

## Extractive-photometric Determination of Cobalt(II) in Steels using 4-(2-Pyridylazo)resorcinol and Xylometazoline Hydrochloride

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Cobalt(II) forms anionic chelates with 4-(2-pyridylazo)resorcinol (PAR) at pH 7.0-8.0, which can be quantitatively extracted into chloroform as an ion-pair with xylometazonium cation (XMH). The ion-association system has an absorption maximum at 535 nm and obeys Beers law in the range 0-1.6 µg of Co/ml with a molar absorptivity 42000 dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>. The Job's method of continuous variations indicated a composition of 1 : 2 : 2 for cobalt : PAR : XMH for the extracting species. Based on this extraction, a highly sensitive and selective spectrophotometric method for the determination of cobalt in various steels, after prior separation of iron, is described.

Many spectrophotometric methods have been reported based on the extraction of anionic cobalt complexes with quaternary ammonium salts<sup>1</sup>, but most of these procedures have difficulties like ease of separation of phases, low sensitivity and removal of excess of reagent<sup>2</sup>.

Cobalt(II) reacts with 4-(2-pyridylazo)resorcinol (PAR) to form a water-soluble, red-colored complex<sup>3</sup> at pH 7.8 with an absorbance maximum at 510 nm. This complex can be extracted into organic phase in presence of a long-chain quaternary ammonium salt, xylometazoline hydrochloride (XMH), which has been used for developing a rapid and sensitive spectrophotometric method for the determination of cobalt in steels.

### Results and Discussion

Of the various solvents studied chloroform was found to be the best for quantitative extraction of the ion-pair. For faster separation of the phases, 2.0 ml of propanol was added. The orange-red complex extracted into chloroform was found to be highly stable for more than 12 h, and a 2 min shaking time found to be sufficient for quantitative extraction of the system. The ion-pair gave maximum constant absorbance in the pH range 5.8-7.4 and the investigation was carried out using a pH 7.0 phosphate buffer. A 10-fold excess of PAR and 50-fold excess of XMH to cobalt(II) were necessary to achieve maximum absorbance for the ion-pair.

The absorption spectrum of the cobalt-PAR-XMH ion-pair in chloroform appears as a systematic curve with maximum absorbance at 535 nm with an average molar absorptivity of 42000 dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>, which is more than those reported for cobalt<sup>4</sup>. This ion-association system obeys Beers law in the range 0-16 µg of Co/ml at 535 nm, and the Sandell sensitivity is 9.5 × 10<sup>-4</sup> µg of Co/cm<sup>2</sup>. The precision of the present method was evaluated by determining different concentrations of cobalt (each analyzed six times) that gave standard deviations in the range 0.068-0.11 for 5-15 µg of cobalt in 10.0 ml of chloroform indicating that this method is highly precise and reproducible.

TABLE 1—DETERMINATION OF COBALT(II) IN SYNTHETIC SAMPLES AND STEELS

Synthetic solutions/ Steel samples*	Co added*	Co Found*	
		Spark Present	
Synthetic mixtures :			
(a) Mn, 100 <sup>a</sup> ; Mo, 50; V, 25; Nb, 10; Sb, 5; W, 50; Ta, 25; Fe, 500	10		9.92
(b) Mn, 10; Si, 5; Cr, 100; Mo, 10; V, 25; Nb, 25; W, 100; Ta, 10; Fe, 250	10		9.95
(c) Mn, 200 <sup>a</sup> ; Ni, 25; Cu, 2; Cr, 10; Mo, 10; V, 50; Ti, 5; Sn, 10; Nb, 5; Sb, 10; W, 10; Ce, 10; Ta, 5	10		9.98
(d) Mn, 50; Ni, 10; Si, 25; Cu, 50; Cr, 10; Mo, 25; Ti, 5; Sn, 50; Nb, 100; Sb, 10; W, 75; Ce, 5; Ta, 10; Fe, 50	10		10.02
(e) Mn, 25; Ni, 5; Si, 10; Cu, 100 <sup>a</sup> ; Cr, 25; Mo, 5; V, 50; Ti, 10; Sn, 25; Nb, 50; Sb, 5; W, 250; Ce, 25; Fe, 100	10		10.04
Low alloy steel :			
(a) ST-01-1	0.003	0.0029	0.0029 ± 0.0006
(b) ST-02-1	0.018	0.0179	0.0178 ± 0.0013
(c) ST-04-1	0.054	0.0540	0.0536 ± 0.0024
(d) C-1	0.200	0.1992	0.2083 ± 0.0140
High speed tool steel :			
(a) SS-486/1	0.030	0.0815	0.0814 ± 0.0034

\* Average of five determinations; ppm for synthetic mixture, and % for steel samples.

<sup>a</sup>After using appropriate masking agent.

**Effect of diverse ions :** The interference of various cations and anions in the determination of 10 µg of cobalt by this method was examined and it was found that phosphate, thiourea, ammonium ions, chloride, bromide, thiosulphate, nitrate, acetate, zinc and cadmium do not interfere even when they are in excess. Perchlorate, ascorbic acid, fluoride, sulphate and citrate do not interfere when they are present below 3000 ppm. The tolerance limit, amount causing an error not exceeding 2% in the absorbance, for Mg, Ta, Pb is 500 ppm and that for Mo, W, Bi, Ti is 250 ppm. 100 ppm of V, In, Ru, La, Cr and 50 ppm of Cu, Ni, Mn, Fe do not interfere. EDTA, cyanide and Pd interfere seriously.

The composition of the ion-association system as determined by Job's method of continuous variations corresponds to 1 : 2 : 2 for cobalt : PAR : XMH.

**Determination of cobalt in steels :** To the sample were added 20% (v/v) sulphuric acid (30 ml) and concentrated orthophosphoric acid (1.5 ml) and the mixture was heated gently, then concentrated nitric acid (1 ml) was added. It was evaporated to dryness followed by addition of concentrated sulphuric acid (2 ml), again evaporated nearly to dryness and the process was repeated twice. After cooling, the mass was dissolved in 20% (v/v) tartaric acid (10 ml) and diluted to 100 ml with distilled water. The solution was diluted appropriately so that it contained upto 5 µg of cobalt, and cobalt was determined by adopting the general extraction procedure.

The method was applied for the determination of cobalt in steels. Before going for the 'real life' samples, tests were carried out in synthetic mixtures corresponding to the composition of steels. The results are shown in Table 1.

### Experimental

A Shimadzu 2100 S spectrophotometer and an Unitech UI-11P pH meter were used.

All reagents were of analytical grade unless specified otherwise. A standard solution (4.9283 mg ml<sup>-1</sup>) of Co<sup>II</sup> was prepared by dissolving cobalt nitrate hexahydrate in water. A 0.01 M solution of PAR<sub>3</sub> was freshly prepared by dissolving the monosodium salt (Riedel), in demineralized water and the purity was checked by spectrophotometric titration<sup>5</sup>. A 0.01 M xyimetazone hydrochloride (Fairdeal Corp.) solution was prepared. A buffer solution of pH 7.0 was prepared by mixing solutions of sodium hydrophosphate and potassium dihydrophosphate. Double-distilled chloroform (B.D.H.) is used.

**General extraction procedure :** To an aliquot (ca 5 ml) of the sample solution containing 0.5–1.5 µg of Co/ml were added, 1 × 10<sup>-3</sup> M PAR (5 ml), 1 × 10<sup>-2</sup> M XMH (2.5 ml) and the phosphate buffer (6.0 ml), and the volume was made up to 20 ml with distilled water. The mixture was shaken for 2.0 min with chloroform (10.0 ml) and propane (2 ml). The absorbance of separated orange-red organic layer was measured at 535 nm against the reagent blank.

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### References

1. R. BHATNAGAR, I. B. BISHNOI, and D. N. PURCHIT, *Rev. Anal. Chem.*, 1991, **10**, 1; S. MOTOMIZU and K. TOEI, *Talanta*, 1982, **29**, 89.
2. K. UEDA, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 1215.
3. M. NAKAMURA, Y. SAKANASHI, H. CHIKUSHI, and F. KAI, *Talanta*, 1987, **34**, 369; H. A. FLASCHKA and A. J. BARNARD, "Chelates in Analytical Chemistry", Marcel Dekker, New York, 1972.
4. P. BERMEJO-BARRERA, J. F. V. GONZALEZ, and F. B. MARTINEZ, *Analyst*, 1985, **110**, 811; G. A. ASUERO, B. ROSALES, and M. M. RODRIGUEZ, *Analyst*, 1982, **107**, 1065.
5. T. IWAMOTO, *Bunseki Kagaku.*, 1961, **10**, 189.