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Extraction and Spectrophotometric Determination of Palladium with Pyridine-2-acetaldehyde Salicyloylhydrazone

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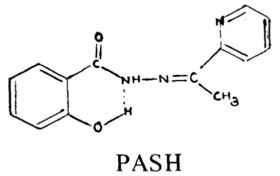
A simple and rapid method is proposed for the separation by solvent extraction and spectrophotometric determination of palladiuim(II) with pyridine-2-acetaldehyde salicyloylhydrazone (PASH). The optimum conditions were evaluated by studying critically pH, reagent concentration, and period of equilibration. The palladiuim was determined by measuring Pd(II)–PASH extracted complex in chloroform at 425 nm. The proposed method offers excellent separation of Pd(II) from rutheniuim, cobalt, nickel, copper, and rhodium. The method was applied for the analysis of palladium catalyst and platinum ores.

Palladium is one of the platinum group metal and finds extensive use in the electrical industry. It is used in grids for electronic tubes, in electrodes for high quality spark plugs, for contact metal in printed circuits. Due to corrosion resistance, nature and in breadth of alloying ability, palladiuim and its alloys have widespread use in dental, medical devices and in jewellery manufacture. Palladium is a good catalyst and is used for hydrogenation and dehydrogenation reactions.

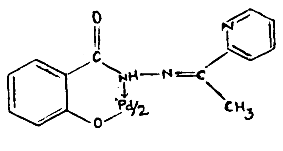
Palladium forms intensely colored complexes with hydrazones, dyes, dithiocarbonates, oximes, and thio compounds. Various extraction methods with di-2-pyridylmethanone-2-(5-nitro)pyridylhydrazone,[1] 3,5-dichloro-2-(2,4-diaminophenyl)pyridine and trichloroacetate,[2] di-2-pyridyl ketone benzoylhydrazone,[3] 2-(2-pyridylmethylimino methyl)pyrrole,[4] isonitrosothiocamphor,[5] *o*-butyl dithiocarbonate,[6] diphenylthiovioluric acid,[7] 2-carboxy-2′-hydroxy-5-methylazobenzene[8] have been reported for the extraction of palladium. However the existing methods suffer from limitations such as longer extraction period,[1–3,7] temperature control,[6] narrow pH range[4–6] less stability,[2] and interference from other ions.[1,6,8] In some methods[3–5] the extraction is not quantitative.

In the present work, we propose a simple and rapid method for the extraction, separation, and spectrophotometric determination of palladium using pyridine-2-acetaldehyde salicyloylhydrazone[9] as a reagent. PASH reacts with palladium to give yellow colored complex extractable into chloroform. Beer's law was obeyed over the concentration range af 0.5 to 3 ppm palladium at 425 nm. Effect of pH, reagent concentration, shaking period, foreign ions etc. on the extraction behavior have been studied.

PASH and its Pd(II) complex has the following structures;



PASH



Pd-PASH

which were confirmed in IR spectrum.

Experimental

Instruments. A Bausch and Lomb spectronic-20 model with glass cells were used for absorbance measurement. A digital ELICO pH meter type LI-120, was employed for pH measurements.

Palladium Stock Solution. This was prepared by dissolving 1 g palladium chloride (Johnson Matthey, London) in 2 ml of concentrated hydrochloric acid, and diluted to 100 cm^3 with double distilled water and standardized with dimethylglyoxime.[10]

PASH was synthesized by the method reported in the literature.[9] For the extraction of palladium 0.1% m/v solution of PASH was used.

All reagents and chemicals used were of A.R. quality. Solutions of other ions were prepared by dissolving the corresponding salts in distilled water or dilute hydrochloric acid.

Extraction of Palladium. To an aliquot of solution containing 30 μg of palladium(II), adequate amount of acetic acid was added to have the desired acidity and the volume was made up to 10 ml. The solution was equilibrated with 10 ml of chloroform containing 1 ml of 0.1% reagent solution in DMF–chloroform for one minute. The organic extract was collected in a 10 ml standard flask and made up to the mark with chloroform, if necessary. The absorbance of the solution was measured at 425 nm. Calibration curve was prepared. Unknown amount of palladium(II) was determined from the calibration curve.

The optimum extraction conditions were established by the studies on effect of pH, reagent concentration, period of equilibration. Tolerance of diverse ions was also studied.

Results and Discussion

Extraction Conditions. The extraction of palladium was carried out over the pH range 0.5 to 10. The results indicate that the quantitative extraction of palladium occurs from pH of 2 to 4.25 (Fig. 1). Above and below this pH range extraction was found to be incomplete.

Absorption Spectra. The absorbance spectrum of the 30 μg of palladium complex extracted into chloroform showed that $\lambda_{\max}$ occurs at 425 nm (Fig. 2). The

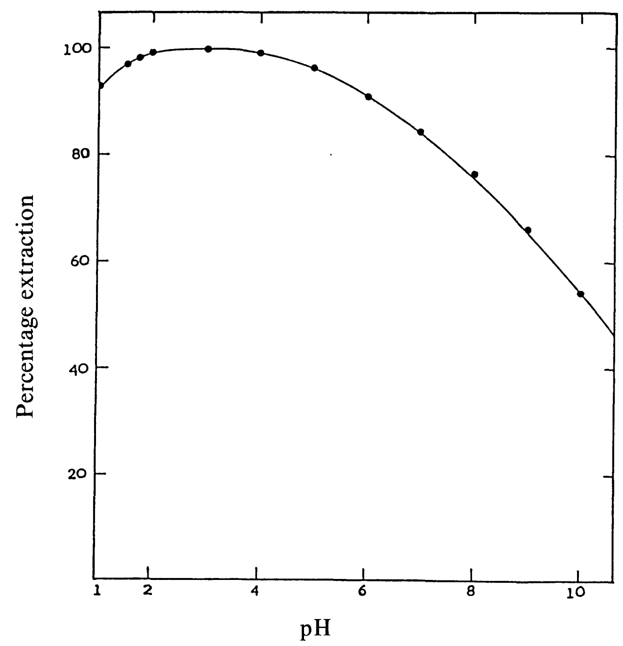


Fig. 1. Effect of pH on the extraction of palladium(II) with PASH into chloroform.

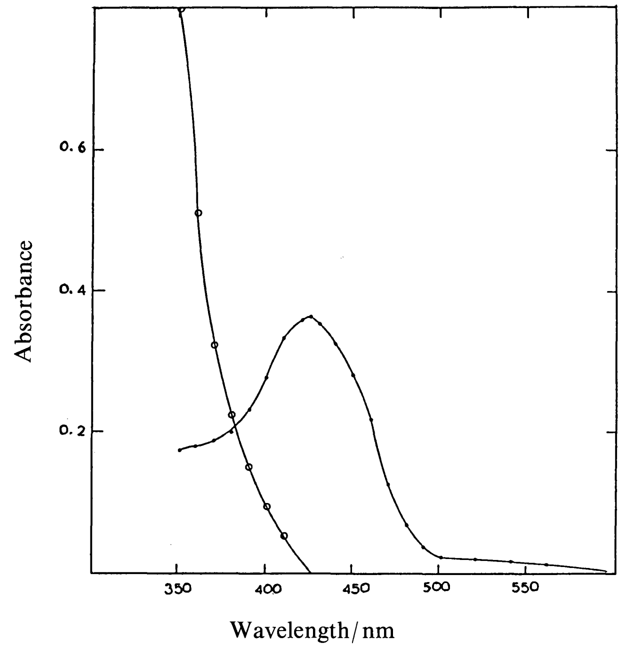


Fig. 2. Absorption spectrum of Pd–PASH complex and PASH in chloroform. Concentration of Pd(II)=2.8×10^{-5} M, concentration of PASH=7.8×10^{-4} M.
(○) reagent vs. chloroform.
(●) Pd–PASH complex vs. reagent.

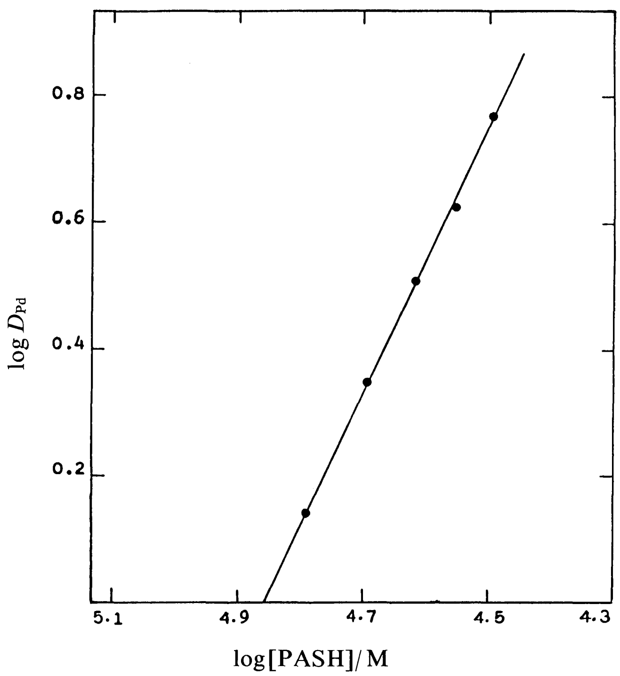


Fig. 3. Distribution ratio of palladium(II) as a function of PASH concentration.
Pd=2×10^{-5} M, shaking time=60 s,
Slope of the plot of log D_{Pd} vs. log C=2.02, C=log [PASH]/M.

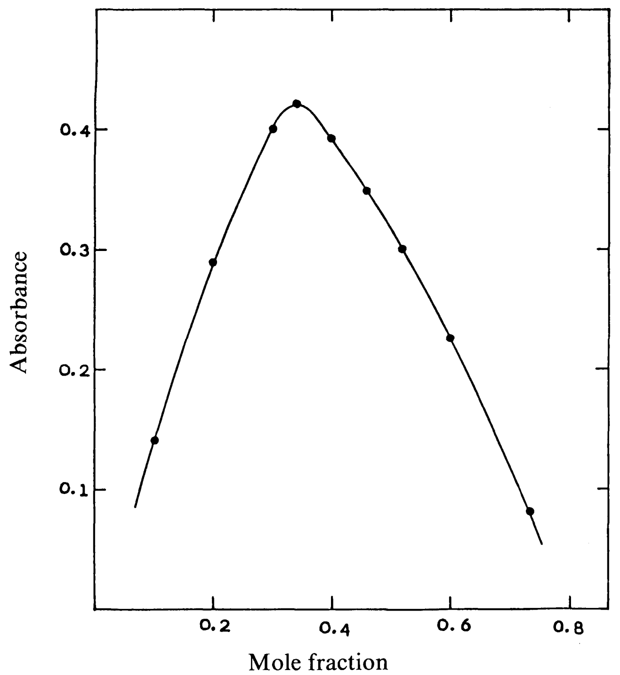


Fig. 4. Plot of composition of the extracted species by Job's continuous variation method.
Concentration of Pd(II) and PASH =2×10^{-4} M.

optimum metal : ligand ratio was found to be 1 : 14. The system obeys Beer's law over the concentration range of 5—30 μg of palladium per 10 cm^3 of organic phase and the absorbance is stable for at least 56 h. It is further noted that extraction is quantitative after 1 min of equilibration time. The sensitivity of the method defined by Sandell's is 8.2 ng cm^{-2} at 425 nm and the molar absorptivity is 13,087.90 l mol^{-1} cm^{-1}.

Nature of the Extracted Species. The composition

Table 1.

Sr. No.	Synthetic mixture/Sample	Pd(II)[b] found: Present method μg	Pd(II)[b] found: Known method[13] μg
	Synthetic mixture[a]		
1	Ru, (100); Rh, (60); Pd, (50).	50.00	50.10
2	Co, (100); Cu, (25); Pd, (20).	19.95	20.00
3	Ni, (50); Cu, (25); Pd, (60).	60.00	60.05
	Samples	Pd(II) found/%	Certified value/%
1	Pt-ore	4.05	4.02
2	Pt-ore	3.03	3.05
3	Pd-$BaSO_4$ catalyst	0.88	0.89
4	Pd-$CaCO_3$ catalyst	4.43	4.44
5	Pd-charcoal catalyst	27.00	27.00

a) Values in parentheses are in μg. b) Average of three determinations.

of the yellow Pd(II) complex was determined by the log-log plot of distribution ratio versus pyridine-2-acetaldehyde salicyloylhydrazone (PASH) concentration, at a fixed pH. It shows molar ratio of 1:2 with respect to PASH (Fig. 3). The composition was verified by Job's continuous variation method[11,12] (Fig. 4). Equimolar solution of reagent and Pd(II) (2×10^{-4} M) were mixed in complimentary mixture of five ml volume. Thus the probable extraction mechanism can be expressed as:

$$Pd(H_2O)^{2+} + 2(C_{14}H_{12}O_2N_3)^- \rightleftarrows Pd(C_{14}H_{12}O_2N_3)_2 + 2H_2O$$

Effect of Foreign Ions. Various cations and anions were investigated in order to assess the tolerance of these ions on the extraction of palladium. The tolerance limit for the variation was fixed at ±2% in absorbance. The results showed that in the extraction and determination of 30 μg of palladium(II), 20 mg each of chloride, iodide, sulfate, nitrite, nitrate, phosphate, thiocyanate, acetate, oxalate, and tartarate did not interfere. Bromide, fluoride, lead(II), calcium(II), uranium(VI), and nickel(II) did not interfere upto 10 mg. Molybdenum(IV) upto 5 mg, bismuth(III), zinc(II), iron(III), and copper(II) upto 2 mg did not interfere. Titanium(IV), thorium(IV), platinum(IV), gold(III), rhodium(III), silver(I), cobalt(II), and selenium(IV) can be tolerated up to 1 mg. Tungsten(V), barium(II), arsenic(III), tellurium(IV), cadmium(II), and chromium(III) upto 500 μg and 200 μg of ruthenium(III) did not interfere. EDTA and thiourea upto 10 mg are masked with copper(II) sulfate (5 mg). Interference of 1 mg of vanadium(V) and 5 mg of Sn(II) masked by sodium fluoride and sodium citrate respectively.

Palladium Estimation: I) Synthetic Mixtures. The separation of palladium(II) from synthetic mixtures of associated metals containing ruthenium(III), cobalt(II), nickel(II), copper(II), and rhodium(III) with varying combinations was carried out. A suitable aliquot of synthetic mixture was taken in a beaker and the pH of the solution mixture was adjusted to 2.0 with 1 ml of 7.5 M (1 M=1 mol dm^{-3}) acetic acid and the volume was made to 10 ml with distilled water. The mixture was extracted with 10 ml of chloroform with 0.1% PASH. The two phases were separated and the organic phase was stripped with 10 ml of 0.75 M acetic acid (pH≈2). The absorbance of the organic phase was measured at 425 nm using reagent blank. The amount of palladium(II) was determined from calibration curve. Number of synthetic mixtures were analyzed by the developed and known method[13] and reported in Table 1. Pd-PASH complex did not show traces of associated metals at the working pH. They show a good agreement between the amount added and estimated.

II) In Catalysts. Palladium catalyst was analyzed. About 0.1 g samples were digested with mixtures of concentrated perchloric acid and nitric acid and brought into solution. An aliquat of the solution was used far the extraction and determination of palladium.

III) In Platinum Ores. Platinum ore of about 0.1 g was digested with 20 cm^3 of aquaregia. The solution was filtered off and then the solution was made up to 25 cm^3. An aliquot of solution was taken and extracted as per general procedure. The values determined by the present method were in good agreement with the certified values. The results of the analysis are presented in Table 1.

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