Extractive Spectrophotometric Determination of Cobalt(II), Nickel(II) & Palladium(II) & Consecutive Determination of Palladium(II) & Nickel(II)/Palladium(II) & Cobalt(II) in Binary Mixtures

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A sensitive method is described for the extraction and spectrophotometric determination of cobalt(II), nickel(II) and palladium(II) using 1-hydroxy-2-acetonaphthoneoxime (I-HANO). The coloured 1:2 (metal-ligand) complexes formed are quantitatively extracted with chloroform in different pH ranges. Beer's law is obeyed in a small range of concentration. The molar absorptivity, Sandell's sensitivity, and formation constants of the complexes have been evaluated. These metal ions in traces can be determined in the presence of large number of interfering ions.

Literature reports the use of 1-hydroxy-2-acetonaphthoneoxime (1-HANO) as a gravimetric reagent for the determination of palladium(II), copper(II) and nickel(II) in various alloys and in ternary mixtures of metal ions. The use of this reagent for the assay of cobalt, nickel and palladium in ppm range by extractive spectrophotometric method is described in this note. Several oximes are available for the spectrophotometric determination of several transition metal ions, but most of these suffer from disadvantages of one or more kinds. However the present reagent, 1-HANO offers better sensitivity and its use is less time-consuming.

1-Hydroxy-2-acetonaphthone-oxime prepared according to literature method was repeatedly recrystallised from ethanol to get analytically pure compound, m.p. 167-69°. A 0.01 M alcoholic solution of the reagent was used for all extraction studies. The reagent is stable at room temperature for almost 10 days.

Standard stock solutions of cobalt(II), nickel(II) and palladium(II) were prepared by dissolving appropriate amounts of AR grade CoCl₂.6H₂O, NiSO₄.6H₂O and LR grade PdCl₂ (Arora Matthey) and standardized.

Analar grade sodium acetate, ammonium acetate-ammonium hydroxide solutions were used for preparing the buffer solutions.

Spectronic-21, Bausch-Lomb spectrophotometer with 1 cm matched glass or quartz cells was used for all absorbance measurements.

General procedure

To an aliquot of metal ion solution (containing 20-70 µg of cobalt, 10-65 µg of nickel and 10-55 µg of palladium) was added the requisite amount of reagent solution, the pH of the solutions adjusted as follows: 8.60 for cobalt(II), 9.0 for nickel(II) and 5.6 for palladium(II). The mixture was allowed to stand for 1 min and to this was added chloroform (10 ml). After shaking for 2 min the chloroform layer was separated, dried over anhydrous sodium sulphate and the absorbance measured against the reagent blank. The amount of metal ion extracted was computed from calibration graph.

The chloroform solutions of the metal complexes of cobalt(II), nickel(II) and palladium(II) exhibited maximum absorbance at 380, 396 and 378-380 nm, respectively; under similar condition the reagent had negligible absorbance at these wavelengths.

The absorbances of metal ion complexes in chloroform show a decreasing trend in both higher and lower pH ranges, than those recorded in Table 1 for maximum absorbance.

Quantitative extractions were obtained when the reagent volume was 0.4, 0.5 and 1.0 ml for 50 µg, each of cobalt, nickel and palladium respectively. The colour of the extracted complexes was found to have a constant absorbance for about 24 hr.

Amongst the solvents such as chloroform, methyl isobutyl ketone, carbon tetrachloride, benzene, amyl acetate and n-butanol tried for extraction of the complexes, chloroform was found to be the most suitable.

The validity of Beer's law, the optimum Ringbom concentration and Sandell's sensitivities are reported in Table 1.

Job's method of continuous variation was employed for the determination of the composition of the complexes. The metal to ligand ratio was found to be 1:2 for all the three metal ions. This conclusion was further supported by the mole ratio method. The formation constants were calculated from the curves obtained by the continuous variation method and adopting the method of Harvey and Manning. The results are presented in Table 1.

The influence of diverse ions on the determination of metal ions using 1-HANO was studied, in the usual manner. The difference of ±2% in the absorbance was taken to cause interference.

In the case of cobalt (50 µg), 2000 µg of acetate, chloride, sulphate, sulphite and nitrate, 500 µg of calcium, barium, strontium, zinc and cadmium; 50 µg
Table 1—Spectral Characteristics of Complexes of Cobalt(II), Nickel(II) and Palladium(II) with 1-Hydroxy-2-acetonaphthone-oxime

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Cobalt(II)</th>
<th>Nickel(II)</th>
<th>Palladium(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colour</td>
<td>Brown</td>
<td>Greenish</td>
<td>Dark yellow</td>
</tr>
<tr>
<td>$\lambda_{max}$ (nm)</td>
<td>380</td>
<td>396</td>
<td>378-380</td>
</tr>
<tr>
<td>pH range</td>
<td>8.4-9.2</td>
<td>8.5-9.5</td>
<td>4.2-5.8</td>
</tr>
<tr>
<td>pH range selected</td>
<td>8.6</td>
<td>9.0</td>
<td>5.6</td>
</tr>
<tr>
<td>Composition (metal:ligand)</td>
<td>1:2</td>
<td>1:2</td>
<td>1:2</td>
</tr>
<tr>
<td>Beer’s law range (µg in 10 ml)</td>
<td>20-70</td>
<td>10-65</td>
<td>10-55</td>
</tr>
<tr>
<td>Ringbom concentration range (ppm)</td>
<td>2.5-6.3</td>
<td>1.5-6.3</td>
<td>1.26-5.01</td>
</tr>
<tr>
<td>Molar extinction coefficient (litre mol⁻¹ cm⁻¹)</td>
<td>$5.66 \times 10^3$</td>
<td>$5.75 \times 10^3$</td>
<td>$9.30 \times 10^3$</td>
</tr>
<tr>
<td>Sandell sensitivity (µg cm⁻²)</td>
<td>0.010</td>
<td>0.010</td>
<td>0.011</td>
</tr>
<tr>
<td>Formation constant</td>
<td>$2.577 \times 10^7$</td>
<td>$4.815 \times 10^7$</td>
<td>$2.369 \times 10^8$</td>
</tr>
</tbody>
</table>

of palladium could be tolerated. Iron(III), nickel, copper and uranium(IV) interfere with the estimation of cobalt(II). Ascorbic acid, hydroxylamine hydrochloride, EDTA and fluoride reduced the absorbance of the complex.

In the case of nickel (50 µg), 2000 µg of acetate, chloride, sulphate, 500 µg of calcium, strontium, barium, zinc; 50 µg of palladium and manganese could be tolerated. Copper, iron(III), cobalt and uranium(IV) all interfered seriously. However 300 µg of iron(III) in the presence of ascorbic acid could be tolerated. Copper(II) when present to the extent of 400 µg could also be tolerated in presence of thiourea. Fluoride, thiocyanate and EDTA reduced the absorbance of the complex.

In the case of palladium (50 µg), 3000 µg of acetate, chloride, sulphate, ascorbic acid; 1000 µg of calcium, strontium, barium, manganese and 50 µg of cobalt and nickel could be tolerated. Copper formed emulsions. Iron(III) interfered seriously. However even 200 µg of iron(III) could be tolerated in the presence of ascorbic acid; EDTA, fluoride and tartrate decreased the absorbance. Among the various platinum group elements, iridium formed a green coloured complex only on heating which was not extractable into chloroform; equal amounts of platinum, rhodium, ruthenium did not interfere in cold condition.

Consecutive determination of palladium(II) and nickel(II)

A mixture containing equal amounts (50 µg each) of palladium(II) and nickel(II) was taken and the acidity adjusted to pH 5.6 with sodium acetate. To this was added 0.01 M reagent solution (1 ml) and shaken for 1 min. The palladium complex formed was extracted with chloroform (2 x 5 ml). The organic layer collected, dried over anhydrous sodium sulphate and its absorbance recorded at 378 nm against reagent blank. The amount of palladium was computed from calibration graph.

For nickel(II) pH of the aqueous layer was raised to 9.0 with ammonium acetate-ammonium hydroxide buffer and the above sequence of steps was repeated. The absorbance of the final solution was recorded at 396 nm against reagent blank. The amount of nickel was computed from calibration graph. The same procedure could be used for the determination of cobalt in the presence of palladium also.

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References
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