Determination of Nickel, Manganese, Cobalt, and Iron in High-Temperature Alloys, Using Anion-Exchange Separations

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A procedure is given for the determination of nickel, manganese, cobalt, and iron in a high-temperature alloy. Niobium, tantalum, tungsten, and silicon are rendered insoluble by hydrochloric acid dehydration after solution of the alloy in aqua regia. Molybdenum and copper are precipitated with hydrogen sulfide, and the solution is filtered. The filtrate is evaporated several times with hydrochloric acid and hydrogen peroxide to obtain a chloride solution of these elements in the proper valence. The resulting solution is transferred to an anion-exchange column containing Dowex-1. The nickel and manganese, with chromium and some other elements, are collected in the first fraction by elution with 9 N hydrochloric acid. Cobalt is collected in a second fraction by elution with 4 N hydrochloric acid, and iron in a third by elution with 1 N hydrochloric acid. The cobalt is determined by electrolysis from a weakly ammoniacal chloride solution containing hydroxylamine hydrochloride, and the other elements are determined by conventional methods.

1. Introduction

The increased use in recent years of high-temperature alloys and alloys of controlled temperature-expansion characteristics has made the problem of determining cobalt, iron, nickel, and manganese in appreciable quantities and in combination a pressing one. Some of the difficulties encountered in this field of analysis have been summarized by Chirnside, Cluley, and Proffitt [3] [1] in dealing with a ternary alloy of iron, nickel, and cobalt. Many of the alloys manufactured today may contain, in addition, appreciable percentages of chromium, molybdenum, titanium, tungsten, niobium, and other elements. The problem of obtaining analyses of sufficient accuracy for the establishment of standards of composition is not an easy one; even the usually simple determination of nickel may become quite complex in these mixtures [7]. A new approach to the problem seems needed in order to put such methods on a basis of accuracy comparable to other less difficult combinations.

The present paper describes the application of anion-exchange separations to the analysis of high-temperature alloys. Kraus and Moore [8, 12] have shown that nickel, manganese, cobalt, and iron, as well as certain other elements, can be separated by selective elution from an anion-exchange resin with hydrochloric acid solutions. These separations depend on the fact that a number of metallic elements [10] can exist in aqueous solutions either as cations or as complex chloro-anions, the relative amounts depending on the element and on the concentration of chloride ions in the solution. The exact mechanism of the combination (or adsorption) of these complexes with the resin has not been established, but it may be related to the existence of these complex anions in solution as strong acids. For example, iron is probably combined in the form of a complex anion, such as $(H_2FeCl_6)^-$, that is free to compete with the chloride ions for a position on the resin column, much as the competition that exists between chloride and bisulfate ions [9]. Though suggested mechanisms are at present speculative, practical and efficient quantitative separations can be made with quantities and volumes commonly used in analytical work.

The procedure outlined below was designed particularly with the analysis of an S–816 type of alloy [2] in mind. After solution of the alloy in aqua regia, the niobium, tantalum, tungsten, and silicon are rendered insoluble by hydrochloric-acid dehydration. The solution is treated with hydrogen sulfide to precipitate molybdenum and copper, and filtered. The filtrate is evaporated several times with hydrochloric acid and hydrogen peroxide to obtain a chloride solution of the elements in the proper valence. The resulting solution is transferred to an anion-exchange column, and the nickel and manganese, with chromium and some other elements, are collected in the first fraction by elution with 9 N hydrochloric-acid solution. Cobalt is collected in a second fraction by elution with 4 N hydrochloric acid, and iron in a third by elution with 1 N hydrochloric acid. Manganese and nickel are determined in aliquots of the first fraction by the persulfate-arsenite titration and dimethylglyoxime gravimetric methods, respectively. Cobalt is determined in the second fraction by electrolysis from a weakly ammoniacal chloride solution containing hydroxylamine hydrochloride, and iron is determined in the third fraction by reduction with stannous chloride and titration with dichromate.

The method requires several days to carry to completion as about 3 hr are required for each of the ion-exchange fractionations. The method is not intended to replace rapid routine procedures, where they can be developed for a particular type [3] of material, but provides an independent checking procedure of general application.

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[1] Figures in brackets indicate the literature reference at the end of this paper.

[2] This alloy contains approximately 40 percent of cobalt, 20 percent of nickel, 20 percent of chromium, and 4 percent each of niobium, tungsten, and molybdenum, the remainder being largely iron, manganese, carbon, and silicon.

2. Apparatus and Resins

The apparatus required for an ion-exchange separation is simple, consisting of a glass column to hold the resin. The column used in this investigation, illustrated in figure 1, is 1 in. in internal diameter and 12 in. long. As most of these separations require several hours, it is convenient to so arrange the columns that a number can be operated with minimum attention. Such an assembly is illustra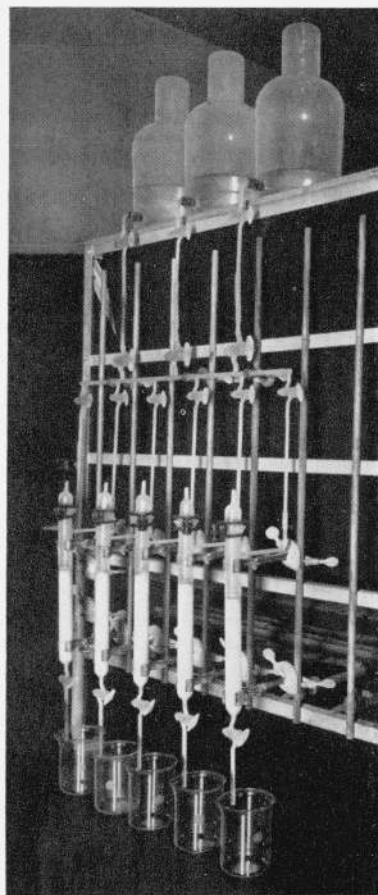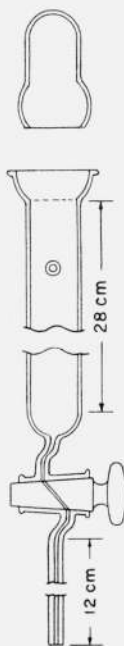ted in figure 2. The solutions necessary for elution are delivered by gravity flow from bottles, placed on the top stand, through a system of stopcocks and capillary tubing, to the columns. Because most of the usable resins are fine-mesh materials that tend to slow the flow of liquid, it is advantageous to have a several-foot head of liquid to control the flow rate.

The resin selected for these columns was 200- to 400-mesh Dowex–1, with 8- or 10-percent cross-linkage.[3] The finest and the coarsest materials are removed by settling the resin in diluted hydrochloric acid $(1+19)$.[4] After several cycles of successively decanting the fine and main portions from the coarse fraction, the column is filled with a slurry of the main portion of the resin to a settled height of 20 to 23 cm (equivalent to approximately 75 g of resin). A plug of glass wool in the bottom of the column serves to retain the resin, and a disk of plastic cloth is placed on top to minimize the disturbance of the resin when solutions are added.

FIGURE 1. *Ion-exchange column.*

3. Procedures

3.1. Preparation of the Solution of the Sample for Ion-Exchange Separation

Transfer an accurately weighed 1 g sample to a 600-ml beaker. Cover the beaker and add 20 ml of aqua regia (3 parts of hydrochloric acid and 1 part of nitric acid). Set the beaker on the side of a steam bath until the reaction ceases, and then warm it gently until the sample is in solution,[5] except for small amounts of carbides and silica.

Wash the cover glass and wall of the beaker with a little diluted hydrochloric acid $(1+19)$ and evaporate to dryness on a steam bath. Treat the dry residue with 10 ml of diluted hydrochloric acid $(1+1)$, warm and mix well with a glass rod, and again evaporate to dryness. Repeat the addition of diluted hydrochloric acid and the evaporation to dryness four times to insure the removal of nitric acid.[6] Finally, add 15 ml of diluted hydrochloric acid $(1+1)$ and warm the solution on the steam bath until the cake is dissolved. Dilute to 300 ml with hot water, and pass a brisk stream of hydrogen sulfide through the solution for 30 min.[7] Let stand for 30 min and filter through a close-textured 11-cm paper containing a little paper pulp. Transfer the precipitate to the paper[8] and wash with a diluted hydrochloric acid $(3+97)$ solution saturated with hydrogen sulfide until the volume of the filtrate and washings is at least 450 ml. Transfer the filtrate and washings to a steam bath and evaporate to dryness.

FIGURE 2. *Assembly of ion-exchange columns.*

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[3] The fine-mesh resins were obtained from The Dow Chemical Co., Technical Service and Development, Midland, Mich.

[4] This denotes 1 volume of concentrated hydrochloric acid, sp gr 1.18, diluted with 19 volumes of water. If no dilution is specified, the concentrated reagent is meant.

[5] Some alloys dissolve slowly, but will dissolve more readily if the chlorine generated by the acid mixture is not driven off by heat.

[6] Manganese appears to form a complex chloromanganite anion of unknown composition in strong hydrochloric acid solutions in the presence of oxidizing agents.

[7] Molybdenum is absorbed in part by the ion-exchange column and soon contaminates all fractions during the separation procedure. It is conveniently removed at this point, along with the dehydrated silica, tungsten, tantalum, and niobium.

[8] This paper can be ignited and the residue examined for manganese, nickel, cobalt, and iron. Examination of residues from an S–816 alloy indicated negligible quantities of manganese and iron, 0.01 percent of nickel, and 0.02 to 0.03 percent of cobalt to be retained by this precipitate.

To the residue add 10 ml of diluted hydrochloric acid (1+1), cover the beaker with a watchglass, and warm. Add 50 ml of warm water, and dissolve any residue on the walls of the beaker by manipulation of the solution with a glass rod. Add 10 drops of hydrogen peroxide (30%) to the covered beaker and digest on a steam bath until reaction stops, then add an additional 10 drops of hydrogen peroxide.[9] When reaction has ceased, wash the cover glass and beaker wall, and evaporate the solution to dryness. Add 10 ml of diluted hydrochloric acid (1+1), warm to dissolve salts, and again evaporate to dryness. Repeat the addition of diluted hydrochloric acid and evaporation to dryness four times.

Add 10 ml of diluted hydrochloric acid (1+1) to the residue, cover the beaker, and warm until the solution clears. Cool, add 10 ml of hydrochloric acid, and mix well with a stirring rod.[10] The solution is now ready for passage through the anion-exchange column.

3.2. Ion-Exchange Separation of Nickel and Manganese, Cobalt, and Iron

Transfer 50 ml of diluted hydrochloric acid (3+1) to the column in small increments (5 to 10 ml), and drain the acid to about 1 cm above the top mat. Place a small funnel in the top of the column. Transfer the concentrated solution of the sample in small increments (5 ml) to the column with the bottom stopcock open. Add the sample as the solution moves down the column until all the sample has been transferred to the column. Always keep the resin completely covered with solution to prevent the formation of air pockets. Replace the "waste" beaker under the column with a clean 600-ml beaker. Wash the beaker that contained the sample with 5-ml portions of diluted hydrochloric acid (3+1), policing the walls with a glass rod, and transfer the washings to the funnel and column until 10 washings have been made. The important point is to get all of the sample solution onto the resin bed. Finally, wash the funnel and the walls of the column above the resin with several small portions of the diluted hydrochloric acid (3+1); a dropping tube and bulb is useful at this point.

Place the cap on the column top, lubricating the joint with a drop or two of water to prevent air leakage, and clamp. Adjust the stopcocks to deliver the diluted hydrochloric acid (3+1) from the reservoir bottle to the column, and adjust the bottom stopcock on the column to a flow rate of 100 to 125 ml/hr. Collect 425 ml of solution, then adjust the stopcocks to deliver diluted hydrochloric acid (1+2) to the column. After 15 min the more dilute acid will be about half way down the column, the beaker containing the nickel and manganese, along with chromium and some other elements, is then replaced with a clean 600-ml beaker. Place the beaker containing the nickel and manganese on a steam bath and evaporate to dryness.

Continue the flow of diluted hydrochloric acid (1+2) at a rate of 100 to 125 ml/hr [11] until 425 ml of the cobalt fraction is obtained, then change the stopcocks to deliver diluted hydrochloric acid (1+11). Replace the beaker containing the cobalt with a clean 600-ml beaker and follow the procedure outlined in the previous paragraph. Place the beaker containing the cobalt on a steam bath, and evaporate the solution to dryness.

Continue the flow of diluted hydrochloric acid (1+11), at a rate of 100 to 125 ml/hr, until 450 ml of the iron fraction is obtained. Close the stopcocks, transfer the beaker to a steam bath, and evaporate the solution to dryness.

3.3. Determination of Nickel, Manganese, Cobalt, and Iron

a. Nickel

REAGENTS

Citric acid solution (250 g/liter). Dissolve 250 g of citric acid in 600 to 800 ml of water, add 20 ml of diluted sulfuric acid (1+1), and dilute to 1,000 ml with water. Filter, if necessary.

Dimethylglyoxime solution (10 g/liter of ethanol). Dissolve 10 g of dimethylglyoxime in 1 liter of ethanol, and filter.

PROCEDURE

Add 10 ml of diluted hydrochloric acid (1+1) to the reserved beaker containing the first fraction from the ion-exchange column, and warm to dissolve the residue. Dilute to 25 ml with warm water, transfer to a 200-ml volumetric flask, policing the beaker well. Cool to room temperature, dilute to the mark, and mix well. Transfer a 50-ml aliquot to a 400-ml beaker, and reserve the remainder of the solution in the volumetric flask for the determination of manganese.

Add 5 ml of hydrochloric acid and 25 ml of citric acid solution to the aliquot in the beaker. Dilute to 100 ml with warm water, and neutralize with ammonium hydroxide, using litmus paper as an indicator. Filter the solution [12] through a 9-cm close-textured paper containing a little pulp into a 600-ml beaker and wash well with hot water.

Adjust the filtrate to a volume of 300 ml and add an excess of 2 to 3 ml of ammonium hydroxide. Add 0.4 ml of dimethylglyoxime solution for each milligram of nickel (in the aliquot) and then 5 ml in excess. Digest for 30 min on a steam bath with occasional stirring, and cool to room temperature. Filter through a weighed 30-ml fritted-glass crucible of medium or fine porosity. Transfer the precipitate to the crucible and finally wash 4 or 5 times with cold water. Dry the precipitate to constant weight at

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[9] This treatment is to remove any residual sulfide by oxidation. It also serves to oxidize any iron to the trivalent form required for the ion-exchange separation.
[10] This treatment adjusts the solution to approximately 9 N hydrochloric acid, which is the correct acidity for the first step of the ion-exchange separation.

[11] The lower viscosity of the more dilute acid usually requires a readjustment of the stopcock at the bottom of the column to maintain the specified flow.
[12] The solution is usually cloudy with resin dissolved in the strong hydrochloric acid used for elution. The paper can be ignited, treated with H_2SO_4-HF to eliminate silica, and the residue dissolved in a few drops of HCl and returned to the main solution.

150° C. Cool in a desiccator and weigh as nickel dimethylglyoxime.

b. Manganese

REAGENTS

Sodium hydroxide solution (300 g/liter). Transfer 30 g of NaOH to a 250-ml beaker, dissolve in 50 ml of water, and dilute to 100 ml.

Sodium bromate.

Mixed-acid solution. Add 100 ml of sulfuric acid to 675 ml of water slowly with good stirring. Cool, and add 125 ml of phosphoric acid (85%) and 100 ml of nitric acid.

Standard sodium arsenite solution (1 ml=0.4 mg of Mn*).* Transfer 4.8 g of As_2O_3 to a 600-ml beaker, add 50 ml of water and 6 g of NaOH. Stir until the oxide has dissolved, dilute to 300 ml with water, and bubble a stream of carbon dioxide into the solution until it is saturated with CO_2. Dilute with water to 4 liters in a glass-stoppered bottle, and mix well. The solution is standardized by titration of known amounts of manganese oxidized with persulfate.

Silver nitrate solution (8 g per liter).

Ammonium persulfate solution (250 g per liter). This solution is not stable, and should be prepared as needed.

PROCEDURE

Transfer a 100-ml aliquot of the solution reserved from the nickel determination to a 400-ml beaker, and dilute to a volume of about 225 ml with warm water. Add the sodium hydroxide solution dropwise until the solution is faintly acid, as judged by the redissolving of the precipitate. Add 3 g of sodium bromate and slowly bring to boiling temperature to oxidize the chromium. Remove from the heat, make just alkaline with the sodium hydroxide solution, and then add 10 ml in excess. Boil gently a minute or two, and allow the precipitate containing the manganese to settle on a steam bath for a few minutes. Filter the hot solution through an 11-cm loose-textured paper containing a little paper pulp and wash 2 or 3 times with a little hot water. Return the paper and precipitate to the beaker,[13] add 10 ml of nitric acid, and mascerate the paper with a glass rod. Warm on a steam bath for a few minutes until the filter is disintegrated, and add 10 ml of water containing a few drops of sulfurous acid. Digest until the precipitate dissolves, dilute with 50 ml of hot water, and boil gently a minute or two. Allow to settle, filter [14] through a 9-cm loose-textured paper, and wash well with hot diluted nitric acid (5+95). Evaporate the filtrate to dryness.

Add 30 ml of acid mixture to the dry residue and digest until complete solution is obtained. Add 100 ml of hot water, 10 ml of silver nitrate solution, and 10 ml of ammonium persulfate solution. Bring to a boil, and boil briskly for 60 to 90 sec. Cool to a temperature of 15° C or lower, add 75 ml of cold water with stirring, and titrate potentiometrically with the standard sodium arsenite solution to the first permanent break.

c. Cobalt

PROCEDURE

Add 20 ml of diluted nitric acid (1+1) to the cobalt residue obtained from the second fraction of the ion-exchange separation. Cover the beaker and digest on a steam bath until the salts are in solution. Add 3 ml of perchloric acid, and dissolve any residue on the walls of the beaker by manipulation of the solution with the glass rod. Transfer the beaker to a hot plate and evaporate to fumes of perchloric acid. Cool, add 5 ml of nitric acid, police the walls of the beaker, and again evaporate the solution to fumes of perchloric acid. Repeat the procedure twice more to destroy the resin.[15] Continue the heating to volatilize most of the perchloric acid, and to convert most of the salt to black oxide.

Cool, add 10 ml of diluted hydrochloric acid (1+1), and warm to dissolve the oxide. Add 10 ml of hot water, and digest until the oxide is in solution. Remove and wash the cover glass, and evaporate the solution to dryness. Repeat the addition of 10 ml of diluted hydrochloric acid (1+1) and evaporation to dryness twice to insure decomposition of nitrates.[16]

Add 30 ml of diluted hydrochloric acid (1+1) to the dried residue and warm to dissolve the salts. Transfer the solution to a 400-ml beaker, washing well with hot water. Adjust the volume to about 150 ml and cool. Neutralize the solution by the dropwise addition of ammonium hydroxide.[17] Add 1 g of hydroxylamine hydrochloride and stir well for a minute or two while the salt is dissolving. Add 5 ml of ammonium hydroxide in excess, and dilute to approximately 275 ml with water.

Transfer the solution to an electrolysis apparatus, cover with a split watchglass, and electrolyze overnight with platinum-gauze electrodes, using a current density of 0.4 amp/dm^2. In the morning, wash the underside of the cover glass, and continue the electrolysis for 30 min. Without interrupting the current, slowly lower the beaker, and at the same time, wash the electrodes with a stream of water.[18] Immediately immerse the electrodes several times in a beaker of water. Interrupt the current and remove the cathode. Rinse the cathode with ethyl alcohol, shake off the excess alcohol, and dry at 110° C in an an oven for a few minutes. Cool in a desiccator, and weigh the deposit as metallic cobalt.

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[13] Alternatively, the paper can be decomposed by fuming with the mixed acid solution and several additions of HNO_3 to destroy the paper. The final nitric acid concentration during the development of the permanganate color is critical, and the solution should contain no more than 3 ml of HNO_3.

[14] The paper can be ignited, treated with H_2SO_4-HF, and any residue can be dissolved in a few drops of HNO_3 and added to the main solution.

[15] Anion-exchange resins usually contain quaternary amine cations and may contaminate a cathode deposit in the electrolysis that follows.

[16] Nitrates inhibit or completely prevent the deposition of cobalt.

[17] A small strip of Hydrion paper will conveniently indicate approximate neutrality.

[18] The electrolyte usually contains from 0.2 to 1 mg of Co. A suitable aliquot can be heated with nitric acid to destroy ammonium salts, and the cobalt determined by the nitroso-R photometric method.

d. Iron

Reagents

Potassium-permanganate solution (25 g/liter).

Stannous chloride solution (150 g/liter of diluted hydrochloric acid (1+3)). Dissolve 150 g of $SnCl_2 \cdot 2H_2O$ in 500 ml of diluted hydrochloric acid (1+1), warming if necessary. Cool and dilute to 1 liter with water.

Mercuric chloride solution (approximately 60 g/liter). Prepare a saturated solution of $HgCl_2$ in water.

Sulfuric-phosphoric acid solution. Mix 150 ml of sulfuric acid with 300 ml of water, cool, add 150 ml of phosphoric acid (85%), and dilute to 1 liter with water.

Sodium diphenylamine sulfonate indicator solution (0.01M). Transfer 0.32 g of barium diphenylamine sulfonate and 0.5 g of Na_2SO_4 to a 250-ml Erlenmeyer flask, add 100 ml of water, and mix well. Decant the supernatant liquid from the precipitated $BaSO_4$.

Standard potassium dichromate solution (0.1N). Transfer 4.904 g of $K_2Cr_2O_7$ (National Bureau of Standards Standard Sample 136) to a 1-liter volumetric flask, dissolve in a little water, dilute to the mark, and mix well.

Procedure

Add 10 ml of diluted hydrochloric acid (1+1) to the beaker containing the dried residue from the third fraction containing the iron. Cover the beaker, and warm until a clear solution is obtained. Dilute to about 25 ml with hot water and add five drops of $KMnO_4$ solution and stir. Heat to boiling, and boil gently for a few minutes to expel free chlorine. Add stannous chloride solution dropwise and with good stirring, until the color of the ferric chloride is discharged, and then 1 or 2 drops (no more) in excess. Wash down the inside of the beaker and cover glass, and quickly cool in ice water. Add, at one stroke, 10 ml of saturated mercuric chloride solution, stir well, and again wash down the inside of the beaker with cool water. Allow the solution to stand for 2 to 5 min.

Dilute to 200 ml with cold water, add 20 ml of sulfuric-phosphoric acid mixture and 4 drops of indicator solution. Titrate the reduced iron with a standard potassium dichromate solution to a clear blue or blue-green end point, which should be permanent for 30 sec.

4. Results and Discussion

The results obtained on a series of synthetic solutions made to simulate some of the cobalt- and nickel-base alloys of interest are given in table 1. Nickel and iron were added as weighed portions of the high-purity metals, manganese was added as aliquots of a manganous nitrate solution prepared from high-purity manganese metal, and cobalt was added as aliquots of a cobalt chloride solution standardized by electrolysis.

The nickel and manganese values require little comment, recoveries being within the limits usually obtained in conventional methods of analysis.

The cobalt recoveries are based on a solution standardized by electrolysis and on a determination finished by electrolysis, and demonstrate the completeness of the recovery in the analytical procedure. They do not, however, indicate the accuracy of the electrolytic procedure for the determination of cobalt. To learn something of the accuracy of the electrolytic deposition method for the determination of cobalt, a batch of approximately 250 g of $Co(NH_3)_6Cl_3$ was prepared [4] from reagent grade $CoCl_2 \cdot 6H_2O$.

The salt was purified by precipitating three times from diluted hydrochloric acid (1+10), finally recrystallizing from water, and drying in a vacuum desiccator over magnesium perchlorate and soda-asbestos. Weighed portions of 3 to 5 g were assayed by reduction to metal under hydrogen in a Rose-type crucible constructed of Vycor. The average of five determinations, involving 21 g of the salt, was 22.041 percent of cobalt, compared to a calculated value of 22.046 percent of cobalt, based on the weight in air of the salt. The salt was apparently quite uniform, the individual values all being within one part in a thousand of the average. The purification process was also effective in reducing the nickel content of the original cobalt salt from 0.08 percent to approximately 0.001 percent of nickel.

Portions of the salt were converted to cobalt sulfate by solution in 20 ml of water and 20 ml of diluted sulfuric acid (1+1) and evaporation to fumes. Cobalt was deposited electrolytically from an ammoniacal ammonium sulfate-sulfite electrolyte, as usually recommended [5]. The values obtained are given in table 2, along with similar data obtained by plating the salt in ammoniacal ammonium chloride solution containing hydroxylamine hydrochloride under the conditions of the recommended procedure. The deposits from the sulfate-sulfite electrolytes are corrected for deposited sulfide sulfur, and all deposits are corrected for the cobalt remaining in the electrolyte. The latter correction was made in a suitable aliquot of the electrolyte by the Nitroso-R-photometric method. The electrolyte contained an average of 0.8 mg of cobalt with a plating current of 0.25 amp/dm², and an average of 0.6 mg of cobalt with 0.4 amp/dm².

The data demonstrate that the electrolytic method for cobalt gives high values similar to those obtained for nickel [6] and that the values obtained by deposition from the chloride solutions are the more nearly correct. The data are typical of approximately 100 determinations [11] made under both conditions from aliquots of several cobalt chloride solutions. The deposition from chloride solution eliminates the necessity for making a sulfur correction.

The recovery of iron is not entirely satisfactory as shown in table 1, the values tending to run 5 or 6 parts in a thousand low. Experiments to determine where the iron was lost in the procedure showed approximately one part in a thousand to be in the

TABLE 1.* Results obtained for nickel, manganese, cobalt, and iron by the recommended procedure on synthetic mixtures

Experiment number	Nickel			Manganese			Cobalt			Iron		
	Taken	Found	Difference	Taken	Found	Difference	Taken	Found	Difference	Taken	Found	Difference
	g	g	g	mg	mg	mg	g	g	g	g	g	g
1	0.4000	0.3998	−0.0002	10.0	10.01	0.01	0.4210	0.4212	0.0002	0.2005	0.1990	−0.0015
2	.4004	.4000	−.0004	10.0	10.02	.02	.4210	.4215	.0005	.1004	.0997	−.0007
3	.4002	.4001	−.0001	10.0	10.01	.01	.4210	.4211	.0001	.0509	.0504	−.0005
4	.0505	.0503	−.0002	10.0	9.99	−.01	.6311	.6313	.0002	.3008	.2991	−.0017
5	.0500	.0499	−.0001	10.0	9.99	−.01	.6311	.6306	−.0005	.1004	.0994	−.0010
6	.4003	.4006	.0003	10.0	10.01	.01	.4212	.4219	.0007	.2005	.1993	−.0012
7	.4004	.4007	.0003	10.0	10.02	.02	.4212	.4222	.0010	.1005	.1000	−.0005
8	.4004	.4004	.0000	10.0	10.02	.02	.4212	.4219	.0007	.0503	.0498	−.0005
9	.0506	.0508	.0002	10.0	9.95	−.05	.6314	.6314	.0000	.3004	.2993	−.0011
10	.0507	.0508	.0001	10.0	9.97	−.03	.6314	.6311	−.0003	.1000	.0994	−.0006
11	.4002	.3998	−.0004	10.0	10.04	.04	.4211	.4216	.0005	.2000	.1993	−.0007
12	.4004	.4001	−.0003	10.0	10.03	.03	.4211	.4217	.0006	.1007	.1002	−.0005
13	.4004	.4000	−.0004	10.0	10.03	.03	.4211	.4215	.0004	.0504	.0500	−.0004
14	.0500	.0500	.0000	10.0	10.03	.03	.6313	.6311	−.0002	.3006	.2995	−.0011
15	.0503	.0504	.0001	10.0	10.03	.03	.6313	.6310	−.0003	.1004	.0996	−.0008

TABLE 2. Results obtained for cobalt by the electrolysis of $Co(NH_3)_6Cl_3$

Taken		Weight of deposit	Cobalt in electrolyte	Sulfur in deposit	Cobalt found	Difference	Remarks
$Co(NH_3)_6Cl_3$	Cobalt						
g	g	g	g	g	g	g	
0.2500	0.0551	0.0555	0.0009	0.0003	0.0561	0.0010	0.25 amp/dm². Ammoniacal ammonium sulfate-sulfite electrolyte.
.2500	.0551	.0564	.0008	.0002	.0570	.0019	
2.0000	.4408	.4426	.0017	.0014	.4429	.0021	
2.0000	.4408	.4438	.0009	.0015	.4432	.0024	
3.0000	.6612	.6647	.0008	.0022	.6633	.0021	
3.0000	.6612	.6641	.0009	.0018	.6632	.0020	
0.2500	.0551	.0555	.0005	.0003	.0557	.0006	0.4 amp/dm². Ammoniacal ammonium sulfate-sulfite electrolyte.
.2500	.0551	.0562	.0006	.0003	.0565	.0014	
2.0000	.4408	.4433	.0008	.0015	.4426	.0018	
2.0000	.4408	.4438	.0007	.0017	.4428	.0020	
3.0000	.6612	.6648	.0007	.0020	.6635	.0023	
3.0000	.6612	.6646	.0006	.0020	.6632	.0020	
0.2500	.0551	.0551	.0006	----------	.0557	.0006	0.25 amp/dm². Ammoniacal ammonium chloride-hydroxylamine hydrochloride electrolyte.
.2500	.0551	.0556	.0006	----------	.0562	.0011	
1.0000	.2204	.2206	.0004	----------	.2210	.0006	
2.0000	.4408	.4415	.0006	----------	.4421	.0013	
2.0000	.4408	.4409	.0007	----------	.4416	.0008	
3.0000	.6612	.6613	.0008	----------	.6621	.0009	
3.0000	.6612	.6614	.0008	----------	.6622	.0010	
0.2500	.0551	.0554	.0006	----------	.0560	.0009	0.4 amp/dm². Ammoniacal ammonium chloride-hydroxylamine hydrochloride electrolyte.
.2500	.0551	.0554	.0004	----------	.0558	.0007	
1.0000	.2204	.2206	.0005	----------	.2211	.0007	
2.0000	.4408	.4416	.0007	----------	.4423	.0015	
2.0000	.4408	.4412	.0006	----------	.4418	.0010	
3.0000	.6612	.6616	.0006	----------	.6622	.0010	
3.0000	.6612	.6612	.0009	----------	.6621	.0009	
0.2500	[1].0551	.0552	.0003	----------	.0555	.0004	Plated, with stirring, at 1 amp/dm². Ammoniacal ammonium chloride-hydroxylamine hydrochloride electrolyte.
.2500	[1].0551	.0556	.0005	----------	.0561	.0010	
3.0000	[2].6612	.6620	.0003	----------	.6623	.0011	
3.0000	[2].6612	.6616	.0006	----------	.6622	.0010	

[1] 3-hr plating time.   [2] 7-hr plating time.

TABLE 3. Results obtained for nickel, manganese, cobalt, and iron by the recommended procedure on a synthetic mixture approximating a high-temperature alloy and on a high-temperature alloy

Sample number	Nickel			Manganese			Cobalt			Iron		
	Taken	Found	Difference	Taken	Found	Difference	Taken	Found	Difference	Taken	Found	Difference
	g	g	g	g	g	g	g	g	g	g	g	g
1	0.2071	0.2071	0.0000	0.0165	0.0165	0.0000	0.3970	0.3971	0.0001	0.0193	0.0193	0.0000
2	.2070	.2072	.0002	.0165	.0165	.0000	.3970	.3970	.0000	.0193	.0192	−.0001
3	.2072	.2073	.0001	.0165	.0166	.0001	.3972	.3977	.0005	.0193	.0194	.0001
4	.2070	.2071	.0001	.0165	.0165	.0000	.3972	.3980	.0008	.0193	.0193	.0000
High-temperature alloy	------	.2071 .2070 .2071 .2069 .2066 .2067	------		.0164 .0164 .0164 .0164 .0163 .0164	------		.4286 .4296 .4290 .4292 .4288 .4291	------		.0214 .0215 .0213 .0213 .0214 .0213	------

cobalt fraction. This loss may possibly be due to a photoreduction [1] of the iron similar to that occurring in the ether-extraction of ferric chloride, because ferrous iron is eluted sufficiently rapidly in 4 N hydrochloric acid to be collected in the cobalt fraction. The remainder was retained by the resin and could be recovered by elution after allowing the resin to equilibrate a day with the 1 N hydrochloric acid.

This slightly low recovery of iron appears to be largely due to the unfavorable diffusion characteristics [14] in the resin column. Qualitative experiments, using commercially available resins of 1- to 10-percent divinylbenzene cross-linkage, indicate the diffusion rates to be more rapid at the 2-percent divinylbenzene level. However, these resins expand and contract so much in going through the analysis cycle that the operation of this type of column is not attractive. Further, a longer column is required, as the bands move much faster under comparable conditions of acidity. The use of colloidal aggregates of the higher cross-linkage resins may be the best answer for quantitative work with this particular type of resin, if the resins can be commercially prepared to allow reasonably rapid flow rates (25 ml or more per hour per square centimeter of cross section).

The results obtained in the analysis of an S–816 type alloy are given in table 3. The values for nickel, manganese, and iron on synthetic control solutions are satisfactory, and good replication of values on the sample is evident, the iron difficulties not being serious at the percentage level of iron in this sample. The cobalt values are subject to the errors of the electrolytic method and are probably 0.5 to 0.8 mg too high as recorded.

It may be mentioned that the ferricyanide titration procedure [2, 13] may prove somewhat more attractive for the rapid determination of cobalt, particularly if good cobalt standards become available. However, it should be kept in mind that manganese interferes quantitatively in this procedure, and that chromium is a disturbing element and must usually be removed if present in any appreciable percentage. Furthermore, the ferricyanide method is limited to approximately 100- to 125-mg quantities of cobalt if good end points are to be obtained.

5. References

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