

Optical Test Strip for Spectrophotometric Determination of Palladium Based on 5(p-dimethylaminobenzylidene)rhodanine Reagent

N. Pourreza* and S. Rastegarzadeh

Contribution from: Chemistry Department, College of Sciences, Shahid Chamran University, Ahvaz, Iran.

Received: August 28, 2004

Accepted (in revised form): November 30, 2004

Résumé

Nous proposons une nouvelle bande d'essai optique pour la détermination du palladium par spectrophotométrie. La bande d'essai a été préparée en mélangeant du PVC, du diméthyle sébacate et du 5(p-diméthylaminobenzylidène)rhodanine dans le THF et en appliquant cette solution sur une plaque transparente en se servant d'un dispositif rotatif. Nous avons étudié l'effet de différentes variables sur la bande et nous avons établi les conditions optimales. La droite de calibration obtenue était linéaire dans la gamme 0.2-20 mg L⁻¹ en palladium avec une coefficient de corrélation de 0.9991. La limite de détection était de 0.1 mg L⁻¹ et l'écart type relatif pour dix mesures répétées de 10 mg L⁻¹ en palladium a été de 3.1%. La méthode a pu être appliquée avec succès pour la détermination du palladium en joaillerie et sur des échantillons synthétiques.

Abstract

A new optical test strip has been established for the determination of palladium by spectrophotometry. The test strip was prepared by mixing PVC, dimethyl sebacate and 5(p-dimethylaminobenzylidene)-rhodanine in THF and coating this solution on a transparent plate using a spin device. The effect of different variables on the strip was studied and optimum conditions were established. The calibration graph was linear in the range of 0.2-20 mg L⁻¹ of

palladium, with a correlation coefficient of 0.9991. The limit of detection was 0.1 mg L⁻¹, and the relative standard deviation for ten replicate measurements of 10 mg L⁻¹ of palladium was 3.1%. The method was successfully applied to the determination of palladium in jewelry and synthetic samples.

Keywords: Optical strip, spectrophotometry, 5(p-dimethylaminobenzylidene)rhodanine, palladium.

Introduction

Palladium is one of the precious metals. Owing to its corrosion resistant nature and alloying ability, palladium is an important element in metallurgy. Its alloys are used in dental and medicinal devices and in jewelry manufacture. Moreover, palladium is used in automobile catalysts together with Pt and Rh (1).

Palladium can be determined by instrumental techniques such as inductively coupled plasma atomic emission spectrometry (ICPAES) and atomic absorption spectrometry (AAS), both flame (FAAS) and electrothermal (GFAAS) (2).

The solid state analysis or dry-chemical methods were introduced in the 1980s. In these methods, all the reagents necessary for analysis are present in a dry state on or in absorptive or swelling carriers or films and are mounted in the form of devices, so-called test carriers, such as test strips or slides (3). While a large variety of devices are possible, they share as a common feature an immobilized reagent phase whose optical properties change upon interaction with the analyte. Depending on the particular device, the optical property measured can be absorbance, luminescence or something else (4).

* Author to whom correspondence should be addressed: npourreza@yahoo.com

Recently, the advent of optical sensors has opened up a new perspective in the search for simple, safe, rapid and remote systems for monitoring some important substances (5).

The key element in the development of an optically sensitive and selective membrane for a given analyte is the availability of a lipophilic, chemically stable and selective ionophore. Different optical membranes for the determination of metal ions based on reversible (6-8) or irreversible (4, 9, 10) processes have been proposed.

In this work, a simple optical test strip for the spectrophotometric determination of Pd (II) by using 5(p-dimethylaminobenzylidene) rhodanine (PDR) immobilized in a thin plasticized poly (vinyl chloride) (PVC) membrane is reported.

Experimental

Apparatus:

Absorbance measurements were made using a Jasco UV-Vis spectrophotometer. The pH values were measured using a Metrohm 632 pH meter and a combined glass electrode.

Reagents:

Analytical grade reagents and double distilled water were used throughout.

A 1000 mg L⁻¹ stock solution of palladium (II) was prepared by dissolving 0.1666 g of palladium (II) chloride (Merck) in 100 mL of water acidified with 3 mL of concentrated hydrochloric acid (Merck). Working solutions were freshly prepared by appropriate dilution of the stock solution with water. Formate buffer solution (pH=3.00) was prepared by addition of 1 mL of formic acid (Merck) to water and dilution to 250 mL. The pH of the solution was adjusted to the desired value using 1 M sodium hydroxide (Merck).

The citrate and phthalate buffers were prepared by dissolving an appropriate amount of sodium citrate (Merck) or potassium hydrogen phthalate (Merck) in a 100 mL volumetric flask and diluting to the mark (0.1 M). The pH of these solutions was adjusted to the desired value by adding 1 M hydrochloric acid and sodium hydroxide, respectively.

Preparation of the optical membrane:

The optical membrane solution was prepared by dissolving a mixture of 90 mg of PVC, 360 mg of dimethyl

sebacate and 8.4 mg of 5(p-dimethylaminobenzylidene) rhodanine (PDR) in 2 mL of THF. A 0.2 mL aliquot of this solution was applied to the surface of a 3 x 2.5 cm transparent plastic plate which was mounted on a rotator. After a spinning time of only 4 seconds, a membrane was produced on the plate (11). This sheet was used as an optical strip for the determination of palladium in further studies.

Jewelry sample:

To 0.282 g of a 17-carat gold sample in a beaker, a mixture of 2.5 mL of hydrochloric acid and 2.5 mL of nitric acid was added, and the beaker was heated at 150 °C on a hot-plate until the solution evaporated to dryness. This procedure was repeated again. 20 mL of water was added to the beaker, and AgCl was filtered off. The precipitated AgCl was yellow in color. Then a few mL of nitric acid (1:6) were added, heated and filtered off again. This procedure was repeated several times until the AgCl produced was white. All filtrates were evaporated to a small volume. After cooling, the solution was diluted to 50 mL in a volumetric flask (12,13).

Recommended procedure:

In a 20 mL volumetric flask, appropriate volumes of Pd (II) solution, 0.2 mL of KSCN (0.1 M) solution and 5 mL of buffer solution were added, thoroughly mixed, and diluted to 20 mL with water. This solution was transferred into a 25 mL cylindrical glass sample cell. An optical strip was placed in the solution, and the solution was stirred with a magnetic stirrer at 250 rpm by a Teflon-coated bar (20 mm x 7 mm diameter).

After stirring for 60 s, the optical strip was removed from the solution, rinsed with a small amount of water, and then wiped to remove any water droplets. The optical strip was placed in the spectrophotometer holder. The absorbance of the colored membrane was measured at 463 and 534 nm and $A_{534} / (A_{463})^2$ was calculated. The same procedure was also carried out in the absence of Pd (II) as a blank.

Results and Discussion

The absorption spectrum of PDR reagent on the strip shows that the maximum absorbance is at 463 nm. After immersion of the strip in the Pd (II) solution, Pd-PDR complex is formed, and the absorbance decreases at 463 nm and increases at 534 nm.

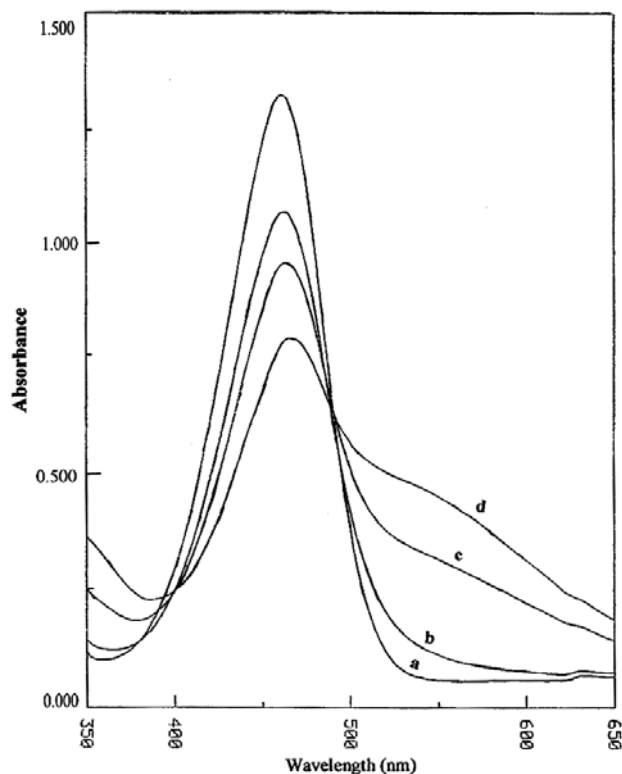
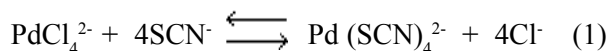


Figure 1. Absorption spectra of optical strip after immersion in a) 0 mg L⁻¹ of Pd; b) 10 mg L⁻¹ of Pd; c) 10 mg L⁻¹ of Pd, 10⁻³ M of SCN⁻; d) 20 mg L⁻¹ of Pd, 10⁻³ M of SCN⁻. pH=3 and 1 minute reaction time.

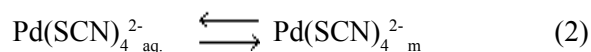
Since the rate of extraction of Pd (II) into an organic phase using common extractants is different in various anion solutions (14), the effect of different anions with the same concentration on the extraction of Pd (II) into the optical test strip was investigated. It was found that thiocyanate ion was most effective in enhancing the rate of extraction. Figure 1 shows the absorption spectrum of the optical strip after immersion in solutions with different concentrations of Pd (II) in the absence and presence of thiocyanate ion.

Aqueous palladium is present as a tetrachloro complex, PdCl₄²⁻, in chloride solution. In the presence of thiocyanate, Pd (SCN)₄²⁻ is formed according to reaction 1 (15):



In the current study, we considered both the water phase (aq) and optical strip phase (m) as two separate

compartments. According to reaction 2, palladium can be distributed in two phases:



Assuming first-order kinetics, the process can then be described by the following expression:

$$d[\text{Pd}(\text{SCN})_4^{2-}]_{\text{m,t}}/dt = k_1[\text{Pd}(\text{SCN})_4^{2-}]_{\text{aq,t}} - k_2[\text{Pd}(\text{SCN})_4^{2-}]_{\text{m,t}} \quad (3)$$

As Pd (SCN)₄²⁻ is adsorbed on the membrane, it forms a complex with PDR; therefore, its concentration in the membrane phase is very small, so:

$$k_2[\text{Pd}(\text{SCN})_4^{2-}]_{\text{m,t}} \ll k_1[\text{Pd}(\text{SCN})_4^{2-}]_{\text{aq,t}} \quad (4)$$

Thus:

$$d[\text{Pd}(\text{SCN})_4^{2-}]_{\text{m,t}}/dt = k_1[\text{Pd}(\text{SCN})_4^{2-}]_{\text{aq,t}} \quad (5)$$

Integration of equation 5 over the interval between zero and t yields equation 6:

$$[\text{Pd}(\text{SCN})_4^{2-}]_{\text{m,t}} - [\text{Pd}(\text{SCN})_4^{2-}]_{\text{m,0}} = k_1 t [\text{Pd}(\text{SCN})_4^{2-}]_{\text{aq,t}} \quad (6)$$

$$\text{at } t=0, [\text{Pd}(\text{SCN})_4^{2-}]_{\text{m,0}} = 0 \quad (7)$$

Thus:

$$[\text{Pd}(\text{SCN})_4^{2-}]_{\text{m,t}} = k_1 t [\text{Pd}(\text{SCN})_4^{2-}]_{\text{aq,t}} \quad (8)$$

$$\text{at } t = 60\text{s}: [\text{Pd}(\text{SCN})_4^{2-}]_{\text{m,60}} = k_1 60 [\text{Pd}(\text{SCN})_4^{2-}]_{\text{aq,60}} \quad (9)$$

Our experimental observations showed that, by repeating the experiments up to 5 times in the same solution, the concentration of Pd (SCN)₄²⁻ does not change very much. This means that only slight amounts of Pd(SCN)₄²⁻ are adsorbed on the membrane in 60 s, and thus the concentration of Pd(SCN)₄²⁻ at 0 and 60s is equal. Therefore:

$$[\text{Pd}(\text{SCN})_4^{2-}]_{\text{m,60}} = k_1 60 [\text{Pd}(\text{SCN})_4^{2-}]_{\text{aq,0}} \quad (10)$$

When the aqueous phase is in contact with the optical strip containing PDR, reaction 11 occurs in which palladium is extracted into the membrane (m):



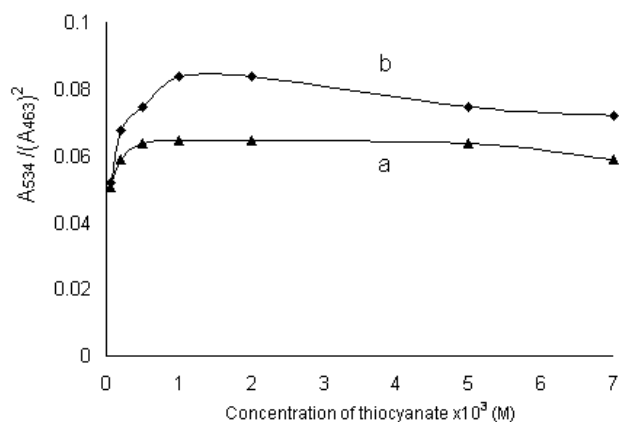


Figure 2. Effect of thiocyanate ion concentration on the optical strip response in a) 0.5, and b) 1 mg L⁻¹ of Pd(II) solution.

$$K_f = \frac{[\text{Pd}(\text{PDR})_2(\text{SCN})_2]_m [\text{SCN}^-]_{\text{aq}}^2}{[\text{Pd}(\text{SCN})_4]_m [\text{PDR}]_m^2} \quad (12)$$

As the complex formation between palladium and PDR in the membrane is very fast, from equation 12 we obtain:

$$[\text{Pd}(\text{SCN})_4]_{m,60} = \frac{[\text{Pd}(\text{PDR})_2(\text{SCN})_2]_{m,60} [\text{SCN}^-]_{\text{aq}}^2}{K_f [\text{PDR}]_m^2} \quad (13)$$

Substitution of equation 13 into equation 10 yields equation 14:

$$k_{f,60} [\text{Pd}(\text{SCN})_4]_{\text{aq},0} = \frac{[\text{Pd}(\text{PDR})_2(\text{SCN})_2]_{m,60} [\text{SCN}^-]_{\text{aq}}^2}{K_f [\text{PDR}]_m^2} \quad (14)$$

According to Beer's law at wavelengths 534 and 463 nm:

$$A_{534} = \epsilon_c b [\text{Pd}(\text{PDR})_2 (\text{SCN})_2]_m \quad (15)$$

$$A_{463} = \epsilon_l b [\text{PDR}]_m \quad (16)$$

where ϵ_c and ϵ_l are the molar absorptivity of Pd (PDR)₂ (SCN)₂ and PDR, respectively, in the strip phase.

Since the complex formation constant of Pd(SCN)₄²⁻ ($pK_f=28.6$) (15) is higher than that of PdCl₄²⁻ ($pK_f=15.5$) (16), equation 1 is nearly complete, and the concentration of Pd(SCN)₄²⁻ is equal to PdCl₄²⁻ as initially present in the solution.

Equation 17 is obtained by substitution of equations 15 and 16 into equation 14. Thus:

$$A_{534} / (A_{463})^2 = \frac{60 k_{f,60} \epsilon_c K_f}{\epsilon_l^2 b [\text{SCN}^-]_{\text{aq}}^2} [\text{PdCl}_4]_{\text{aq},0} \quad (17)$$

Equation 17 shows that there is a linear relationship between $A_{534} / (A_{463})^2$ and concentration of palladium.

Effect of variables

The effect of the pH of the sample solution on the absorbance of the optical strip at 463 and 534 nm was investigated. The appropriate pH was obtained by the addition of dilute hydrochloric acid or sodium hydroxide to the sample solution. The results show that the rate of complex formation is faster when pH=3. Therefore, pH=3 was selected as the optimum value.

The influence of different buffer systems, such as phthalate, citrate and formate, with pH=3 on the optical properties of the test strip was also studied. The absorbance was approximately constant in the presence of these buffer solutions. Therefore, formate buffer solution was used in further studies.

The experiments were carried out to measure the extent of leaching of PDR from the optical test strip after immersion in aqueous solutions at pH=3 for 8 minutes. The extent of leaching was determined by measuring the absorbance of the strip at 463 nm. The results showed that the smallest leaching (0.8%) was seen after 1 minute in a solution with pH=3. Thus all the measurements were made 1 minute after the immersion of the strip in the test solution.

The effect of thiocyanate concentration on the absorbance of the optical strip at 463 and 534 nm for 0.5 and 1 mg mL⁻¹ Pd(II) solutions is shown in Figure 2. As is observed from the results, the maximum $A_{534} / (A_{463})^2$ was obtained at 10⁻³ M thiocyanate ion for both Pd(II) concentrations. Therefore, it was selected for further investigations.

Analytical characteristics

A linear calibration graph of $A_{534} / (A_{463})^2$ vs. Pd(II) concentration in the range of 0.2-20 mg L⁻¹ with regression equation of $A_{534} / (A_{463})^2 = 0.0397 + 0.0461 C_{\text{Pd}}$ and correlation coefficient of 0.9991 was obtained. The limit of detection based on three times the standard deviation of the blank was 0.1 mg L⁻¹. The relative standard deviation for eight replicate measurements of 10 mg L⁻¹ of palladium was 3.1%.

Effect of diverse ions

The selectivity of the optical strip was studied for a 1 mg L⁻¹ solution of Pd(II) in the presence of different amounts of foreign ions using the recommended

Table 1. Effect of interfering ions on determination of 1 mg L⁻¹ Pd(II).

Foreign ions	Tolerance limit (mg L ⁻¹)
K ⁺ , Na ⁺ , Ca ²⁺ , Mg ²⁺ , Citrate, Acetate, I ⁻ , Br ⁻ , CO ₃ ²⁻ , HCO ₃ ⁻	1000
Fe ³⁺ , Cd ²⁺ , Zn ²⁺ , Ni ²⁺ , Cu ²⁺ , Pb ²⁺ , Mn ²⁺ , Co ²⁺ ,	100
Hg ²⁺	100 ^a
Pt ⁴⁺	50
Au ³⁺	30 ^b

^a masked by Cl⁻; ^b masked by I⁻. Ag⁺ precipitated under the recommended procedure and can be easily separated.

Table 2 Determination of palladium in different samples.

Sample	Added Pd (mg L ⁻¹)	Found Pd (mg L ⁻¹)	% RSD (n=3)
Jewelry	0.40	0.45	5.2
	1.50	1.44	4.5
	12.50	12.90	3.8
Synthetic	1.01	1.04	4.8

procedure. The tolerance limit was set as the amount of foreign ion causing $\pm 5\%$ error in the absorbance. The results shown in Table 1 indicate that most cations and anions, with the exception of Hg²⁺ and Au³⁺, do not interfere. The interferences of Hg²⁺ up to 100 times and Au³⁺ up to 30 times were removed by Cl⁻ and I⁻ ions, respectively.

Application

In order to evaluate the analytical applicability of the method, it was applied to the determination of different amounts of Pd(II) spiked into a 17-carat gold jewelry sample solution which was prepared previously. The concentration of Pd(II) was then determined by applying the recommended procedure under the optimum conditions. The results presented in Table 2 show that there are good agreements between the results.

In another experiment, a synthetic mixture containing metal ions similar to the composition of dental alloy (Type IV) was analyzed for the determination of palladium. For this purpose, a solution with a composition of 69% Au, 10% Cu, 12.5% Ag, 3.5% Pd, 3% Pt and 2% Zn was

prepared, and Pd(II) was determined. These results are also presented in Table 2.

Conclusion

The work presented here describes a simple optical test strip method for the determination of trace amounts of palladium. The linear range of the method is 0.2-20 mg L⁻¹, which extends to lower concentrations than flame atomic absorption spectrometry (5-50 mg L⁻¹) (17) and uses less expensive instruments than ICP-MS.

Acknowledgements

Financial support of this work by Shahid Chamran University Research Councils is greatly appreciated.

References

1. A. Tunceli and A.R. Turker, *Anal. Sci.*, **16**, 81 (2000).
2. R.R. Barefoot and J.C. Van Loon, *Talanta*, **49**, 1 (1999).
3. L.F. Capitan-Vallvey, M.D. Fernandez Ramos and P. Alvarez de Cienfuegos-Galvez, *Anal. Chim. Acta*, **451**, 231 (2002).
4. W.R. Seitz, *Anal. Chem.*, **56**, 16A (1984).
5. W.H. Chan, A.W.M. Lee and J.Z. Lu, *Anal. Chim. Acta*, **361**, 55 (1998).
6. M. Lerchi, E. Bakker, B. Rusterholz and W. Simon, *Anal. Chem.*, **64**, 1534 (1992).
7. M. Lerchi, E. Reitter, W. Simon, E. Pretch, D.A. Ghoshdury and S. Kamata, *Anal. Chem.*, **66**, 1713 (1994).
8. X. Yang, K. Wang, D. Xiao, C. Guo and Y. Xu, *Talanta*, **52**, 1033 (2000).
9. X. Liu, W. Xing, G. Ou and Liang, *Anal. Sci.*, **16**, 473 (2000).
10. L.F. Capitan-Vallvey, P. Alvarez de Cienfuegos-Galvez, M.D. Fernandez Ramos and R. Avidad-Castaneda, *Sens. Actuators B*, **71**, 140 (2000).
11. R. Yang, K. Wang, D. Xiao, X. Yang and H. Li, *Anal. Chim. Acta*, **404**, 205 (2000).
12. S. Hoshi, K. Higashihara, M. Suzuki, Y. Sakurada, K. Sugawara, M. Uto and K. Akatsuka, *Talanta*, **44**, 571 (1997).
13. N.H. Furman, "Standard Methods of Chemical Analysis," D. Van Nostrand Company (1962)

496.

14. E. Antico, M. Hidalgo, A. Masona, V. Salvado, J. Havel and M. Valiente, *Anal. Chim. Acta*, **278**, 91 (1993).
15. A.A. Biryukov and V.I. Shlenskaya, *Zh. Neorg. Khim.*, **12**, 2579 (1967).
16. J.A. Dean, "*Analytical Chemistry Handbook*," McGraw-Hill (1995) Sec.2-10.
17. J.W. Robinson, "*Atomic Absorption Spectroscopy*," Marcel Dekker Inc. (1975).