Spectrophotometric determination of cobalt(II) and gold(III) in the presence of potassium persulphate using resacetophenone oxime

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Cobalt(II) and gold(III) react with 2,4-dihydroxy acetophenone oxime (RPO) forming yellowish brown and greyish green coloured soluble complexes respectively. The reactions are very slow but become fast in the presence of $K_2S_2O_8$. This may be due to the enhancement of aeration oxidation of metal complexes with soluble complexes respectively. The reactions are very slow but shows 0.12-1.80 $\mu$g/ml and pH 3.5 where Beer's law is obeyed in the range of lower oxidation states (Co(II)), Au(III)). The complex in solution. The resultant reaction mixture was recrystallised from hot aqueous alcohol (m.p. 199-200°C). An ethanolic solution of RPO (0.01 M) was used in the studies. Solutions of $K_2S_2O_8$ (0.1 M, AR, BDH), cobalt nitrate (0.1 M, AR, BDH) and chloroauric acid (0.01 M, Johnson Mathey) were prepared by dissolving requisite amounts of the respective salts in distilled water and standardized$^{11,12}$. Buffer solution of pH 0.5-3.0 was prepared by mixing suitable volumes of 1 M HCl and 1 M CH$_3$COONa. For buffers in the range pH 3.5-7.0, 0.2 M CH$_3$COOH and 0.2 M CH$_3$COONa and for pH 8.0-12.0, 2 M NH$_4$OH and 2 M NH$_4$Cl were used. Shimadzu UV-vis spectrophotometer (160-A) and ELICO digital pH meter (LI-120) were employed for absorbance and pH measurements respectively.

Procedure

Varying amounts of Co(II) or Au(III) were treated with 10 fold excess of RPO in buffer solution of pH 9.5 or pH 3.5 respectively in the presence of 5 fold excess or 2 fold excess of $K_2S_2O_8$ respectively. A 10% DMF (by volume) was maintained to keep the Au(III) complex in solution. The resultant reaction mixtures were heated on water bath for 10 min, cooled and volume made up to 10 ml. The absorbance of the coloured solutions was measured at 390 nm (for Co(II)) or at 630 nm (for Au(III)) against the reagent blank. The absorbance data were plotted against the amount of metal ion. Linear plots were obtained indicating the obedience of Beer's law.

Results and discussion

Cobalt(II) reacts with RPO in the pH range 8-11 forming a yellowish brown coloured solution. The colour intensity was maximum and constant in the pH range 9.0-10.0. The complex showed $\lambda_{max}$ at 390 nm where the reagent had very low absorbance. Hence further analysis was carried out at pH 9.5 and at 390 nm. Au(III) forms a greyish green coloured turbid solution with RPO in the pH range 1-10. The solution becomes clear showing maximum and constant absorbance in 10% DMF in the pH range 3-4 and again at pH 9.0. However, the absorbance at pH 3.5 was greater than that at pH 9.0. The gold complex shows two maxima at 380 nm and at 630 nm. However, the reagent absorbed considerably at 380 nm with no absorbance at 630 nm. Therefore, studies on the gold complex were made at 630 nm and at pH 3.5. The colour reaction between RPO and either of
Table 1—Analysis of cobalt(II) and gold(III) in pharmaceutical samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Amount of metal ion found*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cert. value</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Vitamin B₁₂ (mg/tablet)</td>
<td></td>
</tr>
<tr>
<td>Thiamin mononitrate(B₁)10; Riboflavin(B₁)10; pyridoxime hydrochloride 3; Nicacinamide 100; Calcium pentothenate 50; Cyanocobalamine 15 mg; Sodium ascorbate 150; Folic acid 1.5</td>
<td>0.552</td>
</tr>
<tr>
<td>Rheumartho with gold</td>
<td></td>
</tr>
<tr>
<td>Sri Baidyanath Ayurvedic Bhavan Ltd, India</td>
<td>1.000</td>
</tr>
</tbody>
</table>

*Average of five determinations

The metal ions studied was quite slow and attained maximum absorbance after 36 hours. When the reaction mixture was heated, the maximum absorbance was attained in one hour. In the presence of 5-fold excess of potassium persulphate in the case of Co(II) or 2-fold for Au(III), the maximum colour intensity was obtained on heating the reaction mixture for only 10 min on a water bath. In aqueous solutions with no complexing agent, Co(II) does not undergo oxidation to Co(III). But in the presence of a complexing agent which forms stable complex with Co(II), the stability of Co(III) is greatly increased. In the present case it is predicted that Co(II) forms a colourless complex with RPO in alkaline medium. This on slow aerial oxidation gives rise to a yellowish brown colour Co(III) - RPO complex. The addition of potassium persulphate may be catalysing the oxidation of Co(II) complex to Co(III) complex. In the same way persulphate might be accelerating the oxidation of Au(III) to Au(V) in acidic medium and the resultant Au(V) species forming a greyish green coloured complex with RPO since Au(V) exists only in the form of chelate complexes with donor ligands. A similar behaviour was observed in our earlier studies in the reaction between Mn(II) and RPO. Beer’s law was obeyed in the range 0.12 - 1.77 ppm and 0.39 - 5.12 ppm for Co(III) and Au(V) respectively. The sensitivity of the method, expressed in terms of molar absorptivity (ε) and Sandell’s sensitivity was calculated as 2.7 x 10⁴ 1 mol⁻¹ cm⁻¹ and 0.002 µg/ cm² respectively for Co(III); and 3.4 x 10⁴ 1 mol⁻¹ cm⁻¹ and 0.0058 µg/cm² respectively for Au(V). The standard deviation of the method for 10 determinations each for Co(III) and Au(V) was obtained as ± 0.00022 and ± 0.00032 respectively. A minimum of 10-fold excess of RPO, 5-fold and 2-fold excess of K₂S₂O₈ were required to obtain complete complexation for Co(III) and Au(V) respectively. The studies on effect of foreign ions on the absorbance of the experimental solution showed that Ni(II), Cr(III), Ag(I) and Hg(II) are tolerated in 70 fold, 30 fold, 18 fold and 10 fold excess respectively in the determination of Co(II). The interference of Fe(III) can be masked with EDTA. All other ions did not interfere even when present in more than 100 fold excess. In the determination of Au(III), the tolerance limits of ions which interfered in the present method are as follows: SO₄²⁻, NO₃⁻ (10-fold); I⁻ (30-fold); Ni(II), Cu(II) (10-fold); Se(IV), Te(IV) (18-fold); As(V), V(V) (30-fold); Sn(II), Sb(V) (40-fold); and Ag(I), Th(IV), Zr(IV), U(VI) (60-fold). Fe(III) was tolerated in 80-fold excess in the presence of citrate. Other ions were tolerated in more than 100-fold excess. The composition of both the complex solutions was determined to be 1:1 by Job’s continuous variation method, molar ratio method and slope ratio method. The stability constants of the complexes as obtained by the continuous variation method were calculated to be 8.99 x 10⁴ and 6.9 x 10⁴ for Co(III) and Au(V) complexes respectively.

Application to real samples

The present method was applied for the determination of cobalt(II) in vitamin B₁₂ tablets and gold(III) in Rheumartho Pharmaceutical sample. The sample solutions were prepared in alcohol and hydrochloric acid respectively and treated with appropriate amount of RPO in suitable buffer solutions and K₂S₂O₈ solution. The ab-
sorbance was measured at the appropriate wavelength and the amount of the metal ions in the samples were computed from pre-determined calibration plots. The results presented in Table 1 indicate the accuracy of the present method in the analysis of natural samples.

The method is simple, sensitive and selective in the presence of potassium persulphate. Many metal ions which are found in association with either Co(II) or Au(III) do not interfere in the present method in reasonably larger quantities. The sensitivity of the present method is greater than some of the reported methods using oximes for Co(II)\textsuperscript{14-17} and for Au(III)\textsuperscript{18-20}. With regard to the determination of Au(III), the present method is more selective than those reported by Kabil et al.\textsuperscript{20}, Nemeceva et al.\textsuperscript{18} and Li et al.\textsuperscript{19}.

References