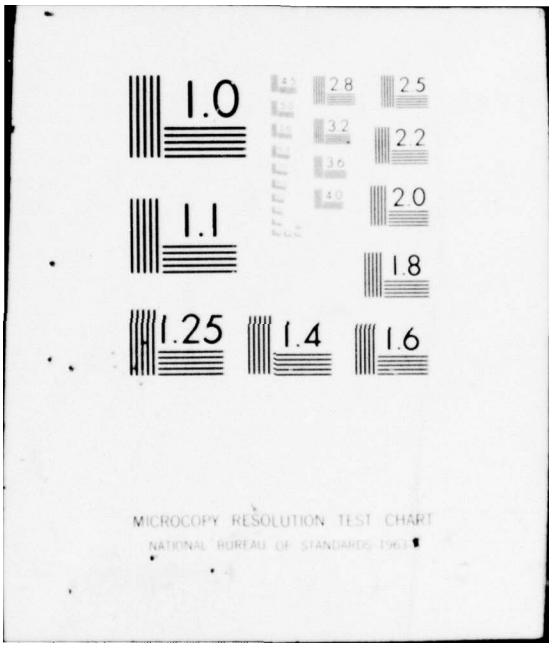
AD-A037 344 FRANKFORD ARSENAL PHILADELPHIA PA F/G 7/2
SPECTROPHOTOMETRIC DETERMINATION OF BORON IN COBALT AND NICKEL --ETC(U)
JUL 76 G NORWITZ, H GORDON

UNCLASSIFIED FA-TT-76035 NL

1 OF 1
AD A037344

END

DATE FILMED 4-77


1.0
1.1
1.25
1.4
1.6
2.8
2.5
3.2
2.2
3.6
2.0
4.0
1.8
MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS 1963

FA-TT-76035

AD

# SPECTROPHOTOMETRIC DETERMINATION OF BORON IN COBALT AND NICKEL COATINGS BY USE OF CARMINIC ACID

by

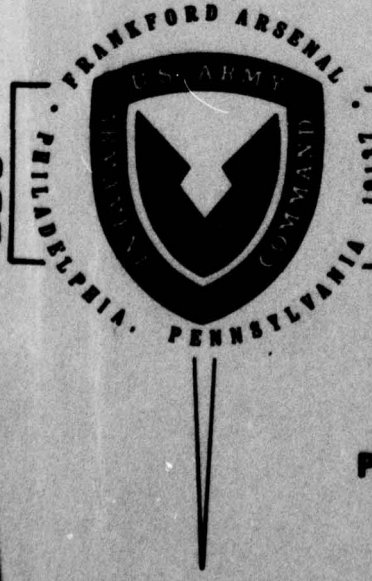
GEORGE NORWITZ
HERMAN GORDON



July 1976








Technical Support Directorate

U.S. ARMY ARMAMENT COMMAND
FRANKFORD ARSENAL
PHILADELPHIA, PENNSYLVANIA 19137

## DISPOSITION INSTRUCTIONS

Destroy this report when no longer needed. Do not return it to the originator.

## DISCLAIMER

**The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.**

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

## REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

(14) 1. REPORT NUMBER: FA-TT-76035

2. GOVT ACCESSION NO. (9)

3. RECIPIENT'S CATALOG NUMBER

(6) 4. TITLE (and Subtitle): SPECTROPHOTOMETRIC DETERMINATION OF BORON IN COBALT AND NICKEL COATINGS BY USE OF CARMINIC ACID.

5. TYPE OF REPORT & PERIOD COVERED: Technical Test Report.

6. PERFORMING ORG. REPORT NUMBER

(10) 7. AUTHOR(s): GEORGE NORWITZ, HERMAN GORDON

8. CONTRACT OR GRANT NUMBER(s)

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Commander
FRANKFORD ARSENAL, ATTN: SARFA-TSE-M-64-1
Philadelphia, PA 19137

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
AMS Code: 53970M6350
PRON: A1-6-08003-F6-NH

11. CONTROLLING OFFICE NAME AND ADDRESS
Commander
Army Material and Mechanics Research Center
ATTN: AMXMR-MO, Watertown, MA 02172

(11) 12. REPORT DATE: July 1976

13. NUMBER OF PAGES: 14

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)

(12) 16p.

15. SECURITY CLASS. (of this report): UNCLASSIFIED

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE: N/A

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

The authors are indebted to Fred Pearlstein of the Chemical Research Division, Frankford Arsenal, for furnishing samples and giving advice.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Boron
Cobalt coatings
Nickel coatings
Carminic acid

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A method is proposed for the determination of boron in cobalt and nickel coatings deposited from borane-type baths by electroless techniques. In the method, the deposit is dissolved in hydrochloric acid in the presence of platinum chloride as a catalyst, potassium chloride and mannitol are added, and the solution is evaporated to dryness. Methyl alcohol is then added, the boron is distilled as methyl borate

(continued)

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

142720

/B

20. ABSTRACT: (continued)

into sodium hydroxide solution, the distillate is evaporated to dryness, and the boron is determined spectrophotometrically using carminic acid. The mannitol prevents loss of boron by volatilization when the solution is evaporated to dryness. The advantage of evaporating the hydrochloric acid solution to dryness is that such treatment eliminates excess acid and water, both of which cause incomplete recovery of boron in the distillation. The potassium chloride, cobalt chloride, and nickel chloride left after the evaporation to dryness dissolve in the hot methyl alcohol during the distillation and do not interfere.

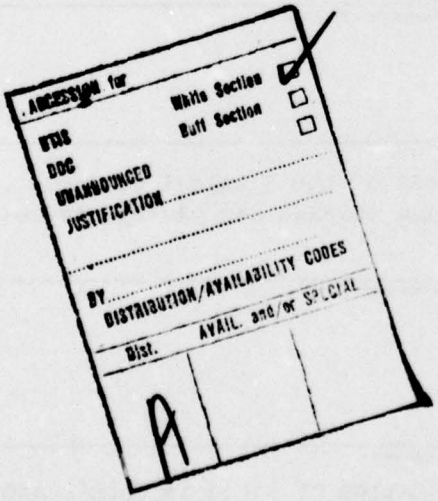


TABLE OF CONTENTS



LIST OF ILLUSTRATIONS



LIST OF TABLES

## INTRODUCTION

The problem of determining boron in cobalt and nickel coatings is important because of the growing use of cobalt and nickel coatings deposited from borane-type baths. Some borane baths[1-3*] tend to give a coating containing several percent boron and the boron content of the coating can be calculated with reasonable accuracy by difference; other borane baths[3-9*] tend to give a coating with a lower boron content and the calculation of the boron by difference is subject to large errors.

In this paper, a spectrophotometric method is proposed for the determination of boron in cobalt and nickel coatings. The sample is dissolved in hydrochloric acid in the presence of platinum chloride as a catalyst[10*], potassium chloride and mannitol are added, and the solution is evaporated to dryness. Methyl alcohol is added, the boron is distilled as methyl borate into sodium hydroxide solution, the distillate is evaporated to dryness, and the boron is determined by use of carminic acid. Feldman[11*] in a comprehensive study of the volatility of boron from solutions, has shown that mannitol prevents the loss of boron when hydrochloric acid solutions containing boron are evaporated to dryness. Many investigators have used carminic acid (in a sulfuric acid medium) for the spectrophotometric determination of boron in various materials.[12-19*]

## EXPERIMENTAL

### Apparatus and Reagents

Distillation apparatus (Figure 1).

Condenser tube, Corning 7280 glass, Corning 72300.

Steel spoon spatula, 9 inches long, Arthur H. Thomas Co. 8339-M10.

Polypropylene graduated cylinders, 10 ml and 50 ml, Arthur H. Thomas Co. 3571-C10 and 3571-C20.

Sulfuric acid, 96% (ACS).

Hydrochloric acid (ACS).

---

* See References

Nitric acid (ACS).

Methanol (ACS).

Hydrogen peroxide, 30% (ACS).

Standard boron solution No. 1 (1 ml = 0.2 mg B). Dissolve 0.5721 g of boric acid (ACS) in water and dilute to 500 ml in a volumetric flask. Store in a polyethylene bottle.

Standard boron solution No. 2 (1 ml = 0.02 mg B). Dilute 25 ml of standard boron solution No. 1 to 250 ml in a volumetric flask. Store in a polyethylene bottle. Prepare fresh weekly.

Carminic acid solution (0.1%). Dissolve 0.500 g of carminic acid (Eastman Kodak) in 500 ml of sulfuric acid. Store in a polyethylene bottle.

Potassium chloride solution (10%). Dissolve 50 g of potassium chloride (ACS) in water and dilute to 500 ml. Store in a polyethylene bottle.

## Key for Figure 1

A. 1500-ml beaker, Pyrex.

B. 300-ml Erlenmeyer flask, Corning 7280 glass, Corning 75000.

C. Connecting tube, Pyrex, each arm 12 mm long, 24/40 ground glass joints, Fisher Scientific Co. 15-322-2.

D. Condenser, Liebig, Pyrex, jacket 400 mm in length, 24/40 ground glass joints, Fisher Scientific Co. 7-721C.

E. Adapter, Pyrex, 11 mm in total length, 24/40 ground glass joint.

F. Tygon tubing.

G. Exit tube, hard plastic tubing, 20 mm long (can be obtained from 500-ml plastic wash bottle, Fisher Scientific Co. 3-409-20C).

H. 250-ml beaker, Corning 7280 glass, Corning 71000.

I. Tripod, 6 inches high, ring of 3 inches (i.d.), Arthur H. Thomas Co. 9481-B10.

J. Wire gauze with asbestos center, 6 inches x 6 inches, Arthur H. Thomas Co. 9931-G28.

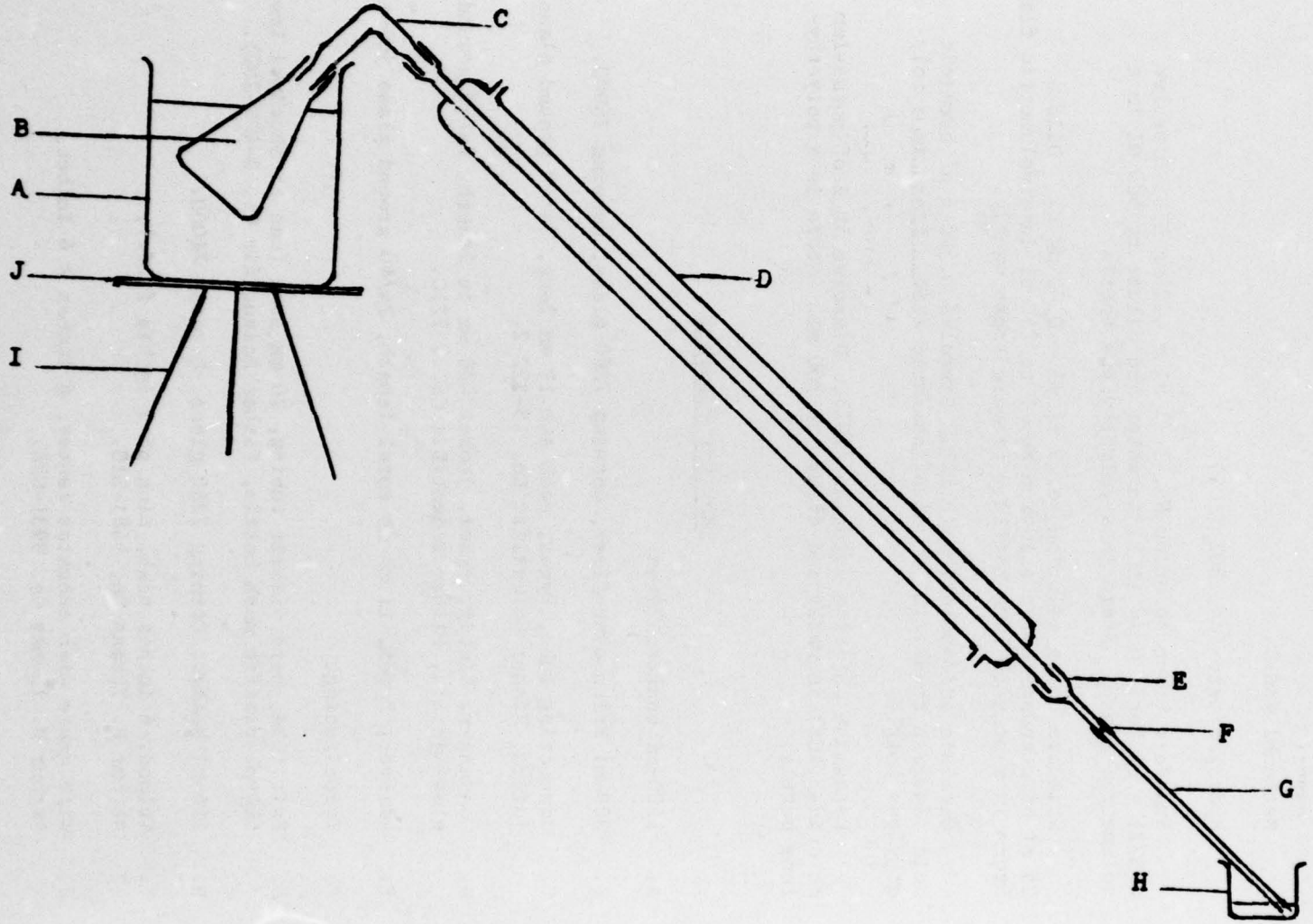



Figure 1. Distillation Apparatus

Mannitol solution (10%). Dissolve 50 g of mannitol (reagent grade) in water and dilute to 500 ml. Store in a polyethylene bottle.

Platinum chloride solution (5%). Fisher Scientific Co. So-P-118.

## Preparation of Calibration Curve

Transfer 1.0, 2.0, 2.0, 3.0, and 4.0 ml of standard boron solution No. 2 (1 ml = 0.02 mg B) to 300 ml Erlenmeyer flasks (Corning 7280 glass). Carry along a reagent blank. Add 10 ml of water, 10 ml of hydrochloric acid, 5 ml of potassium chloride solution (10%), and 10 ml of mannitol solution (10%). Move the flasks to the edge of the hot plate away from direct heat and heat until only one or two drops of liquid remains or until the salts are just dry (do not bake since this will cause the salts to be difficultly soluble). Allow to cool to room temperature. Insert stoppers (Pyrex), add 100 ml of methanol, and allow to stand for 1 hour while swirling frequently. At the end of this time, scrape the salts from the bottom of the flasks with a steel spatula, break up the salts with the spatula, and insert the stoppers.

Add 20 ml of water and 3 ml of sodium hydroxide solution (5%) (measured with 10-ml polypropylene graduated cylinder) to a 250-ml beaker (Corning 7280 glass). Place the beaker under the exit tube of the distillation apparatus (Figure 1) so that the tube reaches diagnally to the corner of the beaker. Attach the Erlenmeyer flask containing the methanol to the connecting tube and place the 1500-ml beaker under the flask so that the bottom of the flask is about 2 inches from the bottom of the beaker. Add tap water until the volume of water in the 1500-ml beaker is about 1 inch from the top. Place a burner under the 1500-ml beaker and heat the water to boiling; then turn down the flame somewhat so that the water boils moderately and continue heating until dry salts remain (the total heating time will be about 15 minutes). Lower the 250-ml beaker and wash down the exit tube with a little water. Place the beaker on a steam bath or an electric hot plate (at low heat) and evaporate just to dryness. Remove from the hot plate and allow to cool (do not cover). Add approximately 35 ml of sulfuric acid and swirl to dissolve the salts. Add 10 ml of carminic acid solution (0.1%) measured from a buret and swirl. Dilute with sulfuric acid to 50 ml in a polypropylene graduated cylinder and then pour the solution back in the beaker. Cover with a watch glass (Pyrex). Allow to stand for 90 minutes and measure the absorbance at 610 nm against the reagent blank. Plot absorbance vs mg of boron (per 50 ml).

## Procedure

Weigh the specimen (preferably 3/4 to 1 sq. inch in area) and calculate the weight of the coating by deducting the original weight of the base metal. Transfer the specimen (squeezing it if necessary) to a 300-ml Erlenmeyer flask (Corning 7280 glass). Add 10 ml of hydrochloric acid and 1 drop of platinum chloride solution (5%). Heat under reflux until the coating has dissolved. If the base metal is copper, the heating need be conducted only until the bright copper surface appears (although complete dissolution of the copper will do no harm). Add 2 ml of hydrogen peroxide (30%) and heat under reflux for 20 minutes to destroy the peroxide. Wash down the interior of the condenser with a little water and detach the flask. Cool, dilute to 500-ml in a volumetric flask and transfer to a polyethylene bottle. Pipet a 5-ml aliquot into a 300-ml Erlenmeyer flask (Corning 7280 glass). Add 5 ml of potassium chloride solution (10%) and 10 ml of mannitol solution (10%), evaporate to dryness, distill, and develop the color as described under preparation of calibration curve. Determine the mg of boron by referring to the calibration curve and calculate the percent boron in the coating as follows:

$$\text{Percent boron} = \frac{\text{mg of boron as found from curve}}{\text{g of coating in aliquot} \times 10}$$

## DISCUSSION AND RESULTS

The advantage of evaporating the hydrochloric acid solution of the sample to dryness is that such a treatment eliminates excess acid and water, Luke[20] has shown (using sulfuric acid solution) that the presence of excess acid and water causes incomplete recovery of boron in the distillation.

The potassium chloride serves the purposes of complexing the boron (as potassium borate) and making the cobalt and nickel chlorides more readily soluble after the evaporation to dryness. Potassium chloride is not readily soluble in methyl alcohol at room temperature but it dissolves when the alcohol is heated close to the boiling point. Sodium chloride is far less soluble in methyl alcohol than is potassium chloride and cannot be substituted for potassium chloride.

---

[20] C. L. Luke, Anal. Chem., 27, 1150 (1959).

Sulfuric acid cannot be used in place of hydrochloric acid because it is not possible to evaporate the sulfuric acid without loss of boron and because the mannitol would be destroyed by the hot sulfuric acid. Also, cobalt and nickel coatings do not readily dissolve in sulfuric acid, and cobalt and nickel sulfates are insoluble in methyl alcohol. Nitric acid cannot be used in place of hydrochloric acid because the mannitol would be destroyed by the hot nitric acid and because residual nitrate (that would be distilled) would interfere with the development of the boron-carminic acid color.

It is essential that the Erlenmeyer flask and condenser used in the dissolution of the sample be made of Corning 7280 glass (low boron, alkali resistant). The combination of high temperature and high acidity will cause high results for boron is glassware of high boron content (Pyrex) is used. The beaker used for the evaporation of alkaline solution after the distillation must also be made of Corning 7280 glass. By reason of the low acidity and relatively low temperature encountered during the distillation, no significant amount of boron is picked up from the connecting tube, condenser, or adapter - (all of which are made of Pyrex).

It is recommended that the color be developed in beakers made of Corning 7280 glass after diluting in a polypropylene graduated cylinder. However, previous investigators have demonstrated that Pyrex glassware can be used for this purpose (after rinsing with sulfuric acid).[18, 21]

The authors used an air condenser in dissolving the sample. It was not necessary to attach a jacket (Pyrex) to this condenser although such a jacket is availabe (Corning 2240, 400 nm). An alternative method dissolving the sample that was found to be equally satisfactory to the use of an air condenser was to cover the Erlenmeyer flask with a 250-beaker (Corning 7280 glass) and then heat the beaker gently at the edge of the hot plate. Cobalt, nickel, and platinum salts are catalysts for the destruction of hydrogen peroxide, so vigorous boiling is not necessary to destroy the peroxide.

---

[18] H. K. L. Gupta and D. F. Boltz, Mikrochim. Acta, 3, 415 (1974)

[21] Amer. Soc. for Testing and Materials, 1975 Annual Book of ASTM Standards, Part 12, Chemical Analysis of Metals; Sampling and Analysis of Metal Bearing Ores, Designation E 34-72, Philadelphia, PA.

The platinum chloride is essential for the dissolution of nickel coatings and less essential (but still recommended) for the dissolution of cobalt coatings.

The maximum amount of cobalt or nickel that can be handled in the distillation is about 0.5 g. The presence of more cobalt or nickel than this can cause bumping.

No residue at all was ever obtained on dissolution of the cobalt and nickel coatings in hydrochloric acid. This indicated that the boron in the coatings was "acid-soluble" (as would be expected).

The concentration of carminic acid used for the development of the color (0.2 mg per ml) is approximately that used by several investigators.[15-17] The absorbance measurements are made at 610 nm as previously recommended.[15, 17]

The recoveries obtained on adding standard boron solution No. 2 to reagent grade cobalt and nickel metal (0.5 g) and carrying the samples through the procedure, using the metal sample as the blank, are shown in Table I. The recoveries were satisfactory. The boron ("acid-soluble") found in the cobalt and nickel samples (using the regular reagent blank) was 0.0002% and 0.0019%, respectively. The results obtained for boron in three coatings of cobalt and one coating of nickel are shown in Table II.

The method in this report will probably be applicable to many other materials besides cobalt and nickel coatings. This was not investigated.

---

[15] H. Kawaguchi, Japan Analyst, 4, 307 (1955).
[16] R. C. Calkins and V. A. Stenger, Anal. Chem., 28, 399 (1956).
[17] D. L. Callicoat and J. D. Wolszon, Anal. Chem., 31, 1434 (1959).

Table I. Recovery of Boron Added to Pure Cobalt and Nickel

| Sample | B Found (mg) |
|---|---|
| 0.5 g Co + 0.020 mg B | 0.021 |
| 0.5 g Co + 0.040 mg B | 0.043 |
| 0.5 g Co + 0.060 mg B | 0.068 |
| 0.5 g Co + 0.080 mg B | 0.081 |
| 0.5 g Ni + 0.020 mg B | 0.018 |
| 0.5 g Ni + 0.040 mg B | 0.040 |
| 0.5 g Ni + 0.060 mg B | 0.057 |
| 0.5 g Ni + 0.080 mg B | 0.077 |

## SUMMARY

A method is proposed for the determination of boron in cobalt and nickel coatings deposited from borane-type baths by electroless techniques. In the method, the deposit is dissolved in hydrochloric acid in the presence of platinum chloride as a catalyst, potassium chloride and mannitol are added, and the solution is evaporated to dryness. Methyl alcohol is then added, the boron is distilled as methyl borate into sodium hydroxide solution, the distillate is evaporated to dryness, and the boron is determined spectrophotometrically using carminic acid. The mannitol prevents loss of boron by volatilization when the solution is evaporated to dryness. The advantage of evaporating the hydrochloric acid solution to dryness is that such treatment eliminates excess acid and water, both of which cause incomplete recovery of boron in the distillation. The potassium chloride, cobalt chloride, and nickel chloride left after the evaporation to dryness dissolve in the hot methyl alcohol during the distillation and do not interfere.

Table II. Results for Boron in Actual Deposits of Cobalt and Nickel

| Type of Coating | Weight of Entire Sample (g) | Weight of Deposit (g) | B Found (%)[a] |
|---|---|---|---|
| Co | 1.4861 | 0.7043 | 0.54; 0.52 |
| Co | 2.7230 | 0.9318 | 0.59; 0.59 |
| Co | 2.8392 | 1.3526 | 0.18; 0.17 |
| Ni | 1.6937 | 0.8027 | 0.56; 0.57 |

[a]The results represent duplicate aliquots.

## RECOMMENDATIONS

It is recommended that the method in this report be submitted to electroplating personnel for evaluation as to implementation.

## REFERENCES


1. K. Lang, Electroplating and Metal Finishing, 19, 86 (1966).

2. H. Narcus, Plating, 54, 380 (1967).

3. G. O. Mallory, Plating, 58, 319 (1971).

4. E. Groshart, Metal Finishing, 70, No. 4, 35 (1972).

5. T. Berzins (to E. I. du Pont de Nemours and Co.), U. S. Patent 3,338,726, August 29, 1967.

6. F. Pearlstein and R. F. Weightman, Frankford Arsenal Report FA-TA-74031, November 1974.

7. Ibid., Frankford Arsenal Report FA-TA-74032, November 1974.

8. Ibid., U.S. Patent 3,578,468, May 11, 1971.

9. Ibid., U.S. Patent 3,917,464, November 4, 1975.

10. C. L. Luke, Anal. Chem., 30, 1405 (1958).

11. C. Feldman, Anal. Chem., 33, 1916 (1961).

12. D. F. Boltz, "Colorimetric Determination of Nonmetals", p. 339, Interscience, New York, 1958.

13. J. T. Hatcher and L. V. Wilcox, Anal. Chem., 22, 567 (1950).

14. W. C. Smith, A. J. Goudie, and J. N. Sivertson, Anal. Chem., 27, 295 (1955).

15. H. Kawaguchi, Japan Analyst, 4, 307 (1955).

16. R. C. Calkins and V. A. Stenger, Anal. Chem., 28, 399 (1956).

17. D. L. Callicoat and J. D. Wolszon, Anal, Chem., 31, 1434 (1959).

18. H. K. L. Gupta and D. F. Boltz, Mikrochim. Acta, 3, 415 (1974).

19. Amer. Public Health Assoc., "Standard Methods for the Examination of Water and Waste Water". 13th ed., p. 72, Washington, DC, 1971.

20. C. L. Luke, Anal. Chem., 27, 1150 (1959).

21. Amer. Soc. for Testing and Materials, 1975 Annual Book of ASTM Standards, Part 12, Chemical Analysis of Metals; Sampling and Analysis of Metal Bearing Ores, Designation E 34-72, Philadelphia, PA.

DISTRIBUTION

Commander
U.S. Army Armament Command
Rock Island, IL 61201

1 Attn: DRSAR-Q, Mr. J. Obren

1 Attn: DRSAR-AQE, Mr. D. Spears

1 Attn: DRSAR-PPW-IR, Mr. E. Case

Commander
Rock Island Arsenal
Rock Island, IL 61201

1 Attn: SARRI-R, Mr. W. Kisner

1 Attn: SARRI-LEQ, Mr. J. Hausman

1 Attn: SARRI-R, Mr. W. McHenry

Commander
Watervliet Arsenal
Watervliet, NY 12189

1 Attn: SARWV-PPI, Mr. L. A. Jette

1 Attn: SARWV-QA, Mr. J. Miller

1 Attn: SARWV-QAS, Mr. J. Monaghan

Commander
Picatinny Arsenal
Dover, NJ 07801

1 Attn: SARPA-C-C-P, Mr. AcAloon

1 Attn: SARPA-VC 2, Mr. T. M. Roach

1 Attn: SARPA-QA-T-T, Mr. D. Stein

Commander
Edgewood Arsenal
Aberdeen Proving Ground, MD 21005

1 Attn: Chief, Programs Division
Mr. W. E. Montanary

1 Attn: SAREA-PATM, Dr. W. J. Maurits

Commander
U.S. Army Electronics Command
Fort Monmouth, NJ 07703

1 Attn: DRSEL-QM

1 Attn: DRSEL-PAE, Mr. S. Alster

Commander
U.S. Army Missile Command
Redstone Arsenal, AL 35809

1 Attn: DRSMI-QLC, Mr. Kenneth E. Parr

1 Attn: DRSMI-QLC, Mr. Knowlen Knowles

Commander
Harry Diamond Laboratories
2800 Powder Mill Road
Adelphi, MD 20783

1 Attn: DRXDO-PP, Mr. Hoke

1 Attn: DRXDO-EDE, Mr. Benjamin F. Willis

Commander
U.S. Army Tank-Automotive Research
and Development Command
Warren, MI 48090

1 Attn: DRDTA-EB, Mr. E. A. Hishon

1 Attn: DRSTA-RKA, Mr. J. Dudzinski

1 Attn: DRSTA-QA, Mr. D. Gamache

Commander
U.S. Army Test and Evaluation Command
Aberdeen Proving Ground, MD 21005

1 Attn: DRSTE-TAA

1 Attn: DRSTE-TO-P, Mr. A. Baldridge

1 Attn: DRSTE-ME, Mr. S. Wise

Commander
Aberdeen Proving Ground
Aberdeen Proving Ground, MD 21005

1 Attn: STEAP-MT-M

1 Attn: STEAP-MT-G, Mr. R. L. Huddleston

Commander
U.S. Army Mobility Equipment Research
and Development Command
Fort Belvoir, VA 22060

1 Attn: DRXFB-QA, Mr. J. K. Mauzy

1 Attn: DRXFB-EM, Mr. S. Levine

1 Attn: DRXFB-RM, Mr. E. York

Commander
U.S. Army Natick Research and
Development Command
Kansas Street
Natick, MA 01762

1 Attn: DRXNM-EM, Mr. S. Werkowski

1 Attn: DRXNM-GE, Mr. M. Budnick

Director
Army Materials and Mechanics
Research Center
Watertown, MA 02172

1 Attn: DRXMR-CT

1 Attn: DRXMR-MI, Mr. H. Hatch

1 Attn: DRXMR-RA, Mr. F. Valente

1 Attn: DRXMR-EM, Mr. T. DeSisto

1 Attn: DRXMR-X, Dr. Wright

1 Attn: DRXMR-PP, Mr. J. O'Connor

Commander
Frankford Arsenal
Philadelphia, PA 19137

1 Attn: SARFA-CO

1 Attn: SARFA-TD

Frankford Arsenal - Cont'd

1 Attn: SARFA-PA

1 Attn: SARFA-QAF-R, Mr. J. Braverman

1 Attn: SARFA-QAA-Q, Mr. J. Barr

1 Attn: SARFA-TS, Mr. H. Sokolowski

1 Attn: SARFA-TSE-M, G. Norwitz

1 Attn: SARFA-TSE-M, H. Gordon

3 Attn: SARFA-TSP-T

Defense Documentation Center
Cameron Station
Alexandria, VA 22314

Printing & Reproduction Division
FRANKFORD ARSENAL
Date Printed: 15 March 1977


FILM