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Procedures for the Analysis of Metals, Alloys, and Other Materials of Research

Part 3—A Spectrophotometric Procedure for the Determination of Trace Amounts of Cobalt in Ferrous Alloys

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PREVIOUS REPORTS IN THIS SERIES

Part 1—"Procedure for the Chemical Analysis of Copper-Base Alloys," O.R. Gates and O. Mylting, NRL Report 6357, Mar. 1966

Part 2—"Determination of Silver and Indium in Magnesium-Base Alloys, Lead in Indium, and Zirconium in Hafnium," O.R. Gates and E.J. Brooks, NRL Report 6427, Sept. 1966

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ABSTRACT

A procedure is presented for the determination of trace amounts of cobalt in ferrous alloys. The cobalt is extracted as tetraphenylarsonium cobaltothiocyanate in chloroform and is determined spectrophotometrically at a wavelength of 620 nm. Cobalt concentrations that range from 0.003 to 0.04% can be determined by this method. The upper concentration limit may be easily increased to cover the analysis of most cobalt-bearing alloys.

PROBLEM STATUS

This is the third in a series of progress reports. Work on the problem is continuing.

AUTHORIZATION

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PROCEDURES FOR THE ANALYSIS OF METALS, ALLOYS, AND OTHER MATERIALS OF RESEARCH

Part 3 — A Spectrophotometric Procedure for the Determination of Trace Amounts of Cobalt in Ferrous Alloys

INTRODUCTION

This is the third in a series of reports which will present progress in analytical methods by the Analytical Chemistry Branch, Metallurgy Division.

During the course of certain radiological studies with special purpose steels it became necessary to establish the cobalt impurity level with a high degree of accuracy. For materials containing traces of cobalt, spectrophotometry holds considerable promise because of the sensitivity of some of the organocobalt complexes. Tetraphenylarsonium chloride is the organic complexing agent chosen for this study.

METHOD OF ANALYSIS

Scope

The method* to be described was developed for the analysis of samples that contain approximately 0.01% cobalt; however, it may be applied without alteration to the determination of cobalt contents that vary between 0.003 and 0.04%. By increasing the volume of the extractant or varying the sample size, the upper limit may be increased to cover the analysis of most cobalt-bearing alloys.

Apparatus

Rubber Pipet Filler (Propipette)

Separatory Funnels — with a capacity of 125 ml

Spectrophotometer and Accessory Equipment

Reagents

Ammonium Bifluoride (20% Solution) — Ammonium bifluoride (100 g) is dissolved in water and diluted to 500 ml. This solution is prepared in a polyethylene beaker and stored in a polyethylene bottle.

Ammonium Citrate (20% Solution) — Ammonium citrate (100 g) is dissolved in water and diluted to 500 ml.

*This is a variation of the Affsprung-Barnes-Potratz spectrophotometric procedure for the determination of cobalt with tetraphenylarsonium chloride; see Ref. 1.

Ammonium Thiocyanate (50% Solution) — Ammonium thiocyanate (500 g) is dissolved in 500 ml of water.

Chloroform — Reagent grade chloroform is used.

Salicylaldoxime (1% Solution) — Salicylaldoxime (5 g) is dissolved in 500 ml of chloroform.

Standard Cobalt Stock Solution (1 ml = 50 μg Co) — High-purity cobalt (0.0500 g) is dissolved in 5 ml of nitric acid and evaporated to fumes with 5 ml of perchloric acid. After cooling, diluting to 100 ml, boiling one minute, and again cooling, the solution is diluted to 1000 ml in a volumetric flask and mixed thoroughly.

Standard Dilute Cobalt Solution (1 ml = 10 μg Co) — A 100-ml aliquot of the cobalt stock solution is transferred to a 500-ml volumetric flask, diluted to the mark, and mixed thoroughly.

Standard Copper Solution (1 ml = 100 μg Cu) — Reagent-grade copper (0.1000 g) is dissolved in 3 ml of water and 3 ml of nitric acid and evaporated to fumes with 3 ml of perchloric acid. After cooling, diluting to 100 ml, boiling one minute, and again cooling, the solution is diluted to 1000 ml in a volumetric flask and mixed thoroughly.

Tetraphenylarsonium Chloride Solution (0.05M) — Tetraphenylarsonium chloride dihydrate (22.7 g) is dissolved in 900 ml of water, then diluted to 1000 ml.*†

Procedure

Preparation of Sample Solution — It is recommended that a standard, which closely resembles the sample under test, be included with each analysis.

A 0.5000-g sample is transferred to a 150-ml beaker. After adding 5 ml of hydrochloric acid and 2 ml of nitric acid, the beaker and contents are heated gently until the sample is dissolved. Five milliliters of perchloric acid is added and the solution is evaporated to heavy fumes, cooled, rinsed down, and, with the cover removed, evaporated to dryness without boiling.‡ The perchlorate salts are then baked until fumes cease to be evolved.

NOTE: In the fuming and baking process, perchloric acid is vaporized and the perchlorate salts are destroyed; also, the chromium, which would interfere in the hexavalent state, is reduced to the trivalent state. It is very important that the perchlorate ions be largely destroyed before the addition of tetraphenylarsonium chloride. The latter is precipitated as the perchlorate (the perchlorate ion replacing the chloride ion), thus markedly reducing its effectiveness as a complexing agent for cobalt.

After cooling, 10 ml of hydrochloric acid (1:1) is added and the contents of the beaker warmed gently to dissolve the residue. To expel the bulk of the acid, the solution is evaporated, again without boiling and in the open beaker, until about 2 ml of liquid remains. The inner wall of the beaker is rinsed and the volume is adjusted to about 30 ml.

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*The tetraphenylarsonium chloride may be obtained from the J. T. Baker Co., Phillipsburg, N.J.

†Stored in a standard 2-liter acid bottle which is fitted with a 50-ml automatic dispensing buret, the solution appears to be stable indefinitely.

‡To prevent sample contamination, evaporations in open beakers should be conducted in a clean or well-shielded hood.

After adding 20 ml of the 20% ammonium citrate solution and a small piece of congo red test paper, the solution is neutralized with ammonia until the test paper begins to turn purple. (For ordinary steels the color of the solution will be greenish. The pH of the solution may vary between 2.5 and 3.5.)

NOTE: The solution is now ready for the salicylaldoxime extraction of the copper. If the copper content of the sample is known to be 200 μg or less, this extraction may be omitted (see Discussion section below).

Salicylaldoxime Extraction* — After transferring the solution to a 125-ml separatory funnel and adding 9 ml of the 1% salicylaldoxime solution, the funnel is shaken vigorously for 30 sec. When the chloroform layer is separated, a 10-ml pipet† is inserted into the funnel using a propipette to expel air from the tip as it passes through the aqueous layer. The chloroform layer is drawn into the pipet and discarded. The aqueous layer is then shaken vigorously for 30 sec with 9 ml of chloroform. After rinsing the pipet, it is again used as previously described to withdraw and discard the second chloroform layer.

Tetraphenylarsonium Chloride Extraction — The aqueous layer in the separatory funnel is shaken vigorously for 10 sec with 5 ml of the 50% ammonium thiocyanate solution, and again 10 sec with 5 ml (use a plastic pipet) of the 20% ammonium bifluoride solution. It is then shaken vigorously for 30 sec with 1 ml of the tetraphenylarsonium chloride solution, and 30 sec again with 5 ml of the chloroform. After the layers have separated, the glass stopper is removed and the chloroform layer carefully drained through the plug into a clean, dry, 10-ml calibrated test tube. The aqueous layer is again shaken vigorously for 30 sec each with 1 ml of the tetraphenylarsonium chloride solution and 5 ml of chloroform, again draining the chloroform layer into the test tube.

NOTE: For many analyses, a single tetraphenylarsonium chloride-chloroform extraction will be adequate for cobalt in the 0.005% range. Typical single extraction recoveries of 28 and 30 μg of cobalt have been obtained for synthetic samples containing 31.5 μg of cobalt, as against 31 and 31.5 μg cobalt recoveries with double extraction experiments. (The calibration curve for evaluating these recoveries was prepared from a doubly extracted aliquot of the standard cobalt solution.)

The volume of the extract in the test tube is carefully adjusted to the 10-ml calibration mark with chloroform. After inserting a rubber stopper and mixing thoroughly, the solution in the tube is filtered through a dry, 9-cm, No. 40 Whatman filter paper, catching about 4 or 5 ml of the latter portion in a clean dry absorption tube.

The spectrophotometer is set at 100% transmission at a wavelength of 620 nm with an absorption tube containing reagent-grade chloroform as a blank. Then the transmittances of the standard and sample solutions are measured and recorded. The values obtained for the standard and blank solutions are used to prepare a calibration curve from which the percentage of the cobalt in the sample is determined.

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*This is a variation of the Dean-Lady flame spectrophotometric procedure for the determination of copper in ferrous alloys; see Ref. 2.

†For ease of manipulation, the pipet used to withdraw the chloroform layer may be cut off several inches above the barrel. To facilitate pipetting, the lower tip opening may be enlarged slightly by cutting the tip back about a quarter of an inch. (Any cut end should be firepolished.) The pipet should be identified as unfit for volumetric work.

DISCUSSION

Calibration Curve

While it is recommended that a standard sample, closely resembling the sample under test, be included in each analysis, experiments have shown that a calibration curve may be prepared with appropriate amounts of the standard cobalt solution, commencing with the tetraphenylarsonium chloride extraction (discussed above). When the instrument is set at 100% transmittance at 620 nm with reagent-grade chloroform, the transmittances of the standards are reproducible from day to day. If similar amounts of cobalt are introduced at various stages of the procedure, only small differences in transmittance are noted.

By using a calibration curve prepared from a standard cobalt solution, the effectiveness of the method may be ascertained with respect to NBS standard samples or synthetic standard samples that closely resemble the sample under test.

Specificity of Tetraphenylarsonium Chloride

Under the conditions of the procedure, no interference was experienced from any alloying constituent or trace impurity normally encountered in ordinary or stainless steels.* If the salicylaldoxime extraction is omitted, copper interferes perceptibly by forming an amber to brownish (depending on the amount of copper present) tetraphenylarsonium cuprothiocyanate color complex. The normal color of the tetraphenylarsonium cobaltothiocyanate color complex is bluish green. The latter color may be almost completely masked by the copper color complex. However, the cobalt color complex absorbs much stronger than the copper color complex at 620 nm. (Generally 1 μg of cobalt exhibits the same amount of absorption as about 20 μg of copper.) Figure 1 shows the absorbance curves for the reagent blank and the cobalt and copper color complexes with the instrument set at 100% transmittance with reagent-grade chloroform for each series of measurements.

Bonding and Distribution

With cobalt the bond arrangement of tetraphenylarsonium appears to be different from that of the corresponding copper complex. In the presence of a (1:1) cobalt-copper combination, a limited amount of the reagent (exactly 5 ml of the tetraphenylarsonium chloride reagent solution after it has been diluted ten times) extracts about four times as much cobalt as copper.

The data in Table 1 were obtained by combining standard solutions of cobalt and copper in the proportions listed in the "Added" column, and extracting from each solution the amount of the element or elements that a limited amount of diluted tetraphenylarsonium chloride would complex. The chloroform extracts were evaporated at room temperature, treated with nitric and perchloric acids, and baked. From this point the sequence followed the procedure as given previously in the section titled Preparation of Sample Solution, beginning with the paragraph following the Note. The copper was evaluated by means of flame spectrophotometry and the cobalt by spectrophotometry.

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*Affsprung et al. (1) claim that pentavalent vanadium interference may be overcome by reducing it to the tetravalent state with ferrous sulfate. Under the conditions of the procedure, the writer experienced no interference from vanadium.

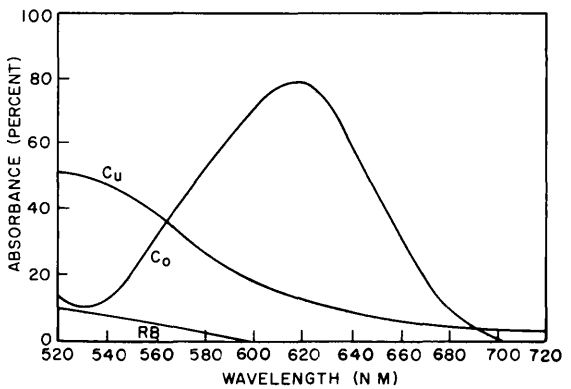

Fig. 1 - Absorbance curves for the chloroform extract of the reagent blank (RB) and the cobalt and copper color complexes. (Each color complex contained 20 μg of the metal per ml of chloroform.)

Table 1
Comparative Amounts of Cobalt and Copper Thiocyanates Extracted with Limited Amounts* of Tetraphenylarsonium Chloride Solution

Sample No.	Added (μg)		Recovered (μg)		Recovery (%)		Co/Cu Recovery Ratio
	Co	Cu	Co	Cu	Co	Cu	
1	1000	—	425	—	42.5	—	—
2	500	500	280	70	56.0	14.0	4:1
3	—	1000	—	210	—	21.0	—

*Five-ml aliquot of (1:10) tetraphenylarsonium chloride solution used for each extraction.

Salicylaldoxime Extraction

Affsprung et al. (1) overcame copper interference by reducing it to the monovalent state with potassium iodide; the resulting free iodine was titrated with a thiosulfate solution.

Under the conditions of the present procedure, the iodide-thiosulfate treatment was not found to be completely reliable. Of the various attempts to minimize or remove copper interference, the salicylaldoxime procedure of Dean and Lady (2) was chosen because its requirements were compatible with the conditions of this procedure.

Whereas Dean and Lady recommended the use of four successive salicylaldoxime extractions to ensure the complete removal of copper, the author found that a single salicylaldoxime extraction, followed by a chloroform rinse, was capable of adequately removing even large amounts of added copper.

Table 2 shows the results of extraction experiments using 0.5-g samples of copper-doped NBS sample 55e. The first four samples were extracted with salicylaldoxime, as described previously, and the chloroform extracts containing the copper were evaporated to dryness, fumed with nitric and perchloric acids, and evaluated for copper. With the

exception of No. 4, the cobalt color complexes were characteristic of pure cobalt extracts. The off-color of cobalt extract from sample No. 4, which contained the equivalent of 2% copper, indicates the presence of a small amount of residual copper.

Table 2
Copper Extraction and Cobalt Recovery

Sample No.	Weight of NBS 55e Sample Used (g)	Copper*			Color of Co Complex	Cobalt	
		Present (mg)	Added (mg)	Total (% of Sample wt)		Present† (%)	Found‡ (%)
1	0.500	0.33	0	0.065	Bluish-Green	0.007	0.0056
2	0.500	0.33	2.0	0.47	Bluish-Green	0.007	0.0058
3	0.500	0.33	5.0	1.07	Bluish-Green	0.007	0.0052
4	0.500	0.33	10.0	2.07	Olive	0.007	0.0074
5	0.500	0.33	0	0.065	Yellowish-Green	0.007	0.0063

*Copper was extracted from all samples except No. 5.
†The NBS certificate value for cobalt in standard sample No. 55e is 0.007%. This value was derived by averaging data that ranged from 0.005 to 0.008%.
‡The cobalt recovery data was obtained from a curve prepared from an aliquot of the standard cobalt solution, the spectrophotometer being set for 100% transmittance at 620 nm with reagent-grade chloroform.

Visual comparison of the cobalt color complexes suggests a greater possible error from copper than is indicated in the reported cobalt results. Reference to Fig. 1 shows the instrumental resolution of the two color complexes.

For alloys containing less than 1% copper, the procedure, as written, with a single salicylaldoxime extraction should be adequate.

SUMMARY

The foregoing procedure provides a rapid means for determining trace amounts of cobalt in a wide variety of iron-base alloys. Under the conditions of the procedure, the included salicylaldoxime extraction removes copper, which is the only element known to the author that forms an interfering tetraphenylarsonium metallothiocyanate complex. Since the copper content of alloys containing trace amounts of cobalt may be relatively high, data is presented that relates to copper as an interferent and its effective removal with salicylaldoxime.

By starting with smaller samples, or increasing the amount of the tetraphenylarsonium chloride solution and chloroform in the extraction process, or a combination of these, the method should also apply to the determination of macro amounts of cobalt in iron-base alloys.

REFERENCES

1. Affsprung, H.E., Barnes, N.A., and Potratz, H.A., Anal. Chem. 23:1680 (1951)

2. Dean, J.A., and Lady, J.H., Anal. Chem. 28:1887 (1956)

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13. ABSTRACT

A procedure is presented for the determination of trace amounts of cobalt in ferrous alloys. The cobalt is extracted as tetraphenylarsonium cobaltothiocyanate in chloroform and is determined spectrophotometrically at a wavelength of 620 nm. Cobalt concentrations that range from 0.003 to 0.04% can be determined by this method. The upper concentration limit may be easily increased to cover the analysis of most cobalt-bearing alloys.

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