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Ion Pair Extraction and Separation Studies of Palladium

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A simple and rapid method is proposed for the extraction, separation, and spectrophotometric determination of palladium from salicylate media using Aliquat 336 dissolved in xylene as an extractant. The optimum conditions were evaluated from a critical study of pH, salicylate concentration, Aliquat 336 concentration, and period of equilibration. The palladium in the Aliquat 336 phase is determined spectrophotometrically with 4-(2-pyridylazo)resorcinol (PAR) at 530 nm. The proposed method described the scheme for the separation of platinum, nickel, copper, cobalt, zinc, and manganese from binary mixtures. The method was extended to the analysis of palladium catalyst and platinum ores.

Palladium, one of the platinum group of metals, find 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. Palladium is a good catalyst and is used for hydrogenation and dehydrogenation reactions. Due to corrosion resistance, non-toxic nature and in breadth of alloying ability palladium and its alloys have widespread use in dental, medical devices and in jewellery manufacture.

Various extraction methods such as dioctylsulphoxide,1) trioctylamine,2,6,9) trilaurylamine,9) tribenzylamine,9) triisooctylamine,10) octylaniline,3) Aliquat 336,4,8) trioctylphosphinoxide,5) and trioctylphosphine7) have been reported for the extraction of palladium from media such as chloride, bromide, nitrate, perchlorate, acetate, succinate, and EDTA. However the existing methods suffer from limitations such as longer extraction period,1—3) narrow pH,4) solvent dependence,5) and temperature control.7) In some instances the extraction is not quantitative.2,3,8,9)

In the present work, we propose a simple and rapid method for the extraction, separation, and spectrophotometric detemination of palladium from sodium salicylate solution using Aliquat 336 as an extractant. The palladium in the Aliquat 336 phase is determined spectrophotometrically with 4-(2-pyridylazo)resorcinol (PAR) at 530 nm.

Experimental

Instruments. Absorbance measurements were made on a Unicam SP 500 spectrophotometer with 1 cm silica cells and pH was measured on a Control Dynamics digital pH meter with a combined glass electrode.

Palladium Stock Solution. This was prepared by dissolving 0.16 g palladium chloride (Johnson Matthey, London) in 100 cm^3 of distilled water containing 2 cm^3 of hydrochloric acid. The solution was standardized by the dimethyl glyoxime method.11) Solutions of lower concentrations were prepared by the dimethyl glyoxime method.11) Solutions of lower concentrations were prepared by appropriate dilution of stock solution.

Extraction Solution. A 5% m/v solution of Aliquat 336 (Fluka) in xylene was prepared, equilibrated with equal volume of 1 mol dm^{-3} sodium silicylate solution and used for the extraction of palladium(II).

Reagent Solution. 4-(2-Pyridylazo)resorcinol (PAR) solution, 0.1% m/v used for palladium determination.

All other chemicals used in this work were of analytical reagent grade.

General Extraction Procedure. To an aliquot of solution containing 4—30 μg of palladium add 0.4 g of sodium salicylate to give concentration of 0.1 mol dm^{-3} in a total volume of 25 cm^3. Adjust the pH of the solution to 5.0 with dilute hydrochloric acid or sodium hydroxide solution and equilibrate the mixture for 30 seconds in a separatory funnel with 10 cm^3 of 5% Aliquat 336 solution. Separate the two layers, discard the aqueous phase and add 2 cm^3 of 0.1% m/v PAR solution to the Aliquat 336 phase. After shaking the mixture for 90 seconds, separate the organic phase, and dry with anhydrous sodium sulphate and measure the absorbance of the orange colored palladium-PAR complex at 530 nm against a reagent blank.

Results and Discussion

Extraction Conditions. The extraction of palladium was carried out over the pH range 3.6—12.0 with various sodium salicylate concentrations (0.0125 to 0.125 mol dm^{-3}) and amine concentration (0.5—5% using xylene as the diluent). The results indicate that

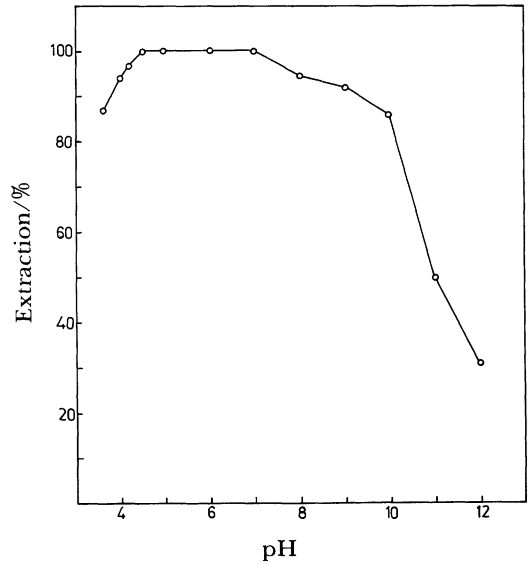

Fig. 1. Extraction of palladium as a function of pH.

the quantitative extraction of palladium occurs from 0.1 mol dm^{-1} sodium salicylate solution adjusted to a pH of 4.5—7.0 (Fig. 1). A single extraction for 30 seconds with 10 cm^3 of 5% Aliquat 336 is adequate for the quantitative extraction of palladium; prolonged shaking has no adverse effect on the extraction. The metal content in the Aliquat 336 phase is determined by measuring the absorbance of the colored complex and referring to the previously constructed calibration curve.

Spectral Characteristics. The extracted palladium may be determined spectrophotometrically in the Aliquat 336 phase with PAR. The palladium-PAR complex shows maximum absorbance at 530 nm (Fig. 2). The color system obeys Beer's law over the concentration range 4—30 μg of palladium per 10 cm^3 of organic phase and the absorbance is stable for at least 36 hours. The characteristic spectrophotometric data are reported in Table 1.

Nature of the Extracted Species. The log-log plot of distribution ratio versus salicylate concentration (at fixed pH and Aliquat 336 concentration) or versus Aliquat 336 concentration (at fixed pH and salicylate concentration) yielded a molar ratio of 1:2 with respect to both Aliquat 336 and salicylate (Figs. 3 and 4). Aliquat 336, which is a quaternary amine, acts as a liquid ion exchanger and extracts the anionic palladium-salicylate complex. Hence the extracted species was thought to be an ion-pair complex of probable composition $(R_4N^+)_2Pd(OC_6H_4COO)_2{}^{2-}$.

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 was defined as the amount of foreign ion required to cause a ±2% error in the recovery of palladium using the proposed method. The results showed that in the extraction and determination of 18 μg of palladium(II), 540 μg of platinum(IV), 360 μg

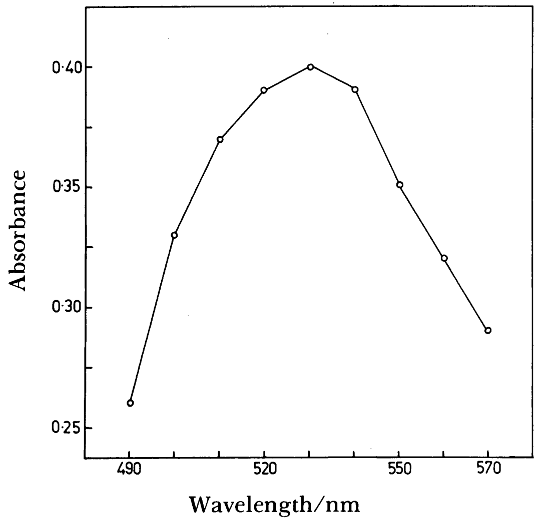

Fig. 2. Absorption spectrum of Pd-PAR complex in Aliquat 336.

Table 1. Spectrophotometric Data for Determination of Palladium after Extraction with Aliquat 336

Parameter	Value
Molar absorptivity	2.36×10^4 mol^{-1} cm^{-1}
Sandell's sensitivity	4.5 ng cm^{-2}
Mean absorbance[a]	0.400
Standard deviation of absorbance	0.006
Coefficient of variation	1.58%

a) Six determinations of 18 μg of palladium.

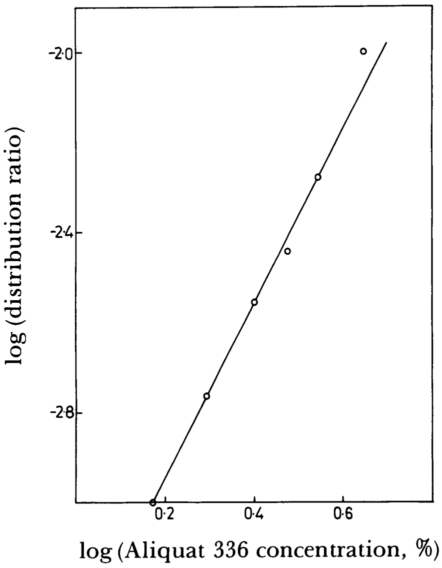

Fig. 3. Plot of log (distribution ratio) versus log (Aliquat 336 concentration) at a fixed salicylate concentration of palladium(II).

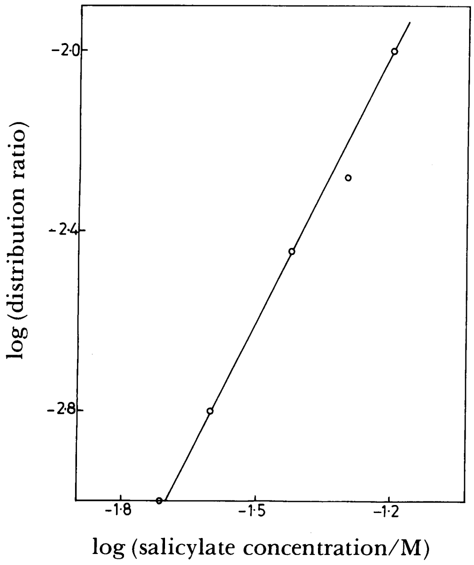

Fig. 4. Plot of log (distribution ratio) versus log (salicylate concentration) at a fixed pH and Aliquat 336 concentration of palladium(II).

Table 2. Analysis of Synthetic Mixtures

Sample	Composition of synthetic mixture[a]	Amount found[b] µg	Recovery/%	Standard deviation	Coefficient of variation/%
1	Pd(18)–Pt(250)	Pd, 17.9; Pt, 248.0	Pd, 99.4; Pt, 99.2	Pd, 0.089; Pt, 0.447	Pd, 0.497; Pt, 0.18
2	Pd(18)–Ni(50)	Pd, 18.0; Ni, 49.7	Pd, 100.0; Ni, 99.4	Pd, 0.109; Ni, 0.089	Pd, 0.605; Ni, 0.179
3	Pd(18)–Co(15)	Pd, 18.0; Co, 15.0	Pd, 100.0; Co, 100.0	Pd, 0.141; Co, 0.126	Pd, 0.783; Co, 0.84
4	Pd(18)–Cu(20)	Pd, 18.0; Cu, 19.9	Pd, 100.0; Cu, 99.5	Pd, 0.109; Cu, 0.155	Pd, 0.605; Cu, 0.779
5	Pd(18)–Zn(20)	Pd, 18.0; Zn, 19.8	Pd, 100.0; Zn, 99.0	Pd, 0.155; Zn, 0.167	Pd, 0.861; Zn, 0.843
6	Pd(18)–Mn(50)	Pd, 17.9; Mn, 49.6	Pd, 99.4; Mn, 99.2	Pd, 0.11; Mn, 0.089	Pd, 0.615; Mn, 0.179

a) Values in parentheses are masses quoted in µg. b) Average of six determinations.

each of aluminium(III), arsenic(III), molybdenum(IV), and tellurium(IV), 270 µg each of tungsten(V) and sulfate, 180 µg each of silver(I) and tartrate, 145 µg each of manganese(II), chromium(IV), bismuth(III), antimony(III), nitrate, bromide, fluoride, and oxalate, 90 µg each of barium(II), titanium(IV), gold(III), iodide, ascorbate, chloride, phosphate, nitrite, and thiocyanate, and 55 µg each of lead(II), citrate, and cyanide did not interfere. By prior washing of the organic phase with water 180 µg each of nickel(II), cobalt(II), and copper(II) do not show interference in the subsequent estimation of palladium with PAR. However, equal amounts of uranium(VI), iron(III), thorium(IV), zirconium(IV), and EDTA interfere severely and must be absent.

Separation of Palladium(II) from Platinum(IV). The extraction of palladium(II) into Aliquat 336 by the recommended procedure facilitates its separation from platinum(IV) as it does not extract into Aliquat 336 and remains completely in the aqueous phase. The aqueous solution containing platinum(IV) is evaporated to dryness, treated with perchloric acid to decompose salicylate and finally taken up in water. Platinum is then determined with tin(II) chloride method spectrophotometrically.[12] The extracted palladium(II) from the organic phase is subsequently determined as described under general extraction procedure. The results of the separation are reported in Table 2.

Separation of Palladium(II) from Nickel(II), Cobalt(II), Copper(II), Zinc(II), and Manganese(II). The separation of palladium(II) from binary mixtures containing nickel(II), cobalt(II), copper(II), zinc(II), and manganese(II) was made possible by stripping nickel, cobalt, copper, zinc, or manganese with water. These metal ions were determined spectrophotometrically using dimethyl glyoxime,[13] 1-(2-pyridylazo)-2-naphthol,[14,15] or 4-(2-pyridylazo)resorcinol[16,17] method. Finally palladium was determined in the organic phase as described in the general extraction procedure. The recovery of palladium and that of the added ion were greater than 99.0%. The separation results of binary mixtures are reported in Table 2.

Analysis of Palladium in Standard Catalyst and Platinum Ores. The proposed method was applied to the separation and determination of palladium in palladium catalyst and platinum ores. Catalyst sample of 0.1 g was digested with mixtures of concentrated perchloric acid and nitric acid and brought into solution. An aliquot of the solution was used for the extraction and determination of palladium. Platinum ore of 0.1 g was digested with 20 cm^3 of aqua regia. The silica was filtered off and then the solution was made up to 25 cm^3. An aliquot of solution was taken and extracted per general extraction procedure. The values determined by the present method were in good agreement with the

Table 3. Analysis of Palladium(II) in Standard Samples

Sample	Palladium present (Certified value)/%	Palladium found/%[a)]	Standard deviation	Coefficient of variation/%
Pd/Charcoal catalyst	27.0	26.8	0.109	0.408
Platinum ore	3.05	3.02	0.025	0.612
Platinum ore	4.02	4.00	0.019	0.628

a) Average of six determinations.

certified values. The results of the analysis are presented in Table 3.

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