

Articles

Highly Selective and Simple Zero and First Order Derivative Spectrophotometric Determination of Palladium by Using α -Benzilmonoxime in Triton X-100 Micellar Solution

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The reaction of α -Benzilmonoxime with palladium(II) produces a green complex in triton X-100 micellar media. Palladium has been determined using zero and first derivative spectrophotometric methods. The absorbances of Pd(II)- α -benzilmonoxime complex at 441.8 and 677.0 nm in 0.10 M perchloric acid solution were monitored and linear working ranges of 0.3-12.0 and 0.7-20 $\mu\text{g mL}^{-1}$ with detection limits of 0.07 and 0.10 $\mu\text{g mL}^{-1}$ were obtained, respectively. Also, recoveries in the range of 92.8 to 100.1% and relative standard deviations in the range of 0.4 to 7.1% were obtained. First derivative spectrophotometry has also been applied for palladium determination under the optimum condition. The linear dynamic range of 0.2-24.0 $\mu\text{g mL}^{-1}$ palladium with relative standard deviations of 0.6-6.9% and recoveries in the range of 94.9-102.5% has been obtained by first derivative spectrophotometry. The method shows high selectivity because of the high concentration of acid used, which prevents formation of complexes of α -benzilmonoxime with the other cations. The palladium complex formed was stable at least one day. The method was successfully applied to the determination of palladium in some synthetic palladium alloys and palladium-charcoal powder.

Key Words : Palladium, α -Benzilmonoxime, Triton X-100, Derivative spectrophotometry

Introduction

Palladium has been applied in various ways as a hydrogenation catalyst, microcontactors in the electronics, hard alloy in dentistry and in the last few years as a component in the three-way catalysts in automobile exhaust-gas 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 polluted soil.¹ Palladium is thought to be one of the strongest allergens from a health hazard viewpoint.² For these reasons, rapid and accurate palladium determination methods for process, quality and pollution control are valuable.

Various spectrophotometric methods for the assay of palladium have been reported. Solvent extraction or sorption-spectrophotometric,³⁻⁶ high performance liquid chromatographic-spectrophotometric,⁷ spectrophotometric procedures using low melting point extractants,⁸⁻¹⁰ simple spectrophotometric methods,¹¹⁻¹⁶ derivative spectrophotometric,^{17,18} flow injection and stopped flow based techniques¹⁹⁻²¹ and spectrophotometric methods using cosolvents or micelles have also been proposed.^{18,22} Among the methods proposed, simplicity,^{6,8,19,21} speed,^{6,8} sensitivity^{7,20} and selectivity^{5,8,12,15,20,22}

limitations have been observed.

When the concentration of surfactant exceeds the critical micelle concentration (CMC), micelles are formed in solutions that appear to be homogeneous.²³ Micelles have unique properties. Non-polar compounds, such as organic molecules or nonionic complexes, are very soluble in the non-polar core of micellar colonies. Micelles can also act as microextraction capsules, equilibrium shifters and powerful stabilizing agents for non-polars. Some references discuss these properties.²³⁻²⁶

Solvent extraction techniques are time consuming, tedious and usually involve harmful chemicals. However, micellar systems have been conveniently used in UV-Vis spectrophotometry,²⁷⁻³⁰ because they show stability, optical transparency, enhanced sensitivity in aqueous solutions and are readily available.

In previous papers,³¹⁻³⁴ some analytical applications of α -benzilmonoxime are introduced. In the present work, palladium has been determined with ideal selectivity using α -benzilmonoxime in triton X-100 micellar media.

Compared with our previous extraction-spectrophotometric methods, time saving, single step palladium determinations, which avoid the use of organic solvents, are free of health and environmental hazards.^{31,34}

Experimental Section

Apparatus and Reagents. A Cecil CE 9020 UV-Vis

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scanning spectrophotometer was used to record the zero and first order derivative spectra of α -benzilmonoxime-Pd(II) complex. A Cecil CE 1021 UV-Vis spectrophotometer equipped with a 10 mm quartz cell was used to measure the absorbencies of the sample solutions. Experiments and measurements were carried out at room temperature.

Water used in this work was doubly distilled and all of the reagents used were of analytical-reagent grade. Triton X-100, tween-80 and sodium dodecylsulfate were purchased from Merck (Germany). The stock solutions of these detergents as 6.0% (wt/v) were prepared in 100.0 mL volumetric flasks. A standard Pd(II) solution ($1000 \mu\text{g mL}^{-1}$) was prepared as stock solution after solubilizing 0.4165 g of palladium(II) chloride (fluka) in 10 mL aqueous solution containing 1.0 mL of concentrated hydrochloric acid and then adjusting the volume of the solution in a 250.0 mL volumetric flask with doubly distilled water. This palladium solution was standardized by a standard gravimetric method using dimethylglyoxime.³⁵ Diluted palladium solutions were prepared daily by diluting the stock solution with deionized water. α -Benzilmonoxime was prepared and purified in our laboratory by the method reported in the literature.³⁶ A 0.050 M stock solution of α -benzilmonoxime was prepared by adding 1.125 g of the reagent to 100.0 mL of ethanol. Diluted α -benzilmonoxime solutions were prepared from the stock solution by diluting with ethanol.

Procedures for non-derivative and first derivative spectrophotometric determination of palladium. 4.0 mL of 3.0% triton X-100 solution, 1.0 mL of 1.0 M perchloric acid and 1.0 mL of ethanolic solution of 7.5 mM α -benzilmonoxime were added to a 10.0 mL volumetric flask, respectively. Then 2.0 mL of Pd(II) solution was added and after 1.0 min standing, the volume was adjusted to 10.0 mL with double distilled water. The sample solution was transferred into a spectrophotometer cell and the absorbance of the sample solution was measured against a blank solution (free from palladium) at 441.8 or 677.0 nm. The palladium concentration can be calculated using the same prepared calibration curves.

For analysis of the palladium sample solution by first derivative spectrophotometry, the prepared sample solution was transferred into one of the two spectrophotometric matched cells and the first derivative spectrum of the solution was recorded against another matched cell containing a reagent blank solution over the wavelength range of 400–800 nm with the $\Delta\lambda = 2$, using a scan speed of 600 nm/min. The analytical signals were the heights of maximum positive to minimum negative amounts of derivative signals between 400 and 550 nm and also 550 and 800 nm of the derivative spectra in these ranges. The palladium content can be calculated using the same prepared first derivative calibration curves.

Results and Discussion

Absorption Spectra. Early experiments show green palladium- α -benzilmonoxime complex is insoluble in water

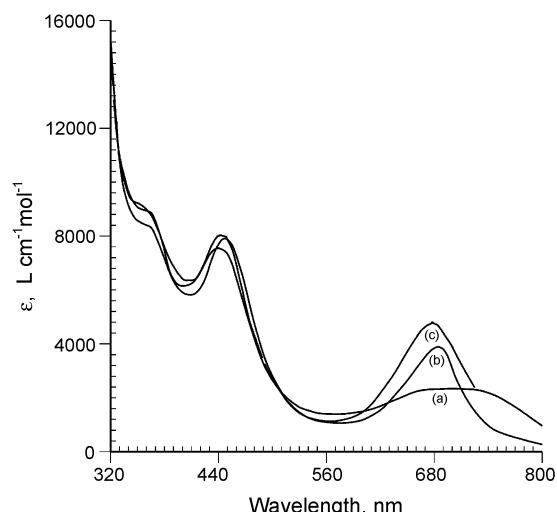


Figure 1. Molar absorptivities of Pd(II)- α -benzilmonoxime complex in the different micellar media. (a) in 1.2% sodium dodecylsulfate (b) in 1.2% tween-80 (c) in 1.2% triton X-100.

Table 1. Spectral characteristics of the palladium complex in the different micellar media

Micellizing agent	Absorption coefficient (Wavelength) L mol ⁻¹ cm ⁻¹ (nm)	
Triton X-100	8000(441.8)	4800(677.0)
Tween 80	7900(447.8)	3900(684.2)
Sodiumdodecylsulfate	7600(442.7)	2400(705.0)

Condition: 10.0 mL aqueous solution containing 7.5×10^{-4} M α -benzilmonoxime, 1.2% micellizing agent and 0.10 M HClO₄.

and immediately after formation is precipitated, but in the aqueous micellar solutions, it is soluble and stable. The absorption spectra of the palladium complex in different micellar media are shown in Figure 1. Two maximum wavelengths have been observed for the palladium complex in the tested micellar solutions: first at about 440 nm and second at about 690 nm with the lower sensitivity. Characteristics of the palladium complex in the various micellar media are shown in Table 1. The spectral characteristics change when the type of the detergent changes. According to the results in Table 1, the molar absorptivity of the palladium complex does not vary for the three different micellar media at the first maximum wavelength, but for the second wavelength, the molar absorptivity changes when the type of the micellizing agent changes. Nonionic micelles often are preferred to anionic micelles for determination of metal ions because attraction forces between the negative head of the micelles and the positive charge of the metal ions causes a lower apparent formation constant between the metal ions and ligands.³⁷ The higher sensitivity using triton X-100 at the second maximum wavelength leads us to the determination of palladium in this micellar medium.

The absorption spectra of α -benzilmonoxime and its palladium complex and also the first and second derivative spectra of the palladium complex in the triton X-100 micellar solution are shown in Figure 2. The maxima of the

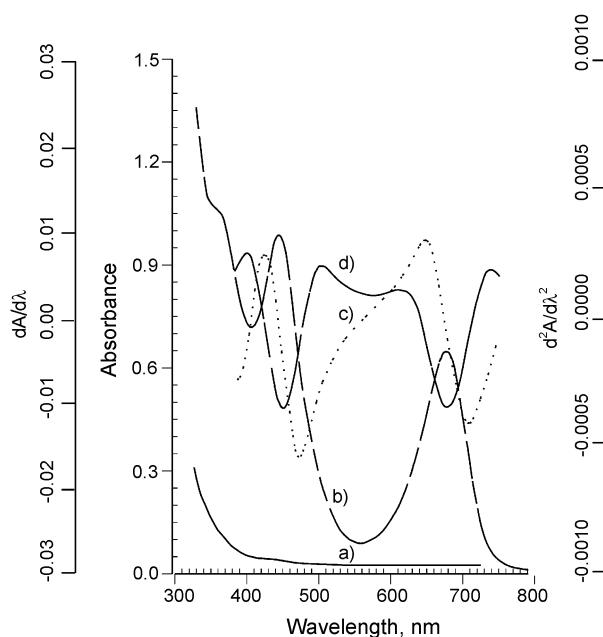


Figure 2. Spectrophotometric spectra of a) α -benzilmonoxime and b) Pd(II)- α -benzilmonoxime complex also c) first and d) second derivative spectra of Pd(II)- α -benzilmonoxime complex.

palladium- α -benzilmonoxime complex at 441.8 and 677.0 nm can be used as practical wavelengths for zero order derivative spectrophotometric determination of palladium because of the fairly small reagent blanks.

When differences between maximum positive and maximum negative of a derivative spectrum are considered as an analytical signal, sensitivity enhancement is obtained that may be an advantage over measuring derivative signal at a fixed single wavelength. According to the first derivative spectra, two regia for sensitive first order derivative spectrophotometric determination of palladium are observed: 400 to 550 and 550 to 800 nm.

Optimization of Parameters. To achieve the best sensitivity for palladium determination, the optimization of conditions is necessary. The net absorbance of the palladium complex at 441.8 nm (absorbancies of the solutions containing fixed amounts of palladium against its reagent blank) was selected as an analytical signal.

A step-wise optimization procedure for obtaining the best conditions was evaluated. Based on this optimization method, acid type and its concentration, α -benzilmonoxime and detergent concentrations were optimized.

Primary experiments show the complex is formed at acidic media. Therefore, different acidifying reagents were tested to select the best ones from the viewpoint of sensitivity. Results of the study are shown in Table 2. According to the results, hydrochloric acid is not a suitable acid. The low sensitivity is probably due to the complexation of palladium (II) with chloride ions that competes with the formation of palladium- α -benzilmonoxime complex. The other acids show nearly similar sensitivity. Perchloric acid was accepted because perchlorate does not complex or precipitate with most metal cations.

Table 2. Effect of acid type on the sensitivity

Acid	Absorbance
Sulfuric acid	0.661
Nitric acid	0.668
Perchloric acid	0.663
Phosphoric acid	0.655
Hydrochloric acid	0.469

Condition: 10.0 mL aqueous solution containing 9.0 $\mu\text{g mL}^{-1}$ of Pd(II), 7.5×10^{-4} M α -benzilmonoxime, 1.2% triton X-100 and 0.10 M acid.

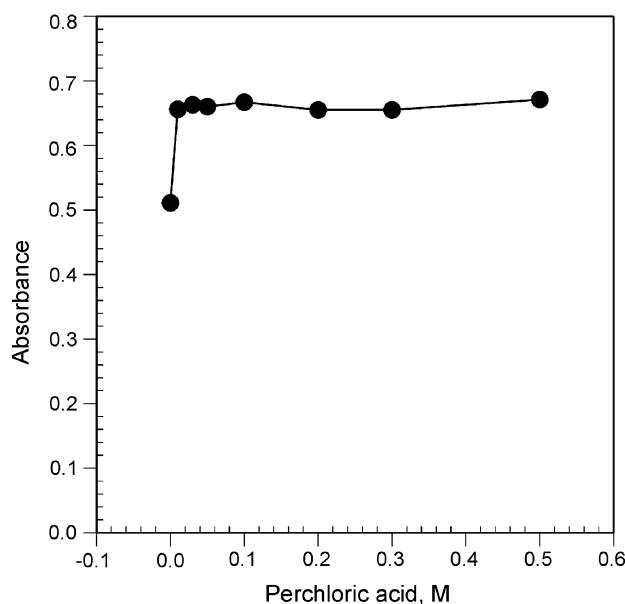


Figure 3. Effect of perchloric acid concentration on the sensitivity. Condition: 10.0 mL aqueous micellar solution containing 9.0 $\mu\text{g mL}^{-1}$ of Pd(II), 7.5×10^{-4} M α -benzilmonoxime and 1.2% triton X-100.

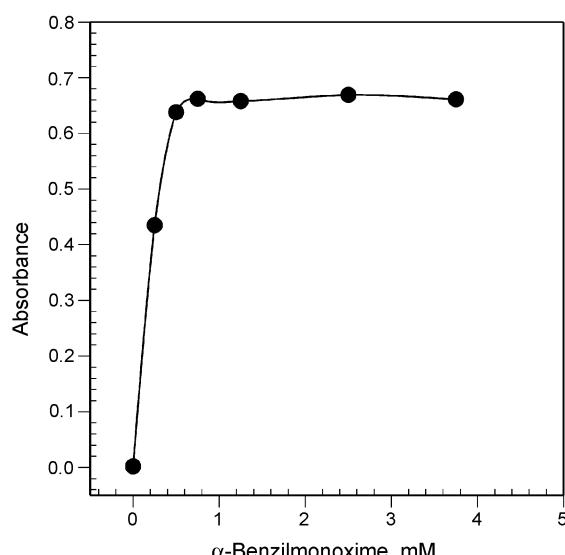


Figure 4. Effect of α -benzilmonoxime concentration on the sensitivity. Condition: 10.0 mL aqueous solution containing 9.0 $\mu\text{g mL}^{-1}$ of Pd(II), 1.2% triton X-100 and 0.10 M HClO₄.

Table 3. Calibration characteristics for the determination of palladium

Calibration equation	Linear range ($\mu\text{g mL}^{-1}$)	Regression
Spectrophotometry:		
Abs. = $4.4 \times 10^{-3} + 7.40 \times 10^{-2} C_{\text{Pd(II)}}$ at 441.8 nm	0.3-12.0	0.9997
Abs. = $6.0 \times 10^{-4} + 4.45 \times 10^{-2} C_{\text{Pd(II)}}$ at 677.0 nm	0.7-20.0	0.9993
Derivative spectrophotometry:		
$\Delta\text{Abs}/\Delta\lambda = 3.3 \times 10^{-5} + 1.59 \times 10^{-3} C_{\text{Pd(II)}}$ in the range of 400-550 nm	0.2-18.0	0.9991
$\Delta\text{Abs}/\Delta\lambda = 4.8 \times 10^{-5} + 1.50 \times 10^{-3} C_{\text{Pd(II)}}$ in the range of 550-800 nm	0.2-24.0	0.9993

The concentration of perchloric acid for obtaining the best concentration was varied. The results are given in Figure 3. Based on the results, sensitivity is not dependent on the perchloric acid concentration and does not decreased at high concentrations of the acid. This may be explained by assuming a high formation constant for the formed palladium complex. For further study, 0.10 M of perchloric acid was selected.

Optimization of α -benzilmonoxime concentration by varying the concentration of the reagent and measuring the absorbance at 441.8 nm was performed. The results in Figure 4 show that for concentrations equal to or more than 7.5×10^{-4} M, sensitivity is high, constant and reproducible. Therefore, for more investigation, an α -benzilmonoxime concentration of 7.5×10^{-4} M was chosen.

The influence of triton X-100 concentration on the absorbance of the palladium complex was investigated by varying the concentration of triton X-100 in the range of 0.0-3.0%. The absorbance of the palladium complex was constant and stable in the triton X-100 concentration range of 0.6-3.0%. Here, a 1.2% solution of this detergent was used as a suitable detergent concentration for further study.

Further study shows the palladium complex is stable. The spectra of the palladium complex were recorded over 24 hrs with measurements every 4 hrs. The obtained spectra show spectral characteristics (maximum wavelengths and their molar absorptivities) did not changed with time at least for one day.

The effect of ionic strength on the determination of palladium was investigated. Different concentrations of sodium sulfate and sodium nitrate as ionic buffers from 0.0 to 0.3 M were tolerated, but no considerable differences in sensitivity were observed.

For investigating interactions between affected parameters, simplex optimization procedure was also evaluated. α -Benzilmonoxime and perchloric acid concentrations as important parameters were evaluated. Based on the results, these two parameters behave independently in a wide range of concentrations and produce a relatively constant absorbance. However, the optimum condition of 7.5×10^{-4} M of α -benzilmonoxime and perchloric acid 0.11 M was selected and proposed by the simplex program. For further study the condition of optimization by the one-at-a-time procedure used here (α -benzilmonoxime 7.5×10^{-4} M and perchloric acid 0.10 M), was considered for further studies as the optimum condition.

Table 4. Accuracy and precision of the first derivative spectrophotometric procedure

[Pd(II)] Taken, $\mu\text{g mL}^{-1}$	400-550 nm		550-800 nm	
	RSD% (n=8)	Recovery%	RSD% (n=8)	Recovery%
0.2	4.5	94.9	6.9	98.4
9.0	1.4	102.5	1.4	101.1
18.0	0.6	98.7	1.0	98.5
24.0	—	—	0.7	100.6

Table 5. Accuracy and precision of the non-derivative spectrophotometric method

[Pd(II)] Taken, $\mu\text{g mL}^{-1}$	441.8 nm		677.0 nm	
	RSD% (n=8)	Recovery%	RSD% (n=8)	Recovery%
0.3	5.5	92.8	7.1	94.4
6.0	0.7	99.5	0.6	100.1
12.0	0.5	99.4	0.4	97.4

Calibration, Accuracy and Precision. Two spectrophotometric and two first derivative spectrophotometric calibration curves were constructed according to the recommended standard procedures. The obtained calibration parameters are shown in Table 3.

The precision and accuracy of the proposed first derivative and non-derivative spectrophotometric methods were also evaluated for replicate analysis of some samples. The results are shown in Table 4 and Table 5, respectively.

Ten absorbance blank measurements at 441.8 and 677.0 nm, show the limit of detections at about 0.07 and 0.10 $\mu\text{g mL}^{-1}$ of palladium, respectively (limit of detections were calculated as $3 \times S_b/m$, where m and S_b are gradients of calibration curves and standard deviations of the reagent blanks, respectively).

The diversity in the calibration equations not only can extend the linear dynamic range of the method but also may be used for selective determination. One foreign ion may produce a colored product that interferes at one wavelength but does not interfere at other wavelengths. Selective determination can be carried out by changing the working wavelength.

Effects of Foreign Ions. When Pd(II) is determined with α -benzilmonoxime, the other ions in real samples might interfere with the palladium complex forming process. The effects of foreign species on the first derivative spectrophotometric determination of 10.0 μg of palladium were

Table 6. Effect of foreign ions on the first derivative determination of palladium

Ions added	Tolerance limit ($\mu\text{g mL}^{-1}$)
Ca(II), Mg(II), Cs(I), K(I), Na(I), ClO_4^- , SO_4^{2-} , NO_3^- , BrO_3^- , IO_3^-	>1000
IO_4^- , ClO_3^- , Sr(II), Mn(II), Fe(III), Mo(VI)	1000
W(VI), Fe(II), Co(II), Cu(II), Ni(II)	500
Zn(II), Cr(III), U(VI), V(V), Cd(II), SO_3^{2-}	200
Os(VIII) ^a , Sn(II), Th(IV) ^a , Ag(I), $\text{C}_2\text{O}_4^{2-}$, Cl^-	100
Rh(III) ^a , Ru(III) ^a , Hg(II), Pt(IV) ^a , Br^-	50
I^- , SCN^-	10

^aMaximum concentration tested.

studied under the one-at-a-time optimum condition. The effects of diverse ions on the determination of palladium are shown in Table 6. Solutions containing 10.0 μg palladium and various amounts of other ions were prepared and the proposed procedure for the determination of palladium was followed. An error of $\pm 3\text{S}$ in the absorbance of 10.0 μg of palladium was considered tolerable. Based on these results,

high selectivity for the palladium determination method was observed. Boiling of the palladium sample in concentrated nitric acid is recommended to remove mild interferences of iodide.³¹ By this manner, interferences of high amounts of iodide are removed.

Application. Synthetic samples based on the composition of some industrial alloys³⁸ and Pd-charcoal laboratory powder were examined according to the recommended procedure to confirm the applicability of the method. Based on the results, the recommended method can be applied to the analysis of some hard and resistant alloys of palladium with good accuracy and precision (Table 7).

Analysis of Pd-Charcoal was performed as follow: 0.100 g of Pd-charcoal was weighed and mixed with 50 mL of 1 M nitric acid in a flask. The mixture was heated for about 2 hours on a hotplate till dry. The residue was mixed with 50 mL of doubly distilled water, filtered and washed with three times with 5 mL portions of distilled water. The filtrate solution was diluted with water in a 250.0 mL volumetric flask, and then 2.0 mL of the solution was used for determination of palladium in Pd-charcoal, using the proposed methods (Table 7). The palladium content of the

Table 7. Determination of palladium in some synthetic and real samples

Sample	Characteristics	Non-derivative (441.8 nm)		First-derivative (550-800 nm)	
		Pd found (n=4)	Recovery%	Pd found (n=5)	Recovery%
Sample 1:		4.07 ± 0.05	101.8	4.03 ± 0.06	100.8
Ni(II)(800 $\mu\text{g mL}^{-1}$)					
Cu(II)(800 $\mu\text{g mL}^{-1}$)					
Pd(II)(4.00 $\mu\text{g mL}^{-1}$)					
Sample 2:		4.01 ± 0.04	100.3	4.07 ± 0.07	101.8
Pd(II)(4.00 $\mu\text{g mL}^{-1}$)					
Ru(III)(50.0 $\mu\text{g mL}^{-1}$)					
Sample 3:	high resistance to oxidation and corrosion	4.05 ± 0.06	101.3	3.95 ± 0.06	98.8
Pd(II)(4.00 $\mu\text{g mL}^{-1}$)					
Ru(III)(0.4 $\mu\text{g mL}^{-1}$)					
Sample 4:	good hardness	3.92 ± 0.04	98.0	3.97 ± 0.06	99.3
Pd(II)(4.00 $\mu\text{g mL}^{-1}$)					
Ag(I)(3.00 $\mu\text{g mL}^{-1}$)					
Cu(II)(3.00 $\mu\text{g mL}^{-1}$)					
Sample 5:	good hardness and resistance to mechanical wear	3.97 ± 0.05	99.3	4.01 ± 0.07	100.3
Pd(II)(4.00 $\mu\text{g mL}^{-1}$)					
Ag(I)(1.44 $\mu\text{g mL}^{-1}$)					
Ni(II)(0.11 $\mu\text{g mL}^{-1}$)					
Sample 6:	good hardness and durability	4.02 ± 0.05	100.5	4.00 ± 0.07	100.0
Pd(II)(4.00 $\mu\text{g mL}^{-1}$)					
Co(II)(16.0 $\mu\text{g mL}^{-1}$)					
Sample 7:	high resistance to corrosion	6.06 ± 0.06	101.0	6.08 ± 0.09	101.4
Pd(II)(6.00 $\mu\text{g mL}^{-1}$)					
Ag(I)(6.00 $\mu\text{g mL}^{-1}$)					
Sample 8:	good hardness and electrical conductance	5.93 ± 0.07	98.8	6.02 ± 0.08	100.3
Pd(II)(6.00 $\mu\text{g mL}^{-1}$)					
Cu(II)(4.00 $\mu\text{g mL}^{-1}$)					
Pd-charcoal:	hydrogenation and dehydrogenation	$(4.64 \pm 0.12)^a$			
5%Pd-95%C	dehydrogenation	4.79 ± 0.07	103.2 ^b	4.74 ± 0.06	102.2 ^b

^aAnalyzed by nitroso-R salt. ^bCalculated based on nitroso-R results.

250.0 mL volumetric flask was analyzed by a standard addition procedure using nitroso-R salt.¹¹

Conclusions

A simple and highly selective method for derivative and non-derivative spectrophotometric determination of palladium has been established with α -benzilmonoxime in the triton X-100 micellar media. The proposed method, owing to the need for solvent extraction, was applied to assays of palladium in Pd-charcoal and synthetic mixtures, according to the composition of some palladium alloys; the analytical results were satisfactory. The diversity in the calibration equations can extend the linear dynamic range without further need for dilution of samples and sample handling also may cause better selectivity. The proposed method should be useful for accurate, precise, rapid, simple and highly selective determination of palladium in alloy and catalyst samples.

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