

## Complexometric Determination of Palladium A Review Study

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### **ABSTRACT**

*A survey of literature since 1976 has been made regarding metallochromic indicators for complexometric determination of Palladium. A brief review of these methods is described below*

**KEYWORDS:** *Metallochromic indicators, Complexometric Determination*

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Complexometric analysis.

Complexometric analysis of palladium lead catalysts (with a  $\text{CaCO}_3$ , carrier) used in the synthesis of linalyl acetate has been reported by Kurekina <sup>1</sup>. A 0.5 g sample was dissolved in dil.  $\text{HCl}$   $\text{HNO}_3$ , and to a portion of the diluted solution excess of  $\text{Na}_2\text{EDTA}$  was added. The total Pd and Pb were then determined by back titration at pH 6 with 0.05 N - Zn acetate using xylenol orange as indicator. However, in another aliquot lead was precipitated as  $\text{Pb(OH)Cl}$  by treatment with aq.  $\text{NH}_3\text{-NH}_4\text{Cl}$  at  $80^\circ$ , and the precipitate was filtered off. The dilute filtrate was adjusted to pH 10 with aq.  $\text{NH}_3$  buffer and in the alkaline solution calcium was determined by titration with EDTA, with Acid chrome dark blue (C. I. Mordant Blue 13) as indicator. The  $\text{Pb(OH)Cl}$  precipitate was dissolved in acetate buffer solution (pH 6), and Pb was determined by back titration with Zn acetate solution after addition of excess of EDTA. The analysis time was 2 h, and the relative error was generally  $\pm 7\%$ .

Postnikova <sup>2</sup> has reported xylenol orange as indicator involving titrations with EDTA at various pH values for determining Pt or Pd in binary or ternary alloys containing lanthanoids, Sc or In. Similar procedures have been proposed for the analysis of Pd-V alloys. The sum of Pd and V is determined with EDTA in the presence of masking agents (depending on the impurities) and after the addition of aq.  $\text{NH}_3$  to mask palladium, titration of V alone is carried similarly.

Tikhonov and Aleksandrova <sup>3</sup> have reported determination of palladium (II) in activator solutions (used in metallisation of printed circuit boards). The sample solution containing up to 2 mg of Pd(II) is mixed with 10 to 15 ml of 5 mM-EDTA, 5 ml of acetate buffer solution (pH 5.5) and 0.5 ml of 0.1% xylenol orange solution. The uncombined EDTA is titrated with 5 mM-ZnCl<sub>2</sub> until the colour changes from yellow to red. Then 1 to 1.5 ml of ethanolic 1% dimethylglyoxime (1) is added and the solution is heated to precipitate the Pd-(II)-1 complex. The other metal impurity is not co-precipitated; and the EDTA equivalent to the Pd is then titrated with  $\text{ZnCl}_2$  solution.

Tikhonov and Stepanova <sup>4</sup> have reported catechol violet as complexometric indicator in presence of hexadecyl trimethyl ammonium ions. On addition of hexadecyltrimethyl ammonium bromide (I) to a test solution during the titration of metal ions with  $\text{Na}_2\text{EDTA}$  or titration of unconsumed EDTA with Bi(III), In(III) or Fe(III) solution with catechol violet as indicator, the sharpness of the colour change at the end point (due to formation of mixed ligand complexes between catechol violet and I) is improved.

Raoot et al <sup>5</sup> have reported the selective complexometric determination of palladium. Palladium has been determined in the presence of various common metal ions and rare earth metals. To a solution containing 3 to 24  $\mu\text{g}$  of Pd(II) an excess of 0.01M-EDTA is added. The mixture is diluted to 100 ml, and the pH is adjusted to 5 to 5.5 with aq. 2% NaOH and acetate buffer solution. The unconsumed EDTA is then titrated with 0.01M- $\text{Pb(NO}_3)_2$  to a red violet end point using xylenol orange as indicator. The titre is equivalent to the content of Pd(II) plus foreign metal ions. To this solution now 10 to 15 ml of ethanolic 5% 1,2,3-benzotriazole is added. The reaction mixture is heated at  $60^\circ\text{C}$  for 10 min., and, after cooling, 15 ml of  $\text{CHCl}_3$  is added. The mixture is vigorously shaken. The liberated EDTA [equivalent to Pd(II)] is titrated with  $\text{Pb(NO}_3)_2$  solution. The method

has been applied to Pd-based binary alloys after dissolution of the sample in aqua-regia, the content of other metal being calculated from the difference between the first and second titres.

Mixture of chrome Azurol S [c.1. Mordant Blue 29] with hexadecyltrimethyl ammonium bromide has been reported as indicator in the determination of palladium (II) by back titration of unconsumed EDTA (added in excess) with aq. FeCl<sub>3</sub>. Milligram amounts of Cu(II), Ga, In, Sc, Y or Fe(III) with Na<sub>2</sub> EDTA have also been determined with the same indicator. For Fe(III) determination (with the solution at 60 to 80° : the pH is maintained at 2 to 4 and with rest of the metals, the titration is made between pH 5 to 6. The colour change at the end point is from blue to red. The quarternary salt improves the colour contrast at the end-point. This method is reported by Tikhonov.<sup>6</sup>

A complexometric method for analysis of palladium-rare earth magnetic alloys has been reported by Raoot and Raoot.<sup>7</sup> The alloy (0.1 to 0.2 g) is dissolved in aqua regia and the solution is diluted to 100 ml. To an aliquot containing 6 to 16 mg of Pd, excess of 0.01M-EDTA is added and the pH is adjusted to 5 to 5.5 with Na acetate - acetic acid buffer solution. Xylenol orange solution is added and the unconsumed EDTA is titrated with 0.01 M-Pb(NO<sub>3</sub>)<sub>2</sub> the value corresponded to Pd plus rare earth ion present. Then 1,10-Phenanthroline is added (four to five times the amount of Pd), and the EDTA liberated is titrated as before; the value corresponded to the Pd(II) present. When > 17 to 18 mg of Pd is present a precipitate is formed on addition of 1,10-phenanthroline. The shaking of the solution with CHCl<sub>3</sub> coagulated the precipitate and facilitated the end point detection. Errors for the method ranged from 0 to 0.83%.

Keshavan<sup>8</sup> has reported a method for rapid direct complexometric determination of palladium (II) with EDTA. To the weakly acid test solution, containing 0.5 to 40 mg of Pd (II) in 90 ml, 10 ml of ag. acetate buffer (pH 5) and 1 ml of 0.2% propionyl promazine phosphate solution (Sayer) is added. It is titrated with 0.02 to 0.05M-EDTA until the red colour is completely discharged. There is serious interference from I<sup>-</sup>, SCN<sup>-</sup>, V(V), Ce(IV), Au and Os (VIII). Tolerance levels (mg) are reported for acetate (150); Po<sub>4</sub><sup>3-</sup> (50); Br<sup>-</sup> (20); F<sup>-</sup> (10); Co(1.0) Ni(II) (0.8) Cu(II) (0.6); Ru(III) (0.6) Rh(III) (1.0); Os(vi) (0.5); Ir(III) (1.5) and Pt (iv) (0.8)

Raoot and Raoot<sup>9</sup> have reported the selective complexometric determination of palladium with thiourea as masking agent. Palladium is determined in the presence of various common metal ions and rare earth metals. To a solution containing 4 to 40 mg of Pd(II), excess of 0.01M-EDTA is added. The mixture is diluted to 100 ml and the pH is adjusted to 5 to 5.5 with dil. NaOH and acetate buffer solution. The unconsumed EDTA is titrated with 0.1M-Pb(NO<sub>3</sub>)<sub>2</sub> with use of xylenol orange as indicator. Then 1% thiourea solution (2 to 20 ml; 4 mg of thiourea for each mg of Pd), is added to decompose the Pd-EDTA complex. The mixture is shaken and the liberated EDTA is titrated with 0.1M-Pb(NO<sub>3</sub>)<sub>2</sub> as before. Interference is caused by Hg or Sn(IV) and by > 5 mg of Mn(II). The method has been applied to alloys of Pd with Cu or Sn after dissolution of the sample in aqua-regia.

A selective complexometric method for determination of palladium in alloys using thiocyanate as releasing agent has been reported by Raoot et al.<sup>10</sup> On addition of 0.01M-EDTA the Pd (II) - EDTA complex and other metal-EDTA complexes are formed and titration of unconsumed EDTA with 0.1M-Pb(NO<sub>3</sub>)<sub>2</sub> is carried out with xylenol orange as indicator. Then 1% NH<sub>4</sub>SCN solution (2 to 12 ml: 100 ml of SCN for each 6 mg of Pd) is added to decompose the Pd-EDTA complex. The mixture is shaken and the liberated EDTA is titrated with 0.1M-Pb(NO<sub>3</sub>)<sub>2</sub> as before. Interference is caused by Hg(II), Ir(III) or Sn(IV) and by >5 mg of Mn(II) (owing to the instability of the Mn EDTA complex). The proposed method is superior to previous methods as the SCN<sup>-</sup> yields a soluble complex with Pd and releases EDTA instantaneously in the cold, and that many foreign cations are tolerated.

Ternary complex system lanthanum (III) xylenol orange hexa decylpyridinium bromide has been used as an indicator in the complexometric determination of palladium in its alloys with copper or nickel by Wu and Zhu<sup>11</sup>. The method is stated to produce a better defined end point as compared to the one reported by Raoot and Raoot<sup>9</sup>.

Raoot and Raoot<sup>12</sup> have reported the complexometric determination of palladium with thiosulphate as masking agent. To a solution containing 3 to 30 mg of Pd(II) and other cations, excess of 0.01M-EDTA is added. The pH of the solution is adjusted with 2% NaOH and the surplus EDTA is back titrated with Pb(NO<sub>3</sub>)<sub>2</sub> solution at pH 5 to 5.5 in Na acetate buffer medium (xylenol orange as indicator) to the sharp colour change from yellow to red. Addition of 3% Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> quantitatively released EDTA equivalent to Pd and this was then titrated with the Pb (NO<sub>3</sub>)<sub>2</sub> to the same end point. Thiosulphate is the most suitable masking agent. It yields a

soluble complex even with large quantities of Pd, releases the EDTA instantaneously in the cold and tolerates a large number of cations. The coefficient of variation are 0.9 and 0.2% (n = 10) at the 2.95 and 14.75 mg levels, respectively. The method is successfully applied to the analysis of alloys.

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