Solvent Extraction & Spectrophotometric Determination of Palladium Using Mixed Ligand Complex Formation with Pyridine, α-Picoline, β-Picoline, γ-Picoline or 2,4,6-Collidine & Thiocyanate

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Palladium forms complexes with pyridine/α-picoline/β-picoline/γ-picoline/2,4,6-collidine in the presence of thiocyanate. These complexes are quantitatively extractable into chloroform and thus provide a method for the estimation of Pd(II). All the species absorb around 310 nm. The sensitivities are 0.0076, 0.0042, 0.0051, 0.0050 and 0.0055 μg Pd(II) cm⁻², and the molar absorptivities of the complexes are 1.39 x 10⁴, 2.51 x 10⁴, 2.46 x 10⁴, 2.13 x 10⁴ and 3.21 x 10⁴ lit mol⁻¹ cm⁻¹ for pyridine, α-pic, β-pic, γ-pic and 2,4,6-collidine systems respectively. Hg(II), Fe(III), Co(II) and Cu(II) interfere in every system, while Ni(II) interferes in all the systems except in α-pic-SCN and 2,4,6-collidine-SCN systems.

Use of pyridine-thiocyanate for extractive-spectrophotometric determination of various metals is well known. But the extractive behaviour of some bivalent metals with methyl substituted pyridines in thiocyanate system has not been studied. We have undertaken a systematic programme to study the extractive behaviour of Pd(II) with pyridine and some of its methyl substituted derivatives in thiocyanate system. Based on these studies, a few rapid and sensitive methods for the extractive and spectrophotometric determination of trace amounts of palladium have been developed. The substituted pyridines used are: α-picoline, β-picoline, γ-picoline and 2,4,6-collidine.

After studying the influence of pH, and concentrations of reagents on the colour formation, the following procedure was adopted for the estimation of Pd(II).

Procedure—An aliquot containing 10-100 μg Pd(II) was mixed with 1.5 ml of 2% (w/v) aqueous ammonium thiocyanate followed by the addition of 1 ml (100%) of pyridine/α-pic/β-pic/γ-pic/2,4,6-collidine. An appropriate amount of dilute HCl/NaOH (0.1 N solution) was added and pH of the resulting solution was measured after extraction. The volume of the aqueous phase was made upto 20 ml with excess of doubly distilled water and then it was equilibrated with 20 ml chloroform by manual shaking for 10 min. The two layers were allowed to settle for 10 min and then separated. Finally, the volume of chloroform extract was made upto 20 ml with excess solvent and its absorbance was measured against a reagent blank. Extracted palladium was determined from a previously prepared calibration curve. The chloroform extract was shaken with anhydrous sodium sulphate prior to the absorption measurement step in order to remove any associated water droplets. All the experiments were carried out at 25-30 °C. The details of the experimental procedure for different systems are given in Table I.

pH of the solution plays an important role in the quantitative extraction of Pd(II) into the organic layer. Study of extractive behaviour of the metal over the pH range 0.5-10 shows that quantitative extraction occurs in the pH ranges 4.9-7.1, 3.5-7.0, 2.6-5.8, 4.9-6.6 and 1.2-2.1 for pyridine, α-picoline, β-picoline, γ-picoline and 2,4,6-collidine systems respectively. In all the cases, 1 ml of 100% base and 1.5 ml of 2% (w/v) NH₄SCN solutions were used. Above or below these pH values, the extractions were found to be incomplete. Different amounts of palladium were extracted, as described in the general procedure earlier, at the corresponding pH and the optical densities were measured. The aqueous phase after each extraction

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Base employed</th>
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<tbody>
<tr>
<td>pH</td>
<td>Pyridine</td>
</tr>
<tr>
<td>4.9-7.1</td>
<td>3.5-7.0</td>
</tr>
<tr>
<td>315</td>
<td>304</td>
</tr>
<tr>
<td>λ max (nm)</td>
<td>315</td>
</tr>
<tr>
<td>Interfering ions</td>
<td>V(IV), molybdate, S₂O₃²⁻</td>
</tr>
<tr>
<td>Molar absorptivity</td>
<td>1.39 x 10⁴</td>
</tr>
</tbody>
</table>

†Concentration of SCN was 1.5 ml (2%, w/v) and that of the base 1 ml (100%,) in each case.
was clear and colourless. The Beer's law was obeyed in the ranges 0.8-7.7, 0.4-4.5, 0.5-5.5, 0.5-5.0 and 0.5-5.5 µg of Pd(II)/ml CHCl₃ for the pyridine, α-picoline, β-picoline, γ-picoline and 2,4,6-collidine systems respectively. Pd(II) was quantitatively extracted into chloroform in a single operation when the layers were shaken for 10 min.

Effect of the variation of concentrations of the reagents was tested at the corresponding pH, the other variables remaining the same. It was found that 0.5 ml of the respective reagents and 1.3 ml of 2% (w/v) aqueous ammonium thiocyanate was sufficient to extract 100 µg Pd(II). Higher concentrations [1 ml for organic reagents and 1.3 ml for 2% (w/v) aq. ammonium thiocyanate] did not affect extraction, but were avoided because of reagent economy.

Sensitivities, in terms of Sandell's definition, are 0.0076, 0.0042, 0.0051, 0.0050 and 0.0055 µg Pd(II) cm⁻² for pyridine, α-picoline, β-picoline, γ-picoline, 2,4,6-collidine systems respectively.

The optical densities of the chloroform extracts, containing 40-160 µg Pd(II) extracted by the recommended procedure, were measured at the different intervals of time and it was found that organic extracts always produced a steady absorbance value for at least 24 hr at room temperature. At the end of 35-40 hr, the absorbance values decreased by about 5-10%. So it seems convenient to measure the optical densities within 24 hr of the extraction.

Effect of diverse ions—In order to study the effect of diverse ions on the extraction behaviour, 40-100 µg Pd(II) was extracted and determined according to the general procedure in the presence of about 10 mg of foreign ions except in the cases of Rh(III) (1.96 mg), Pt(IV) (1.00 mg), Cd(II) (3.2 mg), F⁻ (4.5 mg), Br⁻ (5.8 mg), I⁻ (8.2 mg) and EDTA (4 mg) where more than the amount indicated in the brackets caused serious interference. Interference due to Fe(III) and Co(II) was avoided by masking them with ammonium hydrogen bifluoride in the aqueous phase, 5.38 mg of Fe(III) and 4.99 mg of Co(II) could be rendered innocuous in this way for each of the systems.

In each case, upto 7.68 mg Hg(II) could be masked by excess EDTA, and 6.014 mg citrate ions could render 2.13 mg of Cu(II) innocuous. Ni(II) interfered only with pyridine/β-pic/γ-pic-thiocyanate systems. When the methyl group is in the 2-position of the pyridine ring, Ni(II) does not form a complex with it; therefore, α-Pic and 2, 4, 6-collidine can be used to separate Pd(II) from Ni(II) without using any other masking agent. Interference due to Sr(II), Ba(II), Zn(II) and Cd(II) in the 2,4,6-collidine-thiocyanate system was successfully avoided by using aqueous ammonium hydrogen bifluoride. In the same system, Pt(IV) always co-extracted with Pd(II), and so in its presence Pd(II) could not be determined. Due to steric factors, 2,4,6-collidine requires highly acidic medium for complexation, and in relatively highly acidic solution only the ions Ba(II), Zn(II), Sr(II) and Cd(II) interfere; thus this system differs markedly from other four systems.

Molybdate and thiosulphate interfered in the extraction of Pd(II) from aqueous phase to the organic phase. Tolerance limit for oxalate in the case of pyridine-SCN and 2,4,6-collidine-SCN systems is relatively low. In these systems, only upto 4.5 mg of oxalate ions do not hamper the quantitative extraction of Pd(II).

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