Chem. Pharm. Bull.
31(8)2905—2909(1983)

Spectrophotometric Determination of Trace Amounts of Palladium in Antibiotics and Catalysts with Thio-Michler's Ketone

SHIGEKAZU TSURUBOU,*,[a] TADAO SAKAI[a] and SHOZO SHIBATA[b]

Department of Chemistry, Gifu College of Dentistry,[a] Takano 1851, Hozumi-cho, Gifu 501-02, Japan and Government Industrial Research Institute,[b] Nagoya, Hirate-machi, Kita-ku, Nagoya-shi, Aichi 462, Japan

(Received December 23, 1982)

In order to determine trace amounts of palladium reproducibly, a spectrophotometric method using thio-Michler's ketone (TMK) was developed. In this method, it was found that addition of hydroxylamine hydrochloride effectively suppressed oxidation and decomposition of TMK and Pd(II)–TMK complex. A good linear relationship was obtained in the concentration range of 0.1—0.5 ppm for Pd(II). The molar absorptivity was 1.9×10^5 $dm^3 \cdot mol^{-1} \cdot cm^{-1}$ and the coefficient of variation was 1%. The method proposed here could be applied successfully to the determination of trace amounts of palladium in antibiotics and in catalysts for automobile exhaust purifiers.

Keywords——spectrophotometry; thio-Michler's ketone; palladium trace amount; antibiotic; catalyst

Although many reagents[1)] have been employed for the spectrophotometric determination of palladium, the sensitivity is not satisfactory for the determination of palladium at the ppb level. 4,4′-Bis(dimethylamino)thiobenzophenone (thio-Michler's ketone, TMK), a sensitive reagent for spectrophotometry, was synthesized by Tarbell *et al.*[2)] at 1946. TMK forms red-colored coordination complexes with metal ions such as Pd(II),[3)] Ag(I),[4)] Hg(II).[5)] In particular, Pd(II)–TMK complex showed a larger molar absorptivity compared with other Pd(II) complexes,[1)] because TMK has a charged quinone structure and is a monodentate ligand. However, in practice, this reagent is not stable because of air-oxidation and photooxidation of the reagent and its complexes. Therefore, the previous method[3)] using TMK was modified to provide a stable and highly sensitive spectrophotometric determination of Pd(II) and this modified method was applied to the determination of trace amounts of Pd(II) in antibiotics and catalysts for automobile exhaust purifiers in this research.

Experimental

Reagents——TMK Solution: TMK was synthesized according to the published procedure.[2)] A 2.5×10^{-3} M solution was prepared by dissolving 17.8 mg of TMK in 25 ml of *N,N*-dimethylformamide (DMF) freshly each day.

Pd(II) Solution: A standard Pd(II) stock solution, 1000 ppm, was prepared by dissolving 166.6 mg of palladium chloride in 17 ml of 6 M hydrochloric acid and diluting to 100 ml with distilled water, and working solutions were prepared by accurate dilution of the stock solution.

DMF Solution (44%): DMF was diluted to 44% aqueous solution with distilled water and acetate buffer solution.

All other chemicals were of guaranteed-reagent grade.

Apparatus——Absorption spectra were determined and absorbance measurements were made with a Hitachi 556 double beam spectrophotometer with a 1 cm quartz cell. A Hitachi 180-80 Zeeman atomic absorption spectrophotometer was also used. pH measurements were made with a Hitachi-Horiba F-7 II pH meter.

Standard Procedure——Transfer 40 ml of 44% DMF solution adjusted to pH 2.8, 1 ml of sample solution containing more than 5 μg of palladium, 1 ml of 2.5×10^{-3} M TMK solution, and 0.5 ml of 15% hydroxylamine hydrochloride solution into a 50 ml volumetric flask and fill up with distilled water. The order of addition is critical.

After allowing the solution to stand for 10 min, measure the absorbance at 530 nm against a reagent blank as a reference. The temperature should be maintained at 20 °C in the cells.

Results and Discussion

Absorption Spectra

Absorption spectra of TMK and Pd(II)–TMK complex in 35% DMF solution are shown in Fig. 1. Curve (A) is the absorption spectrum of 2.5×10^{-5} M TMK in 35% DMF solution and (B) is that of TMK in 35% DMF solution measured after the solution had stood for 24 h. The absorbance at 465 nm (λ_{max}) had decreased considerably and another absorption peak was observed at 610 nm. From these curves, it is assumed that TMK is oxidized and decomposed with time. Curves (C) and (D) show the absorption spectra of Pd(II)–TMK

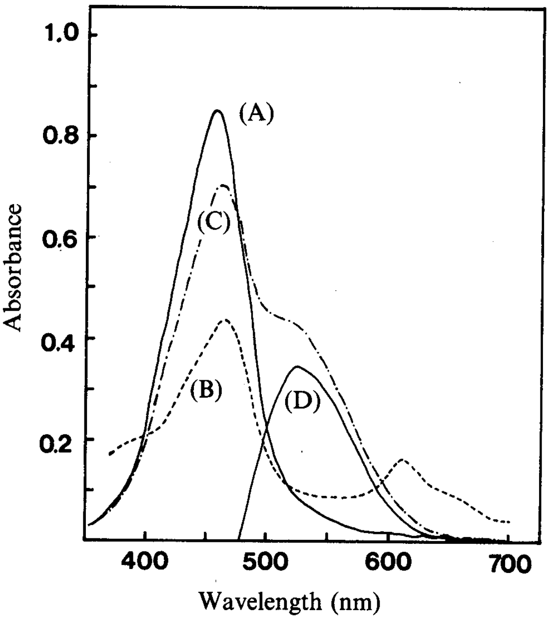

Fig. 1. Absorption Spectra at pH 2.75

(A), 2.5×10^{-5} M TMK in 35% DMF soln., ref. = water; (B), 2.5×10^{-5} M TMK after 24 h; (C) Pd(II)–TMK complex, [Pd(II)] = 0.2 ppm, ref. = water; (D), Pd(II)–TMK complex, [Pd(II)] = 0.2 ppm, ref. = R.B.

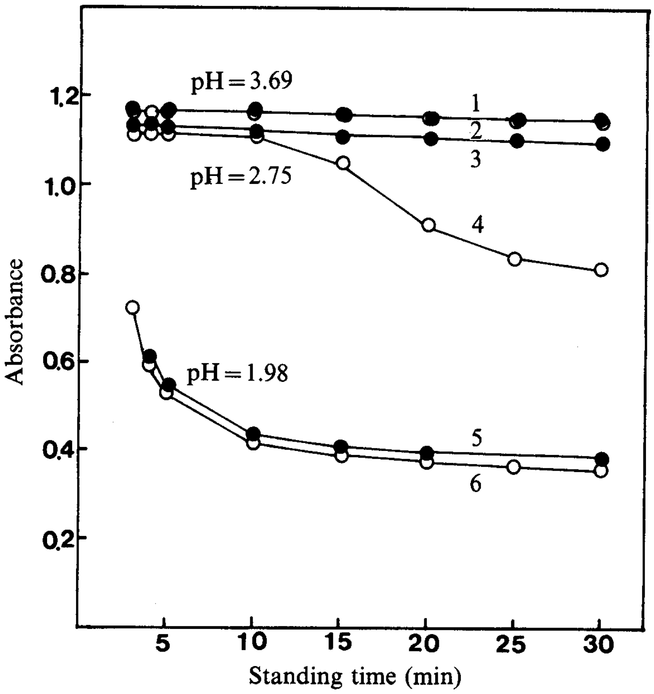

Fig. 2. Effect of Standing Time of TMK in 35% DMF Solution

[TMK] = 2.5×10^{-5} M, λ = 465 nm, ref. = water. ●—●, addition of $NH_2OH \cdot HCl$ (0.15%); ○—○, without $NH_2OH \cdot HCl$.

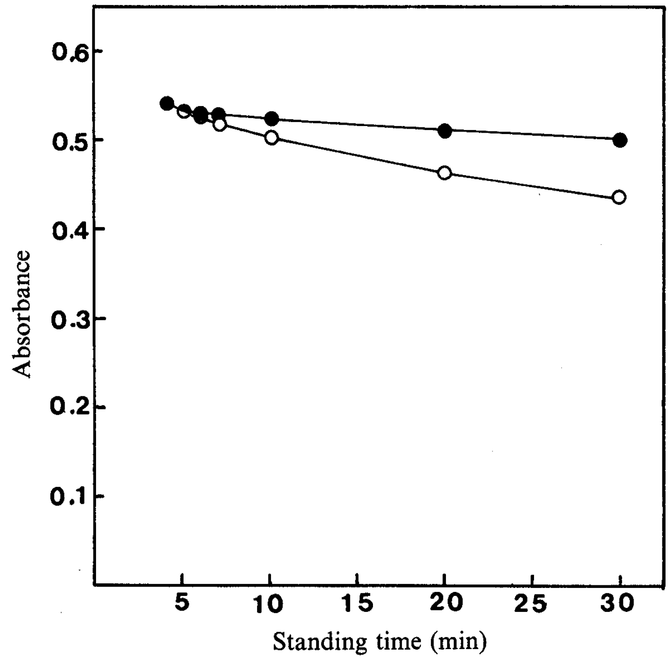

Fig. 3. Effect of Standing Time of Pd(II)–TMK Complexes

[Pd(II)]=0.3 ppm, [TMK]=5×10^{-5} M, pH=2.75, λ=530 nm, ref.=R.B. ●—●, addition of $NH_2OH \cdot HCl$ (0.15%); ○—○, without $NH_2OH \cdot HCl$.

complex against water and reagent blank as references, respectively. It was found that a reagent blank should be used as a reference in order to obtain a clear absorption peak (530 nm) and stable absorbance.

Effects of Standing Time and Addition of Hydroxylamine Hydrochloride

In order to investigate the stability of TMK and Pd(II)–TMK complex, the standing time was examined at different pH values. The results are shown in Figs. 2 and 3. It was reported that TMK reagent is oxidized easily.[6] Therefore, the effect of adding 0.5 ml of 15% hydroxylamine hydrochloride as an antioxidant was examined. TMK in pH 3.69 medium was stable both with and without hydroxylamine hydrochloride (curves 1 and 2 in Fig. 2), but at pH 1.98, the absorbance of TMK decreased considerably in both cases (curves 5 and 6 in Fig. 2). On the other hand, addition of 0.5 ml of 15% hydroxylamine hydrochloride in pH 2.75 medium provided stable and constant absorbance of TMK compared to the case where no hydroxylamine hydrochloride was added (curves 3 and 4 in Fig. 2).

Effects of pH on Formation of the Complex and TMK Concentration

The absorbance of Pd(II)–TMK complex with 0.15% hydroxylamine hydrochloride in 35% DMF solution was constant and maximum in the pH range of 2.2—2.8 and was stable for at least 30 min, as shown in Fig. 3. It was found that though TMK alone was stable in pH 3.69 medium, it was difficult to form stable complexes with it in the same medium. Moreover, it was found that the concentration of TMK should be maintained at more than 10-fold molar excess over Pd(II) to obtain a constant and maximum absorbance.

Calibration Curve

A calibration curve for the determination of Pd(II) was prepared. A good linear relationship was obtained in the Pd(II) concentration range of 0.1—0.5 ppm and passed through the origin. The molar absorptivity at 530 nm was 1.9×10^5 $dm^3 \cdot mol^{-1} \cdot cm^{-1}$, which is large compared with those of other Pd(II) complexes.[1] The reproducibility of the method was examined for 0.3 ppm Pd(II) solution and the coefficient of variation was 1% for ten determinations.

Continuous Variation Plots

The composition of the Pd(II)–TMK complex was examined by the continuous variation method. The molar ratio of Pd(II) to TMK was found to be 1 : 4, so the composition of the complex is assumed to be $Pd(TMK)_4$. This is in accordance with published data.[3]

Interference

The effect of foreign ions on the determination of 0.2 ppm of Pd(II) was examined. Up to 100-fold excess amounts of the following ions did not interfere with the assay; Al(III), Bi(III), Ca(II), Cd(II), Mn(II), Mg(II), Ni(II), Pb(II), Zn(II) and Ti(IV). Five-fold excess amounts of Co(II), Cu(II), Cr(VI) and equimolar amounts of Fe(III) and Mo(VI) with respect to Pd(II) did not interfere. However, Ag(I), Hg(II), and Pt(II) interfered severely with the same amount of Pd(II).

Applications to Practical Samples

The method developed here was applied to the determination of trace amounts of palladium in antibiotics, and also to the catalysts for the clean-up of car exhaust gases. Sample solutions were prepared as follows.

Antibiotics: Several kinds of commercial antibiotics (5.0—12.5 g) were decomposed in a quartz beaker in an electric furnace (650 °C, 24 h). The residues were dissolved in aqua regia, the insoluble portion was filtered off, and the filter paper was ashed with a gas burner. Then the ash was dissolved in hydrofluoric acid and perchloric acid mixture and the mixture was evaporated to dryness. Finally, the filtrate and residues were mixed and evaporated to dryness. The residues were dissolved in 10 ml of 0.1 M hydrochloric acid. When the decomposition of antibiotics was insufficient, a positive error was caused in the determination of palladium because a new and high peak appeared at 610 nm in the absorption spectrum.

Catalyst: Palladium catalysts were supported on carriers made of silica or alumina (bead diameter, 3—5 mm). The sample solutions were prepared by dissolving 0.5 g of catalyst in aqua regia without crushing or grinding. After filtration, the filtrate was evaporated to dryness and the residue obtained was dissolved in 100 ml of 0.1 M hydrochloric acid.

Palladium in the materials described above was determined by the standard addition method, and atomic absorption spectrophotometry was also carried out to measure the

TABLE I. Palladium Contents in Practical Samples

Sample	Sample solution	Pd found (ppm)[a]	
		This method	AAS
Antibiotics			
A	5.0 g/10 ml	1.50	1.41
B	12.5 g/10 ml	N.D.	N.D.
C	10.0 g/10 ml	N.D.	N.D.
Catalyst			
A	0.5 g/100 ml	8.80	8.67
B-1	0.5 g/100 ml	7.80	7.68
B-2	0.5 g/100 ml	6.90	7.02
C	0.5 g/100 ml	N.D.	N.D.

a) In each case, the results given are the mean values of 3 determinations. N.D., not detected; AAS, atomic absorption spectrophotometry.

palladium contents. The results are shown in Table I. It appears that this method may be applicable for the sensitive and simple determination of trace amounts of Pd(II) in materials such as antibiotics and catalysts.

References and Notes

1) F. E. Beamith and J. C. van Loon, "Recent Advances in the Analytical Chemistry of the Noble Metals," Pergamon, Oxford, 1972.
2) D. S. Tarbell and V. P. Wystrach, *J. Am. Chem. Soc.*, **68**, 2110 (1946).
3) A. T. Pilipenko, O. P. Ryabushko and G. S. Matsibura, *Zh. Anal. Khim.*, **35**, 1545 (1980).
4) K. L. Cheng, *Mikrochim. Acta*, **1967**, 820.
5) G. Ackermann and H. Röder, *Talanta*, **24**, 99 (1976).
6) K. Tôei, Y. Ono, T. Wakimoto and H. Miyata, *Bunseki Kagaku*, **31**, 458 (1982).