

2-MERCAPTOETHYLAMINE AS A MASKING AGENT FOR THE COMPLEXOMETRIC DETERMINATION OF PALLADIUM(II) IN CATALYSTS, ALLOYS AND COMPLEXES

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ABSTRACT

A simple, rapid and accurate complexometric method for the determination of palladium in the presence of other metal ions is described, based on the selective masking ability of 2-mercaptoethylamine (MEA) towards Pd(II). Palladium(II) along with other associated metal ions present in a given sample solution is first complexed with an excess of EDTA and the surplus EDTA is titrated with zinc sulphate solution at pH 5-6 (acetic acid-sodium acetate buffer) using xylenol as indicator. A known excess of 0.2% aqueous solution of MEA is then added to displace EDTA from Pd(II)-EDTA complex and swirled well. The released EDTA is again titrated with zinc sulphate solution as before. The method works well in the range 2-20 mg of palladium(II) with the relative error ± 0.27 and the relative standard deviation $< 0.35\%$. The effect of the presence of various diverse ions on the accuracy of the results has been studied. The method has been satisfactorily applied for the determination of palladium in catalysts, alloys and complexes.

Key words: palladium determination, complexometry, masking reagent, 2-mercaptoethylamine

INTRODUCTION

Palladium finds extensive applications as a catalyst in hydrogenation and dehydrogenation reactions. It also tends to retard the formation of silver sulphide and has become a common component of medicinal devices and dental alloys. The high melting point of Pd and its alloys provide high resistance to corrosion, and hence it is widely used in electrical contacts. Metallic Pd and its alloys serve as substitutes for Pt in jewellery. Since it is much lighter than Pt, Pd has been used for the construction of astronomic and sensitive instruments. It was thus considered worthwhile to explore the possibilities of developing a simpler, selective, rapid and accurate analytical method for the determination of Pd(II) in various samples. In this context, an attempt has been made to explore the utility of 2-mercaptoethylamine as a selective masking reagent for the complexometric determination of Pd(II).

The earlier reported methods for the complexometric determination of

Pd(II) employed dimethylglyoxime¹, 1,2,3-benzotriazole², 1,10-phenanthroline³, thiourea⁴ and pyridine⁵ as masking reagents. All these methods involve time consuming steps like heating, cooling or extraction and hence are not rapid. Several common metal ions show interference in 4-amino-5-mercapto-3-propyl-1, 2, 4-triazole⁶, thiosemicarbazide⁷, and 4-amino-3-mercapto-1, 2, 4-triazine-5-one method⁸. Thiocyanate⁹, hydroxylamine hydrochloride¹⁰, N-(2-pyridyl) thiourea¹¹, DL-cystein¹², 3-mercapto propane-1, 2-diol¹³, 2-mercapto propionyl glycine¹⁴ and thioacetamide¹⁵ are some of the other reported masking agents for palladium.

We are now reporting the application and advantages of 2-mercaptoethylamine as a selective masking reagent for the complexometric determination of Pd(II). The proposed method is free from various common interfering ions and does not require any heating or extraction step.

A comparison of the proposed method with other reported methods for palladium determination is given in Table 1.

Table 1. Comparison of MEA with reported masking agents for Pd determination

Masking agent	Interference	Comments	Ref.
Pyridine	Hg(II), Ir(III), Pt(IV), Mn(II)	Requires heating. Reagent is water insoluble	5
4-amino-5-mercapto-3n-propyl-1,2,3-triazole	Ag(I), Hg(II), Sn(II), Mn(II), Fe(II), Sb(III), Al(III), Tl(III)	Works for 0.5-5mg of Pd. Water insoluble reagent, which requires preparation.	6
Thiosemicarbazide	Cu(II), Fe(II), Sn(II), Hg(II), Tl(III), Bi(III), Al(III), Cr(III)		7
4-amino-3-mercapto-1,2,4-triazine-5-one	Ag(I), Hg(II), Sn(II), Mn(II), Fe(II), Sb(III), Al(III), Tl(III)	Works for 0.5-5mg of Pd. Water insoluble reagent, which requires preparation.	8
Thiocyanate	Hg(II), Ir(III), Tl(III), Mn(II), Sn(IV)		9
Hydroxylamine hydrochloride	Hg(II), Cd(II), Cr(III), Al(III), Tl(III)	Requires readjustment of pH	10
N-(2-pyridyl thiourea)	Hg(II), Cr(III), Tl(III)	Water insoluble reagent, which requires preparation	11
DL-cystein	Cu(II), Hg(II), Tl(III), Zr(IV), Sn(IV)	-	12
3-mercapto propane-1,2-diol	Hg(II), Tl(III), Cr(III), Bi(III), Sn(IV), Mn(II)	-	13
2-mercapto propionyl glycine	Cu(II), Hg(II), Tl(III), Cr(III), Sn(IV)	-	14
Thioacetamide	Hg(II), Tl(III), Cr(III), Sn(IV)	-	15
2-mercaptoethylamine (MEA)	Hg(II), Tl(III), Cu(II), Sn(IV). Interference from Hg(II) & Sn(IV) can be suitably avoided by premasking.	Reagent is readily available and soluble in water. Stringent conditions like heating, readjustment of pH or extraction are not required	Present method

EXPERIMENTAL

Materials

All the chemicals used were of analytical reagent grade. A stock solution of Pd(II) was prepared by dissolving PdCl₂ (Merck) in minimum volume of concentrated HCl and making up to a known volume. The solution was standardized gravimetrically by dimethylglyoxime method¹⁶. Zinc sulphate solution (0.01M) was prepared by dissolving a known amount of zinc sulphate (Merck) in distilled water and standardized gravimetrically by salicylaldehyde method¹⁶. EDTA solution (0.01M) was prepared by dissolving the required amount of disodium salt of EDTA (Merck) in distilled water. A freshly prepared solution (0.2%) of 2-Mercaptoethylamine (Fluka, Switzerland) in distilled water was used as the masking reagent. A freshly prepared aqueous solution of xylenol orange (0.5%) was used as the indicator.

Standard Procedure

To a solution containing 2-20 mg of palladium(II) and varying amounts of diverse metal ions taken in a 250 mL conical flask, an excess of 0.01M EDTA was added. The solution was diluted to 60-70 mL with distilled water. The pH of the solution was initially adjusted between 4 and 5 by the drop-wise addition of diluted sodium hydroxide solution and finally to 5-5.5 with the addition of acetic acid-sodium acetate buffer. The surplus EDTA was titrated with 0.01M zinc sulphate solution using few drops of xylenol orange indicator to a sharp color change from yellow to red. To this, a 0.2% solution of MEA was added in required amounts and swirled well. The released EDTA was again titrated with the same 0.01M zinc sulphate solution as before. The second titre volume corresponds to the palladium content in the aliquot.

RESULTS AND DISCUSSION

Masking property of 2-Mercaptoethylamine

2-Mercaptoethylamine (MEA) is a potential bidentate ligand containing sulphur of mercapto group and nitrogen of amino group as donor atoms. It has been reported that MEA forms a strong 1:2 (M : L) neutral complex with Pd(II) by coordinating through deprotonated sulphur of thiol group and neutral nitrogen atom of amino group^{17,18}. These results in the formation of a stable five membered chelate. This is very well in agreement with the consumption of two moles of MEA for each moles of palladium for the quantitative release of EDTA from Pd(II)-EDTA complex. The stability constant of the Pd(II)-EDTA complex is reported to be 26.4¹⁹. However, no data on the stability constant of the Pd(II)-MEA are given in the literature. The quantitative release of EDTA from Pd(II)-EDTA complex by MEA at room temperature itself indicates that Pd(II)-MEA complex is more stable than Pd-EDTA complex under the experimental conditions employed. This finding show that Pd(II) forms a stable complex with MEA than with EDTA and reverse is true with common metal ions. For instance, the EDTA complexes of Zn(II), Ni(II), Cd(II), Pb(II) are more stable (log K= 16.5, 18.6, 16.5, 18.0) compared to their respective complexes with MEA (log K= 7.21, 9.58, 7.38, 10.1)²⁰.

Effect of 2-Mercaptoethylamine concentration

In order to find out the exact amount of MEA required for the quantitative release of EDTA from Pd-EDTA complex and the influence of excess reagent on the accuracy of the result, titrations were carried out with solutions containing 10.42 mg of Pd(II) and varying amounts of 0.2% MEA solution added. From the plot (Fig. 1) of the volume of reagent added versus the recovery of Pd, it is clear that about 8 ± 0.5 mL solution of 0.2% MEA is required for each 10.42 mg of Pd. Addition of excess of the reagent over the required amount has no adverse effects on the experimental results.

Reliability of the proposed method

To evaluate the precision and accuracy of the proposed method, determination of palladium at different concentration levels were carried out under optimized experimental conditions. Reproducible and accurate results (Table 2) are obtained in the range 2-20 mg of palladium with the relative error ± 0.27 and the relative standard deviation (n=6) not exceeding 0.35%.

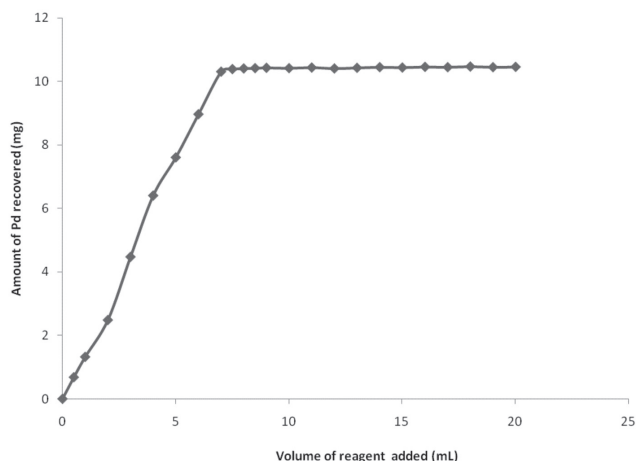


Fig. 1. Effect of 0.2% 2-mercaptoethylamine on the release of 10.42 mg of Pd(II)

Effect of diverse ions

The recommended procedure was followed to study the possible interference due to various diverse metal ions with solutions containing 5.21mg of Pd. The results obtained are presented in Table 3. The presence of the following ions did not interfere with in the concentration range studied: 100 mg of Zn(II), Pb(II); 40mg of Cd(II), Ni(II), Co(II), Bi(III); 30 mg of Fe(III), Al(III), Ti(IV), Ce(III); 25 mg of V(IV), Mo(VI); 20 mg of Pt(IV), Os(VIII), Zr(IV), Au(III), As(V), U(VI); 10 mg of Ru(III), Rh(III), Ir(III), Mn(II); 100 mg of SO₄²⁻, PO₄³⁻, NO₂⁻, F⁻, Cl⁻, Br⁻, acetate, oxalate, citrate and tartarate. However, metal ions like Hg(II), Tl(III), Cu(II) and Sn(IV) show interference giving positive error, which is perhaps due to simultaneous release of EDTA from their respective M-EDTA complexes along with Pd(II)-EDTA complex. The interference of Hg(II) (up to 10 mg) can be obviated by the addition of 5% acetyl acetone (5 mL) prior to EDTA complexation as secondary masking agent. Similarly, the interference due to Sn(IV) (up to 10 mg) can also be avoided by the addition of 2% NH₄F (5 mL) as secondary masking agent.

Table 2. Determination of Pd(II) in palladium chloride solution

Palladium , mg		Relative error (%)	RSD (%)
Taken	Found*		
1.56	1.56	0.00	0.33
2.60	2.60	0.00	0.31
3.65	3.64	-0.27	0.22
5.21	5.20	-0.19	0.15
7.81	7.82	0.13	0.13
10.42	10.41	0.10	0.19
15.63	15.62	-0.06	0.10
20.84	20.87	0.14	0.10

*Average of six determinations
RSD = Relative standard deviation

Table 3. Determination of Pd(II) in the presence of diverse ions (Pd(II) taken in solution = 5.21 mg)

Diverse ion	Quantity added (mg)	Pd(II) found* (mg)	Relative error (%)
Zn(II)	100	5.21	0.00
Cd(II)	40	5.23	0.38
Ni(II)	40	5.19	-0.38
Co(II)	40	5.22	0.19
Pb(II)	100	5.21	0.00
Bi(III)	40	5.18	-0.58
Mn(II)	10	5.24	0.58
Fe(III)	30	5.19	-0.38
Al(III)	30	5.22	0.19
Ti(IV)	30	5.23	0.38
V(IV)	25	5.18	-0.58
Ce(III)	30	5.19	-0.38
Pt(IV)	20	5.24	0.58
Ru(III)	10	5.23	0.38
Rh(III)	10	5.18	-0.58
Os(VIII)	20	5.23	0.38
Sn(IV) #	10	5.24	0.58
Zr(IV)	20	5.20	-0.19
Au(III)	20	5.23	0.38
As(V)	20	5.18	-0.58
Hg(II) §	10	5.24	0.58
U(VI)	20	5.19	-0.38
Ir(III)	10	5.18	-0.58
Mo(VI)	25	5.24	0.58
SO ₄ ²⁻	100	5.20	-0.19
PO ₄ ³⁻	100	5.19	-0.38
NO ₃ ⁻	100	5.24	0.58
F ⁻	100	5.22	0.19
Cl ⁻	100	5.18	-0.58
Br ⁻	100	5.19	-0.38
Acetate	100	5.22	0.19
Oxalate	100	5.24	0.58
Citrate	100	5.23	0.38
Tartrate	100	5.19	-0.38

* Average of three determination

Premasked with NH₄F and § Premasked with acetyl acetone**Analytical applications of the method**

In order to demonstrate the analytical usefulness of the proposed method, it was applied to the determination of palladium in catalysts, complexes and synthetic alloy samples.

Determination of palladium in catalysts: A known amount of catalyst sample (0.1-0.2g) was dissolved in minimum amount of aqua regia. The solution was evaporated to near dryness with the addition of three 5 ml portion of concentrated HCl to remove the oxides of nitrogen. The cooled solution was filtered, if necessary and diluted to 100 mL with distilled water in a volumetric flask. Suitable aliquots of this sample solution were analyzed for Pd(II) as per the standard procedure. The results are presented in Table 4.

Table 4. Determination of Palladium in catalysts and complexes

Catalyst / Complex	Palladium present * (%)	Palladium found (%)	RSD (%)
Pd- Charcoal Catalyst	5.14	5.16	0.40
Pd- CaCO ₃ Catalyst	9.88	9.92	0.35
Pd(C ₆ H ₇ N ₃ S ₂) ₂ Cl ₂ ^a	19.42	19.37	0.30
Pd(C ₇ H ₈ O ₂ N ₂) ₂ Cl ₂ ^b	22.09	22.01	0.35
Pd(C ₆ H ₅ N ₃) ₂ Cl ₂ ^c	25.60	25.52	0.24
Pd(CH ₆ N ₄ S) ₂ Cl ₂ ^d	27.31	27.21	0.30
Pd(CH ₅ N ₃ S) ₂ Cl ₂ ^e	29.59	29.48	0.40
Pd(C ₄ H ₇ O ₂ N ₂) ₂ ^f	31.61	31.55	0.24

*Average of three determinations

Determination of palladium in complexes: Some palladium(II) complexes with ligands such as thiophene-2-carboxaldehyde thiosemicarbazone, salicyloyl hydrazide,

1, 2, 3-benzotriazole, thiocarbohydrazide, thiosemicarbazide, and dimethylglyoxime were prepared and purified as per the reported methods²¹⁻²⁴.

A weighed sample of the complex (0.1-0.2g) was carefully decomposed to near dryness with aqua regia. The cooled residue was dissolved in minimum amount of 2N HCl and made up to a mark in a 100 mL volumetric flask with distilled water. Aliquots of this solution were analyzed for palladium as described and the results obtained are tabulated in Table 4.

Determination of palladium in synthetic mixtures with alloy composition: As certified samples of Oakay alloy, Solder alloy, Dental alloy and Jewellery alloy were not available, synthetic mixtures with the same composition were prepared. Palladium content in these samples was determined by the procedure described and the results are given in Table 5.

Table 5. Determination of palladium in synthetic mixture with alloy composition

Alloy	Synthetic mixture composition (%)	Palladium found*(%)	RSD (%)
Oakay alloy	Pd 10.5; Ni 60.0 Pt 20.0; V 9.5	10.54	0.40
Solder alloy	Pd 30.0; Pt 10.0 Au 60.0	30.10	0.30
Dental alloy	Pd 34.0; Ni 34.0 Co 22.0; Au 10.0	34.12	0.35
Jewellery alloy	Pd 50.0; Au 50.0 Pd 95.5; Ru 4.5	49.86 95.61	0.24 0.30

*Average of three determinations

Pd complex with thiophene-2-carboxaldehyde thiosemicarbazone^a, salicyloyl hydrazide^b, 1,2,3-benzo-triazole^c, thiocarbohydrazide^d, thiosemicarbazide^e, dimethylglyoxime.^f

CONCLUSIONS

The proposed method for the complexometric determination of Pd(II) offers advantages of simplicity, rapidity and reasonable selectivity over the other methods. The masking reagent, 2-mercaptoethylamine forms a soluble complex with palladium, releases the EDTA instantaneously at room temperature and tolerates the presence of a number of metal ions without the need for the time consuming steps like heating or solvent extraction. Because no solvent extraction is required, the use of organic solvents, which are generally toxic pollutants, is avoided. In conclusion, the simplicity of the analytical procedure and the use of inexpensive facility make the technique very attractive for a wide spectrum of application.

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