Extractive Photometric Determination of Palladium(II) with 4-Nitrosoresorcinol in Presence of Pyridine & Some of Its Methyl Substituted Derivatives

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Received 18 June 1987; revised 14 September 1987; accepted 11 December 1987

An extractive photometric method is proposed for the determination of Pd(II) using 4-nitrosoresorcinol and pyridine/substituted pyridines. The mixed-ligand complexes of palladium(II) with 4-nitrosoresorcinol and pyridine/its methyl derivatives are extractable into chloroform and obey Beer's law. The molar absorptivities of the complexes are (2.6-3.5) × 10^4 I mol⁻¹ cm⁻¹ at λ_max 395-400 nm and Sandell's sensitivities are 0.003-0.004 μg Pd(II)/cm². The influence of foreign ions is studied.

The use of pyridine-thiocyanate for extractive photometric determination of various metals is well established. 4-Nitrosoresorcinol reacts with cobalt(II) and palladium(II) to form red complexes which are insoluble in chloroform. The reaction was used for detection and determination of the metals in aqueous solution by colour comparison. In the present note we report the extractive photometric determination of Pd(II) with 4-nitrosoresorcinol in presence of pyridine and some of its methyl substituted derivatives like α-picoline, β-picoline, γ-picoline and 2,4,6-collidine, extractable into chloroform under optimum conditions.

The absorbance measurements were made with a Shimadzu PR 1 spectrophotometer equipped with stoppered quartz cells of 10 mm path length. An ECL 5651 digital pH meter was used for pH measurements.

Palladium chloride (Johnson & Matthey) (1 g) was dissolved in hot conc. HCl (1 ml) and diluted to 250 ml with distilled water followed by standardisation with dimethylglyoxime. A working solution (210.5 μg Pd/ml) was prepared by dilution. Chloroform (E. Merck), pyridine (BDH), α-picoline (Riedel), β-picoline, γ-picoline (BDH), (Fluka) and 2,4,6-collidine (BDH) were distilled before use.

4-Nitrosoresorcinol was prepared according to the known procedure. The light yellow crystalline solid, which was formed, was filtered off and recrystallized from dilute ethanol. The reagent in the solid state is very unstable, but its ethanolic solution is stable.

General procedure

An aliquot of sample solution was mixed with 0.2 ml of 1% ethanolic solution of 4-nitrosoresorcinol followed by addition of (0.5 ml, 100%) pyridine/α-picoline/β-picoline/γ-picoline/2,4,6-collidine. The pH of the solution was adjusted to 2 with KCl-HCl buffer. The volume of the aqueous phase was maintained at 10 ml. The solution was then equilibrated with 10 ml of chloroform in a separating funnel for 1 min. The two layers were allowed to settle. The separated organic layer was shaken with anhydrous sodium sulphate to remove any moisture. Finally the absorbance of the organic extract was measured at the corresponding absorption maxima (Table 1) against a palladium-free reagent blank. The amount of palladium(II) was determined from a previously prepared calibration curve.

The extraction of palladium complexes was investigated in the pH range 0-11. Chloroform extracts showed maximum and steady absorbance when the extractions were carried out in the pH range 1-8. When the extraction was repeated with the same aqueous phase, the organic extract virtually showed no absorbance. The aqueous phase, after extraction, was also tested for palladium by an independent method. This indicated a complete and quantitative extraction of palladium in this pH range.

The spectra of the mixed-ligand complexes were scanned in the wave-length region 300-600 nm against the corresponding reagent blanks. The Pd(II)-complexes showed absorption maxima at 395-400 nm. As the reagent blanks showed some absorbances in the aforesaid wave-length region, all the analytical measurements were carried out against the respective reagent blanks. Figure 1 shows the spectrum of Pd(II)-4-nitrosoresorcinol-γ-picoline system and the corresponding reagent blank. The optimum concentration of the reagents for the purpose of quantitative extraction of the complexes was ascertained by extracting palladium(II) at various concentrations of 4-nitrosoresorcinol and pyridine bases. Extraction was found to be quantitative when 0.2 ml of 1% ethanolic solution of 4-nitrosoresorcinol and 0.5 ml of pyridine/α-picoline/β-picoline/γ-picoline/2,4,6-collidine were used. Under these optimum conditions 84.2 μg of Pd(II) was found to be quantitatively extracted. The higher concentrations of the reagents had no adverse effects on the extraction.

The quantitative extraction of palladium occurred in a single operation when the layers were shaken
Table 1—Details of Extractive Methods

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Pyridine</th>
<th>α-picoline</th>
<th>β-picoline</th>
<th>γ-picoline</th>
<th>2,4,6-collidine</th>
</tr>
</thead>
<tbody>
<tr>
<td>λ_{max} (nm)</td>
<td>395</td>
<td>400</td>
<td>395</td>
<td>395</td>
<td>400,410*</td>
</tr>
<tr>
<td>Molar absorptivity (l mol^{-1}cm^{-1})</td>
<td>3.28 x 10^4</td>
<td>2.68 x 10^4</td>
<td>3.44 x 10^4</td>
<td>3.52 x 10^4</td>
<td>3.47 x 10^4</td>
</tr>
<tr>
<td>Sandell's sensitivity (µg/cm^2)</td>
<td>0.0032</td>
<td>0.0039</td>
<td>0.0030</td>
<td>0.0029</td>
<td>0.0031</td>
</tr>
</tbody>
</table>

*shoulder

Palladium(II) (84.2 µg) can be determined without interference in presence of 50-60 fold excess of Ni(II), Cd(II), Hg(II), Zn(II), V(V), Pt(IV), Rh(III), Mn(II) and Be(II). The system tolerated 20-25-fold excess of Mo(VI), Zr(IV), U(VI), La(III), Al(III), Ti(III), Pb(II) and Cr(III). 10-fold excess of Fe(III) and Cu(II) could be tolerated in presence of ammonium bifluoride and citrate respectively. High results were obtained in presence of Co(III).

Among the anions tested, 100-fold excess of borate, phosphate, bromide, iodide, phthalate, acetate, tartrate, citrate, fluoride, ascorbate, oxalate did not interfere. 30-fold excess of EDTA did not have any effect. Thiocyanate and thiosulphate interfere seriously. More than 100-fold excess of chloride, nitrate and sulphate was found to be harmless.

With γ-picoline the precision and accuracy of the proposed method was tested by analyzing solutions containing a known amount of Pd(II) following the recommended procedure. The average of six determinations of 84.2 µg Pd was found to be 83.4 µg with the relative mean deviation of ±1%.

References