a</sup>	Slope of Curve Figure 16
gm	mg		A <sub>s</sub> / 0.1 mg Co
0.00	0.0100	0.020	
0.00	0.0500	0.105	
0.00	0.1000	0.206	
0.00	0.1500	0.301	
0.00	0.2000	0.400	0.210
0.00	0.2500	0.54	
0.00	0.4000	0.83	
0.00	0.5000	0.96	
0.25	0.0000	0.025	
0.25	0.1000	0.260	0.217
0.25	0.2000	0.470	
0.25	0.4000	0.90	
0.50	0.0000	0.060	
0.50	0.0500	0.180	
0.50	0.1000	0.300	0.213
0.50	0.2000	0.50	
0.50	0.4000	0.96	
1.0	0.0000	0.130	
1.0	0.1000	0.348	0.212
1.0	0.2000	0.54	
1.0	0.4000	1.0	

<sup>a</sup>One centimeter cells.

Cobalt-60 Check on Cobalt Extraction. The data for these tests are presented in Table XV, page 62.

These tests were conducted to determine the efficiency of the extraction of the cobalt complex by the liquid resins.

Each test consisted of the following: (1) adding a known amount of cobalt-60 to the aqueous phase, (2) extraction of the cobalt, as the thiocyanate complex, with a resin-xylene mixture, and (3) determining the amount of cobalt-60 remaining after extraction. Relative counting techniques were used for these determinations.

Determination of the Extraction Isotherm for the Cobalt Thiocyanate Complex. The data for these tests are presented in Figure 17 and Table XVI, pages 63 and 64.

The test consisted of equilibrating ten milliliters of a 1:9 Amberlite IA-1: xylene mixture with aqueous solutions containing known amounts of cobalt.

The data presented in Table XVI was then determined by analysis of the aqueous phase only.

Spectrographic Determination of the Metals Extracted with Amberlite IA-1. The data for these determinations are presented in Figure 18 and Table XVII, pages 65 and 66.

An artificial nickel sample containing selected impurities was prepared. (See appendix B). The sample was put into solution and split into two parts.

To the first part sulfuric acid was added and the

solution evaporated to dryness. The resulting salts were then converted into oxides in a muffle furnace.

The second part was processed by the procedure developed. (See page 72). The resulting aqueous phase was evaporated to dryness and the salts converted into oxides.

The spectrograms obtained for the oxide samples in an initial and an extracted condition gave qualitative information as to which metals were extracted.

Comparative Analysis. The data for these analysis are presented in Figure 19 and Table XVIII, pages 67 and 68.

The cobalt content of each sample was found by the procedure developed. (See page 72).

Stripping the Adsorbed Cobalt Thiocyanate from Amberlite LA-1 with Sodium Carbonate. The data for these tests are presented in Figure 20 and Table XIX, pages 69 and 70.

The test consisted of equilibrating ten milliliters of a 1:9 Amberlite LA-1: xylene mixture, containing 0.01892 grams of cobalt, with aqueous solutions containing known amounts of sodium carbonate.

The data presented in Table XIX was then determined by analysis of the aqueous phase by the procedure developed. (See page 72).

Cobalt-60 Check on Cobalt Thiocyanate Stripping. The data for these tests are presented in Table XX, page 71.

The tests were conducted to check the data obtained on

the stripping of the cobalt complex from the liquid resin Amberlite LA-1.

Each test consisted of taking the extract resulting from the extraction tests (see page 59) and stripping it with known amounts of a sodium carbonate solution. The extract was then counted and the amount of cobalt removed determined.

Relative counting techniques were used in these determinations.

TABLE XV

Cobalt-60 Check on Cobalt Extraction

Extractant	Volume of Extractant	Initial Cond. of Sample	Co <sup>60</sup> Added <sup>a</sup>	Co <sup>60</sup> After Ext. <sup>a</sup>	Apparent Removal
	ml		Counts/min.	Counts/min.	Per Cent
Amberlite IA-2 and Xylene (1:1)	10	1.25 gm Ni 0.163 mg Co 2.5M NH <sub>4</sub> CNS pH = 1	192	1.5	>99
Amberlite IA-1 and Xylene (1:1)	10	1.25 gm Ni 0.163 mg Co 2.5M NH <sub>4</sub> CNS pH = 1	4320	7.4	>99
Amberlite IA-1 and Xylene (1:19)	10	1.25 gm Ni 0.163 mg Co 2.5M NH <sub>4</sub> CNS pH = 1	3200	50.1	>98
Amberlite IA-1 and Xylene (1:1)	10	1.25 gm Ni 0.063 mg Co 2.5M NH <sub>4</sub> CNS pH = 1	6860	58.9	>99

<sup>a</sup>Corrected for background.

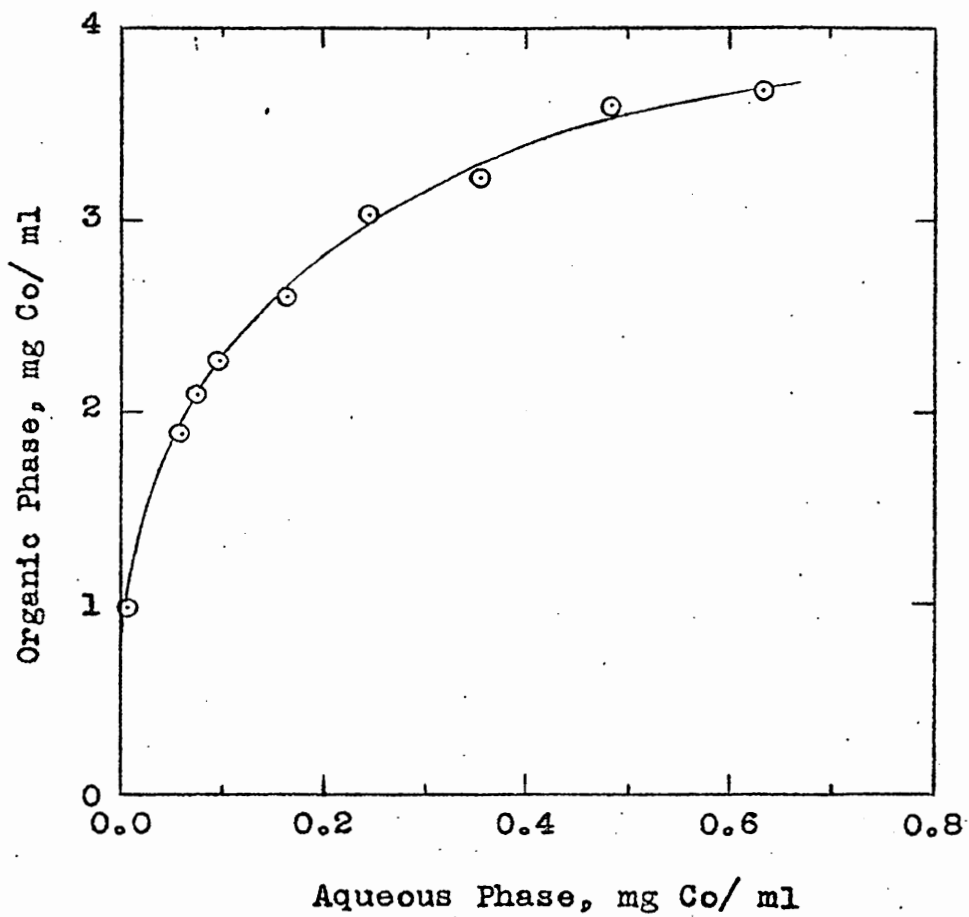


Figure 17. Extraction Isotherm for the Cobalt Thiocyanate Complex with Amberlite LA-1

TABLE XVI

Extraction Isotherm for the Cobalt  
Thiocyanate Complex with Amberlite IA-1

Phase Ratio Organic : Aqueous	Conc., Organic <sup>a</sup>	Conc., Aqueous <sup>b</sup>
	mg/ml	mg/ml
1 : 1	0.99	0.01
1 : 2	1.88	0.06
1 : 2.25	2.09	0.073
1 : 2.5	2.27	0.092
1 : 3	2.51	0.16
1 : 4	3.03	0.242
1 : 5	3.21	0.358
1 : 7	3.63	0.482
1 : 10	3.68	0.632

<sup>a</sup> Organic: 10 ml 1:9 Amberlite IA-1:xylene.  
<sup>b</sup> Aqueous: 1.000 mg Co/ml, 2.0M NH<sub>4</sub>CNS,  
 pH = 1, before extraction.

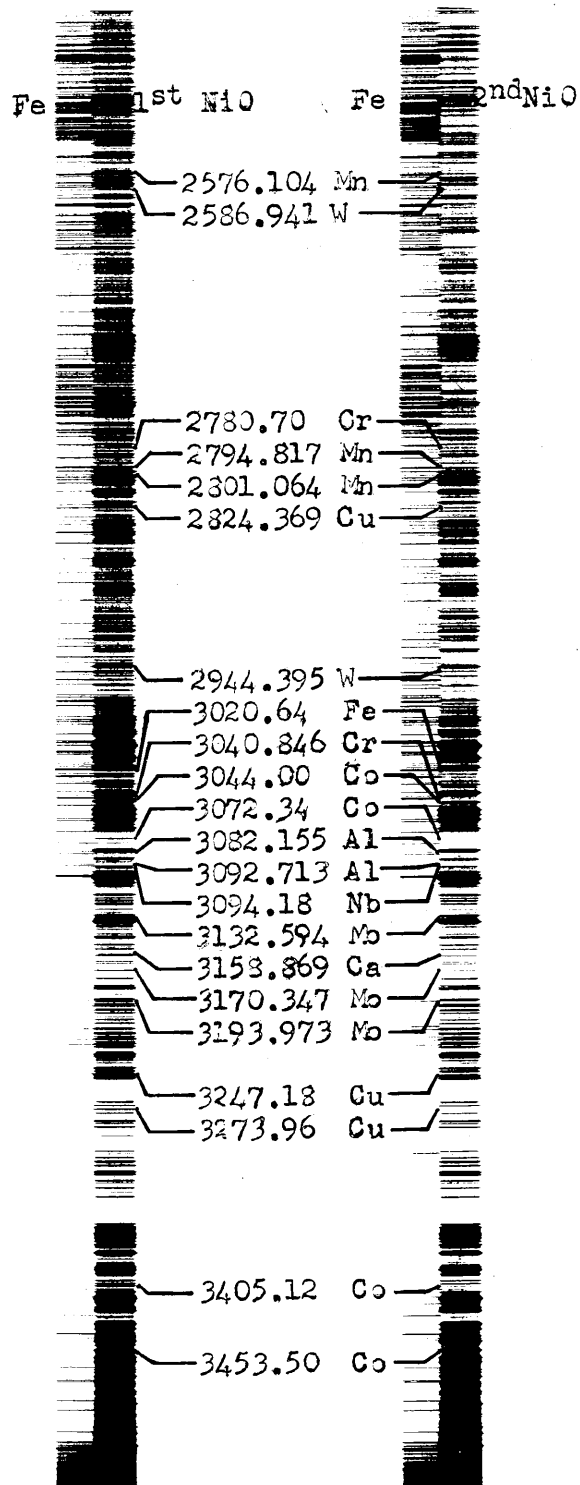


Figure 18. Spectrograph for Nickel Oxide



TABLE XVII

Spectrographic Determination of Metals  
Extracted with Amberlite LA-1

Element	Line Angstroms	Relative Intensity	Indicated Results
Aluminum	3082.155	800	Not Removed
	3092.713	1000	
Calcium	3158.869	100	Removed
Cobalt	3044.00	400r	Removed
	3072.34	200r	
	3405.12	2000r	
	3453.50	3000r	
Copper	2824.369	1000	Removed
	3247.18	80	
	3273.96	3000r	
Chromium	2780.70	600R	Removed
	3040.846	500R	
Iron	3020.64	1000r	Removed
Manganese	2576.104	300R	Removed
	2794.817	1000R	
	2801.064	600R	
Molybdenum	3132.594	1000R	Removed
	3170.347	1000R	
	3193.973	1000r	
Niobium	3094.18	100	Removed
Tungsten	2586.941	75	Removed
	2944.359	30	

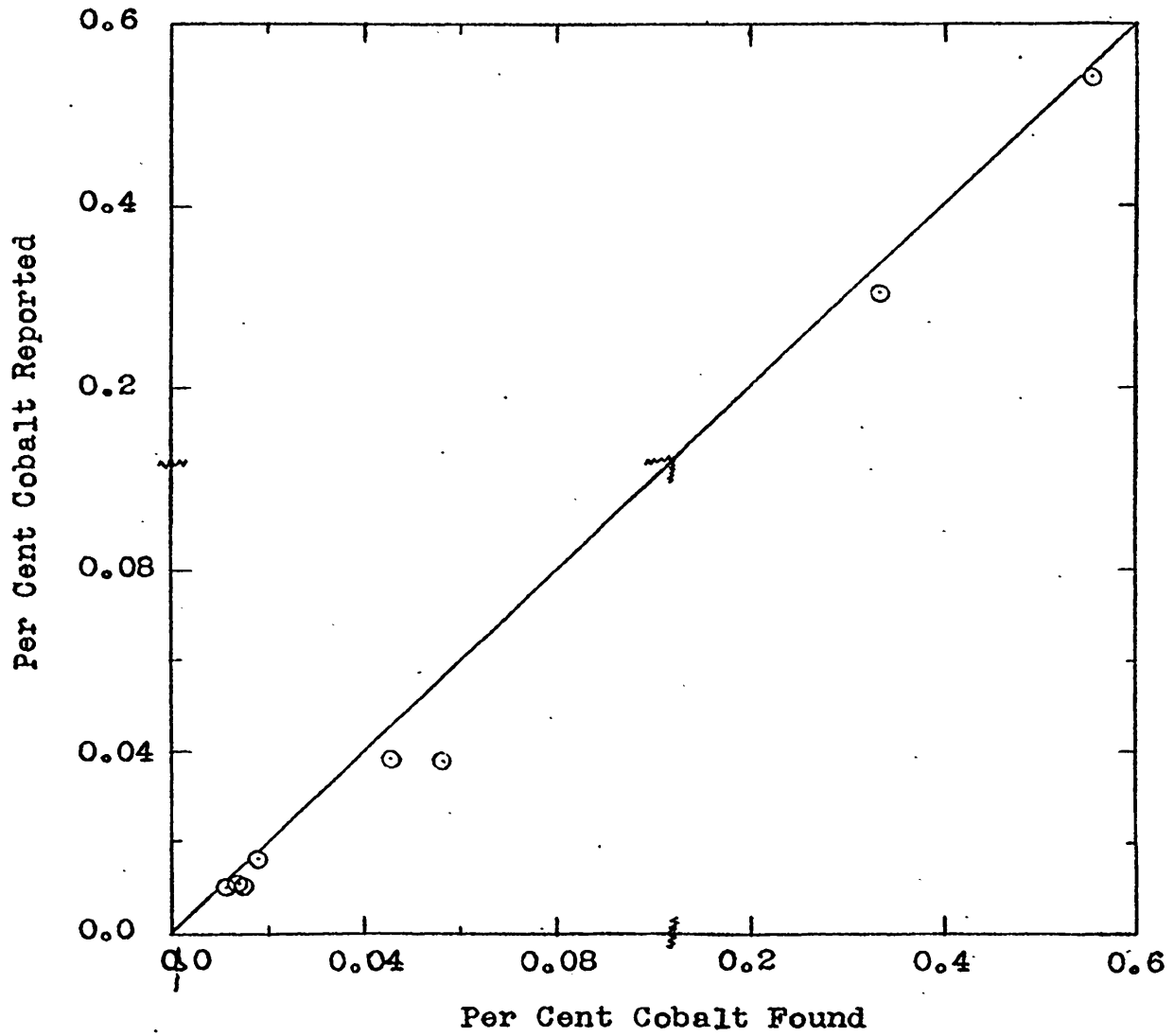


Figure 19. Comparative Analysis for Cobalt in Nickel

TABLE XVIII

Comparative Analysis for Cobalt  
in Nickel

Sample Form	Supplier	Per Cent. Cobalt Reported	Per Cent Cobalt Found
NiCl <sub>2</sub> ·6H <sub>2</sub> O	Fisher Scientific Co.	< 0.00 <sup>b</sup>	0.0032
NiSO <sub>4</sub> ·6H <sub>2</sub> O		< 0.009 <sup>b</sup>	0.0054
NiO	U.S. Bureau of Standards	0.55 <sup>c</sup>	0.548
		0.31 <sup>c</sup>	0.332
		0.016 <sup>c</sup>	0.0178
	J.T. Baker Co.	0.01	0.0123
Ni (metal)	U.S. Bureau of Mines <sup>a</sup>	0.038 <sup>d</sup>	0.0569
		0.038 <sup>d</sup>	0.0456
		0.010 <sup>d</sup>	0.0149
		0.011 <sup>d</sup>	0.0143

<sup>a</sup>Samples prepared at Rolla Station.

<sup>b</sup>Lot Analysis.

<sup>c</sup>Certificate of Analysis in appendix D, E, and F.

<sup>d</sup>Results obtained from Spectra Chemical Research Inc., Chicago, Ill. (Spectrographic Analysis)

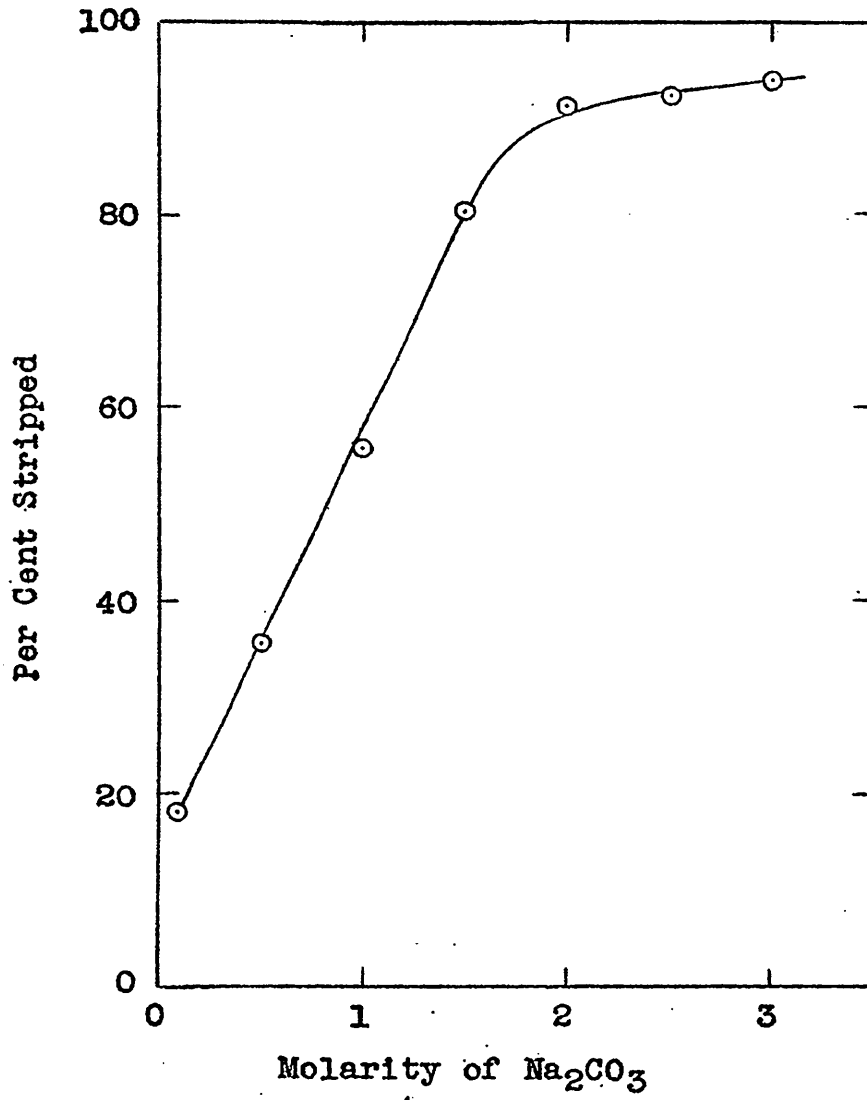


Figure 20. Stripping the Adsorbed Cobalt Thiocyanate from Amberlite LA-1 with Sodium Carbonate

TABLE XIX

Stripping the Adsorbed Cobalt Thiocyanate from  
Amberlite LA-1 with Sodium Carbonate<sup>a</sup>

Molarity of Na <sub>2</sub> CO <sub>3</sub>	Cobalt Removed <sup>b</sup>	Per Cent Stripped
	mg	
0.1	3.25	17.2
0.5	6.65	35.2
1.0	10.48	55.4
1.5	15.24	80.6
2.0	17.25	91.2
2.5	17.50	92.5
3.0	17.88	94.5

<sup>a</sup> 1:3 O:A phase ratio, 1:9 Amberlite  
LA-1:xylene organic phase.

<sup>b</sup> Cobalt initially on resin: 18.92 mg.

TABLE XX

Cobalt-60 Check on Cobalt Stripping

Eluent	Volume of Eluent	Initial Cond. of Sample	Cobalt on Resin <sup>a</sup>	Cobalt in Stripper <sup>a</sup>	Apparent Removal
	ml		Counts/min.	Counts/min.	Per Cent
2.0 Molar Na <sub>2</sub> CO <sub>3</sub>	50	0.163 mg Co 10 ml of 1:19 Amberlite LA-1:xylene	3150	2918	>92
2.0 Molar Na <sub>2</sub> CO <sub>3</sub>	100	0.063 mg Co 10 ml of 1:1 Amberlite LA-1:xylene	6800	4926	>72

<sup>a</sup>Corrected for background.

The result of this investigation is the following quantitative method for the separation and determination of cobalt.

Determination of Trace Amounts of Cobalt in High Purity Nickel by the Thiocyanate--Liquid Ion Exchange Method.

- A. Principle of Method. Cobalt forms a blue thiocyanate complex which is quantitatively adsorbed by a liquid, secondary amine, ion exchange resin. Spectrophotometric measurement is made at 630 millimicrons.
- B. Concentration Range. The recommended concentration range is from 0.05 to 0.25 milligrams of cobalt in ten milliliters of extractant, using a cell length of one centimeter.
- C. Stability of Color. The color is stable for more than fifty hours.
- D. Interfering Elements. The amounts of copper, iron, and manganese ordinarily present in high purity nickel samples do not interfere.
- E. Reagents.

1. Standard Cobalt Solution. (0.01mg/ml)

Weigh out 0.1000 gram of cobalt, 99.99% pure.

Put in a beaker. Add concentrated nitric acid drop-wise, heat to dissolve. Cool. Add concentrated sulfuric acid drop-wise, heat to dense white fumes and cool. Add water to

dissolve. Transfer to a one-liter volumetric flask and dilute to mark, mix well. Transfer 100 milliliters of this solution to a one-liter volumetric flask, dilute to mark, mix well.

2. Extractant Solution. (1:1 liquid resin:xylene)  
Transfer 100 milliliters of Amberlite IA-1 (or Amberlite IA-2) to a 200 milliliter volumetric flask. Dilute to mark with xylene.
3. Ammonium Thiocyanate. (crystals)

#### F. Preparation of Calibration Curve.

1. Calibration Solutions. Transfer 5, 10, 15, 20, 25, 30, 35, and 40 milliliters of the standard cobalt solution to eight 100 milliliter beakers and dilute to 40 milliliters. Proceed in accordance with F-3 and F-4.
2. Reference Solution. Transfer 40 milliliters of water to a 100 milliliter beaker. Proceed in accordance with F-3 and F-4.
3. Complex Formation. Add 9.5 grams of ammonium thiocyanate and dissolve. Check pH, adjust to between one and seven if necessary. Transfer to a separatory funnel and dilute to approximately 50 milliliters.



4. Extraction. Transfer exactly ten milliliters of extractant solution to a separatory funnel. Shake to extract the cobalt complex. Let stand until phases separate. Drain off heavier aqueous phase. Centrifuge extractant phase until all occluded water is separated.
5. Spectrophotometry. Transfer the centrifuged extractant phase for the reference solution to a standardized quartz absorption cell, the wave length set at 630 millimicrons, and adjust the spectrophotometer to the initial setting by the appropriate method. Transfer the centrifuged calibration solutions to standardized quartz absorption cells. Take absorbance readings.
6. Calibration Curve. Plot the absorbance readings for each calibration solution against the amount of cobalt in each sample.

G. Procedure for Unknown.

1. Sample Solution. Weigh out a sample containing from 0.05 to 0.25 milligrams cobalt. Put in a beaker and add concentrated nitric acid drop-wise. Heat to dissolve. Add one milliliter of concentrated sulfuric acid per gram of nickel, evaporate to white fumes. Cool.

Add water and dissolve. Proceed as described in F-3 and F-4.

2. Reference Solution. Proceed as described in F-2, F-3 and F-4.
3. Spectrophotometry. Proceed as described in F-5.
4. Determination of Cobalt Content. Convert the absorbance readings obtained for the sample into grams of cobalt from the calibration curve. Calculate the per cent cobalt in the sample.

#### IV. DISCUSSION

The data obtained is discussed in the same order as the data is presented in the preceding section.

Distribution Coefficients. The data and results of these determinations are presented in Figures 1 to 7 and Tables I to VII, pages 25 to 38.

Manganese (II) Thiocyanate. The data shows that the adsorption characteristics for the manganese complex are approximately the same at a pH of 1 and 7 for each thiocyanate concentration. The shape of the curve in Figure 1 indicates that the amount of manganese complexed as an anion, depends on the thiocyanate concentration of the aqueous phase.

Iron (III) Thiocyanate. The data shows that the adsorption characteristics for the iron complex are essentially constant for thiocyanate concentrations above 0.5 molar, at a pH of 1. At a pH of 7 the thiocyanate complex was not strong enough to eliminate precipitation of the iron as the hydroxide.

Cobalt (II) Thiocyanate. The data shows that the cobalt complex is more strongly adsorbed at pH values of 1,3,5 and 7 by Dowex-1x10% than by Dowex-2x10%. The shapes of the curves in Figures 3 and 6 both indicate the dependence of the thiocyanate concentration on the

amount of complex formed.

At a pH of 9, both resins exhibited decreased adsorption of the cobalt complex. Although the adsorption of the cobalt complex by Dowex-2x10% increases with increasing thiocyanate concentration, the adsorption of the complex by Dowex-1x10% decreases with increasing thiocyanate concentration.

Nickel (II) Thiocyanate. The data shows that the nickel complex is more strongly adsorbed at pH values of 1,3,5 and 7 by Dowex-1x10% than by Dowex-2x10%. The shapes of the curves in Figures 4 and 7 indicate dependence of the thiocyanate concentration on the amount of complex formed. The fact that the curves go through a maximum, indicate that at high ammonium thiocyanate concentrations, ammonia substituted complexes are formed.

At a pH of 9 the amount of nickel complex adsorbed by both resins decreased appreciably; indicating more complete ammine formation.

Copper (II) Thiocyanate. The data shows that formation of the copper complex is dependent on both the thiocyanate concentration and the pH.

At a pH of 1, thiocyanate concentrations above one molar were required to complex the copper and keep it in solution, while at a pH of 7 thiocyanate concentrations greater than 3.5 molar were required.

The decreased adsorption of the copper complex with increased thiocyanate concentration could possibly be attributed to the formation of an ammonia substituted complex.

The data obtained for Dowex-1x10% showed that the cobalt complex was the more strongly adsorbed of the metal complexes studied. It was indicated that the order of adsorption for the thiocyanate complexes at a pH of 1 to 7 was:  $Co > Fe > Mn > Cu > Ni$ . With Dowex-2x10%, the thiocyanate complexes of cobalt and nickel exhibited approximately the same adsorption characteristics:  $Co > Ni$ .

Column Separations. The data for these tests are presented in Table VIII, page 39.

The tests with the ammonium thiocyanate system indicated: (1) Dowex-1 could be used to adsorb the cobalt complex and that Dowex-3 was unsuitable, (2) the resin could be initially in the thiocyanate or the chloride form with little difference in adsorption, and (3) the influent must be acid to realize good adsorption characteristics.

The tests with the nitrite complex of cobalt indicated that the complex was adsorbed by the resin. Even though favorable results were obtained using this complex, the tests were abandoned because of the gassing that occurred in the column as the solution came in contact with the resin.

The nitroso-R-salt complex of cobalt was found to be

adsorbed by Dowex-1. The resin in the acetate form gave a better adsorption than when it was in the hydroxide or chloride form. The amount of cobalt in the effluent was found to be higher with nickel present in the influent. The tests with this complex were abandoned because of the results obtained.

Column Elution. The data for these tests are presented in Table IX, page 42.

The tests with water as an eluent for the thiocyanate complexes of cobalt and nickel showed that only the nickel complex was eluted. This was advantageous because the amount of nickel in the final cobalt fraction can be lowered by eluting most of the nickel with water.

The tests conducted with Amberlite IR-120, to determine if cobalt and nickel could be selectively eluted from the resin, were all unfavorable. The results showed that: (1) cross contamination of the two occurred when the cations were eluted with ammonium thiocyanate, (2) water was not sufficient to elute cobalt (III) and nickel (II) amines, (3) sodium chloride and ammonium acetate solutions showed no selectivity for either cobalt (III) or nickel (II) amines, and (4) ammonium hydroxide would not elute cobalt (II) and nickel (II) amines.

Absorption Tests. The absorption curves obtained for the thiocyanate complexes of cobalt, iron, manganese and

nickel adsorbed on Amberlite LA-2 are shown in Figure 8, page 43. They indicate that the adsorbed complex of cobalt could be used in a spectrophotometric analytical method with no interference from the other metals. The maximum for the cobalt absorption curve occurred at 630 millimicrons. This was in the range expected because of the blue color of the cobalt complex.

Figure 9, page 44 indicated that Amberlite LA-1 could be used as well as Amberlite LA-2, and that a slight increase in sensitivity could be obtained. The maximum for the cobalt absorption curve was again at 630 millimicrons.

The absorbance curve for the cobalt chloride complex adsorbed on Amberlite LA-2 is shown in Figure 10, page 45. The maximum absorbance obtained in the range scanned showed that this complex would not be as sensitive as the thiocyanate complex for a spectrophotometric method. The absorbance curve also indicated the possibility of several adsorbed complexes of various colors. This was not expected because the cobalt complex, when formed in eight molar hydrochloric acid and when adsorbed on an ion exchange resin, is blue.

Effect of Ammonium Thiocyanate Concentration on the Adsorbed Cobalt Complex. The effect of the ammonium thiocyanate concentration of the aqueous solution before extraction of the cobalt is shown in Figure 11 and Table X, pages 46 and 48.

The data shows that no change in the absorbance occurs with ammonium thiocyanate concentrations between 1 and 2.5 molar. Below one molar concentration there is a definite decrease in the absorbance. This indicates that excessive amounts of thiocyanate are required to completely complex the cobalt and give consistent results for cobalt determinations.

Effect of pH on the Adsorbed Cobalt Complex. The effect of the pH of the aqueous solution on the adsorbed cobalt complex after extraction is shown in Figure 12 and Table X, pages 47 and 48.

It is seen that with a pH of 1 to 7, little change in the absorbance of the adsorbed cobalt complex occurs. While with pH values greater than 7, there is a definite decrease in the absorbance. This could be caused by a decreased adsorption of the complex by the resin or by the formation of a less colored complex in the basic solution.

The results indicated that any pH between one and seven should be sufficient for reliable cobalt determinations.

Effect of Time on the Adsorbed Cobalt Complex. The data is presented in Figure 13 and Table XI, pages 51 and 52.

It is seen from the data that very little change in the absorbance of the adsorbed complex occurs. The slight deviations during the first fifty hours are believed to have been caused by deviations in the instrument used to



measure them. The increase in absorbance obtained from 120 to 165 hours was caused by evaporation of the liquid resin medium. Any decomposition of the cobalt complex would have caused a decrease in absorbance.

The data has shown that time is not important in the formation of a stable cobalt complex. The complex is formed immediately and the color is stable for many days.

Effect of Resin Concentration on the Adsorbed Cobalt Complex. The effect of resin concentration is shown in Figure 14 and Table XII, pages 53 and 54.

The curve obtained, indicated that the cobalt complex formed, was dependent on the amount of resin in the extractant. At resin concentration above 25 per cent, the rate of change of the absorbance was slight compared to that at lower concentrations.

The data indicated that for accurate absorbance measurements, the extractant should contain an amount of resin between 25 and 60 per cent and should be kept constant for any series of determinations.

Calibration Curve for Cobalt Analysis. The data obtained from these determinations are shown in Figure 15 and Table XIII, pages 55 and 56.

The standardization curves obtained for the adsorbed cobalt complex on both Amberlite LA-1 and Amberlite LA-2 were found to follow Beer's Law, with a cobalt concentration

from 0 to 0.4 milligrams in ten milliliters of extractant.

The curve for Amberlite LA-1 was found to have a slope greater than the one for Amberlite LA-2. This was predicted in Figures 8 and 9, pages 43 and 44. The reason for this is probably due to slight differences in the co-ordinating ability of the two resins.

The Amberlite LA-2 extractions were not centrifuged before the absorbance was determined. This caused the variations in the data.

Effect of Nickel Concentration on the Adsorbed Cobalt Complex. The data obtained from these tests are shown in Figures 16 and Table XIV, pages 57 and 58.

No definite trend in interference was found with the various amounts of nickel studied. The slight increase in the slopes of the curves from the slope of the standard curve were within the limits of error of the spectrophotometer.

The fact that the amount of nickel in the sample does not interfere in the cobalt determination eliminates dilutions and preliminary separations from the method.

Cobalt-60 Check on Cobalt Extraction. The tests conducted with the cobalt-60 tracers all showed very favorable results. In each test the amount of cobalt extracted was 99 per cent or greater with a single ten milliliter extraction.

The test with the 1:19 extraction mixture proved that the major portion of the cobalt was extracted even though the absorbance decreased. (See Figure 14, page 53)

From the data obtained, with the amount of cobalt-60 used, a definite extraction efficiency for the cobalt extraction could not be determined.

Determination of the Extraction Isotherm for the Cobalt Thiocyanate Complex. The data from these tests are presented in Figure 17 and Table XVI, pages 63 and 64.

The data obtained supplements that obtained by the cobalt-60 check on the adsorption. (See Table XV, page 62) At low cobalt concentrations, the cobalt is essentially all in the organic phase. As the amount of cobalt initially in the aqueous phase is increased, the major portion is still extracted by a single batch extraction. The reason all of the cobalt complex is not extracted is because the capacity of the resin is being approached at the higher concentrations.

The results indicate that ten milliliters of a 1:1 liquid resin mixture will be adequate for all trace analysis.

Spectrographic Determination of the Metals Extracted with Amberlite LA-1. The data is shown in Figure 18 and Table XVII, pages 65 and 66.

The results showed that the procedure used for the removal of cobalt from nickel could also be used to remove copper, chromium, iron, manganese, molybdenum, niobium and

tungsten. From these results the possibility of adsorption of all the thiocyanate anion complexes exist.

The fact that all of these metals were removed by the developed procedure, and the fact that these metals are usually the ones present in trace quantities in nickel, indicate that the procedure developed could be used to prepare nickel of extreme purity.

Comparative Analysis. The data for these analysis are presented in Figure 19 and Table XVIII, pages 67 and 68.

The results showed that from 0.01 to 0.55 per cent cobalt, in a nickel sample, could be analyzed by the method developed with as much accuracy as is attained with spectrographic analysis.

Samples containing less than 0.01 per cent cobalt were not available for comparative analysis.

Stripping the Adsorbed Cobalt Thiocyanate Complex from Amberlite LA-1. The data shown in Figure 20 and Table XIX, pages 69 and 70, indicated that the cobalt complex could be stripped from the liquid resin by sodium carbonate solutions. For a single batch stripping, sodium carbonate concentrations above 1.5 molar were found to be more efficient than lower concentrations. This type of stripping is advantageous because the resin is left in the free base form.<sup>(1)</sup> The resin is then in the form that is used to adsorb the cobalt complex. Thus, the resin could be reused if desired.

Cobalt-60 Check on Cobalt Thiocyanate Stripping. The results shown in Table XX, page 71, indicate that the cobalt complex can be almost completely removed from the resin with a single batch extraction.

The amount of cobalt remaining on the resin, after both extractions, was approximately the same. This indicates the possibility that some cobalt will remain on the resin after continued stripping.

Determination of Trace Amounts of Cobalt in High Purity Nickel by the Thiocyanate-Liquid Ion Exchange Method. Considering the data obtained, it is evident that the solid ion exchange techniques investigated would not be suitable for the quantitative separation and determination of cobalt in nickel.

The thiocyanate-liquid anion exchange technique investigated, exhibited all the characteristics desirable for the quantitative separation and determination of cobalt in nickel and was therefore selected as the basis for the method presented on page 72.

## V. CONCLUSIONS

An analysis of the data obtained from the various separation procedures investigated, resulted in the following conclusions.

### Solid Ion Exchange Resins.

#### A. Anion Exchangers.

1. Cobalt and nickel can be quantitatively separated by selective adsorption of the cobalt thiocyanate complex, although the cobalt could not be quantitatively recovered from the resin, with eluent techniques employed in this work.
2. Cobalt and nickel could not be quantitatively separated by selective adsorption of the cobalt nitroso-R-salt complex or the cobalt nitrite complex.

#### B. Cation Exchangers.

1. Cobalt and nickel could not be quantitatively separated by selective elution with ammonium thiocyanate or with hydrochloric acid.
2. Cobalt and nickel amines could not be quantitatively separated by selective elution with water, sodium chloride

solutions or ammonium hydroxide solutions.

Liquid Ion Exchange Resins. The data obtained showed that trace amounts of cobalt in high purity nickel can be quantitatively removed by selective adsorption of the cobalt thiocyanate complex on a liquid resin. The data further showed that a direct determination of the adsorbed cobalt complex can be obtained with the use of a spectrophotometer.

The following conclusions were made concerning the analytical procedure developed: (See page 72)

A. Nickel and the amounts of other impurities usually present in high purity nickel (iron, copper, and manganese) do not interfere.

B. Any aqueous phase pH between one and seven is satisfactory for the determination.

C. Slight changes in the concentration of the ammonium thiocyanate between one and three molar do not cause significant changes in the absorbancy for any sample.

D. The complex color develops immediately and is stable for adequate time to complete an analysis.

E. Slight variations in the resin concentration of the extractant phase, between 25 and 60 per cent liquid resin, will not cause significant absorbance change in the extracted cobalt sample.

F. The amount of cobalt that can be accurately determined is dependent only on the amount of the sample that can be dissolved, held in solution, and efficiently extracted with the prescribed amount of extractant.

G. The method is less time consuming, requires a less skilled analyst, less costly equipment, and is as accurate as spectrographic analysis for nickel samples containing from 0.01 to 0.55 per cent cobalt.

H. The method is far superior to the potassium nitrite - nitroso-R-salt method (see Appendix G) because of the drastic reduction in the time required for, and the number of steps involved in, the analysis.



## VII. RECOMMENDATIONS

There are many ways in which this research could be extended. The first being the determination of the distribution coefficients for the other elements not studied in the thiocyanate-solid anion resin system. These coefficients could be used to predict separations which could be carried out with this system.

A second extension would be an investigation of the elution of the cobalt complex from the anion exchange resin. If an eluent could be found that would remove the cobalt complex easily and completely, the system investigated would become useful for separating cobalt from nickel.

A third extension would be an investigation of anion complexes of metals (including other metal thiocyanates) which could be adsorbed by the liquid resins and used for analysis in a method similar to the one developed for cobalt.

A fourth extension which might prove very interesting entails the application of liquid resins, containing adsorbed metal complexes, to flame photometric and chromatographic methods of analysis.

The last and most important extension that should come from this work would be the development of an industrial process for the production of extremely pure nickel (99.99%).

## VII. SUMMARY

The separation of trace amounts of cobalt from massive amounts of high purity nickel by the use of ion exchange techniques has been investigated.

Exchange studies with solid cation exchangers and the metal ions and ammine complexes showed that quantitative separation was not attained.

Exchange studies with solid anion exchangers and the nitrite and nitroso-R-salt complexes of cobalt, showed that a quantitative separation could not be effected. The studies with the thiocyanate complex of cobalt showed that a quantitative separation could be attained, but the elution of the complex was difficult.

Exchange studies with liquid anion exchangers and the thiocyanate complex of cobalt were found to give quantitative separation, with a direct determination of the cobalt content by spectrophotometric techniques.

A method for the separation and direct microdetermination of the cobalt content of high purity nickel is presented. The spectrophotometric method developed was found to be independent of pH, time, and reagent composition, within broad limits, and the lower limit of the determination was dependent only on the size of the sample that could be

adequately handled. It was also found that the method was at least as accurate as a spectrographic analysis for cobalt concentrations from 0.01 to 0.55 per cent, and that a cobalt content below 0.01 per cent could be determined with little difficulty.

VIII. APPENDICES

APPENDIX A

Methods Used In Chemical Analysis

Nitroso-R-Salt Method for Cobalt. Transfer 1.0 ml of a sample solution containing 0.005 to 0.1 mg of cobalt, as sulfate, to a 50 ml beaker, dilute to 10 ml. Add 5.0 ml of sodium acetate buffer solution (500 gm/l), followed by 2.0 ml of nitroso-R-salt solution (7.5 gm/l), mixing the solution after each addition. (The pH at this point should be about 5.5) Cover the beaker, heat to boiling, and maintain just under the boiling temperature for 1 to 2 min. Add 5.0 ml of  $\text{HNO}_3$  (1:2) and boil gently for 1 to 2 min. Cool to room temperature, transfer to a 50 ml volumetric flask, dilute to mark, and mix. Transfer to an adsorption cell and read at 520  $m\mu$  against a reagent blank.

Pyridine Method for Cobalt and Nickel Analysis. Transfer an aliquote of sample containing 0.005 to 0.025 mg of cobalt or nickel, as sulfate, to a 50 ml beaker, dilute to 10 ml. Add 8 ml of pyridine, dilute to 40 ml. Adjust pH to 5.5 with cone, HCl. Transfer to a 50 ml volumetric flask, dilute to mark, and mix. Transfer a known amount to a polarographic cell, determine current-voltage curve. The amount of cobalt in the sample is then determined by the standard addition method.

The standard addition method involves; Obtaining the polarogram of the unknown solution, adding a known amount

of standard solution and, obtaining the polarogram of the resultant solution. The amount of cobalt present in the unknown solution is then obtained by use of the following equation:

$$C_x = \frac{-vC_s h}{hV - H(V+v)}$$

Where:  $C_x$  = Concentration of sample (gm/ml).

$C_s$  = Concentration of standard added (gm/ml).

$h$  = Height of current curve for sample alone (mm).

$H$  = Height of current curve for sample plus standard addition (mm).

$V$  = Volume of sample (ml).

$v$  = Volume of standard addition (ml).

Dimethylglyoxime Method for Nickel. Transfer a sample containing 0.5 to 3.5 mg of nickel, sulfate form, to a 500 ml beaker. Add 10 ml hydrochloric acid, add 2 gm tartaric acid and 2 gm ammonium chloride. Make solution slightly alkaline with ammonium hydroxide. Heat to boiling. Add dimethylglyoxime (1% alcoholic solution), until the weight of reagent is about seven times the assumed weight of nickel present. Add ammonium hydroxide, if necessary, until faint but distinct odor of it is apparent. Stir the solution and allow to digest at 80°C for 1 hour. After digestion, filter the solution through a fritted crucible and wash the precipitate with hot water. Dry the precipitate in an oven at 110°C, and weigh to a constant weight.

Ceric Ammonium Sulfate Method for Iron. Transfer sample solution to a 400 ml beaker, add 15 ml hydrochloric acid (1:1). Add stannous chloride solution (saturated) until iron color disappears, then add 6 drops excess. Dilute to 100 ml. Add 10 ml mercuric chloride solution (1gm/ml) and 15 ml Rhinhardt's Solution. (6 gm  $MnSO_4$ , 16 ml  $H_2SO_4$  and 16 ml  $H_3PO_4$  per 120 ml) Add 4 drops of Barium Diphenylamine Sulfonate indicator (1.2668 gm/400ml). Titrate to a violet end point with a standardized solution of ceric ammonium sulfate.

Gm Iron = (titer value)(ml used).

Thiosulfate - Iodide Method for Copper. Transfer sample to 250 ml  $H_2SO_4$ . Evaporate to dryness, add  $HNO_3$  and heat to dissolve, then take to dryness on sand bath. Take up in 100 ml  $H_2O$  and heat to boiling. Add 4 drops of NaOH (6% solution) or until black ppt. forms. Add 10 ml acetic acid, and boil. Cool. Add KI until solution clear, add 5 ml starch solution (saturated). Titrate to blue end point with a standardized sodium thiosulfate solution.

Gm Copper=(titer value)(ml used).

Bismuthate Method for Manganese. Transfer sample to a 600 ml beaker. Add 15 ml HCl and 10 ml H<sub>2</sub>SO<sub>4</sub>. Evaporate to dryness. Add 175 ml H<sub>2</sub>O and 75 ml HNO<sub>3</sub>, dissolve. Cover and boil 5 minutes. Cool. Add sodium bismuthate in excess. Filter through medium fritted filter. Wash with HNO<sub>3</sub> (1%). Add a standard solution of ferrous ammonium sulfate until colorless. Titrate with a standard potassium permanganate solution until pink.

$$\text{Gm Manganese} = [(A)(B) - (C)] (D)$$

Where: A = ml Fe(NH<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub> solution added.

B = ml KMnO<sub>4</sub> solution/ml Fe(NH<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub> solution.

C = ml KMnO<sub>4</sub> solution used in titration.

D = titer value of KMnO<sub>4</sub> solution (gm Mn/ml).



APPENDIX B

Artificial Sample Prepared to Determine  
the Metals Extracted with Cobalt  
by Amberlite LA-1

The following materials were used in preparing this sample: (1) 20.0000 gm nickel oxide (obtained from International Nickel Co.), (2) 0.0300 gm iron (99.99% Fe) (obtained from Merck and Co.), (3) 0.1000 gm nickel oxide (USBS No. 167\*), (4) 0.1000 gm nickel oxide (USBS No. 162\*).

The following table is the calculated composition of the resulting sample on a metal in metal basis.

Element	Percent
Ni	99.104
Co	0.272
Cu	0.182
Mn	0.025
Cr	0.127
Fe	0.204
Mo	0.024
W	0.028
Nb	0.020
Al	0.001
Others	0.013

\*Analysis in Appendix C.

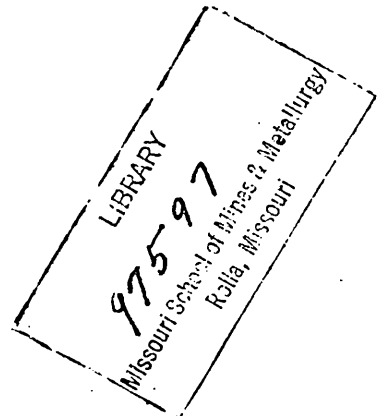
APPENDIX C

Certificate of Analysis Standard Sample No. 162

Element	Percent
C	0.11
Si	0.67
Co	0.54
Al	0.23
Mn	2.34
Cu	28.93
Fe	0.34
Ti	0.20
S	0.002
Ni	66.38
Cr	0.24

Certificate of Analysis Standard Sample No. 167

Element	Percent
C	0.38
S	0.007
Ni	20.65
Cr	20.00
W	4.50
Mn	1.64
Si	0.44
Co	42.90
V	0.01
Nb	3.15
P	0.01
Cu	0.03
Fe	2.13
Mo	3.90
Ta	0.08



## APPENDIX D

Provisional Certificate of Analysis  
Standard Sample 671, Nickel Oxide, No. 1<sup>a</sup>

Method	Per Cent of the Element in Nickel Oxide								
	Co	Cu	Fe	Mg	Mn	Si	Ti	Al	Cr
Chemical	0.29	0.196	0.39	--	0.129	0.048	0.024	--	0.026
	0.30	0.199	0.40	--	0.133	--	0.024	--	--
	0.29	0.190	0.40	--	0.118	0.048	0.024	--	0.023
	0.29	0.190	0.40	--	0.134	--	0.025	0.0088	0.022
	0.32	0.198	0.38	--	0.129	--	0.023	--	--
	--	--	--	0.029	--	0.047	--	--	--
	0.32	0.202	0.40	0.031	0.129	0.045	0.025	--	--
	0.32	--	0.35	0.028	0.12	--	0.024	0.0094	0.024
	0.30	0.21	0.40	--	0.13	0.048	0.023	--	--
	Spectro- chemical	0.32	0.20	0.38	0.031	0.130	--	0.025	0.0092
0.32		--	0.39	0.032	0.115	--	0.026	0.011	0.024
0.32		0.198	0.42	0.031	0.134	0.052	0.023	0.0092	0.030
0.32		0.165	0.40	0.026	0.123	0.044	0.024	0.0084	0.025
--		--	0.39	--	0.13	--	--	--	--
Recommended Value	0.31	0.20	0.30	0.030	0.13	0.047	0.024	0.009	0.025

<sup>a</sup>U.S. Department of Commerce, National Bureau of Standards, Washington, D.C. (1956)

APPENDIX E

Provisional Certificate of Analysis  
Standard Sample 672, Nickel Oxide, No. 2<sup>a</sup>

Per Cent of the Element in Nickel Oxide									
Method	Co	Cu	Fe	Mg	Mn	Si	Ti	Al	Cr
Chemical	0.55	0.017	0.078	--	0.099	0.112	0.0088	0.0045	0.0021
	0.55	0.018	0.082	--	0.096	--	0.0086	--	--
	0.53	0.017	0.073	--	0.093	0.11	0.010	--	0.0032
	0.54	0.016	0.081	--	0.095	--	0.0090	0.0033	0.0032
	0.56	0.017	0.079	--	0.094	--	0.0082	--	--
	--	--	--	0.019	--	0.12	--	--	--
	0.52	0.020	--	0.023	0.099	0.107	0.010	--	--
	0.59	0.019	0.079	0.017	0.094	--	0.010	0.0039	0.0032
	0.54	0.018	0.081	--	0.10	0.11	0.009	--	--
	Spectro-chemical	0.55	0.017	0.077	0.019	0.093	0.096	0.0097	0.0035
0.53		0.017	0.085	0.023	0.084	--	0.0078	0.005	< 0.005
0.56		0.018	0.075	0.020	0.093	0.10	0.0082	0.0047	< 0.005
--		0.018	0.078	0.018	0.084	0.098	0.0106	0.0044	0.0032
--		0.018	0.079	--	0.086	--	--	--	--
Recommended Value	0.55	0.018	0.079	0.020	0.095	0.11	0.009	0.004	0.003

APPENDIX F

Provisional Certificate of Analysis  
Standard Sample 673, Nickel Oxide, No. 3<sup>a</sup>

Per Cent of the Element in Nickel Oxide									
Method	Co	Cu	Fe	Mg	Mn	Si	Ti	Al	Cr
Chemical	--	--	--	--	--	0.0076	--	--	--
	--	0.0024	0.023	--	0.0041	0.0033	0.0032	0.0013	0.0003
	0.019	0.001	0.028	0.0042	0.0027	--	0.0026	0.0009	0.0014
	0.020	--	--	0.0018	--	0.0066	--	0.001	<0.001
	0.014	0.0024	0.032	0.0035	0.0036	0.0035	0.0028	0.0010	0.0003
Spectro- chemical	0.015	0.0024	0.031	0.0029	0.0041	0.0074	0.0030	0.0013	0.0004
	--	0.0018	0.028	0.0020	0.0037	0.0047	0.0035	0.0009	0.0002
	0.015	0.0016	0.029	0.004	0.0039	--	0.0025	0.0012	<0.001
	0.016	0.0024	0.031	0.0028	0.0034	0.0055	0.0040	--	0.0004
	0.013	0.0012	0.029	0.0025	0.0042	0.0057	0.0032	0.0014	0.0011
	0.019	0.0012	0.023	0.0021	0.0040	0.0066	0.0036	--	<0.001
Recommended Value	0.016	0.002	0.029	0.003	0.0037	0.006	0.003	0.001	0.0003

<sup>a</sup>U.S. Department of Commerce, National Bureau of Standards, Washington, D.C. (1959)

APPENDIX G

Potassium Nitrite Separation for Cobalt (0.01 to 10 per cent) in Various Alloys, Prior to Estimation by the Nitroso-R-Salt Photometric Method. The following procedure (32) was supplied by the International Nickel Co., Inc.

(a) Transfer a 2 g. sample to a 400 ml. beaker, and decompose about as below, the amount of acid specified being regulated to that necessary for rapid decomposition without excessive neutralization later. Use of more than about 1 ml. of perchloric acid is to be avoided, because of the insolubility of its potassium salt, and sulfuric had better be limited to not more than 2 or 3 ml., because the quantity of sodium sulfate produced during subsequent neutralization is difficult to keep in solution, in the small volume required during the nitrite separation.

<u>Alloy</u>	<u>Acid or Mixture</u>
Nickel-Copper and Similar	15 ml. of nitric acid
Nickel alloys including high Mn, high Ti, high Al	30 ml. of nitric acid (1:1)
Nickel-chromium alloys, stainless steels, high temperature alloys	25 ml. of hydrochloric- nitric acid (3:2)

If necessary, heat gently to effect solution, controlling the heating to prevent as much as possible the hydrolysis of titanium and/or columbium-tantalum, if present. NiCrMo alloys may require further small additions of hydrochloric

acid, to overcome passivity. 4 or 5 drops of hydrofluoric acid may be added to assist in the decomposition of refractory alloys, or to dissolve gelatinous silicic acid appearing in solutions of cast materials. The insoluble metallic residues, that often deposit from solutions of alloys containing high tungsten and/or columbium should be digested with the nitro-hydrochloric and hydrofluoric acid mixture until completely decomposed, the tungsten oxidized, and the columbium either in solution or partially hydrolyzed.

(b) When solution is adjudged complete, which may require some experience in the case of high temperature alloys, rinse and remove the cover, add 5 drops of hydrofluoric acid, or sufficient to dissolve any silicic acid, (if hydrofluoric has not already been used), followed by 25 ml. of hot water and 10 ml. of citric acid (250 g. per liter). Mix, and heat gently for 10 to 15 min. If tungstic acid, chromium carbides, or hydrolyzed compounds are apparent in the solution, filter through an 11 cm. medium paper with paper pulp into a 400 ml. beaker, and wash with hot water, limiting the filtrate to about 100 ml.

(c) Neutralize the cooled filtrate, or cooled original solution, if clear, with anhydrous sodium carbonate, introducing the reagent in about 1 g. portions, covering immediately, and waiting each time until the previous reaction subsides, before adding the next portion. As the speed of reaction decreases as the solution approaches neutrality,

mix very thoroughly after each addition, to avoid over-neutralization. The approach of the end-point is generally signalled by the formation of green or brown precipitates in the solution, (the colors depending on the major elements in the alloy), and addition of carbonate must then be controlled so that only a small amount remains unreacted as action ceases.

(d) Cautiously add 40 ml. of glacial acetic acid to the solution, and allow to stand, with occasional swirling, until the excess carbonate is decomposed. A precipitate, remaining after the evolution of gas has ceased, usually indicates salts insoluble because of the low volume, and water should be added in small quantities, with thorough mixing, until the precipitate just disappears.

(e) Add 50 ml. of potassium nitrate solution (500 g. per liter) to the cool solution, swirl to mix, and let stand six hours, or overnight, at about 60°C. The volume at this point should be not less than 200 ml. to prevent separation of insoluble salts, or more than 250 ml. to avoid interference with the precipitation of potassium cobaltinitrite.

(f) Filter, using an 11 cm. medium paper with a generous quantity of paper pulp, bringing the level of liquid only about two thirds of the way up the paper at each addition, to prevent creeping of the precipitate. As much as possible of the precipitate should be kept in the beaker.



at this point. Decant all possible of the supernatant liquid with the filter, wash the sides of the beaker down with 50 ml. of potassium nitrite solution (50 g. per liter). swirl, and decant this wash liquid into the filter, observing the same precautions as before. Do not wash the top of the paper at any time, to minimize creeping of the precipitate. Repeat the washing procedure just described. Return the washed paper and precipitate to the beaker, and discard the filtrate.

(g) For work of the highest accuracy, the precipitation must be repeated, as described in Paragraph (i) in routine work, the precipitate will often be sufficiently free of interfering elements that it can be prepared at this point for photometric analysis. If the filter paper shows no green or brown precipitates, and the top of the paper has drained reasonably free of color, proceed as in (h).

(h) Add 35 ml. of nitric acid, and 1 ml. of sulfuric acid for each 50 ml. of final dilution required for the photometric analysis. Cover, and evaporate slowly to fumes on an asbestos pad on the hot plate. Cool somewhat, add 3 ml. of nitric acid, and again take slowly to fumes. Repeat this operation, if necessary to insure complete destruction of organic matter. Finally, cool, wash down the cover and sides of the beaker with about 10 ml. of water, evaporate to fumes once more, and cool. Continue as directed in

Paragraph (j).

(i) If reprecipitation is necessary, add 35 ml. of nitric acid, 3 ml. of sulfuric acid, and 1 ml. of perchloric acid. Cover, and evaporate slowly to fumes on an asbestos pad on the hot plate. Cool somewhat, add 50 ml. of warm water and 10 ml. of citric acid (250 g. per liter), mix, and heat gently, if necessary to dissolve the salts. Cool the solution, and neutralize with anhydrous sodium carbonate as before, with care to control the additions so that only a small amount remains unreacted as action ceases. There is no indication of the approach of the end-point other than the decrease in the speed of reaction. Continue as directed in Paragraphs (d), (e), (f), and (h).

(j) Add 20 ml. of water, or more, with due regard to the size of flask to be used for the photometric analysis. Mix, and heat gently, if necessary to dissolve salts. Cool, and transfer the solution to a volumetric flask of suitable size, in accordance with the amount of cobalt expected, dilute to the mark and mix, at room temperature.

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XI. VITA



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