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ARTICLES

Spectrophotometric Determination of Palladium(II) Based on Its Catalytic Effect on the Reduction of Azure I by Sodium Hypophosphite[1]

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Abstract—A catalytic-spectrophotometric method for the determination of traces of palladium(II) is proposed. The reaction is based on the catalytic action of palladium(II) on the reduction of azure I (λ_{max} = 647 nm) by sodium hypophosphite. The various variables affecting the sensitivity were studied, and a study of interfering ions was also carried out. The reaction gave a detection limit of 4.3 ng/mL palladium(II) and good reproducibility with a relative standard deviation of 1.53–1.98% in the palladium(II) concentration range 40–200 ng/mL. The method yielded another linear range (5–40 ng/mL) when using slightly different conditions. In this case, the detection limit was 0.78 ng/mL palladium(II), and the relative standard deviation for ten replicate analyses of 20 ng/mL palladium(II) was 2.05%. The method was applied to the determination of palladium in a sample of activated charcoal.

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The demand for highly sensitive methods for determining ultratrace amounts of palladium has increased in industrial and environmental analysis. Several spectrophotometric methods for the determination of palladium have been described [1–18]. Most of these methods for the determination of palladium have low sensitivity and are not sufficiently selective. Several spectrophotometric reagents were used in the complex formation with palladium, but there are few data concerning the determination of trace amounts of palladium by kinetic methods.

In this work, the kinetic determination of palladium based on its catalytic effect on the reduction of azure I by sodium hypophosphite was studied. The proposed method is highly sensitive and simple.

EXPERIMENTAL

Reagents. All solutions were prepared from analytical-reagent grade substances (Fluka, Merck) and doubly distilled water. A 1000-μg/mL solution of palladium(II) was prepared by dissolving 0.1666 g of $PdCl_2$ in 100 mL of 0.01 M hydrochloric acid, and its accurate concentration was determined complexometrically with EDTA and Zinc(II) using eriochrom black T as an indicator. Working palladium(II) solutions of appropriate concentrations were prepared daily by serial dilution of the stock solution.

A 0.34 M solution of sodium hypophosphite and a 1.4×10^{-4} M solution of azure I ($C_{15}H_{16}N_3SBF_4$) were used. Buffer solutions were prepared by mixing certain volumes of 0.1 M sodium acetate and 0.1 M acetic acid.

Apparatus. Absorbances were measured at 647 nm with a MiltonRoy Spectronic 20D spectrophotometer with a 1-cm glass cell. All spectra were obtained with a JASCO model 7850 UV/V spectrophotometer. A Metrohm model 632 pH meter and a Metler AC100 balance with a precision of ±0.0001 g were used. The reaction was performed at 25 ± 0.1°C using a W.C. Heraues Hanau thermostat.

Procedure. Quantities of 1.6 mL of azure I solution (1.4×10^{-4} M), 2 mL of sodium hypophosphite solution (0.34 M), and 2 mL of acetate buffer (pH 4) were placed in a 10-mL volumetric flask. The solution was kept in a thermostatically controlled water bath at 25.0°C until the temperature remained stable; 0.0–1 mL of palladium(II) solution (2 μg/mL) was then added, and the start of the reaction was registered. The solution was diluted to the mark with doubly distilled water. The reaction mixture was shaken, and a portion of it was transferred into a 1-cm glass cell. After 2 min from the start of the reaction, the absorption was measured exactly at 647 nm. Blank determinations were run in the same way, and a plot of absorbance vs. added palladium(II) concentration was constructed.

RESULTS AND DISCUSSION

Figure 1 shows that the difference between the rates of the catalyzed and uncatalyzed reactions decreases with increasing azure I concentration. A concentration

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[1] The text was submitted by the authors in English.

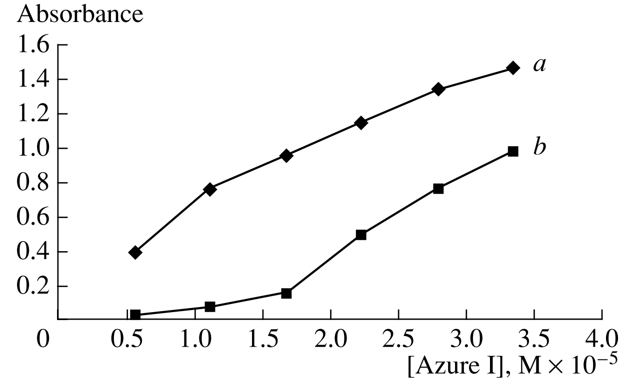

Fig. 1. Effect of azure I concentration on the rates of the uncatalyzed (*a*) and catalyzed (*b*) reactions. Conditions: 0.2 µg/mL palladium(II), 6.4×10^{-2} M hypophosphite, pH 4, 25°C, 647 nm.

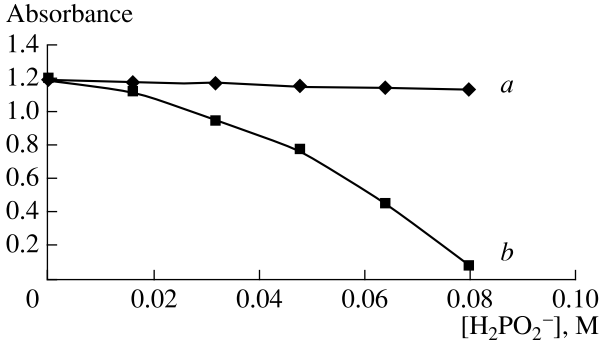

Fig. 2. Effect of hypophosphite concentration on the rates of the uncatalyzed (*a*) and catalyzed (*b*) reactions. Conditions: 0.2 µg/mL palladium(II), 2.24×10^{-5} M azure I, pH 4, 25°C, 647 nm.

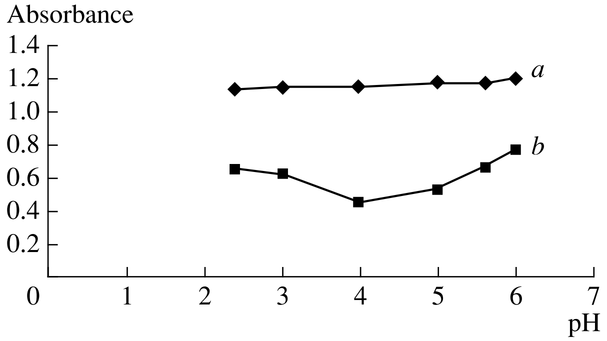

Fig. 3. Effect of pH on the rates of the uncatalyzed (*a*) and catalyzed (*b*) reactions. Conditions: 0.2 µg/mL palladium(II) 2.24×10^{-5} M azure I, 6.4×10^{-2} M hypophosphite, pH 4, 25°C, 647 nm.

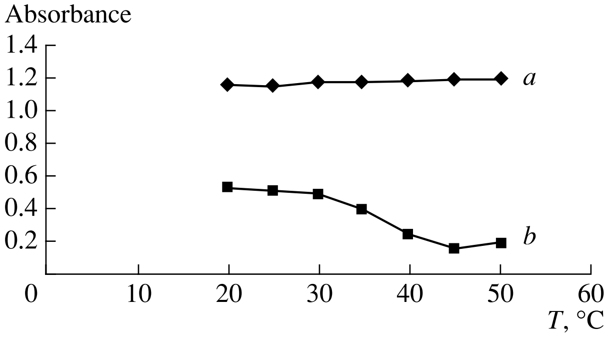

Fig. 4. Effect of temperature on the rates of the uncatalyzed (*a*) and catalyzed (*b*) reactions. Conditions: 0.2 µg/mL palladium(II), 6.4×10^{-2} M hyophosphite 2.24×10^{-5} M azure I, pH 4, 25°C, 647 nm.

of 2.24×10^{-5} M azure I was chosen as the most convenient one.

Higher concentrations of azure I gave a greater error of photometric measurement ($A \gg 1$). Lower concentrations of azure I caused difficulties in the recording of the absorbances, because the rate of the catalyzed reaction was very high. So, as a compromise between sensitivity and time, a concentration of 2.24×10^{-5} M azure I was used for the procedure. Various concentrations of sodium hypophosphite were examined over the range 0–0.8 M. It was found that a concentration of 6.4×10^{-2} M hypophosphite afforded the best results as regards sensitivity and reproducibility (Fig. 2). Higher concentrations of hypophosphite gave higher sensitivities for the determination of palladium(II), but, in the presence of higher concentrations of hypophosphite, the catalyzed reaction was completed in about 2 min. Hence, a concentration of 6.4×10^{-2} M hypophosphite was specified in the procedure.

In Fig. 3, the effect of pH over the range 2.4–6 on the catalyzed and uncatalyzed reactions is presented. A change in pH has no considerable effect on the uncatalyzed reaction. The results showed that the acetate buffer of pH 4 is the most suitable solution, because it produced a maximum difference between the rates of the catalyzed and uncatalyzed reactions and had no side effects.

The volume of buffer solution of pH 4 has no considerable effect on the uncatalyzed reaction. The difference between the rates of the catalyzed and uncatalyzed reactions increases up to a volume of 1.5 mL. Then, the reaction rates remain constant in spite of a considerable increase in the amount of buffer solution. A volume of 1.5 mL buffer solution was selected as the optimum.

The influence of temperature was studied (Fig. 4). The rate of the uncatalyzed reaction remains unaffected when the temperature is varied from 20 to 50°C. With an increase in temperature, the rate of the catalyzed

Effect of foreign species on the determination of 0.1 μg/mL of palladium(II)

Species	Concentration ratio [Ion]/[palladium]	Species	Concentration ratio [Ion]/[palladium]
Na^+, NH_4^+, Ba^{2+}	2000	Tartrate, Ascorbate, NO_3^-	2000
Ni^{2+}, Al^{3+}, Mg^{2+}	1500	PO_4^{3-}, CO_3^{2-}	1500
Ce^{4+}, Sr^{2+}	1200	SO_4^{2-}, ClO_4^-, Cl^-, BrO_3^-	1000
Co^{2+}, Cd^{2+}, Th^{4+}	1000	Br^-, $S_2O_5^{2-}$	500
Zn^{2+}	800	F^-	350
Fe^{2+}, Mn^{2+}	500	$S_2O_8^{2-}$	200
Pb^{2+}	350	IO_3^-, Citrate	100
V^{4+}	200	IO_4^-, NO_2^-	50
In^{3+}, Cr^{3+}	150	WO_4^{2-}	25
Bi^{3+}	50	I^-, S^{2-}	
MO^{6+}	25		
Au^{3+}, Pt^{4+}, Hg^{2+}	5 (interfers)		5 (interfers)
Cu^{2+}, Zr^{4+}	2 (interfers)		

reaction increases and the difference in the reaction rates becomes larger. For practical purposes (low reaction background and good reproducibility), a temperature of 25 ± 0.1°C was selected.

Calibration. The calibration plot was linear in the range of 40–200 ng/mL palladium(II). The regression equation was $\Delta A = -0.1165 + 3.745 \times 10^{-3}c$ with a correlation coefficient of $r = 0.9988$. The limit of detection was 4.3 ng/mL (signal/noise = 3). The reproducibility was satisfactory, with relative standard deviations of 1.53 and 1.98% for ten determinations of 160 and 100 ng/mL palladium(II), respectively.

By changing the variables affecting the sensitivity, another linear plot was obtained for a lower concentration range, 5–40 ng/mL palladium(II). The slightly different conditions are as follows. 20 ng/mL palladium(II); 1.57×10^{-5} M azure I; 9.6×10^{-2} M hypophosphite; 2.0 mL of acetate buffer (pH 4) in a 10-mL volumetric flask; a temperature of 25 ± 0.1°C; λ_{max} = 647 nm; and a fixed time of 2 min.

The regression equation was $\Delta A = -0.056 + 0.0145c$ ($r = 0.9984$). The limit of detection was 0.87 ng/mL palladium(II). The RSD was 2.05% for ten determinations of 20 ng/mL palladium(II).

Interference study. The influence of other ions on the background reaction was studied. The results show that the other ions have no influence on the background reaction. The rate of the background reaction increases only in the presence of palladium(II).

Solutions containing 0.1 μg/mL palladium(I)) and different concentrations of other ions were examined according to the catalytic fixed-time method. The tolerable limit of a foreign species was taken if it caused a relative error of less than 5%. The tolerable ratio of some interfering ions are listed in the table. One of the main sources of interference was caused by Cu^{2+}, which can be masked by adding an excess amount of ascorbic acid. Another was caused by Zr^{4+}, which can be masked by tartrate.

Sample analysis. The good sensitivity and the low detection limit of the proposed method permitted the determination of traces of palladium(II) in a sample of activated charcoal (following the procedure described in [19]). The RSD for three replicate analysis of an activated charcoal sample with an average content of palladium solution of 2.3 μg/mL was 2.9%. The results obtained by the proposed method agreed with those obtained by the AAS method (with a relative error less than 5%).

REFERENCES

1. Marczenko, Z. and Jarosz, M., *Talanta*, 1981, vol. 28, p. 561.
2. Riyazzuddin, P., *Talanta*, 1982, vol. 29, p. 1122.
3. Montes, R. and Javier Lasena, J., *Analyst*, 1985, vol. 110, p. 1339.
4. Sanches Pedreno, C., Garcia Carcia, M.S., and Alberto Quinto, M.I., *Anal. Quim.,* 1987, vol. 32, p. 198.
5. Pitombo, L.R.M. and Flumignan, E., *Anal. Lett.*, 1988, vol. 21, no. 7, p. 1259.
6. Tuwar, S.M., Nandibewoor, S.T., and Raju, J.R., *Indian. J. Chem. Sect. A*, 1990, vol. 29, p. 825.
7. Tikhonova, L.P., Goncharik, V.P., Kozhara, L.I., and Savarkovskaya, I.P., *Zh. Anal. Khim.*, 1991, vol. 46, no. 10, p. 2009.
8. Kock, K.R. and Auer, D., *Talanta*, 1993, vol. 40, no. 12, p. 1975.
9. Miletic, G.Z. and Mitic, S.S., *J. Anal. Chem.*, 1994, vol. 49, no. 5, p. 458.
10. Lu Hailing, Duan Yanping, and Lihua Jianyan, *Huaxue Fence*, 1995, vol. 31, no. 6, p. 333.

11. Wang, Z. and He, P., *Guijinshu*, 1996, vol. 17, no. 3, p. 31.
12. Liu, C., Liu, H., and Lihua Jianyan, *Huaxue Fence*, 1997, vol. 33, no. 1, p. 29.
13. Hanna, W.G., *Talanta*, 1999, vol. 50, no. 4, 809.
14. Huang, Z., Yang, G., Yin, J., and Xu, Q., *Guijinshu*, 1999, vol. 20, no. 3, p. 39.
15. Bhalotra, A. and Puri, B., *Mikrochim. Acta*, 2000, vol. 134, nos. 3–4, p. 139.
16. Meiwauki, M.B. and Seetharamappa, J., *J. Saudi. Chem. Soc.*, 2000, vol. 4, no. 2, p. 165.
17. Ensafi, A.A. and Keyvanfard, M., *Anal. Lett.*, 2002, vol. 35, p. 423.
18. Ensafi, A.A. and Keyvanfard, M., *Spectrochimica. Acta. Part A. Molecular*, *Biomolecular Spectroscopy*, 2002, vol. 58, no. 8, p. 1567.
19. Rosales, D., Gomez Ariza, J.L., and Asuero, A.G., *Analyst,* 1986, vol. 111, p. 449.