Extractive-photometric Determination of Cobalt with Isonitrosothiocamphor

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Received 14 November 1984; revised and accepted 5 June 1985

Cobalt(II) forms a 1:3 complex with isonitrosothiocamphor (INTC). A single extraction from 1 M hydrochloric acid medium is adequate for quantitative extraction of cobalt. Beer's law is obeyed in the range 0.2-1.5 ppm. The system tolerates a thousand-fold excess of diverse ions. Cobalt has been determined successfully in synthetic mixtures using the proposed method.

The potential of isonitrosothiocamphor (INTC) as an analytical reagent for cobalt remains unexploited and this has stimulated our interest in the title investigation. Previous use of the reagent has been reported in the extraction of copper. In the presence of acetate, cobalt(II) gives a violet colour instantaneously when treated with an ethanolic solution of INTC and the coloured chelate so formed is extractable into chloroform. Taking advantage of this behaviour, a rapid spectrophotometric method for the determination of cobalt has been developed.

A Shimadzu PR 1 spectrophotometer was used for absorbance measurements. A 0.04% ethanolic solution of INTC was used in the present work. A stock solution of Co(II) was prepared by dissolving a known weight of Co(II) chloride hexahydrate of a guaranteed reagent grade in distilled water followed by standardisation by EDTA titration. A working solution of Co(II) (10 µg) was prepared by dilution. Chloroform was distilled before use. All the other reagents were of AR grade and were employed without further purification.

General procedure

An aliquot containing 5-15 µg cobalt was transferred to a 100 ml separating funnel followed by the addition of 0.1 ml of aqueous sodium acetate (1%) and 1 ml of an ethanolic solution of INTC (0.04%). The aqueous phase was diluted to 10 ml and adjusted to 1 M hydrochloric acid. The solution thus prepared was then equilibrated with 10 ml of chloroform for 1 min. The organic extract was washed with 0.5 M sodium hydroxide and the absorbance measured at 350 nm against the corresponding reagent blank. Cobalt was determined from a calibration curve.

Effect of pH on the extractibility of Co-INTC complex into chloroform was examined in terms of the absorbance of the chelate. A complete and quantitative extraction is found to be accomplished in the medium ranging from 1 M hydrochloric acid to 1 M sodium hydroxide.

The cobalt complex shows absorption maxima at 240, 295 and 325 nm. The reagent blank itself shows absorption maxima at 240 nm and 295 nm, with negligible absorbance beyond 340 nm. The absorbance measurement was, therefore, performed at 350 nm.

The complex obeys Beer's law in the concentration range 0.2-1.5 ppm of cobalt at 350 nm. At this wave length the molar absorptivity of the complex is 1.7 x 10^4 lit mol^-1 cm^-1 and the sensitivity is 0.0025 µg/cm² for an absorbance of 0.001.

One ml of 0.04% ethanolic solution of INTC is sufficient to extract 10 µg cobalt. The colour of the complex is quite stable for several days.

Effect of foreign ions

The effect of foreign ions on the determination of cobalt according to the above procedure was noted in individual cases. A thousand-fold excess of the following ions does not interfere in the determination of 10 µg of cobalt: Hg(II), Ni(II), Mo(IV), Fe(II), Fe(III), Zr(IV), Th(IV), Mn(II), Cd(II), Ba(II), Sr(II), Zn(II), Ca(II), Mg(II), U(VI), Cr(III), Al(III), Pt(IV), Rh(III), Pb(II), Ag(I) and As(III). The system tolerates a ten thousand-fold excess of anions like acetate, sulphate, oxalate, phosphate, borate, phthalate, citrate, tartrate, fluoride, nitrate, thiocyanate and thiocyanate. EDTA interferes if the operation is carried out at pH > 6. Interference due to Cu(II) was avoided by carrying out the extraction in presence of tartrate. Co-extraction of Pd(II) was checked using thiourea as the masking agent.

Table 1—Determination of Cobalt in Synthetic Mixtures

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Composition</th>
<th>Co found (µg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Co(10 µg) + Ni(500 µg) + Cu(500 µg) + Fe(500 µg) + tartrate (3 mg)</td>
<td>10.05</td>
</tr>
<tr>
<td>2.</td>
<td>Co(10 µg) + Pd(500 µg) + Pt(500 µg) + Rh(500 µg) + thiosulfate (3 mg)</td>
<td>10.20</td>
</tr>
<tr>
<td>3.</td>
<td>Co(10 µg) + Zn(500 µg) + Hg(500 µg) + Cd(500 µg)</td>
<td>9.95</td>
</tr>
<tr>
<td>4.</td>
<td>Co(10 µg) + Zn(500 µg) + Th(500 µg) + U(500 µg)</td>
<td>10.15</td>
</tr>
<tr>
<td>5.</td>
<td>Co(10 µg) + Mn(500 µg) + Cr(500 µg) + Mo(500 µg)</td>
<td>10.00</td>
</tr>
<tr>
<td>6.</td>
<td>Co(10 µg) + As(500 µg) + Ag(500 µg) + Pb(500 µg)</td>
<td>10.15</td>
</tr>
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</table>
The Co-INTC chelate was scarcely back extracted from chloroform extract with 1-12 $M$ hydrochloric acid. It is also interesting to observe that the absorbance of the organic extract remains unaffected even after washing with 2 $M$ sodium hydroxide.

*Analysis of synthetic mixtures*

In absence of real samples, the method has been tested on a number of synthetic mixtures and the results are shown in Table 1.

The average of six determinations for 10 μg is 10.03 μg and the standard deviation is 0.08 μg.

The authors thank the Head of the Department of Chemistry, North Bengal University for laboratory facilities.

References