The Extraction Spectrophotometric Determination of Palladium with Monothiodibenzoylmethane

B. N. Prabhu and S. M. Khopkar

Department of Chemistry, Indian Institute of Technology, Bombay 400076, India

(Received July 14, 1975)

Monothiodibenzoylmethane (HSDBM) was used for the quantitative extraction of palladium. It was extracted at pH 3.5—6.5, with 0.001 M HSDBM in benzene, as an orange-red colored complex and measured spectrophotometrically at 470 nm. Beer's law was valid in the concentration range of 0.6 to 3.6 μg of palladium per ml. The complex was stable for at least 144 h. Ten milliliters of 0.001 M HSDBM in benzene was adequate for quantitative extraction of palladium. The optimum period of equilibration was 10 min. It was possible to extract palladium in the presence of a large number of elements.

Monothiodibenzoylmethane (3-mercapto-1,3-diphenyl-2-propen-1-one) HSDBM, a monothio-substituted derivative of dibenzoylmethane was used for the extraction and photometric determination of several transition elements.[1] Further studies revealed that it is possible to extract palladium(II) at pH 3.5—6.5 as the orange-red colored complex and determine photometrically at 470 nm.

Amongst β-diketones, acetylacetone[3] was used for the extraction of palladium at pH 8.0. The extractions with benzoylacetone were complete between the pH range of 1.2 to 10.[3] The extractions with dibenzoylmethane were not only incomplete, but also the rate of equilibration was slow. With 2-thenoyltrifluoroacetone (HTTA), palladium was extracted as an orange-yellow complex, in methyl propyl ketone.[4] It was successfully separated from platinum in HTTA-butanol.[5] Monothiothenoyltrifluoroacetone[6,7] was used for the extractive spectrophotometric determination with some advantages. Recent methods for the solvent extraction[8] and photometric determination[9] are summarized in recent monographs.

The method proposed in this paper is simple, rapid and selective and is applicable at tracer concentrations; the special feature being, palladium can be separated from other noble metals by extraction.

Experimental

Apparatus and Reagents. Spektromom-204 spectrophotometer with matched 10 mm quartz cells. Type FEK-57 photoelectric filter photometer with 10 mm corex glass cuvettes. Cambridge pH-meter with glass and calomel electrodes. Wrist action flask shaker. Monothiodibenzoylmethane was prepared from dibenzoylmethane (Koch-light, England), by the procedure of Chaston *et al.*[10] About 0.001 M HSDBM in benzene was used. The reagent may be preferably preserved in the refrigerator.

A stock solution of palladium was prepared by dissolving 1.002 g of palladium chloride (Johnson Matthey and Co., London) in 500 ml distilled water containing 5% concentrated hydrochloric acid. The solution was standardized gravimetrically with dimethylglyoxime.[11] It contained 1.2 mg/ml of palladium. The dilute solution containing 6 μg/ml of palladium was prepared by appropriate dilution.

General Procedure. An aliquot of solution containing palladium (30 μg) was taken. The pH of the solution was adjusted to 5.0 on pH meter with 0.01 M hydrochloric acid or 0.01 M ammonium hydroxide. The total volume of the aqueous phase was made up to 25 ml. The solution was transferred to a separatory funnel. Ten ml of 0.001 M HSDBM in benzene was added to it. Then the solution was shaken on the wrist action flask shaker for about 10 min. The layers were allowed to settle and separate. The aqueous phase was carefully withdrawn. The orange-red colored palladium complex in the organic phase was transferred into a 10 ml volumetric flask. The absorbance of the complex was measured, at 470 nm, against the reagent blank. The amount of the palladium was computed from calibration curve.

Results and Discussion

Absorption Spectra. The absorption spectra of palladium-SDBM complex ($Pd = 2.819 \times 10^{-5}$ M), against the reagent blank (A), is shown in Fig. 1. The spectrum of the reagent blank against benzene (B) is also shown. The complex showed maximum absorbance at 470 nm; with minimum absorbance for the reagent blank. Therefore this wavelength was selected for all measurements. The molar absorptivity at 470 nm was 8.868×10^3. The sensitivity (Sandell's definition) was 0.012 μg/ml/cm^2.

Extraction as the Function of pH. The extraction of palladium was carried out between the pH region of 1.0—10.0, with 10 ml of 0.001 M HSDBM in benzene. The results (Fig. 2) showed that the $pH_{1/2}$ was 3.0. The extraction was quantitative in the pH region of 3.5 to 6.5. The extraction was incomplete below and above this region. Hence pH 5.0 was used for all extractions.

Beer's Law. Different amounts of palladium, from 6 μg to 60 μg, were taken and were extracted with 10 ml of 0.001 M HSDBM in benzene. The absorbance of the complexes was measured at 460, 470, and 480 nm. The system conformed to Beer's law in the concentration range of 0.6 to 3.6 μg of palladium per ml at 470 nm. It is possible to expand this range provided, we use high reagent concentration.

Effect of Reagent Concentration. With all other factors kept constant, palladium was extracted with varying volumes and varying concentration of the reagent (Table 1). The results showed that 10 ml of 0.001 M HSDBM in benzene was adequate for quantitative extraction. The extraction was not quantitative at lower reagent concentration while at higher reagent concentration, there was negligible increase in extraction. The variation in volume of 0.001 M HSDBM showed that 10 ml of the reagent was ade-

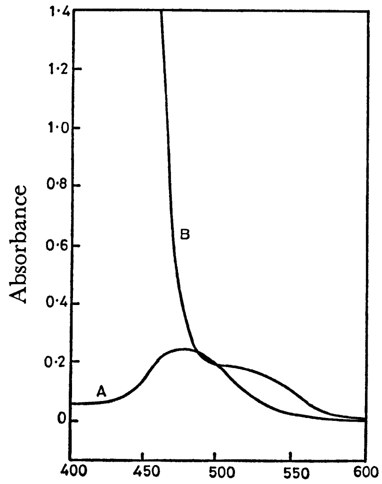

Fig. 1. Absorption spectra of palladium–SDBM complex.
(A): Pd(II)–SDBM complex *vs.* reagent blank. Pd(II)=2.818×10^{-5} M at pH=5.0.
(B): Reagent blank *vs.* benzene at pH=5.0, HSDBM=1.0×10^{-3} M in benzene.

Table 1. Effect of reagent concentration
Pd=30 μg; pH=5.0

Concentration of the reagent ($M\times10^{-3}$)	Amount added ml	Absorbance at 470 nm
0.25	10	0.090
0.50	10	0.180
0.75	10	0.240
1.00	10	0.250
1.25	10	0.250
1.50	10	0.250
2.00	10	0.250
2.50	10	0.250
1.00	2.5	0.120
1.00	5.0	0.150
1.00	7.5	0.195
1.00	15	0.250
1.00	20	0.250
1.00	25	0.250

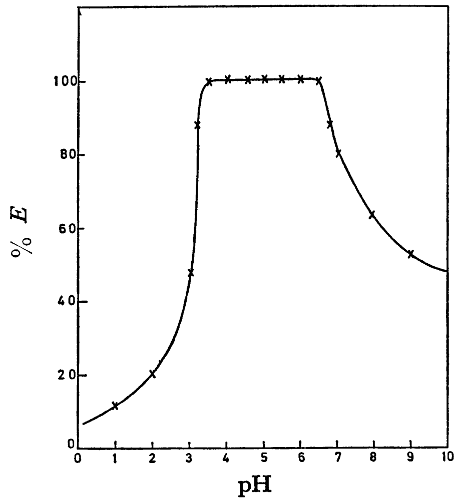

Fig. 2. Extraction as function of pH.

Table 2. Effect of diverse ions
Pd=30 μg; pH=5.0; SDBM=1×10^{-3} M in benzene

Tolerance limit (μg)	Foreign ion present
5.0×10^4	Ca^{2+}, Mg^{2+}, Na^+, K^+, Li^+, NO_3^-, SO_4^{2-}.
2.5×10^4	Sr^{2+}, $tart^{3-}$.
1.0×10^4	Tl^+, UO_2^{2+}, Cs^+, Rb^+, F^-, Cit^{3-}, thiourea, CrO_4^{2-}, $Mo_7O_{24}^{6-}$, ReO_4^-, SeO_3^{2-}, VO_3^-.
0.5×10^4	Ge^{4+}, Ba^{2+}, Be^{2+}, Br^-, AsO_3^-.
0.3×10^4	Sb^{3+}, Os^{8+}, Rh^{3+}, Pt^{4+}, Al^{3+}, Th^{4+}, Zr^{4+}, Y^{3+}, Mn^{2+}, Ga^{3+}, Ce^{4+}, SCN^-, TeO_3^{2-}, WO_4^{2-}.
0.1×10^4	Ti^{4+}, Bi^{3+}.
0.05×10^4	Pb^{2+}, Cd^{2+}, Cr^{3+}, Co^{2+}, Ru^{3+}, Ir^{4+}, Zn^{2+}, In^{3+}.
None	Hg^{2+}, Cu^{2+}, Au^{3+}, Fe^{3+}, Ni^{2+}, CN^-, $EDTA^{4-}$, $S_2O_3^{2-}$, mal^{2-}, $C_2O_4^{2-}$.

quate for quantitative extraction of palladium. However, for very high metal ion concentration, it is preferable to use high reagent concentration.

Effect of Salting-out Agents. With all other conditions same, the chlorides of lithium, sodium, potassium, ammonium, magnesium and calcium in the concentration range of 0.5—5 M were used as salting-out agents. The results showed that none of them were effective, possibly on account of high ionic concentration. In few cases, the extraction substantially decreased due to competitive action of chloride ion with reagent anion for central metal atom to form complex. Similar phenomenon was also observed by previous workers.6)

Stability of the Color of the Complex. The absorbance of the complex was measured at elapsed intervals of 0, 1, 2, 4, 8, 16, 24, 48, 72, 96, 120, and 144 h. The complex was stable for at least 144 h. In other methods complex was not stable for such long duration.12)

Period of Equilibration. The period of shaking was varied from 2.5 to 30 min. The extraction was incomplete up to a shaking period of 8 min, but was quantitative in 10 min of equilibration. This is more practicable in contrast to the method proposed by earlier workers.3)

Composition of the Extractable Species. An attempt was made to ascertain the composition of the extractable species from the log C_{HSDBM} *vs.* log D plot.13) The concentration of the reagent was varied from 1.0×10^{-4} to 5.0×10^{-4} M. The slope was 1.73, indicating that a di-solvated species is present. Therefore the composition of the extractable species is $Pd(SDBM)_2$.

Effect of Diverse Ions. The effect of several ions on the extraction behavior of palladium was studied (Table 2). The tolerance limit was calculated as described earlier.1) The results showed that the alkali, alkaline earth metals were tolerated in high ratios (>1 : 1000). Thallium(I), uranium(VI) and common oxyanions were tolerated in the ratio of 1 : 300. The noble metals were tolerated in the ratio of 1 : 100. But, mercury, copper, gold, nickel, and iron showed

Table 3. Comparison of methods

Palladium taken (μg)	Palladium found by			
	HSDBM method	HSTTA method[6,7]	2-nitroso-1-naphthol method[14]	2-furildioxime method[15]
6.0	6.05	6.00	6.20	6.10
12.0	12.00	11.95	12.10	12.05
18.0	18.05	18.10	18.20	18.10
24.0	24.10	24.20	23.70	23.90
30.0	29.90	29.95	30.30	30.20

strong interference. The interferences due to some of the ions were eliminated using sequestering agents. Bismuth, chromium, thorium, titanium and gallium were masked with tartaric acid, while zirconium, antimony and aluminium were masked with fluoride. The interference due to osmium(VIII) and cobalt(II) were eliminated by selective extraction with carbon tetrachloride and 1-nitroso-2-naphthol respectively.[8]

Comparison with Other Methods. Four sets of five samples containing various amounts of palladium were taken. Then palladium from each sample was measured with monothiodibenzoylmethane, monothiothenoyltrifluoroacetone (HSTTA),[6,7] 2-furildioxime[14] and 2-nitroso-1-naphthol[15] methods. It was interesting to note (Table 3) that the amount of palladium found by HSDBM method, compares favorably well with other methods of extraction of palladium.

The absorbance of the solutions with 20 determinations was 0.250±0.001. The relative standard deviation was ±0.75%. It was possible to accomplish separation and spectrophotometric determination of palladium in a single operation. The overall process needed 30 min. As little as 0.12 μg of palladium per ml can be determined by this method. The method is selective, as it was possible to separate palladium from many elements including noble metals, with which it is associated.

Thanks are due to the Council of Scientific and Industrial Research (India), for awarding Junior Research Fellowship to one of the authors (B.N.P.).

References

1) R. R. Mulye and S. M. Khopkar, *Anal. Chim. Acta*, **76**, 204 (1975).

2) E. Uhlemann and H. Muller, *Anal. Chim. Acta*, **41**, 311 (1968).

3) J. Stary and E. Hladky, *Anal. Chim. Acta*, **28**, 227 (1963).

4) A. V. Rangnekar and S. M. Khopkar, *Bull. Chem. Soc. Jpn.*, **38**, 1696 (1965).

5) A. K. De and M. S. Rahaman, *Analyst*, **89**, 795 (1964).

6) A. V. Rangnekar and S. M. Khopkar, *Chem. Ind. (London)*, **1969**, 293.

7) A. V. Rangnekar and S. M. Khopkar, *Chem. Era*, **1970**, 42.

8) A. K. De, S. M. Khopkar, and R. A. Chalmers, "Solvent Extraction of Metals," Van Nostrand-Reinhold, London (1970).

9) F. F. Beamish and J. C. Van Loon, "Recent Advances in the Analytical Chemistry of Noble Metals," Pergamon, New York (1972), pp. 48, 332.

10) S. H. H. Chaston, S. E. Livingstone, T. N. Lockyer, V. A. Pickles, and J. S. Shannon, *Aust. J. Chem.*, **18**, 673 (1965).

11) A. I. Vogel, "The Text Book of Quantitative Inorganic Analysis," 3rd ed., Longmans Green, London (1961), p. 511.

12) V. K. Gustin and T. R. Sweet, *Anal. Chem.*, **34**, 44 (1963).

13) A. A. Yadav and S. M. Khopkar, *Bull. Chem. Soc. Jpn.*, **44**, 693 (1971).

14) O. Menis and T. C. Rains, *Anal. Chem.*, **27**, 1932 (1955).

15) K. L. Cheng, *Anal. Chem.*, **26**, 1895 (1954).