

## Spectrophotometric Determination of Palladium by the Colouration with 2-(2-Quinolylazo)-5-diethylaminobenzoic Acid

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Palladium has been used 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 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 soil pollution. Palladium is thought to be one of the strongest allergens from a health hazard viewpoint.<sup>1,2</sup> For these reasons, establishing rapid and accurate methods for the determination of palladium for industrial process, quality and pollution control is important. Many sensitive methods, such as spectrofluorimetry, X-ray fluorescence spectrometry, neutron activation analysis, atomic absorption spectrometry have widely been used for the determination of palladium. However, spectrophotometric methods have gained popularity for palladium determination as advantageous in respect of simplicity and low operating costs. A wide variety of spectrophotometric reagents, such as azo dyes, rhodanine derivatives, porphyrin ligands, thiourea derivatives, 8-aminoquinoline derivatives and nitroso dye have been developed for the determination of palladium.<sup>3-12</sup>

In our previous work, some 2-quinolylazo reagents were reported for the determination of metal ions.<sup>13-16</sup> These reagents have a higher sensitivity than that of pyridylazo reagents because of its larger conjugated system. However, the use of these reagents for the determination of palladium has not been reported yet. We had synthesized 2-(2-quinolylazo)-5-diethylaminobenzoic acid (QADEAB) and used it to the determination of cobalt.<sup>17</sup> This reagent has high sensitivity. In this paper, we thoroughly studied the color reaction of QADEAB with palladium. The results show that QADEAB is a highly sensitive, selective and convenience reagent for palladium. Based on this, a highly sensitive, selective and convenient method for the determination of palladium in water and catalyst was developed.

### Experimental Section

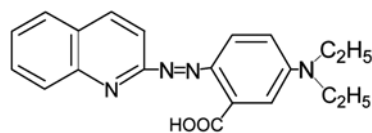
**Experimental Apparatus.** A UV-160-A spectrophotometer (Shimadzu Corporation, Tokyo, Japanese) equipped with 1 cm cells was used for all absorbance measurements. pH values was determined with a Beckman  $\Phi$ -200 pH meter

(Beckman Instruments, Fullerton, CA, USA).

**Synthesis of QADEAB.** QADEAB was synthesized according to the our previous proposed procedure:<sup>17</sup> 7.2 g of 2-aminoquinoline was dissolved in 300 mL of anhydrous ethanol and 2.2 g of sodamide were added. The mixture was refluxed for 6 h in a boiling water bath. Hereafter, 8.5 mL of isoamyl nitrite were added. The mixture was again refluxed for 40 min in a boiling water bath. Then the solution was cooled and kept over night at 0 °C. Diazo salt was obtained with a yield of 93%. The diazo salt was then dissolved in 200 mL of anhydrous ethanol, m-diethylaminobenzoic acid (8.0 g) was added, and carbon dioxide was passed through the stirred solution until pH reached the value of about 8.0. Finally ethanol was evaporated and the residue was recrystallized in 35% ethanol. QADEAB was obtained with a yield of 21%; mp. 241-243 °C. The structure of QADEAB is show in Figure 1.

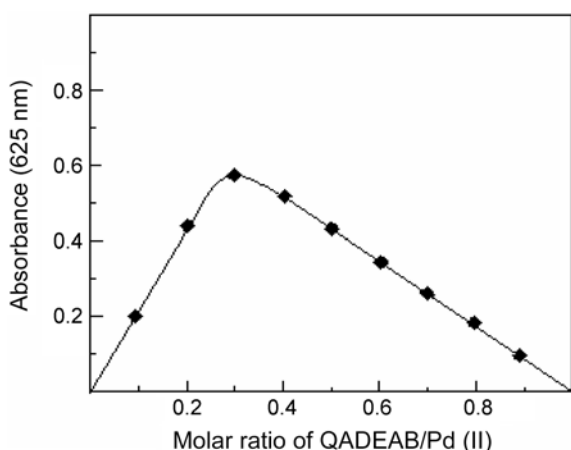
**Reagents.** All of the solutions were prepared with ultra-pure water obtained from a Milli-Q50 SP Reagent Water System (Millipore Corporation, USA). A  $5 \times 10^{-4}$  mol L<sup>-1</sup> of QADEAB solution was prepared by dissolving QADEAB with 95% of ethanol. A stock standard solution of palladium (1.0 mg mL<sup>-1</sup>) was obtained from Chinese Standard Center, and a working solution of 2.0  $\mu$ g mL<sup>-1</sup> was prepared by diluting this solution. A 5 mol L<sup>-1</sup> of hydrochloric acid was used. Cetyl trimethylammonium bromide (CTMAB) solution (1.0% (w/v)) was prepared by dissolving CTMAB with 20% ethanol. All chemicals used were of analytical grade unless otherwise stated.

The river water for determination was collected from Panglog River, Kunming, P. R. China according to literature.<sup>18</sup> The Plating Effluents for determination were collected from Yunnan Smelt Factory, Kunming, P. R. China according to literature<sup>18</sup> too. The catalyst for determination is a Chinese Certified Reference Standard Material (GBW(E)070029) obtained from Chinese Standard Material Centre. The certified standard palladium value is (0.538  $\pm$



**Figure 1.** The structure of QADEAB.





**Figure 4.** Composition of Pd(II)-QADEAB complex by continuous variation method. The concentration of Pd(II)+QADEAB was  $1.5 \times 10^5 \text{ mol L}^{-1}$ , other conditions as in standard procedure

**Table 2.** Tolerance limits for the determination of 5  $\mu\text{g}$  of Pd(II) with QADEAB (relative error  $\pm 5\%$ ).

Ion added	Tolerate (mg)
$\text{NO}_3^-$ , $\text{K}^+$ , borate, Na, $\text{Cl}^-$ , $\text{Mg}^{2+}$ , $\text{SO}_4^{2-}$ , $\text{ClO}_4^-$	200
$\text{Li}^+$ , $\text{Al}^{3+}$ , $\text{PO}_4^{3-}$ , $\text{NO}_2^-$ , $\text{ClO}_3^-$	20
$\text{Ca}^{2+}$ , $\text{Sr}^{2+}$ , $\text{IO}_3^-$ , $\text{BrO}_3^-$ , B(III)	10
$\text{Mn}^{2+}$ , Ce(IV), $\text{Fe}^{3+}$ , Mo(VI), V(V)	5
Ti(IV), Bi(III), Cr(VI), $\text{Ba}^{2+}$ , W(VI), U(IV), $[\text{Co}^{2+}]^*$	1
$\text{Cd}^{2+}$ , $\text{Pd}^{2+}$ , $\text{Cr}^{3+}$ , $\text{La}^{3+}$ , $\text{Zn}^{2+}$ , Zr(IV), $[\text{Ni}^{2+}]^*$	0.5
Bi(III), $\text{Pb}^{2+}$ , $\text{Hg}^{2+}$ , $\text{Sb}^{3+}$ , Th(IV), Sn(IV)	0.1
Se(IV), Te(IV), $\text{Au}^{3+}$ , $\text{Cu}^{2+}$ , $\text{Ag}^+$	0.05
$\text{Ni}^{2+}$ , $\text{Co}^{2+}$	0.01

\*masked with 2 mL of 10% citric acid

**Table 3.** Determination of palladium in the water and catalyst samples.

Samples	AAS method	Found	RSD% (n=5)	Recovery (%) (n=5)
River water	0.0285 ( $\mu\text{g mL}^{-1}$ )	0.0274 ( $\mu\text{g mL}^{-1}$ )	2.6	93
Plating effluents	0.278 ( $\mu\text{g mL}^{-1}$ )	0.285 ( $\mu\text{g mL}^{-1}$ )	2.2	96
Catalyst	0.544 (%)	0.541 (%)	1.4	102

**Table 4.** Comparison of reagents for spectrophotometric determination of palladium.

Reagent	Medium/Solvent	$\lambda_{\text{max}}$ (nm)	$\epsilon (\times 10^4)$ $\text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$	Linear Range ( $\mu\text{g/mL}$ )	Ref
5-(5-Nitro-2-pyridylazo)-2,4-diaminotoluene	In hydrochloric acid medium	592	1.9	0-0.9	4
<i>o</i> -Hydroxyacetophenone thiosemicarbazone	In aqueous at pH 6.0	370	0.90	0.42-10.6	5
1-(2-Pyridylazo)-2-naphthol	By solid-liquid extraction at 90 °C	678	1.2	0.1-1.8	6
2-(5-Nitro-2-pyridylazo)-5-(N-propyl-N-3-sulfopropylamino)-phenol	In weak acidic media	612	10.8	0-2.5	7
N-Dodecyl-N'-(sodium p-aminobenzenesulfonate)-thiourea	In the presence of CTMAB and NaAc-HAc buffer solution	296	7.41	0-0.5	8
Pyridoxal-4-phenyl-3-thiosemicarbazone	Extracted into benzene at pH 3.0	460	2.20	0.4-6.4	9
2,2'-Dithiodianiline	Extraction of isobutyl methyl ketone at pH 3	397	14.7	0.003-0.2	10
2-(2-Quinolinyloxy)-5-diethylaminobenzoic acid	0.5-2.5 mol $\text{L}^{-1}$ of HCl and CTMAB medium	625	15.1	0.01-0.6	This work

**Interference.** The selectivity of the proposed method was investigated by the determination 5  $\mu\text{g}$  25  $\text{mL}^{-1}$  of Pd(II) in the presence of various ions within a relative error of  $\pm 5\%$ . The results are given in Table 2. The results shows that the Ni(II) and Co(II) have a low tolerance limits. However, the Ni(II) and Co(II) can be masked with citric acid. The tolerance limits reaches 1 mg for Co(II) and 0.5 mg for Ni(II) when asked with citric acid. This method has high selectivity.

**Application.** The proposed method has been successfully applied to the determination of palladium in water and catalyst.

For water sample, taking an appropriate volume (plating effluents 20 mL, river water 500 mL) of water sample in a 500 mL flask. The samples were concentrated to about 10 mL by heating on a hot plate. 5 mL concentrated nitric acid and 2 mL of 30% hydrogen peroxide were added in this solution. The mixture was heated on a hot plate and evaporated to near dryness. The residue was dissolved with 5 mL of 5% hydrochloric acid and transferred into a calibrated flask. 2 mL of 10% citric acid was added to mask the nickel and cobalt, and the solution was neutralized with sodium hydroxide. The palladium content was analyzed by general procedure. The recovery test of palladium was determined by adding 1.0  $\mu\text{g}$  of palladium to water samples. A standard method using flame atomic absorption spectrometry together with preconcentration as literature<sup>19</sup> was also used as reference method. The results are shown in Table 3.

For catalyst, 0.1 g of samples was weighted accurately into the Teflon high-pressure microwave acid-digestion bomb (Fei Yue, Analytical Instrument Factory, Shanghai, China). 3.0 mL of concentrated nitric acid, 2 mL of hydro-

chloric acid and 5.0 mL of 30% hydrogen peroxide were added. The bombs were sealed tightly and then positioned in the carousel of the microwave oven (Model WL 5001, 1000 W, Fei Yue Analytical Instrument Factory, Shanghai, China). The system was operated at full power for 10 min. The digest was evaporated to near dryness. The residue was dissolved with 10 mL of 10% of hydrochloric acid, then transferred into a 50 mL of calibrated flask and diluted to volume with 10% of hydrochloric acid. 5 mL of 10% citric acid was added to mask the nickel and cobalt. The palladium content was analyzed according to general procedure. The recovery test of palladium by adding 1.0  $\mu\text{g}$  of palladium in sample was carried out, and a standard method using flame atomic absorption spectrometry as literature<sup>19</sup> was also used as reference method. The results are shown in Table 3 too.

### Conclusion

A comparison of the proposed methods with other spectrophotometric methods (Table 4) shows the QADEAB is one of the most sensitive, selective and convenient spectrophotometric reagents for palladium.

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### References

1. Patrick, G.; Michel, P. *Platinum. Met. Rev.* **2003**, *47*, 60-72.
2. Caroli, S.; Alimonti, A.; Petrucci, F.; Bocca, B.; Krachler, M. *Spectrochim. Acta B* **2001**, *56*, 1241-124.
3. Zeng, Y. E.; Zhang, H. S.; Chen, Z. H. *Handbook of Modern Chemical Reagents*, The Forth Fascicule, Chromogenic Agent of Inorganic Ion, 1st ed; Chemical Industry Press: Beijing, P. R. China, 1989.
4. Yang, H. Q.; Zhang, G.; Zhang, L. L.; Liu, G. Q.; Zhang, X. H. *Talanta* **1996**, *43*, 747-753.
5. Murthy, G. V. R.; Reddy, T. S. *Talanta* **1992**, *39*, 697-701.
6. Gao, J. H.; Peng, B.; Fan, H. Y.; Kang, J. W.; Wang, X. D. *Talanta* **1997**, *44*, 837-842.
7. Mori, I.; Kawakatsu, T.; Fujita, Y.; Matsuo, T. *Talanta* **1999**, *48*, 1039-1044.
8. Ma, D. L.; Cui, F. L.; Xia, D. S.; Wang, L. L. *Anal. Lett.* **2002**, *35*, 413-421.
9. Sarma, L. S.; Kumar, J. R.; Reddy, K. J.; Kumar, A. K.; Reddy, A. V. *Anal. Sci.* **2002**, *18*, 1257-1261.
10. Gholivand, M. B.; Nozari, N. *Talanta* **2000**, *52*, 1055-1060.
11. Reddy, B. K.; Reddy, K. J.; Kumar, J. R.; Kumar, A. K.; Reddy, A. V. *Anal. Sci.* **2004**, *20*, 925-930.
12. Maria, B.; Katarzyna, P. *Chem. Anal.* **2003**, *48*, 87-95.
13. Hu, Q. F.; Yang, G. Y.; Yin, J. Y. *J. Environ. Monit.* **2002**, *4*, 956-959.
14. Yang, G. Y.; Hu, Q. F.; Huang, Z. J.; Yin, J. Y. *Anal. Sci.* **2003**, *19*, 299-302.
15. Yang, G. Y.; Huang, Z. J.; Hu, Q. F.; Yin, J. Y. *Talanta* **2002**, *58*, 511-515.
16. Hu, Q. F.; Yang, G. Y.; Tang, D. Y.; Yin, J. Y. *Chinese J. Anal. Chem.* **2002**, *30*, 699-701.
17. Wang, L.; Yang, G. Y.; Hu, Q. F.; Yin, J. Y. *Chem. Anal.* **2003**, *48*, 767-773.
18. *Analysis Method of Water and Wastewater*, 3rd ed.; Chinese Environment Protection Agency, Ed.; Environmental Science Press: Beijing, P. R. China, 1989; pp 465-458.
19. Dong, S. A.; Chen, J.; Wu, R. L. *Analysis Methods of Precious Metals*, 1st ed.; Chinese Science Press: Beijing, P. R. China, 1995; pp 263-268.