Separation & Purification Reviews
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597294

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Abraham Warshawsky[a]
[a] Department of Organic Chemistry, Weizmann Institute of Science, Rehovot, Israel

To cite this Article Warshawsky, Abraham(1983) 'Ion Exchange Separation of Platinum and Palladium by Nucleophilic Displacement With Thiocyanate or Thiourea[1,2]', Separation & Purification Reviews, 12: 1, 37 — 48
To link to this Article: DOI: 10.1080/03602548308068396
URL: http://dx.doi.org/10.1080/03602548308068396

SEPARATION AND PURIFICATION METHODS, 12(1), 37-48 (1983)

ION EXCHANGE SEPARATION OF PLATINUM AND PALLADIUM BY NUCLEOPHILIC DISPLACEMENT WITH THIOCYANATE OR THIOUREA[1,2]

Abraham Warshawsky
Department of Organic Chemistry
Weizmann Institute of Science
Rehovot, Israel

Abstract

The separation of platinum and palladium, by adsorption onto weak base anion exchange resins, Amberlite XE 299, or ionex (derived from Amberlite XE-305) from 1M hydrochloric acid, followed by ligand substitution with sulfur nucleophiles is described.

In the thiourea system, cationic thiourea complexes are produced, which cannot be readsorbed into the resin. In the thiocyanate system the formation of $Pd(SCN)_4^{2-}$ is favored in both solution and polymer phases. The $Pd(SCN)_4^{2-}$ readsorption into the anion exchange resin is the basis for the separation of platinum from palladium.

1. Introduction

In a previous paper in this series we have presented a method of separating platinum from palladium by coextraction into a teriary amine solution, followed by selective stripping of platinum with thiocyanate and selective stripping of palladium with thiourea.[3] Both methods rely on the lability of the d^8, square-planar complexes [Pd(II)] and the relative inertness of d^6, octahedral complexes [Pt(IV)].

In the present paper, the same principles were applied to the separation of platinum and palladium by selective elution from anion exchange resins.

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Two resins, a commercial anion exchanger, Amberlite XE-299, a weak base resin with some quaternary functional groups and a tertiary amine resin prepared from chloromethyl Amberlite XE-305 by reaction with diethyl amine (designated ionex) were tested.

2. Absorption of the Platinum Group Metals (PGM) from 4M HCl Solution in Presence of Base Metals

The absorption of the chloride complexes of the transition metals ions, including the PGM ions, onto anion exchange resins is acid dependent. The absorption of platinum, palladium ("primary PM") and gold is highest from dilute HCl solutions (0.01-0.5 M), whereas the absorption of Rh, Ir, Ru, Os (secondary PM) and the other transition metals (particularly Fe, Ni, Cu, Co), increases with increasing HCl concentration.

The experiments were conducted from 4M HCl in order to allow some absorption of the secondary PM's and base metals. This in order to test the efficiency of the washing and stripping procedures.

The coabsorption of metal ions from a solution containing a representative mixture of the ions, onto Ionex is shown in TABLE I and Figure 1. Amongst the PGM the absorption order (in terms of increasing breakthrough volumes) is:

$$\mathrm{Rh} < \mathrm{Ru} < \mathrm{Pd} < \mathrm{Ir} \simeq \mathrm{Pt}$$

amongst the base metals the absorption order is:

$$\mathrm{Ni} < \mathrm{Cu} < \mathrm{Fe}$$

The same absorption order, in slight variations, is observed for Amberlite XE-299 (TABLE II).

TABLE I

ABSORPTION OF METAL IONS ON IONEX[a] FROM 4 M HCl SOLUTION

Volume passed (ml)	Metal Ion Concentration in Solution (p.p.m.)							
	Pt	Pd	Ir	Rh	Ru	Cu	Ni	Fe
0[b]	7735	4620	228	259	256	1010	2200	7160
10	3,6	0,3	<1	<0,1	0,4	0,4	<0,2	<0,2
20	1,8	0,5	4,1	46,9	5,2	295	1050	212
30	1,8	0,3	8,1	145	13,6	346	1650	------
40	3,6	0,7	15,4	255	26,5	412	2090	0,8
50	5,3	0,5	19,0	259	40,5	1010	2320	180
60	7,1	30,5	19,0	264	110	1035	2310	1820
70	25	285	20,4	264	173	1070	2274	3410
80	109	1225	24,5	262	239	1090	2270	4990
90	353	2760	25,8	256	259	1080	2320	5896
100	763	4170	29,1	255	-----	1090	2300	6090
110	1590	------	35,4	260	-----	1080	2210	7360
120	2860	4890	41,0	256	-----	1060	2220	7010
130	3943	4550	45,6	258	-----	1065	2220	-
140	4830	4670	50,6	257	-----	1030	2210	-

[a] IONEX is diethylpolybenzyl amine, prepared from Amberlite XE-305.

[b] i.e. concentration in starting solution.

3. Elution with Thiourea (Tables III, IV)

The elution of the absorbed PGM ions with 20 g/l thiourea is a ligand substitution reaction between the resin-bound PGM chloride complex and thiourea as follows:

$$[\textcircled{P} - NR_3H^+]_{(x-n)}\,[MCl_x^{(x-n)^-}] \xrightarrow[HCl]{X.Tu} [\textcircled{P} - NR_3H^+]Cl^- + xCl^- + M(Tu)_4^{2+} + M(Tu)_6^{3+} + M(Tu)_6^{4+}$$

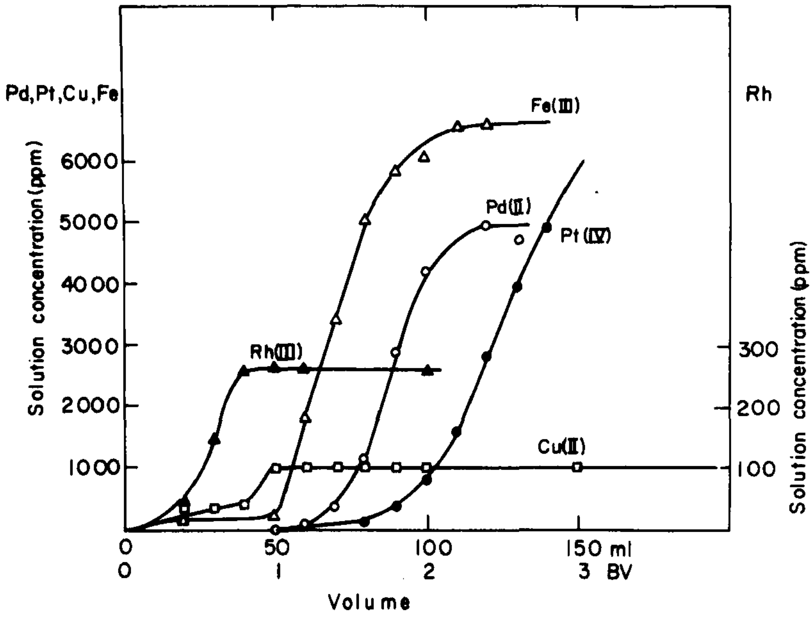

Figure 1

where: M = metal ion in various oxidation states (2^+, 3^+, 4^+)

n = charge on metal ion

x = number of chloride ligands

Tu = thiourea

The high nucleophilicity of the incoming thiourea ligand drives the transformation of the anionic chloride complexes of the PGM to cationic thiourea complexes of the PGM. In contrast to the selective stripping of palladium from tertiary-amine solvents[4] the thiourea elution is nonselective. The reason for this is the short and controlled stripping time in the liquid-liquid extraction step. In comparison, the reaction time in the ion-exchange elution step is much longer (approximately 50 minutes), which allows the slower Pt(II) and Pt(IV) complexes, to react, with thiourea.

TABLE II

ABSORPTION OF METAL IONS ON AMBERLITE XE-299 FROM 4 M HCl

Volume Passed (ml)	Metal Ion Concentration in Solution (p.p.m.)							
	Pt	Pd	Ir	Rh	Ru	Cu	Ni	Fe
0	7735	4620	228	259	256	1010	2200	7160
10	6,6	1,3	<5	<1	1,4	3,8	7,7	4,5
20	13,3	0,9	5	1,8	5,2	61,6	954	197
30	8,8	0,3	5	8,4	3,2	5,4	1929	15,4
40	8,8	0,4	5,5	15,1	5,4	11,2	2049	17,9
50	8,8	1,4	5,6	18,7	9,7	35,6	1984	30,6
60	6,1	0,4	7,4	28,8	13,1	413	2023	582
70	6,1	0,7	14,5	49,1	19,3	917	2185	1880
80	9,4	1,1	23,3	81,5	29,1	1179	1941	3511
90	17,7	2,3	17,3	165,5	49,3	1333	2144	5319
100	10,0	1,0	24,0	282	68,3	1283	1987	6039
110	6,6	4,2	71,0	282	100	1346	2226	7099
120	9,2	99	133	260	139	1321		7071
130	15,9	975	190	263	221	1386		7061
140	57	3116	187	249		1381		7012
150	202	4867	134			1298		7042
160	415	4569				1278		
170	911	4608		269	281	1050	2200	

4. Elution with Thiocyanate (Table V, Figure 2)

The elution of the PGM-loaded resin with 30 g/l thiocyanate is mechanistically more complicated than the thiourea elution. The mechanism of this reaction can be explained by analogy to the corresponding reaction with a tertiary-amine solvent, as follows:

a. Elution of chloride complexes by anion replacement

TABLE III

ELUTION OF IONEX[a] WITH THIOUREA (20 g/l)

Solution volume (ml)	Metal Ion Concentration in Solution (p.p.m.)							
	Pt	Pd	Ir	Rh	Ru	Cu	Ni	Fe
10	7,9	3,3	8,3	14,7	1,0	<1	<1	9,2
20	3,9	2,2	2,8	11,8	2,1	"	"	4,6
30	166	7,2	<1	11,8	1,0	"	"	5,5
40	2786	1548	5,5	11,8	1,0	"	"	4,6
50	4460	2692	<1	17,7	4,2	"	"	3,7
60	5252	2477	<1	17,7	5,2	"	"	10,2
70	6313	2013	2,8	29,5	3,1	"	"	3,7
80		637	<1	29,5	2,1	"	"	5,5
90	4108	443	"	23,6	3,1	"	"	6,5
100		130	"	17,6	2,1	"	"	7,4
110	3571	280	"	26,5	1.0	"	"	2,8
120	3701	209	"	23,6	<1	"	"	3,7
130		148	"	23,6	<1	"	"	5,5
140	3636	73	"	17,7	2,1	"	"	3,7
150	1295	29,1	"	14,7	<1	"	"	4,6

[a] After loading as described in TABLE I.

$$[\textcircled{P} - NR_3H^+]_{(x-n)}\,[MCl_x^{(x-n)^-}] \xrightarrow{NaSCN} [\textcircled{P} - NR_3H^+]SCN^- +$$

$$[MCl_x^{(x-n)^-}]$$

b. Ligand-substitution in solution phase:

$$MCl_x^{(x-n)^-} + xSCN^- \longrightarrow M(SCN)_x^{(x-n)^-}$$

TABLE IV

ELUTION OF AMBERLITE Xe-299[a] WITH THIOUREA (20 g/l)

Solution volume (ml)	Metal Ion Concentration in Solution (p.p.m.)							
	Pt	Pd	Ir	Rh	Ru	Cu	Ni	Fe
10	86	82	<1	3,7	8,1	0,7	2,2	7,7
20	12,4	6,0	"	2,1	9,4	0,6	1,1	7,0
30	5,7	3,0	"	2,5	5,4	1,5	1,1	12,1
40	1867	760	"	2,8	5,4	16,9	5,8	47
50	6118	4122	"	6,2	9,0	2,4	7,2	20
60	6410	5274	"	3,1	11,2	18,9	16,3	36
70	6883	5332	"	3,6	13,5	10,7	16,3	35
80	6857	4008	"	4,0	13,5	2,4	7,2	26
90	6650	2506	"	5,0	10,8	1,9	5,8	22
100	3587	695	"	6,4	18,0	3,9	11,6	23
110	2976	372	12,3	3,5	5,9	4,2	6,7	24,6
120	2841	239	<5	4,8	5,5	3,8	4,8	24,6
130	2941	147	<5	1,8	5,9	2,7	7,7	27,6
140	2841	112	<5	3,3	6,5	3,0	4,3	23,7
150	2874	104	<5	3,5	5,5	3,1	5,3	25,9
160	3049	80	22,5	0,4	10,1	6,3	7,2	35,9
170	3333	81	13,5	3,9	9,5	4,6	5,7	52,7

[a] After loading as described in Table 2.

Fast for: d^8 square-planar complexes [Pd(II)]

Slow for: d^6 octahedral complexes [Pt(IV), IR(III), Ru(III), Rh(III).]

c. Readsorption of thiocyanate complexes:

$$[\textcircled{P} - NR_3H^+]SCN^- + [M(SCN)_x^{(x-n)^-}] \longrightarrow [\textcircled{P} -$$

TABLE V

ELUTION OF IONEX[a] WITH NaSCN (30 g/l)

Solution volume (ml)	Metal Ion Concentration in Solution (p.p.m.)							
	Pt	Pd	Ir	Rh	Ru	Cu	Ni	Fe
5	8,7	3,6	3	1,6	21,9	ND	ND	ND
15	8,5	4,2	3	1,3	16,1			
25	11,1	7,3	3	1,1	13,5			
35	20,2	9,2	8,0	0,6	14,7			
45	1070	7,9	388	2,0	41			
55	3620	4,7	1850	3,8	87			
65	7810	1,6	1770	4,2	95			
75	6330	1,0	118	1,7	33			
85	4370	0,9	3	0,7	9,4			
95	3190	0,7	"	0,6	4,4			
105	2720	0,6	"	0,6	2,5			
115	2520	0,8	"	0,4	2,5			
125	2080	0,7	"	0,4	1,9			
135	1880	0,7	"	0,2	1,3			
145	1670	0,7	"	0,4	1,5			
155	1550	1,2	"	0,3	1,5	ND	ND	ND

[a] After loading as described in TABLE I.

ND = not detected.

$$NR_3H^+]_{(x-n)}[M(SCN)_x^{(x-n)^-}]$$

occurs with Pd(II) only.

d. Direct ligand substitution in polymer phase

$$[\textcircled{P} - NR_3H^+]_{(x-n)}[MCl_x^{(x-n)^-}] \xrightarrow{xSCN^-} [\textcircled{P} -$$

$$NR_3H^+]_{(x-n)}[M(SCN)_x^{(x-n)^-}] + xCl^-$$

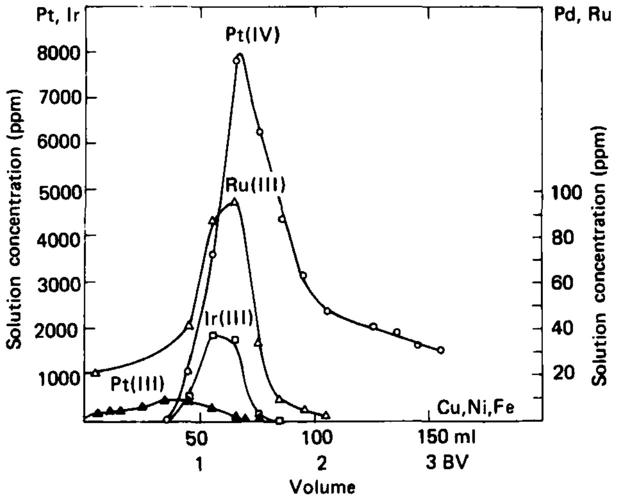

Figure 2

The experimental data (Table V, Figure 2) shows that all the d^6 octahedral complexes (Pt, Rh, Ru, Ir) are eluted with thiocyanate but the d^8 square planar Pd(II) is not eluted

In our earlier studies on tertiary-amine-thiocyanate system,[4] it was established that the reactions analogous to reactions (a) and (c) are fast, and consequently reactions (b) and (d) are the rate-determining steps, and their control will determine the efficiency of the Pd/Pt separation.

Examination of the shape of the elution curves (see Figure 2) indicates a considerable tailing of the Pt elution curve, indicating that $Pt(Tu)_4^{2+}$ readsorption is indeed taking place.

5. Discussion

The separation of platinum and palladium by "reactive elution" of their polymer-bound chloride complexes, with strong sulfur nucleophiles, has been studied for:

(i) neutral thiourea ligand

(ii) anionic thiocyanate ligand

Although both ligands possess high nucleophilicity constants,[5] the mechanism of those two reactions are completely different. In the thiourea elution step, separation may be achieved only if the results of substitution of the polymer-bound chlorocomplexes of palladium and platinum are distinctly different. Since this is not the case, and relatively long elution times are required, the thiourea elution fails to separate between Pd and Pt. Now, the positively charged $Pd(Tu)_4^{2+}$ and $Pt(Tu_6^{4+}$ complexes are stable and inert towards the anion exchange resin.

In the thiocyanate elution step, a much more complicated situation prevails. The products, obtained either by solution phase reaction (b) or by polymer phase reaction (d), are anionically charged and consequently have a larger affinity for the anion exchange resin. The key point in the separation between Pd and Pt is actually the rate of formation of their thiocyanate complexes via reaction (b) (paragraph 4).

Further consideration of the fate of the slow d^8 octahedral complexes shows that they are slowly converted, after separation from resin, into the thiocyanate complexes. Thus a special scheme for the interseparation of those elements (Pt, Rh, Ru, Ir) in the thiocyanate system has been elaborated and will be presented in a forthcoming paper in this series.[5]

The production of pure metal products from the pure platinum-sodium thiocyanate solution has been described in Reference 3. A typical procedure involves precipitation as sulfide followed by oxidative hydrolysis and reduction to a metal sponge. The pure polymer-bound palladium thiocyanate can be eluted with thiourea and precipitated as sulfide,[3] then further converted by oxidative hydrolysis to $PdCl_4^{2-}$ and then reduced to a metal sponge.

6. Experimental

6.1 Materials

Amberlite XE-299 is a product of Rohm & Haas, Philadelphia, U.S.A., Ionex, is prepared from chloromethyl-Amberlite XE-305 by reaction with excess diethylamine. The exchange capacity, for the resins in chloride form is 3.0-3.25 meq/gr.

7. Platinum Group Metal Salts

The platinum group metal salts were prepared at the analytical department of the National Institute for Metallurgy as described in Reference 6. A.R. grade metal was dissolved in HNO_3/HCl or Cl_2/HCl or Br_2/HCl mixtures in sealed tubes. Standard solutions containing the individual metal salts of Pd(II), Pt(IV), Au(III), Rh(III), Ru(III) and Ir(IV) were obtained. Addition of a reducing agent, as hydroquinone or $SnCl_2$, converted Pt(IV) to Pt(II) and Ir(IV) to Ir(III). Stock solutions of the individual metals were mixed at the appropriate ratios in various HCl solutions, to yield the mixed PGM-standard solutions.

8. Analysis of PGM Solutions, Solids, and Resins

A Techtron AA4 atomic-absorption spectrophotometer with a meter, or a digital readout and new Varian-Techtron hollow-cathode lamps were used in the accurate work. Routine analysis was carried on Techtron AA-1000 spectrophotometer. The wavelength at which absorption measurements were those of the most sensitive lines as follows (Å): Pt-2659, Pd-2448, Rh-3435, Ru-3499, Au-2428, Ir-2640.

Air-acetylene flame and a standard Techtron 10 cm grooved burner were used. Maximum sensitivity for Pt, Pd, Au was obtained with a lean flame, Rh required a normal flame, Ru a rich flame. 1% uranium as U_3O_8 was added as a releasing agent in standard analysis.

The determination of base metals is carried out directly for the major components (Ni, Cu, Fe). The minor components are determined after matching with standards prepared by sealed tube dissolution and addition of major base metal components.

X-ray fluorescence, has been used for determination of PGM in solids or resin samples. For the lighter elements, Ru, Rh, Pd, Ag, the K_2 lines are used for measurement. The heavier metals, Os, Ir, Pt and Au, are excited by gold and tungsten target tubes. In X-ray fluorescence analysis, inaccuracies most frequently result from variations in sample composition, the so-called "matrix effect". Emission spectroscopy was used to analyze base metal residues in pure PGM salts.

9. Metal Absorption and Elution Experiments (Tables I-V)

Columns, consisting of 25 ml of fully settled resins, were equilibrated with 4M HCl, and then a solution of 4M HCl containing (in g/l): Pt-7.735; Pd-4.62; IR-0.228; Rh-0.259; Ru-0.256; Cu-1.010; Ni-2.20; Fe-7.16, was passed at a rate of 1 ml/minute. Samples of 5 ml each, were collected and analyzed. After the adsorption experiment, excess 0.2 M HCl was passed to wash out any entrained ions.

The elution experiments were made on samples loaded separately, with solution of 20 g/l thiourea or 30 g/l thiocyanate at the same flow rates. Samples of 5 ml were taken and analyzed.

References and Notes

1. This work was initiated while the author has been employed by the National Institute for Metallurgy (now The Council for Mineral Technology), Randburg, South Africa, and in collaboration with T. Murphy.
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