THE POLAROGRAPHIC DETERMINATION OF COBALT IN POTASSIUM IODIDE

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by
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THESIS APPROVAL SHEET

The thesis of Donald Lee Kiser, Contribution of the Graduate School, Indiana State Teachers College, Series I, Number 809, under the title--THE POLAROGRAPHIC DETERMINATION OF COBALT IN POTASSIUM IODIDE is hereby approved as counting toward the completion of the Master's Degree in the amount of 6 semester hours' credit.

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CHAPTER I

INTRODUCTION

Cobalt is found in a variety of systems. Cobalt compounds are used as pigments in enamels, glasses, and pottery. Cobalt is present in some alloys to strengthen the alloy and to provide resistance to corrosion. Some organic compounds of cobalt are used to facilitate drying of paints. Cobalt is present as a catalyst in many systems.

It is desirable to have a variety of methods of analysis for any metal, so that if one avenue of approach is blocked, another method may be utilized. This paper introduces another approach to the analysis of cobalt solutions.

Statement of the Problem

This study was undertaken to investigate some of the polarographic characteristics of cobalt in a potassium iodide supporting electrolyte and to attempt to develop a polarographic method for the determination of cobalt. The effect of each of the variables of such a procedure, such as the supporting electrolyte concentration and the maximum suppressant concentration, was to be checked to determine the optimum conditions. Attempts were to be made to make the method adaptable to both liquid and solid samples.

Cobaltous ions do not oxidize iodide ions; however, cobaltous solutions that need to be determined in practical work, often contain other metal ions, some of which oxidize iodide ions. Therefore, any method developed, to be practical, had to provide for the easy masking or the elimination of free iodine formed by oxidation.

Importance of the Study

The proposed method is simple and rapid. Consideration of the potassium iodide electrolyte for the analysis of cobalt would give the analyst greater flexibility in choosing the electrolyte best suited to a situation.

Flexibility. In polarographic work it is desirable to have a variety of methods and electrolytes available for each reducible metal, so that if one approach is blocked, another is available to be tried.

The half-wave potential of each metal varies slightly with a change in the electrolyte. Metals having waves that have close-lying or overlapping waves in one electrolyte, may be sufficiently separated in another electrolyte to allow their simultaneous determination. For example, cobalt(II) and nickel(II) have half-wave potentials that are separated by only 0.1 volt in a potassium chloride supporting electrolyte, but in a potassium thiocyanate electrolyte, there is a 0.33 volt separation, so that one wave does not interfere with the other.

In some situations, the change in half-wave potentials may be even greater. In potassium chloride, copper(II) is reduced before lead(II) and therefore small amounts of copper can be determined in large amounts of lead. On the other hand, in potassium cyanide the order of reduction is reversed. Lead is reduced before copper, permitting small amounts of lead to be determined in large amounts of copper.[1]

The use of potassium iodide as a supporting electrolyte for cobalt may produce other useful relationships.

Speed and Simplicity. A method that utilizes a potassium iodide electrolyte would be convenient to use where it is desirable to make a series of on-stream polarographic analyses of an iodide solution.

The proposed method requires fewer operations than some other polarographic methods for cobalt. When working with cobalt solutions in which some of the cobalt could be in the cobaltic state, it is necessary to convert all of the cobalt to the same oxidation state if quantitative results are to be obtained. This is usually done by adding an oxidizing or reducing agent. The added reagent must not

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[1] Walter G. Berl (ed.), Physical Methods in Chemical Analysis, Vol. III (New York: Academic Press Incorporated, 1956), p. 75.

cause interference or it must be removed before the polarogram is made.

J. I. Watters and I. M. Kolthoff used sodium perborate to form the cobaltic ammonia complex.[2] The excess perborate was removed by boiling. Watters used lead dioxide to oxidize cobaltous oxalate.[3] This process included a five minute shaking followed by filtration.

The proposed potassium iodide method eliminates the need for extra reagents to adjust the oxidation state. Any cobaltic ions are reduced to the cobaltous state by the large excess of iodide ions present.[4]

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[2] J. I. Watters and I. M. Kolthoff, Anal. Chem., 21, 1466 (1949).

[3] J. I. Watters, Ph.D. Thesis, University of Minnesota, 1943 as reported by I. M. Kolthoff and J. J. Lingane, Polarography (second edition; New York: Interscience Publishers, Incorporated, 1952), II, p. 485.

[4] H. A. Laitinen and L. W. Burdett, Anal. Chem., 23, 1268-70 (1951).

CHAPTER II

BACKGROUND INFORMATION ON POLAROGRAPHY

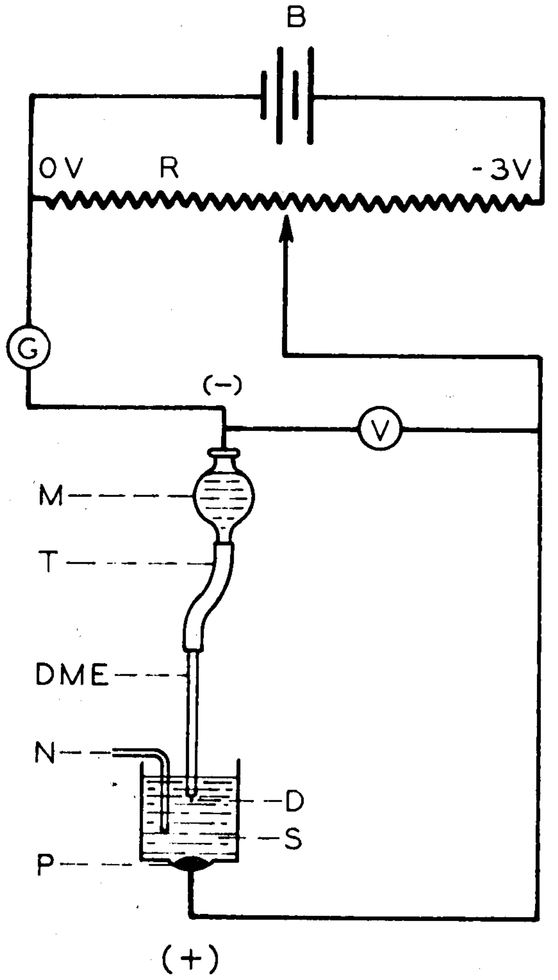
The polarograph was invented by J. Heyrovsky and M. Shikata in 1925. Heyrovsky has been the leader in the field for most of the period since then. He was awarded the Nobel Prize in Chemistry in 1959 for his efforts.

Principles

Polarography is the study of the current-voltage relationships of reducible ions in a small electrolysis cell. The reduction, or in some cases oxidation, takes place at the surface of the small mercury drops that form and fall from a small bore capillary inserted in the solution.

A simple polarographic circuit is shown in Figure 1. The circuit is designed so that any potential between zero and minus three volts can be applied between the mercury pool and the mercury drop.

Solution S contains the reducible ions. D, the mercury drop, serves as the cathode of an electrolysis cell. As the mercury drop that forms in the solution is made increasingly negative, at some potential the ions in the solution around the mercury drop begin to reduce, causing an increased current flow. As the solution in the vicinity



KEY

B	THREE VOLT BATTERY
R	SIDE WIRE RESISTER
G	GALVANOMETER
V	VOLTMETER
M	MERCURY RESERVOIR
T	FLEXIBLE TUBE
DME	DROPPING MERCURY ELECTRODE
N	NITROGEN INLET
S	SOLUTION
D	MERCURY DROP
P	MERCURY POOL

FIGURE 1
SIMPLE POLAROGRAPHIC CIRCUIT

of the drop becomes depleted in ions, other ions from the more concentrated areas diffuse into the depleted area. More reduction takes place on the mercury drop and again new ions diffuse to the depleted area. The rate of diffusion of ions into the depleted area is proportional to the concentration of the ions in the solution. Therefore, a measure of the resulting diffusion current is a measure of the ion concentration.

Each reducible ion has its decomposition potential at which reduction takes place. As the potential applied to a drop is decreased slowly from zero to minus three volts, the most easily reduced group of ions will reduce first, followed by the second most easily reduced and so on.

Some metal ions, such as ferric and cupric ions, are easily reduced and others, such as calcium and magnesium, are reduced only with difficulty. As mentioned above, the potential at which each group of ions is reduced depends, in part, on the nature of the supporting electrolyte.

Terminology

DROPPING MERCURY ELECTRODE. A glass capillary, inserted into the solution, that permits mercury flowing through it to form into small drops which fall each few seconds. The reduction of reducible ions takes place at the surface of the mercury drops.

SUPPORTING ELECTROLYTE. A solution of a salt that is neither oxidized nor reduced over the applied potential range and which is present in a high concentration in the polarographic cell to make the current due to the migration of the reducible ions negligible in size.

RESIDUAL CURRENT. The small steady current recorded before the decomposition potential is reached. A polarogram of cobalt in potassium iodide is shown in Figure 2. In this case the residual current is the part of the polarogram recorded before -0.7 volt.

LIMITING CURRENT. The high steady current recorded shortly after the decomposition potential has been passed. In Figure 2, the limiting current is recorded after -1.0 volt.

DIFFUSION CURRENT. The increase in current determined by the diffusion of reducible ions into an area near the dropping mercury electrode that is deficient in the reducible ions. The diffusion current is directly proportional to the concentration of the reducible ions. On any polarogram the diffusion current is equal to the limiting current minus the residual current.

MAXIMUM. The sharp peak sometimes recorded as the current increases from the residual current to the limiting current.

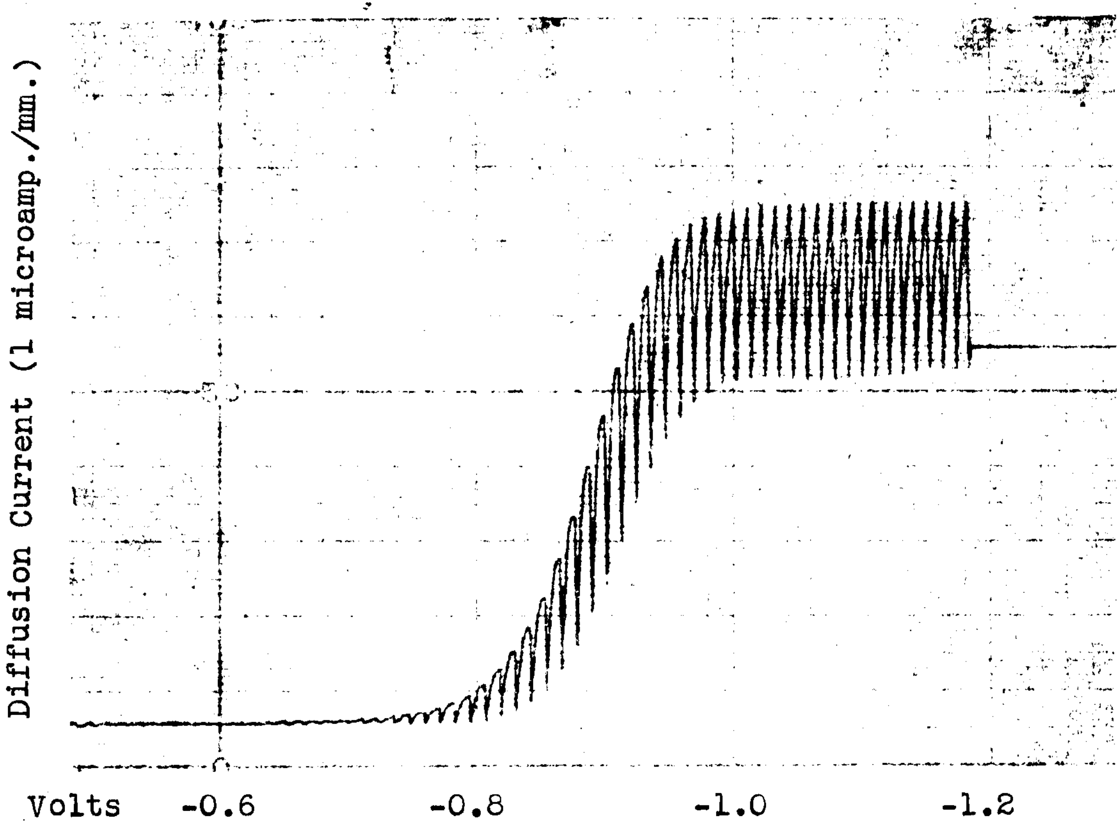


FIGURE 2

TYPICAL POLAROGRAM OF COBALT IN ONE-TENTH NORMAL POTASSIUM IODIDE

SUPPRESSANT. Any chemical that is capable of suppressing the maximum.

HALF-WAVE POTENTIAL. The potential at which the recorded current is one-half way between the residual and limiting currents.

Uses

Polarographic methods for the quantitative determination of most metals have been developed. Many organic compounds which have reducible groups can be determined also.

Polarography is best suited for dilute solutions of metal ions. Solutions of metals of 10^{-2} to 10^{-5} molar concentration can be determined directly. More concentrated solutions need to be diluted.

CHAPTER III

REVIEW OF THE LITERATURE

Hexaquo Complex

The first important work on cobalt was done by R. Brdicka in 1930.[5] From his work, Brdicka theorized that, in aqueous solutions cobalt forms the hexaquo complex, $Co(H_2O)_6^{++}$.

This theory was supported by Willis, Friend, and Mellor in their study of the polarographic reduction of some cobaltamines and related compounds.[6] They reported that the investigated amines reduced in two steps. The first step corresponded to the reduction and disruption of the cobaltic complex to form the hexaquo complex. The second step resulted from the reduction of the hexaquo complex to cobalt. They found that the half-wave reduction potential of the first wave varied from compound to compound. However, the second wave always had the same half-wave potential when the supporting electrolyte remained the same, supporting the theory that the same complex was

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[5] R. Brdicka, Collection Czechoslov. Chem. Commun., 2, 489, 545 (1930); 3, 396 (1931), as reported in I. M. Kolthoff and J. J. Lingane, Polarography (New York: Interscience Publishers, Incorporated, 1941), p. 284.

[6] J. B. Willis, J. A. Friend, and D. P. Mellor, J. Am. Chem. Soc., 67, 1680-83 (1945).

responsible for the second wave of each compound.

Effect of Electrolyte Concentration

These authors found that the concentration of the supporting electrolyte had some effect on the half-wave potential.

Brdicka found that when large concentrations of chloride ion were added to his cobalt solution, the half-wave potential shifted to more positive values and the slopes of the waves increased.[7] He reported that cobalt was then in the chloro complex, $Co(H_2O)_2Cl_4^{--}$, rather than in the hexaquo complex.

Willis, Friend, and Mellor found the half-wave potential of the hexaquo complex to be -1.208 volts (versus the saturated calomel electrode) in one-tenth normal potassium sulfate and -1.428 volts in one normal potassium sulfate.[8] That is, they found a shift of the half-wave potential in the negative direction with an increase in the potassium sulfate concentration.

Cobalt and Nickel Separations

Cobalt(II) and nickel(II) frequently need to be

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[7] Brdicka, *loc. cit.*

[8] Willis, Friend, and Mellor, *loc. cit.*

[9] S. P. Shaikind, *J. Appl. Chem.*, *(U.S.S.R.)*, *18*, 322-28 (1945), as reported in *Chem. Abstr.*, *40*, 3362 (1946).

determined in the same solution. In 1941, J. J. Lingane and H. Kerlinger found that the two metals have close-lying half-wave potentials in a one normal potassium chloride electrolyte. Since there was only a one-tenth volt difference in the waves, neither metal could be determined satisfactorily in the presence of the other. In their search of other supporting electrolytes, they found that a one normal ammonium chloride-ammonium hydroxide electrolyte gave a 0.18 volt separation, while one normal potassium chloride in the presence of five-tenths molar pyridine gave a 0.29 volt separation.[10] They obtained a good separation of the metals' waves in a one normal potassium thiocyanate electrolyte. The difference in half-wave potentials was 0.33 volt. However, the authors recommended that the potassium chloride-pyridine electrolyte be used, for the thiocyanate caused irregularities in the diffusion current.

They reported that small amounts of copper do not interfere, but large amounts, if present, must be removed.

Latest Improvements on Cobalt Methods

A. J. Eve and E. T. Verdier got a good separation of cobalt and nickel in a sodium fluoride electrolyte.[11]

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[10] J. J. Lingane and H. Kerlinger, Ind. Eng. Chem., Anal. Ed., 13, 77-80 (1941).

[11] A. J. Eve and E. T. Verdier, Anal. Chem., 28, 537 (1956).

They reported the fluoride electrolyte to be more suitable and more pleasant to use than pyridine. However, a considerable waiting period was required. A forty-eight hour waiting period gave the best results, although a period of forty-five minutes gave satisfactory results. The precision of the method was reported to be of the order of 4 to 5 per cent.

The Kolthoff and Waters procedure, using sodium perborate to oxidize cobalt to the cobaltic state, was mentioned earlier. Louis Meites noted that it took considerable time to rid the solution of perborate and then to cool the solution.[12] He chose to oxidize all of the cobalt to the cobaltic state by using potassium permanganate in an ammoniacal ammonium chloride solution. He then destroyed the permanganate by adding excess hydroxylammonium sulfate. No heating was required. He reported that the results should be reproducible to within about plus or minus 5 per cent.

Resorcinol

Resorcinol, one of the reagents of the method proposed in this thesis, is not reduced at the dropping

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[12] Louis Meites, Anal. Chem., 28, 404 (1956).

mercury electrode, according to Kolthoff and Lingane.[13]

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[13] I. M. Kolthoff and J. J. Lingane, Polarography (second edition; New York: Interscience Publishers, Incorporated, 1952), II, p. 705.

CHAPTER IV

MATERIALS USED AND TECHNIQUE

Apparatus

POLAROGRAPH, Sargent Model XXI, automatic recording.

ELECTROLYSIS VESSEL, Sargent No. S-29385, two-piece type, using a mercury pool anode.

Reagents

COBALTOUS ACETATE, containing 1 mg. Co(II) per ml., prepared by dissolving 2.113 g. of C.P. cobaltous acetate tetrahydrate in water and diluting to 500 ml. This cobalt concentration equals about 1.7 x 10^{-2} molar.

POTASSIUM IODIDE, 1 M, prepared by dissolving 16.6 g. of A.C.S. Reagent grade potassium iodide in water and diluting to 100 ml.

RESORCINOL, 0.1 M, prepared by dissolving 1.1 g. of U.S.P. Recrystallized grade resorcinol in water and diluting to 100 ml. This reagent is used only if copper(II) or other oxidizing agents are present to oxidize iodide ions.

GELATIN, 0.5 per cent, prepared by putting 0.5 g. of Knox brand unflavored gelatin in about 75 ml. of water and letting stand for 15 minutes; then heating gently on a steam bath to make a clear solution. The clear solution was diluted to 100 ml. with water. Fresh gelatin solution was prepared every two days, or every three days when the solution was stored in the refrigerator.

NITROGEN, high purity, dry.

Technique

Solutions to be polarographed were usually one-tenth normal in potassium iodide and were ten milliliters in volume. Each solution was deaerated with a stream of nitrogen, then an eye dropper was used to add about ten drops of mercury to form a pool for the anode at the bottom of the polarographic cell. Next, the dropping mercury electrode was inserted and a polarogram recorded between -0.4 and -1.4 volts as described below.

The instrument was set to span two volts, starting at zero. The bridge was adjusted to apply 20 per cent of the span voltage, or -0.4 volt. The instrument and recorder were then turned on and the bridge allowed to advance automatically to the 70 per cent span voltage position, or -1.4 volts. At that point the polarogram was terminated. This technique provided a recorded polarogram on chart paper on which each major division represented two-tenths volt.

After it was determined that cobalt gave a reduction wave in potassium iodide, the variables of the system were checked, one at a time.

It was found that large amounts of iodine interfere. Heat and the reagents ascorbic acid and resorcinol were checked to determine the feasibility of using one of them for the removal of iodine.

The developed procedure for the determination of cobalt and the effects of the variables are given below.

CHAPTER V

PREPARATION OF THE CALIBRATION CURVE AND THE DETERMINATION OF COBALT SAMPLES

Preparation of the Calibration Curve

The following solutions are required.

(1) 1000 micrograms (1 mg.) of cobalt(II) per ml., prepared as directed under Reagents, page 16.

(2) 100 micrograms of cobalt per ml., prepared by diluting 10 ml. of (1) to 100 ml.

(3) 10 micrograms of cobalt per ml., prepared by diluting 1 ml. of (1) to 100 ml.

To each of the aliquots of the solutions listed in Table I, add 1 ml. of the potassium iodide solution plus 0.2 ml. (or four drops) of the gelatin solution. Then dilute to 10 ml. Shake the solution briefly, then pour into the polarographic cell. Bubble nitrogen through the solution for about eight minutes, then polarograph between -0.6 and -1.3 volts.

Make plots of cobalt concentration versus diffusion current (in this case, wave height multiplied by the current sensitivity factor selected on the polarograph). Plots of 0 to 100, 0 to 1,000, and 0 to 10,000 micrograms of cobalt are convenient. For a small number of analyses, a smaller number of standard solutions covering a more limited range

TABLE I

DILUTIONS OF STANDARD SOLUTIONS TO USE FOR PREPARING CALIBRATION SOLUTIONS

For Standard (micrograms)	Use Ml.	of Solution
30	3	(3)
60	6	(3)
100	1	(2)
300	3	(2)
600	6	(2)
1,000	1	(1)
3,000	3	(1)
6,000	6	(1)
8,000	8	(1)

can be used.

Record the mercury height to the nearest one-tenth centimeter. Readjust the mercury to that height before cobalt determinations are made. The calibration curve should be valid until the dropping mercury electrode used for calibration is damaged or exchanged.

Procedure for Cobalt Samples

Solid Samples. Determine the approximate sample size to use from Table II. Weigh the sample and put it into an appropriate size evaporating dish. Dissolve the sample in a minimum amount of dilute hydrochloric acid. Evaporate to dryness on a steam bath.

Take up the green residue with two to three milliliters of water and transfer to the appropriate size volumetric flask. Rinse with two other approximately 1 ml. portions of water. Make a dilution if necessary. Place the appropriate size aliquot into a 10 ml. volumetric flask. Add 1 ml. of the potassium iodide solution and 0.2 ml. (or four drops) of the gelatin. Dilute to 10 ml. with water, shake the solution briefly and pour the contents into the polarographic cell. Deaerate by bubbling nitrogen through the system for about eight minutes, then polarograph between -0.6 and -1.3 volts.

TABLE II

SUGGESTED DILUTIONS FOR SOLID SAMPLES

Per cent cobalt in sample	Sample Weight	Dilute to	From the dilution use
3.0 - 30	0.5 g.	100 ml.	1 ml.
0.3 - 3.0	0.5 g.	10 ml.	1 ml.
0.03 - 0.3	1.0 g.	no dilution	entire sample
below 0.03	1 to 5 g.	no dilution	entire sample

Liquid Samples. Weigh the size sample determined from Table III and make any necessary dilution. Place an aliquot into a 10 ml. volumetric flask. Add 1 ml. of potassium iodide and 0.2 ml. (or four drops) of gelatin. Dilute to 10 ml. with water and polarograph as directed for solid samples.

Irregular Samples. Liquid samples may contain reducible organic components. If any abnormalities occur on or near the cobalt wave, the liquid sample should be evaporated to dryness according to the procedure given for solid samples.

Samples may contain components that oxidize some of the electrolyte to iodine. Small amounts of iodine do not interfere. If large amounts of iodine are formed and the charging current of each drop of mercury is large, prepare a new sample adding 1 ml. of the resorcinol solution before dilution of the aliquot to 10 ml.

If resorcinol is used in the procedure, a separate calibration curve should be prepared, using 1 ml. of resorcinol in each calibration solution.

If only a small number of samples having large amounts of iodine are to be run, the iodine can be removed by heating the solutions on a steam bath until the dark yellow color fades. Samples prepared in this manner can be determined by using the initial calibration curve described above.

TABLE III

SUGGESTED DILUTIONS FOR LIQUID SAMPLES

Per cent cobalt in sample	Pipet then Weigh	Dilute to	From the dilution use
3.0 - 30.0	1 ml.	100 ml.	1 ml.
0.3 - 3.0	1 ml.	10 ml.	1 ml.
0.03 - 0.3	1 ml.	no dilution	entire sample
below 0.03	1 to 5 ml.	no dilution	entire sample

CHAPTER VI

EFFECTS OF VARIABLES, DIFFUSION CURRENT LINEARITY, AND OTHER OBSERVATIONS

Effect of the Electrolyte Concentration on the Diffusion Current and the Half-wave Potential

Four solutions were prepared, containing identical concentrations of cobalt. The potassium iodide concentration varied from 0.05 M in the first to 0.6 M in the fourth. All solutions contained 1 ml. of 1.00×10^{-2} M cobalt, x ml. of 1.00 M potassium iodide, 8.9-x ml. of water, and 0.1 ml. of gelatin solution. The diffusion currents and the half-wave potentials of the solutions are given below.

Ml. KI added	Electrolyte Molarity of the Solution	Wave Height (mm.)	Half-wave Potential (v.)
0.5	0.05	85.2	-0.89
1.0	0.10	85.6	-0.90
3.0	0.30	85.4	-0.84
6.0	0.60	85.8	-0.82

The concentration of the supporting electrolyte has little, if any, effect on the diffusion current. The variances in the wave height were well within experimental error. The half-wave potential shifted in the positive direction with increasing iodide concentration; however, the shift does not affect the quantitative results.

Deaeration Time

Dissolved oxygen in a solution will reduce at the dropping mercury electrode. Oxygen reduces in two waves, the second being at -0.9 volt. Since cobalt also reduces near that potential, dissolved oxygen must be removed.

A 10 ml., 1.00×10^{-3} M solution of cobalt was deaerated for the following times with nitrogen (at about fifty bubbles in fifteen seconds) and the resulting wave heights measured.

Deaeration Time (minutes)	Wave Height (mm.)
0	116
3	91.6
6	88.6
13	89.0

Ninety per cent of the oxygen was removed in three minutes and the deaeration was quantitatively complete in six minutes. A slightly longer time should be allowed for more dilute solutions.

Gelatin Concentration

Equal volumes of identical concentrations of cobalt solutions in 0.1 N potassium iodide contained the below listed amounts of five-tenths per cent gelatin solution.

From the figures given it is seen that the addition of gelatin to cobalt solutions, decreases the diffusion current to a slight extent. The results for all these concentrations were reproducible within experimental error.

Ml. of 0.5% Gelatin	Gelatin Concentration	Wave Height
0.0	0.0 %	85.4 mm.
0.1	0.005	84.8
0.2	0.01	84.8
0.4	0.02	83.6
1.0	0.05	82.8

Diffusion Current Linearity

The procedure previously given for the preparation of a calibration curve was used to prepare the concentrations of cobalt given in Table IV. All solutions were identical except for cobalt concentration.

The waves for the ten and twenty microgram solutions were not distinct enough to give reproducible results. Thirty micrograms was the lowest concentration for reliable results.

The diffusion current values for cobalt quantities above thirty micrograms increased with an increase in the cobalt concentration but not quite linearly. When diffusion current was plotted against cobalt concentration, the plot was essentially a straight line. However, since the

TABLE IV

COBALT CONCENTRATION - DIFFUSION CURRENT RELATIONSHIPS IN ONE-TENTH NORMAL POTASSIUM IODIDE

Micrograms of Cobalt in 10 ml.	Diffusion Current (Wave height times current sensitivity) (microamperes)
10	0.131 (indistinct)
20	0.228 (indistinct)
30	0.390
60	0.782
100	1.32
200	2.73
500	7.04
1,000	13.9
2,000	27.4
3,000	41.8
4,000	57.5
6,000	90.0
8,000	116.8

diffusion current was not quite linear, a calibration curve would need to be used for the best results on cobalt analyses, especially for the higher cobalt concentrations.

The reproducibility of Table IV values was checked two days later.

Micrograms of Cobalt	Table IV Diffusion Current Values	Diffusion Current of Check Solutions
60	0.782 microamp.	0.774 microamp.
100	1.32	1.33
1,000	13.9	13.9

Even though the diffusion current is not directly proportional to the cobalt concentration, the results are closely reproducible.

Effect of Resorcinol Concentration on the Diffusion Current

The following amounts of one-tenth molar resorcinol solution were present in otherwise identical 10 ml. solutions of cobalt in potassium iodide.

Ml. Resorcinol	Resorcinol Concentration	Diffusion Current (mm.)
0	0.0 M	84.0
1	0.01	90.2
2	0.02	120.0
4	0.04	134.2
6	0.06	137.0

The diffusion current increased rapidly with an increase in resorcinol concentration. For solutions above 0.04 M in resorcinol, the rise in diffusion current was not so rapid and appeared to be leveling off for concentrations above 0.06 M. Solutions above this value were not tried because the waves tended to become distorted the higher the concentration of resorcinol.

This enhancement of the diffusion current by resorcinol makes it necessary to prepare a new calibration curve when resorcinol is to be used in the cobalt solutions.

Linearity of Diffusion Currents With Concentration of Solutions Containing Resorcinol

Calibration solutions of cobalt were prepared as described previously, except 1 ml. of 0.1 M resorcinol was added before the solutions were diluted to 10 ml. The diffusion currents are listed in Table V.

The ten microgram solution gave a very poor wave. The diffusion currents of these solutions deviated more from linearity than did the diffusion currents of normal cobalt solutions. The solution of 6,000 micrograms gave a smaller diffusion current than expected.

When solutions are to contain resorcinol, the cobalt concentration should be limited to between sixty and one thousand micrograms in a 10 ml. solution.

TABLE V

COBALT CONCENTRATION - DIFFUSION CURRENT RELATIONSHIPS IN SOLUTIONS CONTAINING RESORCINOL

Micrograms of Cobalt in 10 ml.	Diffusion Current (Wave height times current sensitivity)
10	indistinct
60	0.835 microamp.
100	1.42
600	8.90
1,000	14.9
6,000	77.0

Interfering Agents

Metals which oxidize iodide ions or reduce polarographically before cobalt will interfere if present in more than small amounts. Copper(II), such an interfering agent, was used to obtain an estimate of tolerance permitted. To 1 ml. of 1.00 x 10^{-2} M cobalt was added 0.1 ml. of gelatin solution and varying amounts of 1.00 x 10^{-2} M cupric chloride solution. The solutions were diluted to 10 ml. and the diffusion currents determined.

Ml. of Copper(II) Solution	Diffusion Current (mm.)
0.0	84.8
0.1	84.7
0.4	84.3
0.8	84.4
1.0	83.0

Precipitation of cuprous iodide was observed. The diffusion current values decreased slightly with increasing copper concentration. The quality of the wave decreased with increased copper concentration. The maximum amount of cupric chloride tolerable was near equal that of the cobalt concentration.

Acidity of the Solution

Runs were made of cobalt in solutions buffered at the pH values 4, 5, 6, 7, 8, and 10. The solution buffered at pH 4 gave no cobalt wave. A rapidly rising current developed in the cobalt reduction region, but did not level off. This may have been due to hydrogen discharge.

The solution buffered at pH 5 showed this rapidly rising current, but it appeared after the cobalt reduction. At pH 6, the interfering current was even farther removed.

The diffusion current of the cobalt solution buffered at pH 8 was much lower than the diffusion currents at pH 6 and 7. At pH 10, no diffusion current was indicated. The polarogram appeared as a simple residual current.

The wave of best quality appeared to be obtained between pH 6 and 7. To more completely evaluate the effect of the solution acidity, Sorensen's phosphate buffer solutions of pH 6.47, 6.64, 6.81, and 6.98 were prepared.[14] Cobalt samples run with these buffers produced better wave quality as pH 7 was approached. However at the higher pH values, as the concentration of cobalt was increased, some cobalt was precipitated, probably as cobaltous phosphate.

Solutions of 10^{-3} M cobaltous acetate in one-tenth normal potassium iodide have a pH of about 4.7, and develop

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[14] Wendell M. Latimer and Joel H. Hildebrand, Reference Book of Inorganic Chemistry (third edition; New York: The Macmillan Company, 1955) p. 564.

good quality waves. Solutions buffered near pH 4.7 with a sodium acetate-acetic acid buffer and at the pH values 4, 5, and 6 with commercial buffers gave poor waves. It was concluded that the reagents in the buffer solutions were affecting the cobalt reduction wave. Since unbuffered cobalt solutions gave near linear diffusion currents, buffered solutions were not investigated further.

Other Observations

Occasionally, during the study of cobalt solutions, the half-wave potential would appear at about -1.4 volts instead of the regular -0.9 volt potential. The cause of this shift was not found. On one occasion, merely bubbling more nitrogen through the solution caused the wave to reshift to its normal position.

Besides resorcinol, heat and ascorbic acid were tried as means of removing large amounts of iodine. Solutions heated on a steam bath had iodine removed to a satisfactory degree, but each sample required a considerable time. Samples containing ascorbic acid had the iodine rapidly removed, but when polarographed the limiting current was not level and the wave was distorted.

Alpha-naphthol was tried as a maximum suppressant, with fair results, but gelatin, when present in equal concentration, was the more efficient suppressant.

Nickel and cobalt, both 1.0×10^{-4} M, were run in an electrolyte one molar in potassium iodide and five-tenths molar in pyridine. The maximum was suppressed with gelatin. The half-wave potential of nickel in this electrolyte was -0.40 volt and that of cobalt was -0.74 volt. The nickel wave was not steep, but both waves were well defined and sufficiently separated for quantitative determination of each.

CHAPTER VII

DISCUSSION

As mentioned in Chapter III, cobaltous cobalt is believed to form the hexaquo complex in aqueous solutions and this complex usually reduces in the -1.2 to -1.4 volt range. Therefore one would expect cobalt in the potassium iodide electrolyte to reduce somewhere near one of these potentials.

Usually cobaltous solutions in the one-tenth normal potassium iodide used in this work reduced at about -0.9 volt. Occasionally, the system responded quite differently and the half-wave potential of cobalt shifted to -1.4 volts. It may be that the hexaquo complex is occasionally formed in the potassium iodide and in those cases is reduced at -1.4 volts. A different complex may be present when the usual reduction potential of -0.9 volt is observed.

The cause or conditions of the cobalt reduction at -1.4 volts was not determined. When the late reduction was first experienced, it was believed to be due to the use of stale gelatin. This probably was not the case, since the unusual system could be upset, sometimes by just adding a little more of one of the reagents, such as one milliliter of one normal potassium iodide or a few drops of additional gelatin. On at least one occasion the wave shifted from

-1.4 volts to the usual -0.9 volt after nitrogen had been allowed to pass through the solution for about a minute.

It was considered that the polarograph or the recorder could be not functioning properly when the unusual reduction potential of cobalt was observed. This was checked by making runs of cobalt in a one-tenth normal potassium chloride solution. The half-wave potential was recorded then at -1.4 volts, which is the normal potential in that electrolyte. From this it was concluded that the cause of the shift must be a chemical change in the solution.

The -1.4 volts half-wave potential was noted most frequently over a period of three or four days and then most often on solutions of relatively high concentrations of cobalt, about 5 x 10^{-3} molar. The fact that it was observed most frequently over a short period of time suggests that the result may have been caused by one of the reagents used during that period. Since it was noted at higher concentrations, it may be that when in the presence of excess complexing agent, such as iodide ions, the cobalt formed one complex, but when the complexing agent was in a lesser proportion to cobalt, the cobalt formed the hexaquo complex.

Because the complex that reduced at -1.4 volts could not be formed at will, its nature was difficult to study.

Cobalt in one-tenth normal potassium iodide supporting electrolyte produces a diffusion current that is not quite linear with concentration. In electrolytes, such as potassium chloride, in which the diffusion current is directly proportional to the concentration, only one standard solution needs to be run before an unknown can be determined. With potassium iodide electrolyte, the one-standard method of calibration is not usable. Even so, this is not a big disadvantage, for good results can be obtained using a correctly prepared calibration curve.

Nickel and cobalt are well separated in the potassium iodide-pyridine electrolyte mentioned previously. The waves were well defined and were separated by 0.34 volt, which is 0.01 volt better separation than the potassium thiocyanate electrolyte used by J. J. Lingane and H. Kerlinger and 0.05 volt better than the potassium chloride-pyridine electrolyte that they recommended for the separation of the two metals.[15]

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[15] See p. 13.

CHAPTER VIII

SUMMARY

It is desirable to have a variety of methods of analysis for any metal, so that if one avenue of approach is blocked, another method may be utilized. This work was undertaken to investigate some of the polarographic characteristics of cobalt in a potassium iodide electrolyte and to attempt to develop a polarographic method for the determination of cobalt.

The half-wave potential of each metal varies slightly with a change in the electrolyte. In some cases, even the order of reduction of two metals may be reversed with an electrolyte change. Therefore the use of potassium iodide as an electrolyte would offer greater flexibility to those confronted with cobalt and other metal analyses.

The potassium iodide method is faster and simpler than some extablished cobalt methods. No preliminary adjustment of the oxidation state is required. The iodide ions in the electrolyte reduce any cobaltic ions to the cobaltous state.

A system was developed that is capable of determining from thirty to eight thousand micrograms (eight milligrams) of cobalt in ten milliliters of a one-tenth normal potassium iodide supporting electrolyte. Gelatin was used as a maximum suppressant.

The diffusion current was not directly proportional to the cobalt concentration, being higher than expected at higher concentrations of cobalt. However the diffusion currents were reproducible, so that good results could be obtained on unknown cobalt samples if a calibration curve was used.

Metal ions that oxidize iodide ions to iodine cause interference if present in more than small amounts. Resorcinol can be used to remove iodine from such systems, but a separate calibration curve must be prepared with standard solutions containing resorcinol if quantitative results are to be obtained. If resorcinol is used in the solution, the cobalt concentration should be limited to between sixty and one thousand micrograms in a ten milliliter solution.

Nickel and cobalt have close-lying waves in most electrolytes. These two metals were run in an electrolyte one molar in potassium iodide and five-tenths molar in pyridine. The waves of both metals were well defined and separated by 0.34 volt, which should be sufficient for the quantitative determination of each.

The potassium iodide electrolyte should reveal other interesting relationships.

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