

## Complexo-Titrimetric Determination of Palladium(II) Using 1, 3, 4, 6-Tetrahydropyrimidine-2-Thione as a Replacing Reagent

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A simple, rapid, convenient, accurate and selective complexo-titrimetric method using the masking technique is proposed for the determination of palladium(II). In presence of diverse metal ions palladium(II) is complexed with a known excess of EDTA and the uncomplexed EDTA is back titrated with lead nitrate solution in acetic acid-sodium acetate buffer (pH 5.0-6.0) to the sharp end point of xylenol orange indicator. A 0.5% solution of 1, 3, 4, 6-tetrahydropyrimidine-2-thione (TPT) in acetone is added to displace EDTA quantitatively from the Pd-EDTA complex. The released EDTA is titrated against standard lead nitrate solution.

### INTRODUCTION

The direct complexometric methods for palladium determination have mostly dealt with its determination in pure solution or in presence of platinum group metals which do not normally react with EDTA. Determination of palladium in presence of common metal ions, using some selective masking agents is important in the analysis of its alloys with copper and nickel which are widely used as contact materials. It is well known that the Pd-EDTA complex can be selectively decomposed using organic reagents such as dimethylglyoxime<sup>1,2</sup> and benzotriazole<sup>3</sup>. The methods are not rapid in that they require extraction of the precipitate and heating of the reaction mixture for the quantitative liberation of EDTA. The method using 1,10-phananthroline<sup>4</sup> is not universal since it is applicable to the study of interference by rare-earth ions only. The thiourea<sup>5</sup> method though selective requires heating. Besides, common metals like copper, mercury etc. interfere severely. The pyridine<sup>6</sup> method is not convenient because it involves heating and readjustment of pH before the final titration. The method of estimation of Pd(II) using 4-amino-5-mercapto-3-n-propyl-1,2,4-triazole<sup>7</sup> and thiocyanate<sup>8</sup> as replacing reagents are however reliable besides being convenient. The work now reported highlights the merits of 1,3,4,6-tetrahydropyrimidine-2-thione (TPT) as a selective masking agent for the complexometric determination of Pd(II) by EDTA titration.

## EXPERIMENTAL

## Reagents

1,3,4,6-tetrahydropyrimidine-2-thione was synthesized as reported in literature<sup>9</sup> and used as a 0.5% solution in acetone. EDTA solution (approx. 0.02M) was prepared by dissolving the disodium salt of EDTA in distilled water. Palladium chloride solution was prepared by dissolving PdCl<sub>2</sub> in excess of KCl and then standardised by the dimethylglyoxime method<sup>10</sup>. Lead nitrate solution (0.01M) was prepared from the analytical grade reagent and standardised by the chromate method<sup>10</sup>.

## Procedure

To an aliquot of the neutral solution containing 2–19 mg of Pd(II), a known excess of 0.02M EDTA solution is added. The pH of the solution is adjusted between 5.0–6.0 by adding acetic acid-sodium acetate buffer. The uncomplexed EDTA is back titrated against the standard lead nitrate solution to the sharp colour change of the xylenol orange indicator from yellow to red. To this is then added an excess of 1,3,4,6-tetrahydropyrimidine-2-thione solution in acetone (one fold excess over the molar ratio of 1 : 2), the contents are mixed well and allowed to stand for 3–5 minutes. The liberated EDTA is titrated against the lead nitrate solution. The second titre value corresponds to Pd(II) present in the aliquot. The results of analyses are presented in Table 1.

TABLE 1  
RELIABILITY OF PALLADIUM(II) DETERMINATION  
IN ITS SOLUTION

Palladium(II) taken (mg)	Palladium(II) found* (mg)	Standard deviation	Recovery %
1.93	1.94	0.02	100.52
3.85	3.86	0.01	100.26
7.70	7.73	0.01	100.39
9.63	9.67	0.02	100.42
11.55	11.55	0.02	100.00
15.40	15.48	0.03	100.52
19.25	19.16	0.02	99.53

\*Average of five determinations.

### Analysis of palladium complexes

A number of palladium(II) complexes with some sulphur containing ligands were prepared by the conventional methods and their purity checked from elemental analysis. About 0.2–0.3 g of the complex was decomposed by evaporation to near dryness with aqua regia. The residue was then cooled, dissolved in water and made upto 100 ml. Aliquots of 10 ml were used for the estimation as per recommended procedure. The results of analyses are presented in Table 2.

TABLE 2  
ANALYSIS OF PALLADIUM COMPLEXES

Complex	Pd found %	Pd present %
$\text{Pd}(\text{C}_3\text{H}_3\text{N}_4\text{OS})_2^a$	27.19	27.11
$\text{Pd}(\text{C}_{10}\text{H}_{11}\text{N}_4\text{OS})_2^b$	18.38	18.45
$\text{Pd}(\text{C}_4\text{H}_7\text{O}_2\text{N}_2)_2^c$	31.71	31.62
$\text{Pd}(\text{C}_9\text{H}_7\text{N}_4\text{OS})_2^d$	19.42	19.54

- Palladium complex of 4-amino-5-mercapto-1,2,4-triazine-(4H)-5-one.
- Palladium complex of 3-(*o*-cresyloxymethyl)-4-amino-5-mercapto-1,2,4 triazole.
- Palladium complex of dimethyl glyoxime.
- Palladium complex of 4-amino-5-oxo-3-thioxo-6-phenyl-2,3,4,5 tetrahydro-1,2, 4 triazine.

### RESULTS AND DISCUSSION

The fact that TPT displaces EDTA quantitatively from Pd-EDTA complex indicates that Hg-TPT complex is more stable than the Pd-EDTA complex. EDTA from the complex is released quantitatively and instantaneously at room temperature itself. Pd-TPT complex is highly soluble in the medium under the experimental conditions. Thus absence of any precipitate in the reaction mixture makes the end point sharp. A minimum of onefold excess of the reagent over the molar ratio of 1:2 is required for the complete release of the complexed EDTA. A large excess of the reagent however has no adverse effects.

The results of determination of palladium(II) from its solution and from the palladium complexes show that reproducible and accurate results are obtainable. The effect of common metal ions and rare-earth ions on the quantitative determination of Pd(II) was studied with aliquots containing 3.85 mg of palladium. However cations like Sn(IV), Tl(III), Fe(III) and Hg(II) show severe interference. But this interference can be got over by

using secondary masking agents such as fluoride for Sn(IV), ascorbic acid for Tl(III), phosphate for Fe(III) and acetyl acetone for Hg(II). The results of analyses are presented in Table 3.

TABLE 3  
DETERMINATION OF PALLADIUM IN PRESENCE OF DIVERSE  
METAL ION

(Palladium present in the solution 3.85 mg)

Diverse metal	Level of conc.	Amount of Palladium* found mg	Mean	Recovery
Zn(II)	5	3.84	3.84	99.74
	25	3.83		
Cd(II)	16	3.84	3.84	99.74
	32	3.84		
Cu(II)	6	3.85	3.86	100.26
	30	3.86		
Ni(II)	6	3.86	3.85	100.00
	30	3.84		
Co(II)	6	3.85	3.86	100.26
	30	3.86		
Mn(II)	2.5	3.83	3.83	99.48
	5	3.83		
Al(III)	5.5	3.84	3.84	99.74
	27.5	3.83		
Bi(III)	5	3.85	3.85	100.00
	25	3.85		
Rh(III)	4	3.85	3.85	100.00
	8	3.85		
Ru(III)	4	3.83	3.84	99.74
	8	3.85		
Au(III)	4	3.83	3.84	99.74
	8	3.84		
La(III)	14	3.87	3.87	100.52
	28	3.86		
Cr(III)	5	3.84	3.83	99.48
	10	3.82		

TABLE 3 (contd.)

Ce(III)	14	3.85	3.84	99.74
	70	3.83		
V(IV)	5	3.86	3.86	100.26
	25	3.86		
Ti(IV)	5	3.83	3.83	99.48
	25	3.83		
Zr(IV)	9	3.83	3.84	99.74
	18	3.84		
U(VI)	12	3.84	3.85	100.00
	24	3.86		
Sn(IV)	5	3.84	3.84	99.74
	10	3.84		
Tl(III)	2	3.84	3.85	100.00
	10	3.86		
Fe(III)	6	3.83	3.83	99.48
	30	3.83		
Hg(II)	50	3.85	3.84	99.74
	25	3.83		

\*Average of three determinations.

### Advantages

The speciality of the reagent is that it does not form any precipitate with either Pd(II), the metal ion to be estimated or Pb(II) the titrant, under the experimental conditions. This facilitates sharp detection of the end point without necessitating the use of end point sharpeners. The method works well in the conc. range of 2–19 mg of palladium. The main advantage of the proposed method is that it does not require heating or cooling either for the formation of the Pd-TPT complex or for the decomposition of the Pd-EDTA complex. Since many metal ions do not interfere with palladium in its estimation by this method, the method is suitable for the estimation of Pd in Pd-alloys. The method does not involve extraction of the Pd-TPT complex and hence is convenient and can be rapidly carried out in a single stage. The EDTA solution need not be standardised. Besides, the method requires no readjustment of pH.

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