Amperometric Study of 
the Vanadium(IV) and 
Hexacyanoferrate(II) Reaction

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Potassium hexacyanoferrate(II) reacts with many metals forming complex precipitates. 
The reaction with vanadium(IV) has received little attention. Two studies, one involving 
a conductometric (1) and the other a potentiometric (2) approach, have reported the composition of the precipitate to 
correspond to \((\text{VO}_2\text{Fe(CN)}_6)_3\) and \(K_2\text{Fe(CN)}_6\), respectively. A polarographic 
and amperometric study has now been effected and the latter composition has been 
confirmed.

Reagents & Apparatus. Vanadyl sulfate soln. was standardized against std. K\text{MnO}_4 soln. at 80° (3) 
and the potassium hexacyanoferrate(II) soln. against std. K\text{MnO}_4 soln. using N-phenylanthranilic acid as indicator (4).

For the amperometric study, titrations were effected using an H-cell of Lingane type with a 
dropping mercury electrode as cathode and a satd. calomel electrode as anode.

Experimental. Polarographic study. The polarographic behavior of vanadium(IV) in 
0.1 molar sulfuric acid was studied in the presence and absence of 10% ethanol and the half-wave potentials were found to be 
-1.01 and -0.92 volt vs. saturated calomel electrode. Hexacyanoferrate(II) did not 
give a cathodic wave and therefore, a potential of -1.1 volt was chosen as the diffusion 
current potential for the amperometric study.

Amperometric study. An aliquot of 0.1 molar vanadyl solution was pipetted into the wide limb of the H-cell, maintaining a 
sulfuric acid concentration at 0.1 molar and the total volume at 50 ml. The solution was deaerated by bubbling hydrogen gas through 

<table>
<thead>
<tr>
<th>Ethanol, % vol.</th>
<th>VCSO₄, Millimoles</th>
<th>Fe(CN)₆³⁻, Millimoles</th>
<th>Molar ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.3000</td>
<td>0.1921</td>
<td>31.82</td>
</tr>
<tr>
<td>0</td>
<td>0.2000</td>
<td>0.1220</td>
<td>31.83</td>
</tr>
<tr>
<td>0</td>
<td>0.1000</td>
<td>0.0607</td>
<td>31.82</td>
</tr>
<tr>
<td>0</td>
<td>0.0800</td>
<td>0.0499</td>
<td>31.87</td>
</tr>
<tr>
<td>10</td>
<td>0.4000</td>
<td>0.2659</td>
<td>31.98</td>
</tr>
<tr>
<td>10</td>
<td>0.2000</td>
<td>0.1333</td>
<td>3.20</td>
</tr>
<tr>
<td>10</td>
<td>0.1000</td>
<td>0.0662</td>
<td>3.19</td>
</tr>
<tr>
<td>10</td>
<td>0.0800</td>
<td>0.0528</td>
<td>3.19</td>
</tr>
</tbody>
</table>

it for 15 min. (and for 1 min. after each 
titrant addition). The titration was performed at a potential of -1.1 volt and the 
galvanometer readings were recorded with the flow of hydrogen gas interrupted. The 
readings corrected for volume changes were plotted against the titrant volumes and the 
lines were extrapolated to their intersection.

The amperometric titration was also performed in a medium 10-30% in ethanol. 
Typical molar ratios obtained in the presence and absence of ethanol are summarized in Table I. The molar ratio of vanadium(IV) 
to hexacyanoferrate(II) of 3:2 is closely approximated in the presence of ethanol, which 
reduces the solubility of the precipitate. The composition \(K_2(\text{VO}_2\text{Fe(CN)}_6)_3\), previously 
advanced (2), is thereby confirmed. The results indicate that this amperometric titration 
the ethanol-containing medium might be applied to the practical determination of either vanadium(IV) or hexacyano
ferrate(II).


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\[ \text{o-Hydroxyacetophenone Phenylhydrazone as a Gravimetric Reagent for Palladium} \]

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The possibility of using the phenylhydrazones of a number of \( \text{o-hydroxyaldehydes and ketones, viz. salicylaldehyde, resacetophenone, o-hydroxyvanillin, o-hydroxyacetophenone and 2-hydroxy-1-naphthaldehyde as gravimetric reagents for the estimation of palladium has been examined. o-Hydroxyacetophenone phenylhydrazone has been found to be the best reagent for the estimation of palladium in the range 15-47 mg.} \]

A good deal of work has been done on the use of oximes as gravimetric reagents for palladium. However, a study of phenylhydrazones as the reagents for this metal has not so far been made. We have examined a few phenylhydrazones of \( \text{o-hydroxyaldehydes and ketones, viz. salicylaldehyde, resacetophenone, o-hydroxyvanillin, o-hydroxyacetophenone and 2-hydroxy-1-naphthaldehyde as gravimetric reagents for the determination of palladium. It was found that all these reagents (10 per cent aqueous solution) reacted quantitatively with palladium in alkaline medium in the presence of sodium acetate yielding coloured precipitates, viz. deep green with salicylaldehyde phenylhydrazone, grey with resacetophenone phenylhydrazone, brown with o-hydroxyvanillin phenylhydrazone and pale yellow with 2-hydroxy-1-naphthaldehyde. 2,4-Dinitrophenylhydrazone of salicylaldehyde gave only a coloured solution.}

The palladium complexes could not, however, be directly weighed for the estimation of the metal, since excess of the reagent could not be removed by washing. Experimental work conducted with all these reagents showed that \( \text{o-hydroxyacetophenone phenylhydrazone was the best reagent for the estimation of palladium. With this reagent, the removal of the organic residue by ignition was very facile.}

Procedure — A known volume of the standard palladium solution, containing 15-47 mg. Pd, was taken in a clean beaker (400 ml) and diluted to about 200 ml. Sodium acetate (5-6 g) was added and the solution heated nearly to boiling. An excess alcoholic solution of the reagent was added slowly with constant stirring; reagent should be about 10 times the amount of palladium present. The mixture was made alkaline with ammonia (5 to 6 ml. of 2N ammonia), heating continued for a few minutes and the mixture kept on a water-bath for 30 min. The precipitate was allowed to settle at room temperature for 2-3 hr and filtered through Whatman No. 42 filter paper, washed, dried and ignited. The residue was weighed and one or two drops of formic acid and heated over a very low flame, cooled and immediately weighed as palladium metal.

Some typical determinations of palladium by this method are given in Table 1.

### Table 1 — Determination of Palladium Using \( \text{o-Hydroxyacetophenone Phenylhydrazone} \)

<table>
<thead>
<tr>
<th>Palladium, mg.</th>
<th>Error %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Taken</td>
<td>Found</td>
</tr>
<tr>
<td>14.89</td>
<td>14.78</td>
</tr>
<tr>
<td>23.77</td>
<td>23.80</td>
</tr>
<tr>
<td>30.95</td>
<td>30.92</td>
</tr>
<tr>
<td>41.00</td>
<td>41.0</td>
</tr>
<tr>
<td>47.55</td>
<td>47.50</td>
</tr>
</tbody>
</table>

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References