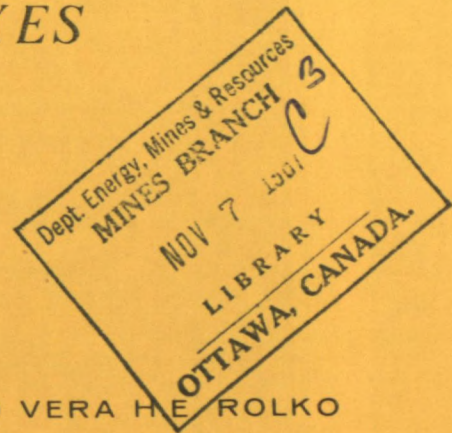




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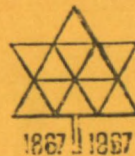
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OTTAWA

*DETERMINATION OF COBALT AND ZINC IN
NICKEL METAL BY ATOMIC - ABSORPTION
SPECTROPHOTOMETRY AFTER
SEPARATION BY SIMULTANEOUS
CHLOROFORM EXTRACTION OF THEIR
THIOCYANATE - DIANTIPYRYLMETHANE
COMPLEXES*



ELSIE M. DONALDSON AND VERA HE ROLKO
MINERAL SCIENCES DIVISION

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OF THEIR THIOCYANATE-DIANTIPYRYLMETHANE COMPLEXES

by

Elsie M. Donaldson* and Vera H. E. Rolko**

ABSTRACT

An atomic-absorption spectrophotometric method for determining cobalt and zinc in the range 0.0005 to 0.10% in nickel metal is described. After sample dissolution, cobalt and zinc are separated from the matrix element by simultaneous chloroform extraction of their thiocyanate-diantipyrylmethane ion-association complexes from a citric acid medium at pH 3.25. Interference from copper and various elements (i.e. titanium, vanadium, molybdenum, tungsten, etc.) is eliminated with thiourea and ammonium fluoride, respectively. Cadmium, iron and chromium also interfere under the chosen experimental conditions, but the amounts of these impurities present in nickel metal are so low that their interference effects are negligible. Other impurities do not interfere in the proposed method.

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Direction des mines
Bulletin technique TB 93

DOSAGE SPECTROPHOTOMÉTRIQUE PAR ABSORPTION ATOMIQUE
DU COBALT ET DU ZINC DANS LE NICKEL MÉTAL APRÈS
SÉPARATION PAR EXTRACTION SIMULTANÉE AU CHLOROFORME
DE LEURS COMPLEXES THIOCYANATE ET DIANTIPYRYLMÉTHANE

par

Elsie M. Donaldson* et Vera H. E. Rolko**

RÉSUMÉ

Les auteurs décrivent une méthode de dosage du cobalt et du zinc pour des niveaux allant de 0.0005 à 0.10% dans le nickel métal par spectrophotométrie d'absorption atomique. Après dissolution de l'échantillon, le cobalt et le zinc sont séparés du nickel par une extraction simultanée au chloroforme de leurs complexes d'associations ioniques thiocyanate et diantipyrylméthane à partir d'un milieu d'acide citrique à pH 3.25. L'interférence causée par le cuivre et divers éléments (i.e. le titane, le vanadium, le molybdène, le tungstène, etc.) est respectivement éliminée par la thiourée et le fluorure d'ammonium. Le cadmium, le fer et le chrome gênent également dans les conditions expérimentales choisies, mais les quantités de ces impuretés présentes dans le nickel métal sont si faibles que leur influence est négligeable. Les autres impuretés ne gênent pas dans le dosage proposé.

*Préposée aux recherches scientifiques, et **agent scientifique,
Division des sciences minérales, Direction des mines, ministère de
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INTRODUCTION

With the advent of atomic-absorption spectrophotometry to the Mines Branch Laboratories, much investigational work has been performed to determine the applicability of this sensitive and selective analytical technique to the routine determination of various elements in many diverse materials. As part of this project, the present investigation was undertaken to assess the analytical potential of this method for the determination of trace amounts of cobalt and zinc in nickel metal.

Published information pertaining to the determination of small amounts of cobalt and zinc in nickel metal by atomic-absorption spectrophotometry is sparse. Recently, Ott and Hatch (1) described a method for the direct determination of zinc in electrolytic nickel, at a concentration as low as 2.5 ppm, utilizing standard calibration solutions prepared from nickel samples of known zinc content. However, this method was not considered suitable in the present work, because the accuracy attainable is directly dependent on the reliability of the zinc results obtained for the nickel samples used to prepare the calibration solutions. In addition, their calibration curve does not pass through zero because of a constant background absorbance equivalent to their limit of detection for zinc. Similarly, McPherson et al.(2) have reported that small amounts of cobalt ($\ll 0.01\%$) can also be determined directly in pure nickel by atomic-absorption spectrophotometry, but no data were presented to substantiate their statement.

At the beginning of this investigation, preliminary experiments with synthetic nickel samples revealed that the accurate determination of small quantities of cobalt and zinc by direct measurement of their respective absorbances in highly concentrated nickel solutions was not feasible. Erratic results were obtained in these tests, presumably due to interelement and/or viscosity effects resulting from the high concentration of the matrix element present in the solutions taken for analysis. Consequently, it was considered that the development of a suitable atomic-absorption procedure for determining trace amounts of cobalt and zinc in nickel metal would require prior separation of these elements.

Many of the existing methods for determining cobalt and zinc in nickel-base and other materials depend on their separation from the matrix elements by solvent extraction of their anionic thiocyanate complexes (3-11, 17, 18), or the neutral thiocyanate-ion-association compounds produced with various organic reagents (i.e. tetraphenylarsonium chloride (12, 13), diantipyrylmethane (14, 16, 20), acridine sulphate (19)) capable of forming cations of large ionic size in solution. Although many metallic ions, particularly copper^{II} and iron^{III}, are known to interfere in the above methods by

the formation of similar extractable species, their interference effects can generally be eliminated with suitable masking agents (e.g., thiourea, potassium iodide, citric acid, ammonium fluoride). Because Jankovský (20) has reported that the thiocyanate-diantipyrilmethane complexes of cobalt and zinc can be extracted into chloroform from solutions containing thiourea and ammonium fluoride under essentially the same experimental conditions, it was decided to investigate the possible application of this separation procedure in the present work.

This report describes the successful application of a modified version of Jankovský's extraction method to the separation and subsequent determination of small amounts of cobalt and zinc in nickel metal by atomic-absorption spectrophotometry. Under the proposed experimental conditions, cadmium and iron are partially extracted and chromium causes emulsification in the organic phase. However, moderate amounts of these elements do not interfere in the extraction procedure or in the final determination of cobalt and zinc.

APPARATUS AND REAGENTS

Apparatus

Atomic-absorption spectrophotometer: Techtron Model AA-3 equipped with a Photovolt Varicord Model 43 recorder, a 10-cm laminar-flow-air-acetylene burner and cobalt and zinc hollow-cathode lamps.

pH meter: Leeds and Northrup.

Reagents

Standard Cobalt Solution, 200 ppm

Dissolve 0.8075 g of cobaltous chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) in water and dilute to 1 litre. Prepare working solutions containing 1, 2, 3, 4, 5 and 6 ppm of cobalt by appropriate dilution of this stock solution, and adjust the hydrochloric acid concentration of the resulting solutions to approximately 0.10 N.

Standard Zinc Solution, 200 ppm

Decompose 0.2000 g of pure zinc metal with 20 ml of 1:4 hydrochloric acid solution, evaporate the resultant solution to dryness, dissolve the residue in water, and dilute to 1 litre. Dilute 25 ml of this stock solution

to 100 ml with water (i.e. 50 ppm zinc solution), then prepare working solutions containing 0.20, 0.40, 0.60 and 0.80 ppm of zinc by appropriate dilution of this solution and adjust the hydrochloric acid concentration of the resulting solutions to approximately 0.10N.

Diantipyrylmethane Solution, 2%

Dissolve 5 g of 4,4'-diantipyrylmethane (Aldrich Chemical Co., Inc.) in ethyl alcohol and dilute to 250 ml with ethyl alcohol.

Ammonium Chloride - Ammonium Hydroxide Solution

Dissolve 25 g of ammonium chloride in water, add 25 ml of concentrated ammonium hydroxide, and dilute to 1 litre.

Sodium Thiocyanate Solution, 50% w/v

Ammonium Fluoride Solution, 5% w/v

Citric Acid Solution, 50% w/v

Thiourea Solution, 10% w/v

Chloroform

Analytical reagent.

PROCEDURE

Procedure for Nickel Metal

In the following procedure a reagent blank is carried along with the sample.

Transfer a 1.000 g sample of the powdered metal to a 100-ml beaker, add 25 ml of 1:4 hydrochloric acid solution, cover the beaker with a watch glass, and warm gently on the hot plate. Add 30% hydrogen peroxide solution slowly, 1 ml at a time, until all of the metal is in solution. Usually, 5 ml is sufficient. Remove the watch glass and evaporate the resulting solution to dryness in a water bath to remove excess peroxide. Then add 1 ml of concentrated hydrochloric acid and 20 ml of water, and heat gently to dissolve the residue. Add 5 ml of 5% ammonium fluoride solution, 10 ml of 50% citric acid solution, mix well, and then, using a pH meter, adjust the pH of the resulting solution to 3.25 ± 0.10 with concentrated ammonia

solution. Add 5 ml of 10% thiourea solution and 10 ml of 50% sodium thiocyanate solution, mix well after each addition, and readjust the pH to exactly 3.25. Transfer the sample solution to a 125-ml separatory funnel and dilute to approximately 100 ml with water. Add 5 ml of 2% diantipyrylmethane solution, mix well, then add 15 ml of chloroform, stopper, and shake for 1.5 minutes. Allow 3 minutes for the layers to separate, then drain the chloroform extract into a 60-ml separatory funnel. Re-extract the sample solution two more times, using 5 ml of diantipyrylmethane solution and 5 ml of chloroform each time (Note 1, p. 5), then wash the aqueous phase by shaking for 30 seconds with 5 ml of chloroform. Combine these extracts with the first one. Add 20 ml of ammonium chloride-ammonium hydroxide solution to the combined extracts, shake for 30 seconds, allow the layers to separate, and drain off and discard the chloroform layer. Transfer the aqueous layer containing the cobalt and zinc to a 100-ml beaker, add 5 ml of concentrated hydrochloric acid, heat gently to remove excess chloroform, and then evaporate the solution to approximately 15 ml. Cover the beaker with a watch glass, add 5 ml each of concentrated hydrochloric and nitric acids, and boil to destroy ammonium salts and organic material. Remove the cover and gently evaporate the solution to dryness on the hot plate, to remove excess hydrochloric and nitric acids. Add 2 ml of concentrated hydrochloric acid, followed by 5 ml of water, to the residue in the beaker, evaporate the resulting solution to dryness in a water bath (Note 2, p. 5), then add approximately 10 ml of 0.10 N hydrochloric acid solution and heat gently to dissolve the cobalt and zinc salts. Filter, if necessary, using 0.10 N hydrochloric acid solution to wash the beaker and filter paper, dilute to an appropriate volume (25-200 ml) with the same solution, depending on the expected cobalt and zinc contents of the sample (Note 3, p.5), and analyse the solution for cobalt and zinc by the procedure described below.

Procedure for the Determination of Zinc by Atomic Absorption Spectrophotometry

The experimental conditions utilized for the determination of zinc are as follows: wave length, 2139 Å; lamp current, 6 mA; slit width, 300 microns; air pressure, 26 psi; acetylene pressure, 2.5 psi.

Measure the absorbance of both the reagent blank solution (diluted to 25 ml) and the sample solution, and determine the zinc content of each by reference to the absorbance values obtained for two standard solutions containing slightly lesser and slightly greater amounts of zinc. Correct the value obtained for the sample, by subtracting that obtained for the blank.

Procedure for the Determination of Cobalt by Atomic Absorption Spectrophotometry

The experimental conditions utilized for the determination of cobalt are as follows: wave length, 2407 Å; lamp current, 10 mA; slit width, 100 microns; air pressure, 26 psi; acetylene pressure, 2.5 psi.

Measure the absorbance of the sample solution and determine the cobalt content by the procedure described above for zinc (Note 4, p. 5).

Notes

1. Because of the solubility of diantipyrylmethane in chloroform, additional reagent solution must be added prior to each extraction step, in order to recomplex any cobalt and zinc remaining in the aqueous phase after the preceding extraction step. Complete extraction of both cations is obtained when the blue colour of the cobalt thiocyanate complex is no longer visible in the chloroform phase. Fifteen ml of 2% diantipyrylmethane solution is generally sufficient for the extraction of up to 1 mg each of cobalt and zinc under the proposed experimental conditions.
2. Excessive heating of cobalt salts results in the formation of black mixed oxides (Co_3O_4) which are relatively insoluble in water or dilute hydrochloric acid (i.e. 0.10 N) and thus cause low results for cobalt if suitable precautions are not taken. In the proposed procedure this difficulty is circumvented by dissolution of the oxides with concentrated hydrochloric acid, followed by evaporation of the resultant solution to dryness in a water bath.
3. The calibration curves for cobalt and zinc are approximately linear and linear, respectively, in the concentration ranges 0-6 ppm of cobalt and 0-0.80 ppm of zinc under the experimental conditions described in the sections pertaining to the determination of these elements by atomic absorption spectrophotometry. Consequently, the final volume of the sample solution (or a suitable aliquot thereof diluted to an appropriate volume with 0.10 N hydrochloric acid solution) is adjusted so that the resultant cobalt and zinc contents are within the specified ranges.
4. A correction for the reagent blank is not required, because the reagents do not contain cobalt.

EXPERIMENTAL

Effect of pH

Previous investigators have employed solvent extraction of the blue cobalthiocyanate-diantipyrylmethane complex (14,16, 21, 22) for the separation and also the spectrophotometric estimation of cobalt, but the optimum pH range for the complete formation and subsequent extraction of the complex does not appear to have been clearly defined. Although Jankovský (20) has reported that zinc thiocyanate is completely extracted by a chloroform solution of diantipyrylmethane from solutions 3 N in hydrochloric acid to pH 4, and that both zinc and cobalt are extracted from a slightly acid solution (pH \leq 4), preliminary tests carried out in this laboratory showed that the extraction of cobalt is incomplete at this pH. Therefore, in order to define the pH range in which both complexes are completely extracted, tests were performed with a series of solutions of increasing pH (\approx 1 to 5) and containing 250 μ g each of cobalt and zinc. In these tests the addition of reagents (i.e. ammonium fluoride, citric acid, etc.), the extraction procedure, and the subsequent determination of cobalt and zinc were carried out as described under "Procedure". The exact pH at which the complexes were formed in these test solutions was determined by measuring the pH of the aqueous phase after extraction.

The results of these tests (Table 1) show that the extraction of both complexes is complete from at least pH 1.40 to pH 3.45. The upper pH limit obtained for zinc (pH 3.90) corroborates that obtained by Jankovský,

TABLE 1

Effect of pH on the Formation of the Zinc and Cobalt Thiocyanate -
Diantipyrylmethane Complexes

Zinc taken, 250 μg
Cobalt taken, 250 μg

| pH | Co Found, μg | Zn Found, μg |
|------|-------------------------|-------------------------|
| 1.40 | 250 | 248 |
| 2.10 | 254 | 253 |
| 3.00 | 252 | 253 |
| 3.25 | 251 | 250 |
| 3.35 | 251 | 248 |
| 3.45 | 248 | 254 |
| 3.55 | 223 | 251 |
| 3.60 | 177 | 252 |
| 3.65 | 158 | 249 |
| 3.80 | 82 | 246 |
| 3.90 | 25 | 247 |
| 4.05 | 10 | 232 |
| 4.15 | 2 | 152 |
| 5.05 | 0 | 0 |

Effect of Diverse Ions

In preliminary tests carried out to determine the applicability of Jankovský's (20) method for the chloroform extraction of the thiocyanate-diantipyrylmethane complexes of cobalt and zinc to the separation and subsequent estimation of these elements in nickel metal by atomic absorption spectrophotometry, slightly high results were consistently obtained for both elements. In these tests, the final residue containing the cobalt and zinc was dissolved in water, diluted to an appropriate volume, and compared against suitable aqueous cobalt and zinc chloride standard solutions. Further work showed that this positive error was caused by interference from chloride ions resulting from differences in the chloride ion content of the test solutions and the standard calibration solutions. This problem was avoided in subsequent work by preparing both test and standard solutions in 0.10 N hydrochloric acid media.

Although many metallic ions are known to form chloroform-extractable complexes in solutions containing thiocyanate ions and various organic compounds (i.e. diantipyrylmethane (14-16, 20-32), tetraphenylarsonium chloride (12, 13, 33, 34) and bromide (35), triphenylsulfonium bromide (35), triphenylmethylarsonium thiocyanate (36), tetraphenylphosphonium chloride (37), antipyrine (38)), their reactions can generally be prevented or inhibited by the use of suitable masking agents. Previous investigators have employed thiourea or potassium iodide to complex copper^{II} by reducing it to the cuprous state, and ammonium fluoride to render various other ions (e.g. iron^{III}, molybdenum^V, tungsten^V, titanium^{IV}, vanadium^V, bismuth^{III}, uranium^{VI}, etc.) inactive. Jankovský (20) utilized an excess of ammonium fluoride to complex iron^{III} in the presence of thiocyanate and diantipyrylmethane but stated that it is effective only in moderately acidic solutions. This was confirmed in the present work. In the pH range 1.40 to 3.45 required for complete extraction of both the cobalt and zinc complexes, tests showed that iron^{III} is not efficiently complexed with fluoride ions. In addition, it was found that iron cannot be completely prevented from reacting with thiocyanate and diantipyrylmethane by prior reduction to the ferrous state with ascorbic acid or hydroxylamine hydrochloride. Several investigators (3, 5) have employed ammonium citrate (or citric acid) to suppress it on interference during the extraction of the cobalthiocyanate complex and have found that its masking action is also influenced by pH. Experiments performed in this laboratory showed that below approximately pH 3, citrate is ineffective as a complexant for iron. However, tests carried out at pH 3.25 with iron^{III} (5 mg) and excess citric acid (5 g) showed that, although complete complexation of iron is not obtained under these conditions, less than 100 µg are extracted into the chloroform phase. Because this amount does not interfere in the subsequent determination of cobalt and zinc by atomic absorption spectrophotometry, Jankovský's method was modified in the present investigation to include extraction at pH 3.25 from a citric acid medium.

The possible interference effects of various ions that can be expected to occur in small amounts as impurities in samples of nickel metal were tested separately by the proposed method on test solutions containing 250 µg each of cobalt and zinc. The results of these tests (Table 2) showed that, for the quantity of each ion tested, none interfered in the cobalt and zinc determination. However, larger amounts of iron, cadmium and chromium do interfere in the extraction procedure. Low results were obtained in test solutions containing 10 mg of iron^{III}. Because iron is not completely masked with citric acid under the proposed experimental conditions, the uncomplexed portion interferes in two ways: first, it consumes diantipyrylmethane to form a reddish-brown extractable complex and this, in turn, obscures the characteristic blue colour of the cobalt complex in the chloroform phase, thus making it difficult to determine when the extraction of cobalt and zinc is complete. Large amounts of cadmium also interfere by consuming reagent to form a colourless complex which is partially extracted into the chloroform phase. Chromium interferes by partial precipitation, probably as chromium^{III} fluoride (12), which causes emulsification in the chloroform phase, making extraction difficult.

TABLE 2

Effect of Diverse Ions on the Determination of Cobalt
and Zinc by the Proposed Method

Cobalt taken, 250 μ g
Zinc taken, 250 μ g

| Diverse Ion Taken, mg | Co Found, μ g | Zn Found, μ g |
|---------------------------|-------------------|-------------------|
| Fe ^{III} (5 mg)* | 255 | 256 |
| Cu ^{II} (10 mg) | 249 | 250 |
| Cd ^{II} " ** | 250 | 255 |
| Pb ^{II} " | 248 | 248 |
| Mn ^{II} " | 253 | 248 |
| V ^V " | 249 | 249 |
| Mo ^{VI} " | 249 | 248 |
| W ^{VI} " | 247 | 245 |
| Zr ^{IV} " | 251 | 252 |
| Ti ^{IV} " | 257 | 251 |
| Bi ^{III} " | 257 | 251 |
| Sn ^{IV} " | 252 | 246 |
| Sb ^V " | 253 | 252 |
| Cr ^{III} " *** | 255 | 251 |
| Cr ^{VI} " | 254 | 245 |
| As ^V " | 256 | 251 |
| P ^V " | 256 | 248 |

*The reddish-brown iron^{III} complex formed on the addition of diantipyryl-methane is almost completely destroyed by continued shaking with chloroform; approximately 76 μ g of iron were extracted into the chloroform phase.

**Approximately 1.05 mg of cadmium were extracted into the chloroform phase.

***Organic phase turbid and slow in separating; filtered through cotton wool.

Application to Synthetic Nickel Samples

Although standard samples of nickel metal were not available, the accuracy of the proposed method was determined by applying it to the analysis of a series of synthetic samples containing 1 g of nickel and in which the added cobalt and zinc varied from 0.001 to 0.100%. Nickelous chloride hexahydrate (4.049 g) was employed in these tests because the cobalt content of several available samples of nickel metal was too high (>0.05%). The results obtained are given in Table 3.

DISCUSSION

Table 3 shows that the results obtained by the proposed method for synthetic nickel samples agree favourably with the total calculated percentage of cobalt and zinc present.

The proposed method is suitable for samples containing between 0.0005 and 0.10% of cobalt and zinc. It can also be applied to the determination of small amounts of cobalt and zinc in nickel alloys containing large amounts of iron, chromium and copper, if provision is made for the prior removal of the iron and chromium and if a sufficient excess of thiourea is added to mask the copper. Alloys containing more than 0.10% of cobalt and zinc can be analysed directly by atomic absorption spectrophotometry, without prior separation of the elements in question by the proposed extraction method.

TABLE 2

Effect of Diverse Ions on the Determination of Cobalt
and Zinc by the Proposed Method

Cobalt taken, 250 μ g
Zinc taken, 250 μ g

| Diverse Ion Taken, mg | Co Found, μ g | Zn Found, μ g |
|---------------------------|-------------------|-------------------|
| Fe ^{III} (5 mg)* | 255 | 256 |
| Cu ^{II} (10 mg) | 249 | 250 |
| Cd ^{II} " ** | 250 | 255 |
| Pb ^{II} " | 248 | 248 |
| Mn ^{II} " | 253 | 248 |
| V ^V " | 249 | 249 |
| Mo ^{VI} " | 249 | 248 |
| W ^{VI} " | 247 | 245 |
| Zr ^{IV} " | 251 | 252 |
| Ti ^{IV} " | 257 | 251 |
| Bi ^{III} " | 257 | 251 |
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| Sb ^V " | 253 | 252 |
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TABLE 3

The Determination of Cobalt and Zinc in Synthetic Nickel Samples

| Sample | Total Co Present, % | Co Found, % | Total Zn Present, % | Zn Found, % |
|------------------------|---------------------|-------------|---------------------|-------------|
| Ni + 0.0010% Co and Zn | 0.0019 | 0.0020 | 0.0022 | 0.0026 |
| Ni + 0.0050% " " " | 0.0059 | 0.0060 | 0.0062 | 0.0060 |
| Ni + 0.0100% " " " | 0.0109 | 0.0108 | 0.0112 | 0.0107 |
| Ni + 0.0250% " " " | 0.0259 | 0.0259 | 0.0262 | 0.0259 |
| Ni + 0.0500% " " " | 0.0509 | 0.0511 | 0.0512 | 0.0514 |
| Ni + 0.1000% " " " | 0.1009 | 0.0997 | 0.1012 | 0.1011 |

Triplicate determinations of cobalt and zinc in the nickelous chloride hexahydrate by the proposed method gave average results of 9 and 12 μg (or 0.0009 and 0.0012%, calculated on the basis of 1 g of nickel), respectively.

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