



Spectrophotometric determination of micro amounts of Palladium (II) using Thymol Blue as an analytical reagent

Aparna Bhardwaj

Department of Chemistry, Mithibai College, Vile Parle (W), Mumbai, **INDIA**

Email: dr.aparna73@rediffmail.com

Received on 13th August and finalized on 20th August 2013.

ABSTRACT

Thymol Blue dye is used as a reagent for the spectrophotometric determination of Pd(II). The reagent forms a yellow colored complex with palladium(II) instantaneously at pH 3.0-5.0. A twofold molar concentration of the reagent is necessary for the full development of the colour intensity. Beer's law is valid over the concentration range 0.0-9.57 $\mu\text{g ml}^{-1}$ and the optimum range for the effective spectrophotometric determination is 1.06-9.57 $\mu\text{g ml}^{-1}$. The complex has absorption maximum at 470 nm with molar absorptivity $2.12 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ and sensitivity is 0.47 ng ml^{-1} respectively. The standard deviation has been found to be 0.0006.

Keywords: Thymol Blue, Palladium, Spectrophotometry.

INTRODUCTION

Palladium has been used in various ways as a hydrogenation catalyst, microconductors in the electronics, hard alloy in dentistry and in the last few years as a component in the three-way catalysts in automobile exhaust catalytic beads. Due to the introduction of palladium, platinum and rhodium for use in catalytic converters in motor vehicles, the emission of these metals into the environment has increased. In addition, an increased uptake of palladium by plants has led to soil pollution. Palladium is thought to be one of the strongest allergens from health hazard viewpoint [1,2]. For these reasons, establishing rapid and accurate methods for the determination of palladium for industrial process, quality and pollution control is important. Many sensitive methods, such as Spectrofluorimetry, X-ray fluorescence spectrometry, Neutron activation analysis, Atomic absorption spectrometry have widely been used for the determination of palladium. However, Spectrophotometric methods have gained popularity for palladium determination as advantageous in respect of simplicity and low operating costs. A wide variety of spectrophotometric reagents, such as azo dyes, rhodamine derivatives, porphyrin ligands, thiourea derivatives, 8-hydroxy aminoquinoline derivatives and nitroso dye have been developed for the determination of palladium [3-12]. Many organic reagents for the spectrophotometric determination of palladium have been reviewed by Beamish[13]. More recently, procedure based on palladium complex with 3-(2'-thiazolylazo)-2,6-diaminopyridine[14], 2,3-dibromo-4-carboxy benzene-1,10-phenanthroline[15], 1-(5-bromo-2-pyridylazo)-2-naphthol-6-sulfonic acid[16] and pyrogallol red - H_2O_2 [17], But in all the above cases complexation has been reported at an elevated temperature. The sulphur containing ligands form more stable complexes with palladium(II). Some sulphur containing ligands such as substituted thioureas

[18-23], 2-arylythi-p-nitroacetophenone[24], thiosemicarbazones[25], 2,2'-dithiodianiline[26], have been reported for spectrophotometric determination of palladium (II) from associated elements, but these suffer from lack of selectivity and are time consuming.

Some other extractive spectrophotometric methods have also been developed for the determination of palladium (II). Some of them have the advantage of simplicity, sensitivity or specificity. The method described here, however, is superior to each of these in sensitivity, specificity, precision and in the concentration range that can be used. The indicator used is thymol blue.

MATERIALS AND METHODS

An UV-visible spectrophotometer (ELICO, Model SL-159) with quartz cells of 1.0 cm path length was used for absorbance measurement. An ELICO digital pH (Model LI-120) with combined glass calomel electrode was used for pH measurements. All chemicals used were of AR grade (Merck). A 1060 $\mu\text{g ml}^{-1}$ solution was prepared by dissolving 2.134 g of PdCl_2 in 2 ml of concentrated HCl and then diluting to 1000 ml with distilled water and the solution was standardized by known methods reported in the literature [27]. The standard stock solution of thymol blue of 1.0×10^{-2} M concentration was prepared in aqueous alcohol (40% v/v).

Recommended Procedure: An aliquot of solution containing 10.6 $\mu\text{g ml}^{-1}$ palladium (II) was taken in a 10 ml measuring flask, & 2 ml of 1.0×10^{-4} M of the reagent was added to it. The contents were diluted to the mark with aqueous alcohol (40% v/v), keeping the pH constant, the absorption spectrum of the resultant yellow colored palladium (II)-thymol blue complex was recorded against blank from which the value of λ_{max} was obtained. The optimum experimental conditions in regard to - 1. The concentration of the reagent (thymol blue), 2. The concentration of the palladium(II), 3. The pH of the medium and 4. Ascertaining the λ_{max} - of the palladium (II) thymol blue complex were established.

RESULTS AND DISCUSSION

The absorption spectrum of the palladium (II)-thymol blue complex in aqueous alcohol was studied over the wave length range 340-610 nm. The yellow colored complex exhibited absorption maximum at 470 nm, where reagents shows negligible absorption at this wavelength. The effect of the quantity of the reagent on the intensity of color was also studied. It was found that minimum 2-fold excess of the reagent was required for full colour development. The colour develops instantaneously on mixing the two solutions and remains stable for 40 minutes. The optimum pH for the formation of this complex is 4.0.

The system adheres to Beer's law in the range 0.0-9.57 $\mu\text{g ml}^{-1}$ of the palladium (II) with optimum range of 1.06-9.57 $\mu\text{g ml}^{-1}$ of the metal (Figure 1). The molar absorptivity calculated over the range studied was 2.12×10^4 $\text{L mol}^{-1} \text{cm}^{-1}$, while sensitivity was 0.47 ng ml^{-1} . The standard deviation & coefficient of variance as determined of a series of measurements made according to the optimum conditions were 0.0006 and 0.30 respectively. This speaks the volume for the precision for the present spectrophotometric method for the determination of palladium (II) using thymol blue as the analytical reagents. It is worthwhile to mention here that this method has an edge over some recent spectrophotometric methods for the determination of palladium (II) using other reagents (Table 2). Further, the mole ratio method gives the composition of this palladium (II)-thymol blue complex as 1:2 (Pd:T.B::1:2).

The effect of diverse ions on the spectrophotometric determination of Palladium (II), using Thymol Blue as the reagent has been studied in the terms of tolerance limit which was set as the amount ($\mu\text{g ml}^{-1}$) of the diverse ions causing an error of $\pm 1\%$ (table 1). It has been concluded that the following cations and anions do not interfere in the spectrophotometric determination of the Palladium (II).

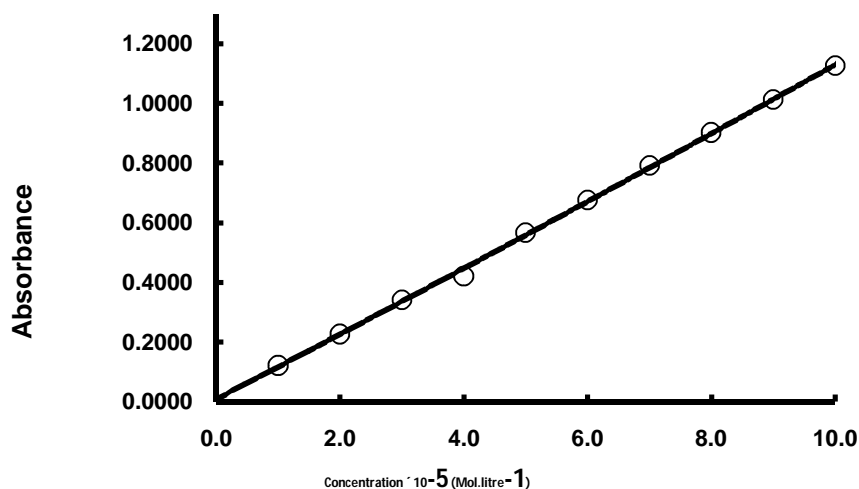


Figure 1. Plot of Absorbance vs Concentration (C) of Palladium(II)- Thymol Blue complex

Table 1. Effect of diverse ions on the Spectrophotometric Determination of Palladium (II) using Thymol Blue as the reagent, Palladium (II) = 2.12 $\mu\text{g mL}^{-1}$

S. No.	Diverse ion	Added as	Amount of a diverse Ion added ($\mu\text{g mL}^{-1}$)	Pd (II) found ($\mu\text{g mL}^{-1}$)	Relative error (%)
1	NO_2^-	NaNO_2	115.8	2.098	-1.03
2	NO_3^-	NaNO_3	149.9	2.110	-0.47
3	CH_3COO^-	CH_3COONa	140.0	2.129	-0.42
4	Cl^-	KCl	178.0	2.135	0.70
5	Br^-	KBr	199.9	2.126	-0.30
6	I^-	KI	317.0	2.127	0.28
7	CO_3^{2-}	Na_2CO_3	154.5	2.11	-0.47
8	SO_4^{2-}	K_2SO_4	238.0	2.126	0.28
9	PO_4^{3-}	$\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$	237.4	2.135	0.70
10	NH_4^+	NH_4NO_3	898.9	2.099	-0.99
11	Na^+	NaNO_3	574.9	2.097	-1.08
12	Pb^{2+}	$\text{Pb}(\text{NO}_3)_2$	518.0	2.144	1.13
13	Hg^{2+}	HgCl_2	494.9	2.10	-0.94
14	Cu^{2+}	$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$	157.0	2.126	0.28
15	Cd^{2+}	$\text{Cd}(\text{NO}_3)_2$	280.0	2.112	-0.37
					Contd.
16	Al^{3+}	$\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$	269.8	2.106	-0.66
17	Fe^{3+}	FeCl_3	1566	2.128	-0.37
18	Cr^{3+}	$\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$	2598	2.139	-0.61
19	Zn^{2+}	$\text{Zn}(\text{NO}_3)_2$	4900	2.126	-0.28
20	Mn^{2+}	$\text{MnSO}_4 \cdot \text{H}_2\text{O}$	1374	2.103	-0.80
21	Ni^{2+}	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	146.7	2.111	-0.42
22	Co^{2+}	$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	735.31	2.105	-0.70
23	Ba^{2+}	$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$	343.0	2.135	0.70
24	Sr^{2+}	$\text{Sr}(\text{NO}_3)_2$	214.0	2.132	0.56
25	Ca^{2+}	$\text{Ca}(\text{NO}_3)_2$	999.4	2.145	1.17
26	Mg^{2+}	$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	564.5	2.112	-0.37
27	K^+	KCl	970.0	2.126	0.28

Table 2. Comparison of the present method with some recent spectrophotometric methods for the determination of Palladium (II)

Reagent	Sensitivity ($\mu\text{g mL}^{-1}$)	Linear range ($\mu\text{g mL}^{-1}$)	Molar absorptivity ($\text{L mol}^{-1} \text{cm}^{-1}$)	Ref. No.
4 – Salicylamido – 1-diacetylmonoxime (SDT)	-	0.09 – 3.6	3×10^4	28
Glyoxal Bis (4 – phenyl – 3 – thiosemicarbazone (GBPT)	-	50 - 500 $\mu\text{g}/25\text{ml}$	(a) 3.2×10^{-3} at (b) 1.5×10^3	29
Phenanthraquinone	0.025	23.4	-	30
Monothiosemicarbazone (PTS)	0.0083	7.2	-	
N – Acetyl – L – Cystine	-	4.0 – 65.3	-	31
4,4' – Bis (dimethylamino) thiobanzophenone (TMK)	-	0 – 0.8	1.96×10^5	32
Disulfoton	-	2 – 17	-	33
5, 6 – Dimethyl – 1, 3 – indanedione – 2 – oxime	-	-	2.98×10^4	34
Pyridine – 2 – Acetaldehyde salicyloyl hydrozone	-	0.12 – 8.0	1.3×10^4	35
2 – (2 – Benzothiazolylazo) – 5 – dimethylamino – 4 – alyl arsomic acid	-	0 – 1.6	6.65×10^4	36
1 – (Thiazolylazo) – 2 – hydroxynaphthalene – 3, 6 – disulphonic acid	-	$2 \times 10^{-6} - 1.5 \times 10^{-4} \text{M}$	1.1×10^4	37
3 – (5' – Tetraazolylazo) – 2, 6 – diaminotoluene	-	-	5.2×10^4	38
1, 4 – Dihydrazino phthalazine	-	0.12 – 8.0	2.6×10^4	39
5 – (5 – Nitro – 2 – pyridylazo) – 2, 4 – diaminotoluene	-	0 – 0.9	1.25×10^5	40
N, N' – Dipirydylythiourea	0.0065	0.24 – 2.88	2.36×10^4	41
1 phenyl – 3 – (2 – thiazolyl) thiourea	-	25 - 180	1.56×10^4	42
2, 4 – dihydroxyacetophenone thiosemicarbazone	-	0.7 – 12.0	1.3×10^4	43
5 – [α - (4 – Chlorophenol) azo] rhodamine	-	0.25 /25 ml	2.96×10^4	44
5 – (3 – Carboxylphenylazo) – 8 – aminoquinoline	-	0 – 10 /25 ml	8.4×10^4	45
2 – (2 – Thiazolylazo) – 5 – dimethylamino benzoic acid	0.391	0.12 – 1.75	8.70×10^4	46
Thymol Blue	0.0032 ng/ml	0 – 10.6	3.1×10^4	Present Method

APPLICATIONS

Present method is rapid and accurate method for the determination of micro amounts of Palladium (II) in different types of samples i.e. in effluent and soil analysis to control Palladium pollution.

It is a simple method and has low operating cost.

It is a sensitive, selective and convenient method for the determination of Palladium.

CONCLUSIONS

A comparison of the proposed methods with other spectrophotometric methods (Table 2) shows the Thymol Blue is one of the most sensitive, selective and convenient spectrophotometric reagents for palladium.

ACKNOWLEDGEMENTS

I am thankful to Principal Agra College, Agra to provide necessary facilities to conduct this pioneer study.

REFERENCES

- [1] G. Patrick, Michel, P. Platinum. *Met. Rev.* **2003**, 47, 60-72.
- [2] S. Caroli, A. Alimonti, F. Petrucci, B. Bocca, M. Krachler, *Spectrochim. Acta B* **2001**, 56, 1241-124.
- [3] Y. E. Zeng, H.S. Zhang, Z. H. Chen, *Handbook of Modern Chemical Reagents, The Forth Fascicule, Chromogenic Agent of Inorganic Ion, 1st ed: Chemical Industry Press: Beijing, P. R. China, 1989.*
- [4] H.Q. Yang, G. Zhang, L. L. Zhang, G. Q. Liu, X. H. Zhang, *Talanta* **1996**, 43, 747-753.
- [5] G. V. R. Murthy, T. S. Reddy, *Talanta* **1992**, 39, 697-701.
- [6] J.H. Gao, B. Peng, H.Y. Fan, J. W. Kang, X. D. Wang, *Talanta* **1997**, 44, 837-842.
- [7] I. Mori, T. Kawakatsu, Y. Fujita, T. Matsuo, *Talanta* **1999**, 48, 1039-1044.
- [8] D. L. Ma, F. L. Cui, D. S. Xia, L. L. Wang, *Anal. Lett.* **2002**, 35, 413-421.
- [9] L. S. Sarma, J.R. Kumar, K.J. Reddy, A. K. Kumar, A. V. Reddy, *Anal. Sci.* **2002**, 18, 1257-1261.
- [10] M. B. Gholivand, N. Nozari, *Talanta* **2000**, 52, 1055-1060.
- [11] B. K. Reddy, K. J. Reddy, J.R. Kumar, A. K. Kumar, A. V. Reddy, *Anal. Sci.* **2004**, 20, 925-930.
- [12] B. Maria, P. Katarzyna, *Chem. Anal.* **2003**, 48, 87-95.
- [13] F. E. Beamish, *Talanta*, **1965**, 12, 743.
- [14] M.I. Toval, P. Richeter, N. Lara, M. Escudera, C. Sotoc, *Anal Lett*, **2000**, 93.
- [15] G. zhongxian, D. Bingfan, Z. Guoxing, Z. Shuyan, *Guijinshu*, **1997**, 18, 38.
- [16] M. Xuequin, T. Fulong, J. Qingping, *Fenxi Huaxue*, **1992**, 20, 951.
- [17] A. A. Ensafi, M. Keyvanfard, *Spectrochim Acta*, **2002**, 58A, 1567.
- [18] M. Donglan, C. Fengling, X. Dongsheng, W. Yulu, *Anal Lett*, **2002**, 35, 413.
- [19] M. Donglan, L. Ying, L. Quanjian, W. Yulu, *J Chinese Chem Soc.*, **2001**, 48, 1111
- [20] D. Guosheng, M. Donglan, *Fenxi Huaxue*, 2001, 29, 740.
- [21] M. Donglan, L. Ying, L. Quanjian, W. Yulu, *Yejin Fenxi*, 2000, 20, 10.
- [22] K.S. Patel, P. C. Sharma, S.G. Agarwal, P. Hoffmann, *Anal Lett*, **2000**, 33, 503.
- [23] S. P. Chaudhari, S. C. Shome, *J. Indian Chem Soc.*, **1997**, 74, 554.
- [24] P. T. Gojare, S. H. Gaikwad, M. A. Anuse, *Res J. Chem Environ*, **2001**, 5, 51.
- [25] G. V. R. Murthy, T.S. Reddy, *Talanta*, **1992**, 39, 697.
- [26] M. B. Gholivand, N. Nozari, *Talanta*, **2000**, 52, 1055.
- [27] A. I. Vogel, *A text book of quantitative Inorganic Analysis, Vth Edn.* Longman Green & Company, London, **1991**.
- [28] M. E. M. Khalifa, K. M. Ibrahim, A. A. El-asmay, *Indian J. Chem.*, **1986**, 25A, 501.
- [29] A. Asuero, A. M. Jimenez, M. A. Herrador, *Analyst*, **1986**, 111, 747.
- [30] K. Shrivah, P. P. Sinha, K. K. Sindhvani, *Analyst*, **1986**, 111, 1339.
- [31] T. S. Javanovic and B. S. Stankovic, *Analyst*, **1989**, 114, 401.
- [32] Z. L. Liu, W.B. Chang, J. H., Y. X. Ci, *Analyst*, **1991**, 116, 213.
- [33] B. Simonovska, J. Marsel, *Analyst*, **1991**, 116, 317.
- [34] D. M. Rao, H. Reddy, D. V. Reddy, *Talanta*, **1991**, 38, 1047.
- [35] S. H. Sinha, A. D. Sawant, *Bull. Chem. Soc. Jpn.*, **1992**, 65, 1622.
- [36] L. Po, L. Hengchuan, W. Cheng, *Talanta*, **1991**, 38, 1143.

- [37] M. Pesavento, C. Riolo, R. Biesuz, *Analyst*, **1985**, 110, 801.
- [38] O. Hernandez, A. J. Jimenez, F. Jiminez, J.J. Arias, J. Havei, *Talanta*, **1994**, 41, 775.
- [39] D. Xu, M. Gong, G. Li, S. Gao, *Fenxi Shiyanshi*, **1996**, 15, 47.
- [40] H. Yang, G. Zhang, L. Zhang, G. Lia, X. Zhang, *Talanta*, **1996**, 43, 747.
- [41] S. P. Chaudhary , S. C. Shome, *J. Indian Chem. Soc.*, **1997**, 74, 554.
- [42] S. Singhal, P. Chandak , S. P. Mathur, *J. Indian Chem. Soc.*, **1997**, 74, 695.
- [43] C. J. Kumar, L. S. Sarma , A. V. Reddy, *Asian J. Chem.*, **1997**, 9, 218.
- [44] Z. Huang, T. Shen, Q. Xu , J. Zhao, *Chem. Abstr.*, **1999**, 130, 133326k.
- [45] X. Tan and J. Pan, *Yejin Fenxi*, **1998**, 18, 4.
- [46] A. Bhalotra, B. K. Puri, *Mikrochim. Acta*, **2000**, 001.