# COULOMETRIC DETERMINATION OF NICKEL AND COBALT

by

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Nickel and cobalt have very similar electrochemical characteristics, and no satisfactory method has previously been described for their electrolytic separation by reduction to the metallic state. BALACHOWSKY<sup>1</sup> attempted the deposition of nickel on a platinum cathode in the presence of cobalt from a buffered thiocyanate solution but the results were far from satisfactory. The usual electrolytic method for separating the two elements, originated by COEHN AND GLÄSER<sup>2</sup> and improved by TORRANCE<sup>4</sup>, involves anodic deposition of the cobalt as cobaltic oxide. However, the latter is invariably contaminated with nickel, and in accurate work the first deposit must be dissolved and the separation repeated. The variable composition of the cobaltic oxide deposit precludes direct weighing, so that the second deposit must be dissolved and the cobalt finally deposited as the metal. More recently NENADKEVICH<sup>7</sup> reported the electrolytic separation of nickel and cobalt from an alkaline cyanide solution. Nickelic oxide deposits on the platinum anode and the cobalt is held in solution as cobalticyanide ion. As with cobaltic oxide the composition of the nickelic oxide deposit is variable, so that it must be dissolved and its nickel content determined by one of the standard methods.

The fact that in thiocyanate or pyridine media  $\pm 2$  nickel and  $\pm 2$  cobalt yield well separated polarographic waves for reduction to the metals<sup>5</sup> prompted this investigation of their separation and coulometric determination on the macro scale by controlled potential electrolysis with a mercury cathode using an aqueous pyridine electrolyte.

## EXPERIMENTAL TECHNIQUE

The electrolysis cell (100 ml capacity and mercury cathode area of 20 cm<sup>2</sup>) was the same as that described by  $LINGANE^4$ . A constant speed (600 r.p.m.) mechanical stirrer was used, with the stirring blades adjusted to keep the mercury-solution interface in rapid but smooth motion. The cell was closed with a Bakelite cover, and dissolved oxygen was removed from the solution with a stream of nitrogen.

Two types of anode, immersed directly in the test solution, were used; a silver anode with either chloride or bromide as depolarizer, and a platinum anode with hydrazine as depolarizer<sup>4</sup>. The silver anode (area 103 cm<sup>2</sup>) was essentially the same as in previous studies<sup>4</sup>. The platinum anode (area 75 cm<sup>2</sup>) was a gauze cylinder, mounted vertically and coaxially with the stirrer shaft.

A potentiostat<sup>4</sup> was used to maintain automatically the potential of the mercury cathode at a constant value against a saturated calomel reference electrode.

The quantity of electricity passed was measured with a hydrogen-oxygen coulometer<sup>4</sup> when the initial current was larger than about 30 milliamp. With smaller initial currents it was found that the hydrogen-oxygen coulometer was subject to a significant negative error. Therefore, when small

quantities (less than *ca.* 20 mg) of metal were determined the quantity of electricity passed was measured with a gravimetric silver coulometer. The electromechanical integrator described by LINGANE AND JONES<sup>6</sup> may be used, and it is more convenient than either the gas or silver coulometers.

The technique of the determinations was as follows. The supporting electrolyte alone was placed in the cell, dissolved air was removed with purified nitrogen, and the solution was subjected to a preliminary electrolysis with the potential of the mercury cathode at ---1.20 V vs. S.C.E. to remove traces of reducible impurities. The preliminary electrolysis was continued until the background current decreased to a constant minimal value, which usually required 30 to 60 minutes. The potentiostat was then set to maintain the potential of the cathode at the value to be used in the determination (--0.95 V vs. S.C.E. for nickel and --1.20 V for cobalt), the sample solution was added, and electrolysis was allowed to proceed under automatic control until the current decreased to a constant minimal value. The total quantity of electricity passed, the electrolysis time, and the final current were noted.

Correction for the quantity of electricity associated with the background current was applied by subtracting the product of the final current (amperes) and the electrolysis time (sec) from the total number of coulombs indicated by the coulometer. The background current probably results from reduction of hydrogen ion, and this method of correction assumes that it is constant throughout the electrolysis.

The quantity of metal deposited W was calculated from the relation

$$W = \frac{M(Q - i_b t)}{2F}$$

where M is the atomic weight, Q the total quantity of electricity (coulombs) indicated by the coulometer,  $i_b$  the final background current (amp), t the electrolysis time (sec), and F is the faraday.

Standard solutions of nickelous chloride and cobaltous chloride were prepared from the purest commercially available salts. The nickel solution was standardized by the dimethylglyoxime method, and the cobalt solution by oxidation to cobaltic oxide with hydrogen peroxide in alkaline medium and iodometric assay of the +3 cobalt. The significant amounts of nickel impurity in the cobalt salt and cobalt impurity in the nickel salt were determined by polarographic methods,<sup>3,5</sup> and the appropriate corrections were applied. The pyridine used (Mallinckrodt Analytical Reagent) was redistilled, and the middle fraction

The pyridine used (Mallinckrodt Analytical Reagent) was redistilled, and the middle fraction boiling within a 2° range was collected.

## RESULTS AND DISCUSSION

The optimum control potentials for the deposition and separation of nickel and cobalt were established by determining the deposition potentials polarographically with the dropping mercury electrode. Polarograms were recorded in the usual manner with a polarograph at a relatively low sensitivity, and the deposition potential was measured by extrapolating the nearly linear steeply rising part of the c.v. curve back to intersection with the residual current.

The deposition potentials (at a metal ion concentration of ca. 0.02M) were determined over a wide range of pH in an electrolyte containing IM total pyridine and 0.5Mchloride ion (added as either hydrochloric acid or potassium chloride). The potentials at which reduction of the supporting electrolyte occurred were also determined.

As shown in Fig. 1, the deposition potentials of both metals are practically constant over the pII range from 4 to 9. In neither case does the reduction of the pyridine-metal ion complex proceed reversibly; if it did the deposition potential would shift to a more negative value with increasing pH because of the increasing concentration of free pyridine. At a pII below about 4 complexation with pyridine is prevented by the conversion of the latter to pyridinium ion ( $pK_a$  for pyridinium ion is 5.4). The abrupt negative shift of the deposition potential of cobalt at pH = 3.5 is simply a manifestation of the well known fact that the overpotential required for the discharge of aquo cobaltous ion is larger than that for the cobaltous-pyridine complex.

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Fig. 1. Deposition potentials of nickel and cobalt at a mercury cathode from aqueous pyridine medium as a function of pH.

From these data a potential of -0.95 V vs. S.C.E. was selected as optimum for the separation of nickel from cobalt over the entire pH range. A potential of -1.20 V is satisfactory for the deposition of cobalt without interference from reduction of the supporting electrolyte.

# Results with silver-silver chloride auxiliary anode

Typical performance data obtained with the silver-silver chloride auxiliary electrode are shown in Tables I and II. Exactly similar data were obtained in a series of experiments with a silver-silver bromide auxiliary electrode, and in another series using a divided cell like that on p. 371 of Reference 4.

The chief factor limiting the precision of these determinations, and the smallest quantity of the metals it is feasible to determine, is the appreciable background current

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TABLE I

SEPARATE DETERMINATIONS OF NICKEL AND COBALT WITH SILVER-SILVER CHLORIDE ANODE

Nickel at									
pH	Nickel laken mg	Initial current m.1	Resulual current m.l	Time min	Total coulombs	Nickel Jound mg	Error mj		
5.3	208.6	250	.4.2	165	7239	207.5	I . I		
5.3	104.3	1.10	1.8	150	359.8	104.5	0.2		
5.3	10.4.3	175	2.7	150	368.1	10.1.6	0.3		
5.3	104.3	160	38	162	383 6	105.4	1.1		
5.3	20.9	66	2.7	105	86.4	21,1	0.2		
5.3	20.9	67	1.6	120	78.0	20.2	0.7		
6.6	104.3	250	2.6	1 50	367.2	10.4.6	0.3		
7.9	104.3	230	1.5	120	354.4	104.5	0.2		
<u>9.0</u>	104.3	1.10	2.2	120	358.1	104.1	0.2		
9.3	104.3	1.48	4.3	157	386.3	105.2	0.9		
							Av. $\pm 0.5$		
		····	Cobalt al -	-1.20 V vs. S	.C.E.				
pН	Cobalt taken mg	Initial current m.1	Residual current mA	Time min	Total coulombs	Cobalt found mg	Error m		
5.3	102.9	130	2.8	17.1	4.10.7	125.7	22,8		
5.3	102.9	170	2.8	120	387.0	112.0	9.1		
5.4	102.9	170	2.2	150	395.9	114.9	12.0		
Ğ.4	102.9	220	2.5	150	359.7	103.0	0,1		
7.4	102.9	230	1.7	180	355.0	102.8	0,1		
9.2	102.9	230	2.8	120	356.I	102.6	0.3		
9.2	51.5	175	3.9	120	198.6	52.1	0.6		
9.2	20.6	83	2.4	120	87.0	21.3	• 0.7		

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Electrolyte 1.00 $M$ total pyridine, 0.50 $M$ chloride Electrolysis at0.95 V vs. S.C.E. for nickel and at 1.20 V vs. S.C.E for cobalt									
	p11	Nickel taken mg	Nickel Jound mg	Error mg	Cobalt taken mg	Cobalt found mg	Error mg		
ı	9.0	104.6	105 3	0.7	:03.3	103.1	O, 2		
2	9.1	10,4,0	105.2	0.6	103.3	103 7	0.4		
4	9.0	104.0	10.4.3	- 0.3	103.3	10.4 2	0.9		

TABLE II

due to reduction of the supporting electrolyte. From experiments in which the gain in weight of the silver anode was compared with the quantity of electricity passed, it was established that about one-half the background current results from the reduction of the constant small concentration of dissolved silver present in the solutions. From the known polarographic behavior of pyridine,<sup>3</sup> the remainder probably results from a catalyzed reduction of hydrogen ion at pII values below about 6 and from reduction of pyridine at higher pII's.

As explained above, correction for the background current was applied by assuming that the background current during the entire electrolysis was the same as the final residual current; *i.e.*, that the background current was not influenced by the metal deposition. The results in Table I demonstrate that this assumption is valid in the case of nickel over the entire pH range, but with cobalt it is valid only when the pH is greater than about 6. At pH values less than 6 the background current while cobalt is being deposited evidently is considerably greater than at the end of the electrolysis. Cobalt is insoluble in mercury, and apparently the hydrogen overpotential on the freshly deposited metal is significantly smaller than after the metal deposit has aged.

# Platinum auxiliary anode with hydrazine as depolarizer

The use of a platium auxiliary anode depolarized by hydrazine is somewhat more convenient than a silver-silver chloride anode<sup>4</sup>. More importantly the background current with the platinum-hydrazine anode is only about half as large as with the silver-silver chloride anode. A further incidental advantage is that the nitrogen produced by the oxidation of the hydrazine, according to  $N_2H_4 = N_2 + 4H^+ + 4e$ , aids in excluding air from the solution.

Since it was expected that hydrazine might form complexes with nickel and cobalt which could change their deposition characteristics, a polarographic investigation of nickel and cobalt in the presence of hydrazine, both with and without pyridine present, was carried out. This showed that above a pH of about 6 both metals do form complexes with hydrazine, whose deposition potentials are about 0.2 V more negative than the pyridine complexes. In the presence of both pyridine and hydrazine both complexes co-exist over the pH range from about 6 to 8, and the polarogram shows a separate wave for each.

This is demonstrated in the case of nickel by the typical polarograms in Fig. 2. The single wave at pH = 5.3 results from reduction of the nickel pyridine complex, while the single wave at pH = 8.5 is that of the nickel hydrazine complex. At intermediate pH values a doublet wave is observed, the first wave being that of the nickel



Fig. 2. Polarograms of nickel in the simultaneous presence of pyridine (1M) and hydrazine (0.2M) at the pit values indicated for each curve. Each curve starts at 0 V versus the saturated calomel electrode. The galvanometer zero was displaced downward for each successive curve to avoid over-lapping.

pyridine complex. The occurrence of the doublet wave shows that the rate of transformation of the hydrazine complex to the pyridine complex is relatively slow.

Some transformation (albeit incomplete during the life of a mercury drop at the dropping electrode) does take place at potentials at which the pyridine complex is reduced. Consequently the ratio of the pyridine and hydrazine complexes in the body of the solution doubtless is somewhat smaller than the relative heights of the two waves.

At pH values below 7.5 both metals can be deposited from the mixed pyridine-hydrazine solution at the same potentials used in the absence of hydrazine, because the hydrazine complexes are transformed to the pyridine complexes as the deposition of the latter proceeds. However, at a pH above 7.5 this transformation is so slow that an inordinately long time is required for complete deposition.

With the pyridine-hydrazine electrolyte nickel can be determined satisfactorily over the pH range from 5.2 to 7.2. However, for determination of cobalt the pH must be above about 6.3 to prevent the catalyzed reduction of hydrogen ion described above. Consequently for the successive determinations of both metals the pH must be between about 6.3 and 7.2. Because the hydrogen ion produced by the oxidation of hydrazine at the anode causes a significant decrease in pH the optimum initial pH is  $7.0\pm0.2$ when the supporting electrolyte contains 1M total pyridine and 0.2M hydrazine.

With up to 100 mg of cobalt in 100 ml the concentration of hydrazine should not be much smaller than 0.2M. With only 0.1M hydrazine a few tenths of a milligram of cobaltic oxide was observed to deposit on the platinum anode, but this does not occur with 0.2M hydrazine.

The data in Table III show that the successive determinations of nickel and cobalt are very satisfactory under the optimum conditions.

Because the deposition of each metal requires 2 to 3 hours the total elapsed time for a successive determination of both is 4 to 6 hours. However, since the electrolyses are automatically controlled by the potentiostat, the actual operator time involved is

### TABLE III

#### SEPARATION OF NICKEL AND COBALT, PLATINUM-HYDRAZINE ANODE

Electrolyte 1.00 M total pyridine, 0.30 M chloride, and
o 20M hydrazine sulfate.
Electrolysis at -0.95 V vs. S.C.E. for nickel
and at -1.20 V for cobalt.

	pH	Nuckel taken mg	Nıckel Jound mg	Error mg	Cobalt taken mg	Cobalt found mg	Lerror mg
1	7.0-6 6	104.6	10.1.8	0.2	103.3	103.0	0.3
2	67-61	104.6	105.1	0.5	103.3	a	•
3	7.1-6.8	87.0	86.5	0.5	17.7	18.5	o.8
4	7 0-0.7	87 o	86.5	0.5	17.7	1.80	0.3
5	7.0-0.6	17.6	17.7	o.ï	85.6	85.5	0.1
Ğ	7.1-6.6	17.6	18.3	07	85.6	85.3	0.3
	·	·	Δ	v. <u>+0.4</u>			Av10.4

a) Final pu too low for cobalt detn.

only that required to reset the potentiostat and observe the coulometer readings. Once the test solution has been prepared the operator time need not exceed about twenty minutes. This is less than the actual operator time required to analyse a mixed nickelcobalt solution with equal accuracy by any of the classical methods.

Commercial nickel salts invariably contain significant amounts of cobalt, and the converse is true of cobalt compounds. Ordinary purification techniques are not very effective in removing small amounts of cobalt from nickel salts, and *vice versa*. Since the controlled potential technique described herein provides a very clean separation of nickel from cobalt, it can be used very advantageously for preparing nickel-free cobalt compounds and cobalt-free nickel compounds.

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#### SUMMARY

A method has been developed for the successive determinations of nickel and cobalt by controlled potential coulometric analysis with a mercury cathode, using an aqueous pyridine electrolyte. Quantities of the metals from about 10 to 100 mg per 100 ml are determinable with an average error of  $\pm 0.5$  mg. Because this controlled potential electrolysis technique produces a clean separation of nickel and cobalt it can be used for preparing nickel-free cobalt compounds and cobalt-free nickel compounds.

## RÉSUMÉ

Une méthode a été mise au point pour doser successivement le nickel et le cobalt par analyse coulométrique à potentiel contrôlé, en solution eau-pyridine, en utilisant une cathode de mercure. Des quantités de ces métaux d'environ 10 à 100 mg/100 ml peuvent être déterminées avec une erreur moyenne de  $\pm$  0.5 mg. Grâce à l'excellente séparation nickel-cobalt, obtenue par cette électrolyse à potentiel contrôlé, cette technique peut être utilisée pour la préparation de composés de nickel exempts de cobalt et de composés de cobalt exempts de nickel.

### ZUSAMMENFASSUNG

Es wurde eine Methode ausgearbeitet, um Nickel und Kobalt mit einer coulometrischen Analyse bei kontrolliertem Potential in einer Wasser-Pyridin Lösung nacheinander zu bestimmen, unter Verwendung einer Quecksilberelektrode. Mengen dieser Metalle von 10 bis 100 mg/100 ml können mit einem mittleren Fehler von  $\pm$  0.5 mg bestimmt werden. Dank der hervorragenden Trennung von Nickel-Kobalt, welche man mit dieser Elektrolyse bei einem kontrollierten Potential erhält, kann diese Technik auch für die Präparation von Nickel-Verbindungen, welche kein Kobalt enthalten, und von Kobalt-Verbindungen, welche kein Nickel enthalten, verwendet werden.

### REFERENCES

- <sup>1</sup> D. BALACHOWSKY, Compt. rend., 132 (1901) 1492. <sup>2</sup> A. COEHN AND M. GLASER, Z. anorg. Chem., 33 (1903) 9
- <sup>3</sup> I. M. KOLTHOFF AND J. J. LINGANE, Polarography, Interscience Publishers, Inc., Nev York, 2nd ed., 1952.
- J. J. LINGANE, Electroanalytical Chemistry, Interscience Publishers, Inc., New York, 1953. 4
- <sup>6</sup> J. J. LINGANE AND H. KERLINGER, Ind. Eng. Chem., Anal. Ed., 13 (1941) 77.
- J. J. LINGANE AND S. L. JONES, Anal. Chem., 22 (1950) 1220.
  K. A. NENADKEVICH, Compt. rend acad sci. U. R.S.S., 49 (1945) 31; C A. 40, (1946) 7055; K. A. NENADKEVICH AND V. S. SALTYKOVA, Anal. Khim., 1 (1946) 123; C.A., 41 (1947) 662.
- \* S. TORRANCE, Analyst, 64 (1939) 109.

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