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Spectrophotometric Determination of Palladium by the Coloration with 2-Mercaptoethanol

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Abstract

A simple and highly sensitive method is proposed for the determination of palladium with 2-mercaptoethanol using spectrophotometer. The Pd(II) formed1:2, a yellow colored complex with 2-mercaptoethanol in a buffer(potassium hydrogen phthalate-hydrochloric acid) of pH 4. The detection limit and quantitation limit of the palladium(II) determination are found to be 0.396 µg cm^{-3} and 1.200 µg cm^{-3} respectively. The Beer's law obeyed over the concentration range 1.39-8.36 µg cm^{-3} of palladium(II). The optimum concentration range for maximum precision was deduced from Ringbom's plot and was found to be 2.79-8.36 µg cm^{-3}. The molar absorptivity and Sandell's sensitivity of the complex were found to be 2.2634 x 10^4 dm^3 mol^{-1} cm^{-1} and 7.2154 x 10^{-3} µg cm^{-2}, respectively. The absorbance value of the complex was not effected by the presence of various cations and anions. The investigated method was applied for the determination of Pd(II) in alloy and catalyst samples.

Keywords: Alloy sample, catalyst sample, 2-mercaptoethanol, palladium determination, spectrophotometry.

Introduction

Palladium was discovered by William Hyde Wollaston and it was named after the asteroid Pallas[1]. Palladium is one among the platinum group elements. It is largely used in catalytic converters[2], jewelry and dentistry[3]. It is also used for the storage[4] and purification of hydrogen gas[1]. During making of white gold, palladium can be used as an alternative to platinum[2]. Catalytic convertors are major sources of increase in palladium content in environment[5]. Pd at very low doses can act as potential allergen[6]. Recently it has been reported that palladium containing dental implants can cause allergic contact dermatitis[7]. Thus a rapid, selective and sensitive method for the determination of palladium is explored.

Various sensitive analytical techniques like neutron activation analysis[8], atomic absorption spectrometry[9] and spectrophotometry[10-29] have been used for the determination of palladium. Spectrophotometric methods are popular for the determination of palladium due to their simplicity and low cost of operation. A variety of organic reagents containing nitrogen and sulphur as donor atoms, has been used for palladium(II) determination. Most of these reagents suffer from limitations such as critical pH, long time for colour development, requirement of heating, interference of other ions e.t.c. In the investigated method, 2-mercaptoethanol has been used as a new analytical reagent for palladium(II) determination using spectrophotometer. The results obtained indicate that 2-mercaptoethanol is a highly sensitive, selective and convenient reagent for the determination of palladium.

Material and Methods

Materials: Measurements of absorbance were made on UV-Visible spectrophotometer (Jasco model V-360 manufactured by Jasco Corporation, Japan) using Quartz cell with a path length of 1 cm. Measurements of pH were made using digital pH meter (model EQ-610) supplied by Equiptronics Instruments (India). 0.2902 g of palladium chloride was dissolved in minimum volume of dilute KCl solution, and then diluted to 250 cm^3 with distilled water to obtain the stock solution. Then the method of gravimetry[30] was used to standardize the stock solution. By dilution of the stock solution to the required volume, working solutions were prepared. A known volume of 2-mercaptoethanol was dissolved in distilled water to get 0.01% solution.

0.2M KCl, 0.1M $C_8H_5KO_4$, 0.1M NaOH, 0.1M KH_2PO_4, 0.025M $Na_2B_4O_7.10H_2O$ solutions were prepared by dissolving the respective salts in appropriate amount of distilled water. 0.1M and 0.2M hydrochloric acid were prepared by diluting the appropriate amount of 10.2M hydrochloric acid using distilled water. These solutions were mixed in required amounts to prepare the buffer solutions of various pH.

Metal salts were separately dissolved in and made up to 100 cm^3 using distilled water to get solutions of respective metal ions. Alkali metal salts were dissolved in distilled water to obtain solutions of anions.

Method: Different amounts (34.84 to 348.35 µg) of Pd(II) were taken in separate 25 cm^3 standard flasks, each containing 10 cm^3 of 0.01% 2-mercaptoethanol solution. Each solution was made up to the mark using buffer solution of pH 4 and shaken well for uniform concentration. A wavelength of 315 nm was used to measure the absorbances of solutions, against reagent blank which is prepared in the identical manner but without the addition of palladium. Absorbances were plotted versus concentration to get the calibration plot.

Analysis of palladium alloy and catalyst samples: To a known weight of alloy or catalyst sample, aquaregia was added and heated until the sample almost advance towards dryness. The dilute hydrochloric acid was added to the residue and the solution was filtered. The filtrate was diluted to a known volume using distilled water. The dimethylglyoximate method [1] was employed to standardize the stock solution. Known volume of the stock solution was used for the determination of palladium as per the investigated procedure.

Results and Discussion

Absorption spectra: Pd(II) formed a light yellow coloured complex with 2 mercaptoethanol. Wavelength region 300-800 nm was selected to record the absorption spectra of reagent solution against buffer blank of pH 4 followed by the solution of Pd(II)- 2-mercaptoethanol complex against reagent blank. The spectra of the complex is presented in the figure-1.

Detection Limit and Quantitation Limit: For the determination of Pd(II), the detection limit[31] was calculated (DL=3.3σ/S) as 0.396 µg cm^{-3} and quantitation limit[31] was found [QL=10σ/S where σ represents standard deviation of the regent blank (n=5) and 'S' represents slope of the calibration curve] as 1.200 µg cm^{-3}.

Effect of pH: The effect of pH on the development of colour intensity of the complex was studied. A plot of pH versus absorbance at 315 nm (figure-2) shows maximum absorbance at pH 4. Hence the further studies were carried out at the optimum pH 4.

Effect of reagent: 0.2 to 3.0 cm^3 of 0.01% 2-mercaptoethanol solution was added to a series of 25 cm^3 standard flasks, each containing 0.4 cm^3 of a 348.35 µg cm^{-3} palladium(II) solution. The solution was made up to the mark using buffer solution of pH 4. Absorbance remained constant (figure-3) from addition of 2 cm^3 to 3 cm^3 of the reagent. Surplus of 2-mercaptoethanol did not affect the absorbance of solution.

Validity of Beer's Law: 0.1-1.0 cm^3 of 348.35 µg cm^{-3} Pd(II) solution and 10 cm^3 of 0.01% 2-mercaptoethanol solution was added to different 25 cm^3 standard flasks. The solution in each standard flask was made up to the mark using the buffer solution of pH 4 and absorbances were measured at 315 nm. A graph plotted between amount of palladium(II) and corresponding absorbance (figure-4), shows the linear plot passing through the origin. It obeys the Beer's Law in the range 1.39 µg cm^{-3} to 8.36 µg cm^{-3} of Pd(II).

Sandell's sensitivity and Molar absorptivity: From Beer's law data, Sandell's sensitivity was calculated as 7.2154 x 10^{-3} µg $cm^{-2}$and molar absorptivity as 2.2634 x 10^4 dm^3 mol^{-1} cm^{-1}.

Ringbom plot: A Ringbom plot (figure-5) was established by ploting log [Pd(II)] versus (100-%T). The optimum range of 2.79-8.36 µg cm^{-3} of the metal was obtained.

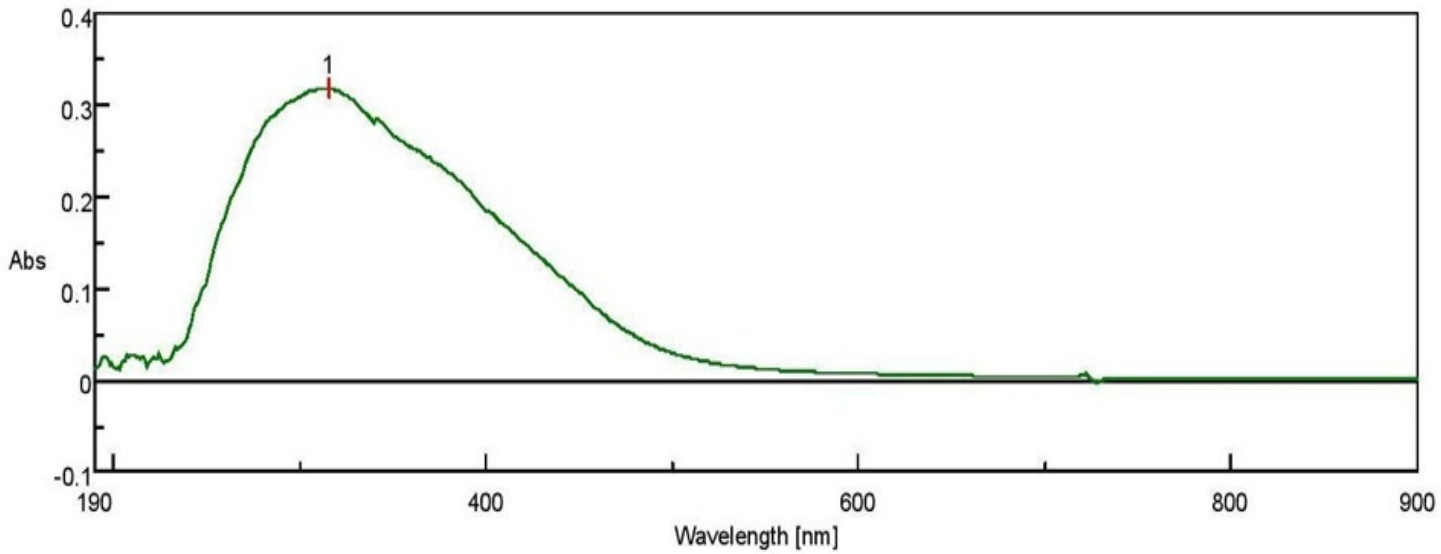

Figure-1
Absorption spectra of Pd(II)-2 Mercaptoethanol Complex

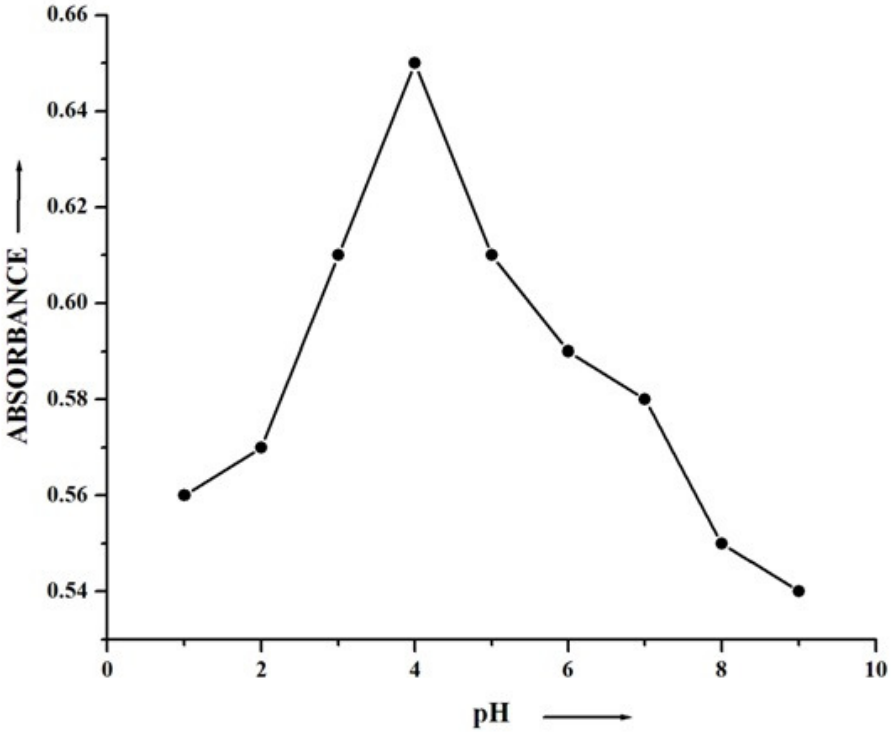

Figure-2
Effect of pH on Pd(II)-2 Mercaptoethanol Complex

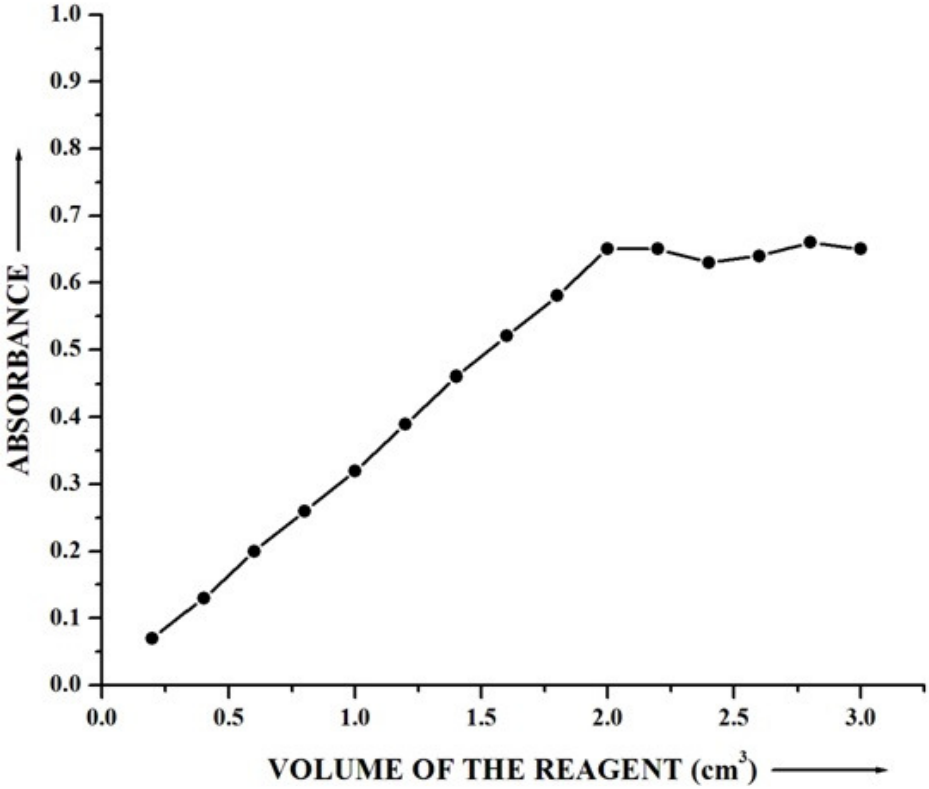

Figure-3
Effect of Reagent concentration on Pd(II)-2 Mercaptoethanol Complex

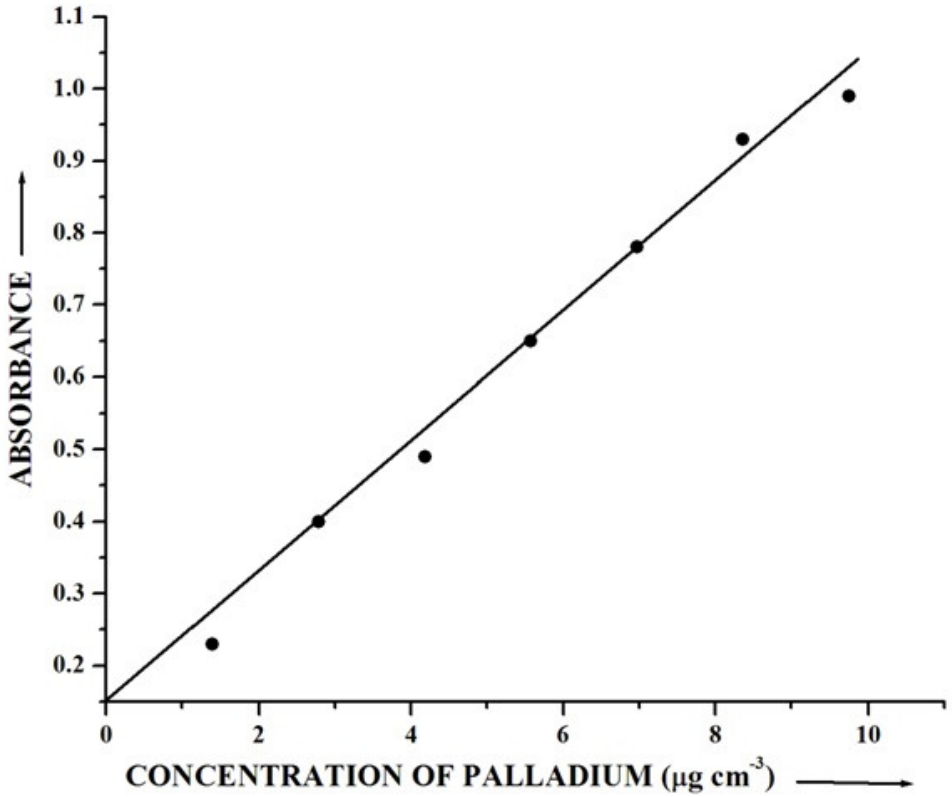

Figure-4
Beer's Law plot of Pd(II)-2 Mercaptoethanol Complex

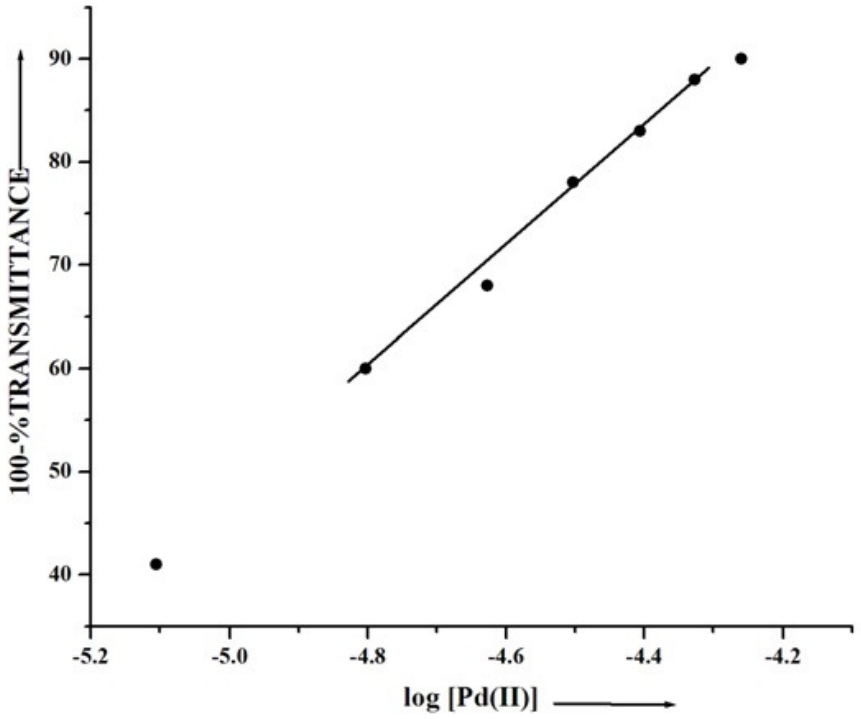

Figure-5
Ringbom plot of pH on Pd(II)-2 Mercaptoethanol Complex

Precision and accuracy: To assess the precision and accuracy of the method, determinations were carried out for a set of five measurements of 2.84-8.16µg cm^{-3} of Pd(II), under the optimized experimental conditions. The results are presented in the table-1. The relative error and relative standard deviation do not exceed ±0.47 % and 0.42 % respectively. The results indicate that the proposed method is precise and accurate.

Composition of the Pd(II) -2-mercaptoethanol complex: By Job's method of continuous variation (figure-6) the composition of the Pd(II)-2-mercaptoethanol was found to be 1:2. It was further confirmed by the mole ratio method (figure-7).

Table 1
Precession and accuracy in the determination of palladium(II)

Pd(II) (µg cm^{-3})		**Relative error (%)**	**Standard deviation (µg cm^{-3})**	**Relative standard deviation (%)**
Taken	**Found***			
2.84	2.83	-0.35	0.012	0.42
4.26	4.24	-0.47	0.007	0.17
5.67	5.65	-0.35	0.012	0.22
7.09	7.07	-0.28	0.02	0.35
8.16	8.13	-0.37	0.012	0.15

*Average of five determinations

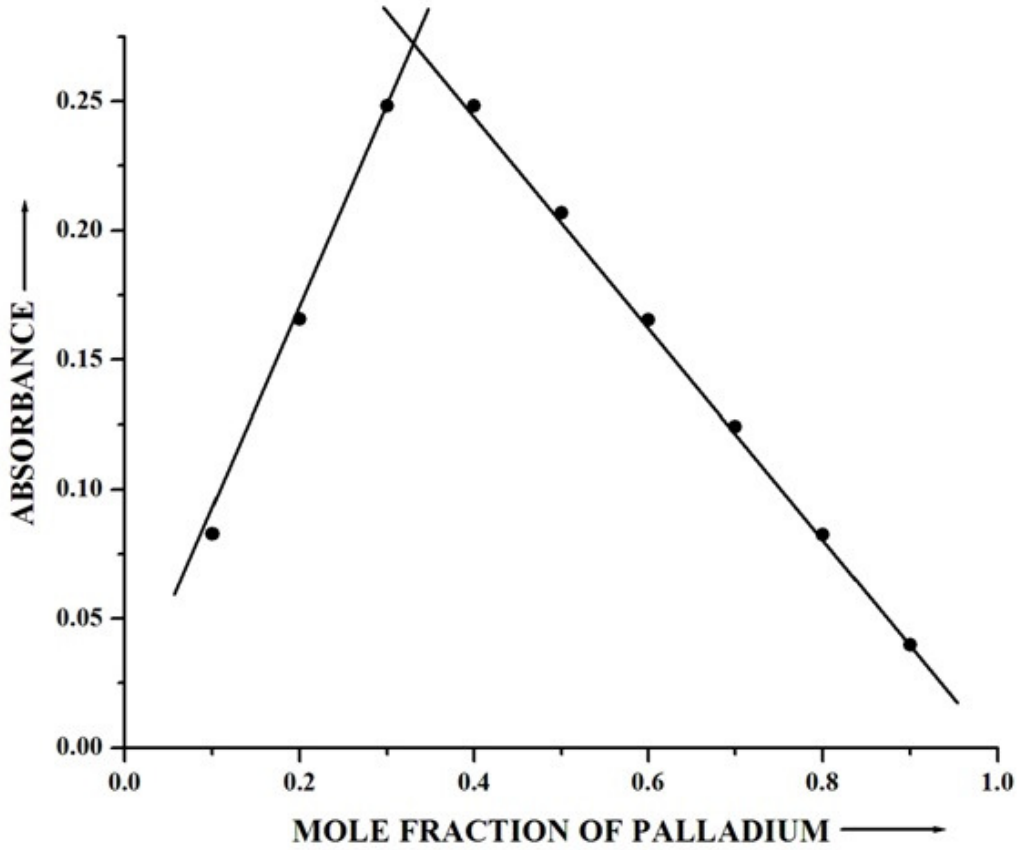

Figure-6
Continuous variation plot of pH on Pd(II)-2 Mercaptoethanol Complex

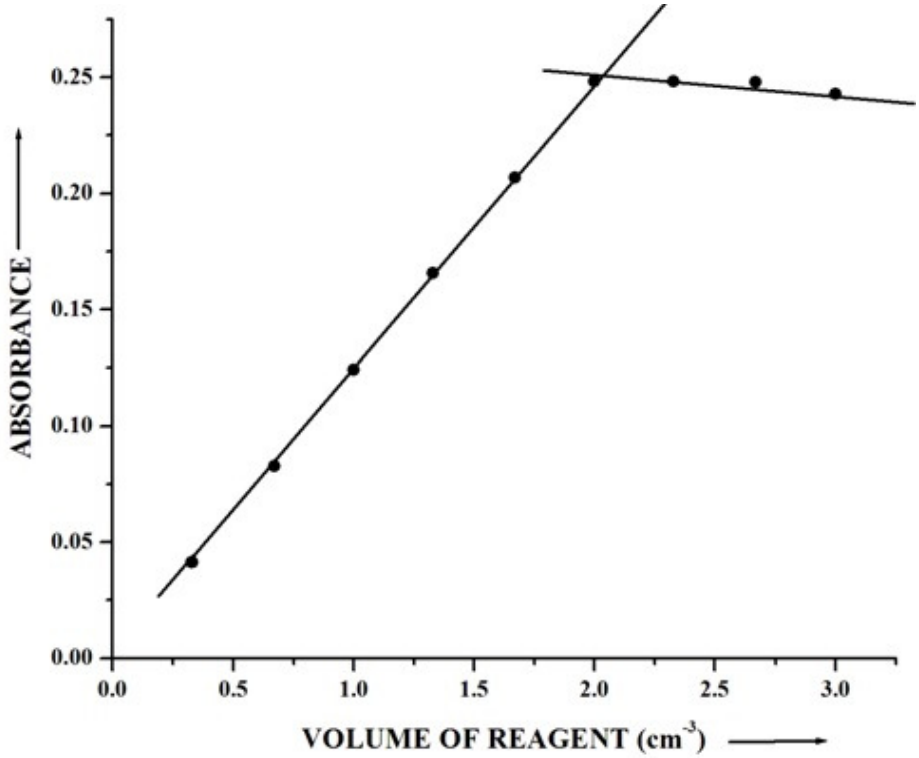

Figure-7
Mole ratio plot of Pd(II)-2 Mercaptoethanol Complex

Effect of diverse ions: The absorbance value of Pd(II)-2-mercaptoethanol [4.26 µg cm^{-3} Pd(II)]complex was studied in the presence of foreign ions. The tolerance limit was fixed as deviation of ±2% in the absorbance value. The following ions did not interfere at the amounts in µg cm^{-3} shown: Ag(I)(05), Ba(II)(140), Zn(II)(1500), Pb(II)(50), Ni(II)(200), Co(II)(50), Ru(III)(10), Au(III)(10) fluoride(200), chloride(300), bromide(500), sulphate(100), phosphate(120), tartarate(150), borate(150), acetate(100), oxalate(250) and nitrate(120).

Applications: Palladium alloy and catalyst samples were explored according to the proposed procedure to affirm the suitability of the investigated method. The results f investigated method has been matched with the results of the reference method [32]. The Student's t-values at α=0.05 and the variance ratio F-values calculated at α=0.05 did not go beyond the theoretical values. The accuracy and precision of the results, of investigated method attune with that of the reference method. Hence it can be effectively applied for the analysis of palladium in alloy and catalyst samples with fair degree of accuracy and precision (table-2 and table-3).

Table 2
Determination of Pd(II) in solutions of alloy composition

	Proposed method				Reference method[32]					
Alloy Composition %	**Pd(II) found[a] (%)**	**Recovery(%)**	**Relative error (%)**	**Relative standard deviation (%)**	**Pd(II) found[a] (%)**	**Recovery (%)**	**Relative error (%)**	**Relative standard deviation (%)**	**[b]F-test**	**[c]t-test**
Dental alloy Ag+Pd+Au 66+23+11	23.9	100.4	0.39	0.068	23.08	100.3	0.35	0.084	1.45	0.91
Gold platinum ceramic alloy Au+Pd+Ru+Ag+In+Sn 28.0+43.9+0.1+19.5+3.5+5.0	43.7	99.5	-0.46	0.1368	43.8	99.8	-0.23	0.2146	1.02	2.00

[a]Average of five determinations, [b]Tabulated t-value for 8 degree of freedom at P (0.95) is 2.306 , [c]Tabulated F-value for (4, 4) degree of freedom at P (0.95) is 6.39

Table 3
Determination of Pd(II) in catalysts

	Proposed method					Reference method[32]				[b]F-test	[c]t-test
Palladium Catalyst	**Pd (%) Certified Value**	**Pd (%) Found[a]**	**Recovery (%)**	**Relative error (%)**	**Relative standard deviation (%)**	**Pd(II) found[a] (%)**	**Recovery (%)**	**Relative error (%)**	**Relative standard deviation (%)**		
Pd-$BaCO_3$	5%	4.97	99.4	-0.60	0.42	4.96	99.2	-0.80	0.41	1.01	0.77
Pd-charcoal	10%	9.97	99.7	-0.30	0.54	9.94	99.4	-0.60	0.49	1.22	0.92

[a]Average of five determinations, [b]Tabulated t-value for 8 degree of freedom at P (0.95) is 2.306, [c]Tabulated F-value for (4, 4) degree of freedom at P (0.95) is 6.39

Conclusion

The method is rapid and reliable. The colour development is rapid and takes place at room temperature. Slight variation of experimental conditions did not affect the intensity of the colored species. The method is useful for the accurate and precise determination of Pd(II) in alloy and catalyst samples. The proposed method doesn't require any solvent extraction, cooling or heating and free from interference from many cations and anions.

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References

1. Hammond C.R., The Elements, in Handbook of Chemistry and Physics, 81st Ed., CRC Press, Boca Raton, Florida, United States, **(2004)**

2. Palladium, United Nations Conference on Trade and Development archived from original Dec06, **(2006)**

3. Roy Rushforth, Palladium in Restorative Dentistry: Superior Physical Properties make Palladium an Ideal Dental Metal, *Platinum Metals Rev.*, **48(1)**, 30-31 **(2004)**

4. Grochala W. and Edwards P.P., Thermal Decomposition of the Non-Interstitial Hydrides for the Storage and Production of Hydrogen, *Chem. Rev.,* **104(3)**, 1283-1316 **(2004)**

5. Krystyna Pyrzynska, Recent advances in solid-phase extraction of platinum and palladium, *Talanta*, **47(4)**, 841-848 **(1998)**

6. Kielhorn J., Melber C., Keller D. and Mangelsdorf I., Palladium-a review of exposure and effects to human health, *Int. J. Hyg. Environ. Health*, **205(6)**, 417-32 **(2002)**

7. Maggie Chow, Nina Botto and Howard Maibach, Allergic Contact Dermatitis Caused by Palladium-Containing Dental Implants, *Dermatitis*, **25(5)**, 273-274 **(2014)**

8. Absalan G., Safavi A., Massoumi A., Extraction Atomic Absorption of Palladium(II) with DDTT, *Microchemical J.*, **37,** 212-215, **(1988)**

9. Lathiri S., Dey S., Baidya T.K., Nandy M., Basu D. and Das N.R., Neutron activation analysis of noble and platinum group of metals in the Proterozoic Dalma rocks of Eastern India, *Appl. Radiat. Isotopes*, **48**, 549-553 **(1997)**

10. Habibollah Eskandari and Gholamhassan Imanzadeh Karkaragh, Highly Selective and Simple Zero and First Order Derivative Spectrophotometric Determination of Palladium by Using α-Benzilmonoxime in Triton X-100 Micellar Solution, *Bull. Korean Chem. Soc.,* **24(12)**, 1731-1736 **(2003)**

11. Rao Mallikarjuna D., Reddy Hussain K. and Reddy Venkata D., Spectrophotometric determination of palladium with 5,6-dimethyl-1,3-indanedione-2-oxime, *Talanta*, **38(9)**, 1047-1050, **(1991)**

12. Orville W. Rollins and Morris M. Oldham, Spectrophotometric determination and spectrophotometric titration of palladium. Formula for the palladium(II)-nitroso R complex, *Anal. Chem.,* **43(2)**, 262-265 **(1971)**

13. Parameshwara P., Karthikeyan J., Shetty Nityananda A. and Shetty Prakash, 4-(N,N-Diethylamino) Benzaldehyde Thiosemicarbazone in the Spectrophotometric Determination of Palladium, *Anal. Chim.,* **97(10)** 1097-1106 **(2007)**

14. Garcia1 Lopez I., Aviles Martinez J. and Cordoba Hernandez M., Determination of palladium with thiocyanate and rhodamine b by a solvent-extraction method, *Talanta*, **5(33)**, 411-414 **(1986)**

15. Ralls J.W., Rapid Method for Semiquantitative Determination of Volatile Aldehydes, Ketones, and

Acids, Flash Exchange Gas Chromatography, *Anal. Chem.,* **32(03)** 332-336, (**1960)**

16. Kuroda Rokuro, Yoshikuni Nobutaka and Kamimura Yoshihiro, Extraction-spectrophotometric determination of traces of palladium with azide and methylene blue, *Anal. Chim. Acta***, 60(1)**, 71-77 **(1972)**

17. Jayaa S., Rao Prasada T. and Ramakrishna T.V., Spectrophotometric determination of palladium using iodide and pyronin G, *J. Less Common Met.,* **91(2)**, 261-265 **(1983)**

18. Marczenko Z., Separation and Spectrophotometric Determination of Elements, John. Wiley and Sons, Inc., Newyork, 566- 602 **(1973)**

19. Hall I.H., Lackey C.B., Kistler T.D., Durham R.W. Jr., Jouad E.M., Khan M., Thanh X.D., Djebbar-Sid S., Benali-Baitich O. and Bouet G.M., Cytotoxicity of copper and cobalt complexes of furfural semicarbazone and thiosemicarbazone derivatives in murine and human tumor cell lines, *Pharmazie,* **55(12)**, 937-941 **(2000)**

20. Reddy Krishna B., Reddy Janardhan K., Rajesh Kumar J., Kiran Kumar A. and Reddy Varada A., Highly Sensitive Extractive Spectrophotometric Determination of Palladium(II) in Synthetic Mixtures and Hydrogenation Catalysts Using Benzildithiosemicarbazone, *Anal. Sci.,* **20(6)**, 925-930 **(2004)**

21. Chhakkar Anoop Kumar and Kakkar Lajpat Rai, Extractive spectrophotometric determination of palladium using 2-(2-hydroxyimino-1-oxoethyl)furan, *Fresenius J. Anal. Chem.***, 350(3)**, 127-131 **(1994)**

22. Uesugi K., Sik L.J., Nishioka H., Kumagai T. and Nagahiro T., Extraction-Spectrophotometric Determination of Palladium with 3-Thiophenaldehyde-4-phenyl-3-thiosemicarbazone, *Microchem. J.,* **50(1)**, 88-93 **(1994)**

23. Shetty Nityananda A. and Gadag Rudrayya V., Spectrophotometric Determination of Palladium(II) Using 4-(Dimethylamino) benzaldehyde Thiosemicarbazone, *Bull. Chem. Soc. Jpn.,* **66(9)**, 2536-2540 **(1993)**

24. Shetty Prakash, Shetty Nityananda A. and Gadag Rudrayya V., Spectrophotometric determination of palladium(II) using piperonal thiosemicarbazone, *Indian J. Chem. Technol.***, 10**, 287-290 **(2003)**

25. Suvarapu Lakshmi Narayana, Reddy Koduru Janardhan, Reddy Somala Adi Narayana, Jyothi Rajesh Kumar and Reddy Ammireddy Varada**,** Synthesis of New Reagent Benzyloxybenzaldehydethiosemicarbazone (BBTSC): Selective, Sensitive and Extractive Spectrophotometric Determination of Pd(II) in Water Samples and Synthetic Mixtures**,** *J. Chin. Chem. Soc.*, **54(5),** 1233–1241 (**2007)**

26. Reddy Janardhan K. , Rajesh Kumar J., Ramachandraiah C., Reddy Adinarayana S. and Reddy Varada A., Selective and sensitive extractive spectrophotometric determination of micro amounts of palladium(II) in spiked samples: using a new reagent N-ethyl-3-carbazolecarbaxaledehydethiosemicarbazone, *Environ. Monit. Assess.,* **136**(1-3), 337-346 (**2008)**

27. Karthikeyan J., Parameshwara P. and Shetty Nityananda A., Analytical properties of *p*-[*N*,*N*-bis(2-chloroethyl) amino] benzaldehyde thiosemicarbazone: spectrophotometric determination of palladium(II) in alloys, catalysts, and complexes, *Environ. Monit. Assess.,* **173**(1-4), 569-577 (**2011)**

28. Pethe Gaurav B., Bhadangel Subhash G., Joshi Mrunmayee D. and Aswar Anand S., Extractive Spectrophotometric Determination of Palladium (ii) with 2-hydroxy-5-methylacetopheneoneisonicotinoylhydrazo-ne (HMAINH), *Adv. Appl. Sci. Res.,* **1(2)**, 58-64 (**2010)**

29. Chandrashekhara K.G, Gopalakrishna Bhat N. and Nagaraj P., Facile and direct spectrophotometric determination of palladium(II) with L-Cystine, *Int. J. Chem. Stud.,* **2(5),** 46-51 **(2014)**

30. Vogel AI, A textbook of Quantitative Inorganic analysis Longman Press, London, 6th Edition, 469-470 **(2000)**

31. Chandrashekhara K.G, Gopalakrishna Bhat N. and Nagaraj P., A highly sensitive spectrophotometric method for the Micro level Determination of Nitrite and Nitrate anions by Coupling of Terazotized Benzidine and N,N-dimethylaniline, *Res. J. Chem. Sci.* **5(2)**, 42-47 **(2015)**

32. Palaniyappan R, Thiosemicarbazone as Analytical reagent; A selective spectrophotometric determination of palladium, *Curr. Sci.,* **58(17)**, 958-961 (**1989)**