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# Colorimetric Determination of Cobalt in Alloys Based on Iron, Nickel & Cobalt

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A simple colorimetric method is proposed for the determination of cobalt at milligram level. It is based on the oxidation of cobalt(II)-EDTA complex by silver(I) sulphate at *p*H 4-5 and 80°C and the measurement of absorbance of the resultant violet cobalt(III)-EDTA complex at 535 nm. Many metal ions including the coloured ones like Cu(II), Ni(II) and Fe(III) do not cause any interference. However, the interference due to chromium(III) is removed by adding iron(III) chloride solution and pyridine followed by the filtration of the hydroxides of iron(III) and chromium(III). The method is fast, accurate and applicable to the analysis of cobalt in alloys based on iron, nickel and cobalt. The accuracy of the method is ±0.1 to ±0.3% in alloys containing cobalt in the range of 8-62%.

The assay of cobalt in its alloys continues to be an interesting area of research. Gravimetric[1], volumetric[1-3] and colorimetric methods[4-6] have been developed. Silverstone and Bach[7] have developed a spectrophotometric method for cobalt in nickel base alloys using EDTA and hydrogen peroxide. However, most of these methods are not free from drawbacks. In a previous investigation[8] from our laboratory, it was shown that silver(I) can be reduced to metal quantitatively with cobalt(II) nitrate in the presence of EDTA in a weakly acidic medium according to the reaction:

$$\underset{\text{orange-red}}{Ag(I) + Co(EDTA)^{2-}} \rightarrow \underset{\text{violet}}{Ag(0) + Co(EDTA)^{-}}$$

The redox nature of the reaction was established by the gravimetric assessment of silver metal[8]. That Ag(I) is able to oxidise cobalt is due to the fact that redox potential of Co(II)/Co(III) system which is 1.79 V is reduced to 0.56 V on complex formation with EDTA. The redox potential of Ag(I)/Ag(0) is 0.8 V. This enables Ag(I) to oxidise quantitatively Co(II)-EDTA (redox potential = 0.56 V) to a violet-coloured Co(III)-EDTA complex.

The oxidation of cobalt(II)-EDTA complex by silver(I) sulphate has been studied in detail and the optimum experimental parameters have been established for the colorimetric determination of cobalt at milligram level. The suitability of this method has been illustrated by estimating cobalt in alloys based on iron, nickel and cobalt.

Standard cobalt solution was prepared by dissolving pure cobalt (1 g) (Johnson-Matthey) in minimum quantity of nitric acid (1:2) and making it upto 1 litre. The solution (0.5%) of silver sulphate (AR, BDH) was prepared by dissolving it (2.5 g) in doubly distilled water (500 ml). EDTA solution (0.25 *M*) was prepared by dissolving disodium salt of EDTA (46.5 g) (E. Merck) in doubly distilled water (500 ml). Iron(III) chloride solution (4%) was prepared by dissolving pure iron (4 g) in hydrochloric acid, oxidising with required quantity of nitric acid and diluting to 100 ml with water. The mixture of nitric acid and hydrochloric acid was prepared by mixing nitric acid (50 ml) (1:1), conc. hydrochloric acid (70 ml) and distilled water (30 ml).

Spectronic 20 colorimeter was used for absorbance measurements using 1.25 cm test tubes. A Metrohm *p*H-meter fitted with a glass-calomel electrode assembly was used for *p*H measurements.

*Analysis of alloys*

The alloy sample (0.1-0.25 g) was dissolved in acid mixture (10 ml). If the alloy contained chromium, iron(III) chloride solution (1 ml) was added. The solution was evaporated to dryness, cooled, sulphuric acid (5 ml) added, fumed and cooled. To this water (20 ml) was added and warmed to dissolve the salts. The solution was boiled, cooled and its volume made upto 75 ml by adding doubly distilled water. Pyridine (15 ml) was added and the volume finally made upto 100 ml with water. The solution was then mixed thoroughly, allowed to stand for 15 min, filtered through a dry Whatman No. 41 filter paper and the filtrate collected. If the alloy did not contain chromium the addition of iron(III) chloride and separation by pyridine were omitted.

To the solution or the filtrate (10 ml) were added acetic acid (5 ml), sodium acetate-acetic acid buffer (5 ml, *p*H 4), EDTA solution (3 ml) and silver(I) sulphate solution (5 ml). The solution was heated to 80°C for 20 min, cooled and the volume made upto 50 ml with distilled water. The elemental silver was allowed to settle and the absorbance of the violet cobalt(III)-complex measured at 535 nm against a blank containing the sample solution and all other reagents except silver(I) sulphate. The amount of cobalt in the solution was directly read from a linear calibration graph obtained over the range of 1-8 mg Co/50 ml solution.

It is found that quantitative formation of the violet complex occurs in the *p*H range 3.0 to 5.5. Hence in the procedure, the solutions were always adjusted to *p*H 4

Table 1—Colorimetric Determination of Cobalt in Various Types of Alloys

| Alloy | Cobalt (%) Present | Found |
|---|---|---|
| *Iron base alloys* | | |
| Co–Mo–W–steel (NBS No. 153A) | 8.47[a] | 8.4; 8.55; 8.57 |
| Fe–Cr–Co magnet alloy | 21.2[b] | 21.0; 21.0; 21.2 |
| AlNiCo magnet alloy (BCS No. 398) | 14.90[a] | 14.83; 14.97; 14.67 |
| Permanent magnet alloy (BCS No. 233) | 23.72[a] | 23.5; 24.0; 24.0 |
| Alcomax III (BCS No. 365) | 24.7[a] | 24.5; 24.9; 24.5 |
| Hycomax III (BCS No. 384) | 33.7[a] | 33.66; 33.66; 34.0 |
| *Nickel base alloys* | | |
| Waspaloy (NBS No. 349) | 13.95[a] | 13.90; 14.1; 13.80 |
| Nimonic-90 (BCS No. 310/1) | 17.0[a] | 17.17; 17.03; 17.0 |
| *Cobalt base alloys* | | |
| Heat resisting alloy (NBS No. 168) | 41.2[a] | 41.3; 40.95; 41.3 |
| Cobalt-samarium alloy | 61.4[b] | 61.6; 61.66; 61.3 |

(a) Standard values; (b) values obtained by the well known redox method of Vydra and Pribil[3].

by the use of sodium acetate-acetic acid buffer of *p*H 4. The use of insufficient EDTA leads to low results while excess reagent has no unfavourable effect on complex formation. 3 ml of 0.25 *M* EDTA are found sufficient for 40 mg sample. 1 ml of 0.5% silver(I) sulphate/1.5 mg cobalt is required for complete oxidation. Large variations in the quantity of pyridine affect colour formation; increase in pyridine concentration causes a decrease in absorbance value. It is found that oxidation of Co(II)-EDTA by Ag(I) does not occur at room temperature (30 C). However at 60 and 80 C, the oxidation is complete in 30 and 15 min respectively.

For interference studies 4 mg/ml solutions of Cu(II), Ni(II), Sn(II), Pb(II), Mn(II), Fe(III), Al(III), Cr(III), Ti(IV), Zr(IV), V(V), Mo(VI) and W(VI) were prepared from AR grade compounds. It is found that only chromium(III) causes serious interference, because it forms similar coloured complex with EDTA. Therefore, in the case of alloys containing chromium, chromium(III) must be removed. In the presence of sufficient amount of iron(III), chromium(III) is precipitated quantitatively with pyridine as a mixture of chromium and iron hydroxides. Al(III), Ti(IV) and Zr(IV) are also precipitated leaving Co(II), Ni(II), Cu(II), Mn(II), V(V) and Mo(VI) in solution. Cobalt(III)-EDTA absorbs maximally at 535 nm at which wavelength the absorption due to EDTA complexes of Ni(II), Cu(II) and Co(II) is negligible. Therefore, by measuring the absorbance of cobalt(III)-EDTA against a blank containing complexes of Co(II), Cu(II) and Ni(II), any interference due to these elements can be eliminated.

The results of the determination of cobalt in alloys based on iron, nickel and cobalt, presented in Table 1, show that the method is accurate and reproducible results are obtained. The results compare well with standard values or those obtained by the well-known redox method of Vydra and Pribil[3].

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