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THE SEPARATION OF PLATINUM GROUP METALS (PGM) IN CHLORIDE MEDIA BY ISOTHIOURONIUM RESINS

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Abstract

Styrene-divinylbenzene copolymers incorporating isothiourea functional groups show a remarkable affinity for platinum-group-metal (PGM) ions in chloride media. The mode of ion binding to the resin depends on the equilibria between isothiourea (free base) form and isothiouronium (conjugated acid) form. This in return is related to matrix structure. A resin, Monivex, which shows high binding capacities for PGM ions in high acidities (2-6M HCl) is described. Equilibrium, rate and selectivity data, as well as process application data is presented and discussed. Electron microprobe studies are used to follow chemical changes in resin beads and ion regeneration patterns.

1. Introduction

The platinum group metals, platinum, palladium, rhodium, iridium, ruthenium, and osmium, called "PGM" for short, belong to the class of rare elements. This, together with the complexity of the minerals in which they occur, side by side with large excess of so called "base metals", makes the winning and separation of this noble group of metals both a challenging and important problem. More so, since many important processes in the chemical industry rely on catalysts prepared from this family of metals.

The current processes of recovery and separation of the PGM[1] are known from almost the early days of the discovery of platinum by Brownrigg and Watson in 1750. These ingenious processes are based on laborious, batch-type crystallization and distillation steps.

The introduction of modern ion exchange techniques has not overpassed those interested in PGM separation chemistry[2]. Yet, the vast number of separation methods in PGM analysis, using ion exchange techniques[3], have not led to new separation processes.

In view of expectations for increased use of platinum in catalytic converters installed in vehicles, the need to revise ion exchange techniques and look for selective resins to extract the PGM and gold, associated with the PGM, has risen. The work described in this paper and consecutive papers in this series, was aimed to devise new separation processes based on selective ion exchange and solvent extraction techniques.

2. Chloride complexes of the transition metal ions[4]

A logical approach to any separation problem brings into account both the aqueous chemistry of the metal ions and the chemistry of the functional group of the separating media. This is true in particular with the PGM, where the complex solution chemistry dictates the separation scheme. In hydrochloric acid media, a variety of metal ions form complexes of the general formula:

$$[MCl_x(OH)_y(H_2O)_z]^{n-x-y}$$

where n denotes the oxidation state of the metal. These complexes can be divided[4] into three distinct classes: The first class contains the true chlorocomplexes which occur through the complete range of HCl concentration, and are described by the general formula y=z=0 and x > n.

The first subgroup of this class contains those metals which form the same complex at all acid concentrations, namely: $AuCl_4^-$, $HgCl_4^{2-}$, $PdCl_4^{2-}$, $PtCl_4^{2-}$.

In the second subgroup, two different chlorocomplexes, equilibrate at intermediate acid concentration by expansion of their coordination spheres:

$AgCl_2^- \rightleftarrows AgCl_4^{3-}$
$TlCl_4^- \rightleftarrows TlCl_6^{3-}$
$BiCl_4^{2} \rightleftarrows BiCl_6^{3-}$

The second class of ions is characterized by the occurrence of a true chlorocomplex only in highly concentrated HCl. At intermediate acid concentrations, several anionic complexes are in equilibrium with each other:

PGM	$RuCl_5(H_2O)^{2-}$	$\rightleftarrows$	$RuCl_6^{3-}$;		
	$RhCl_4(H_2O)^-$	$\rightleftarrows$	$RhCl_5(H_2O)^-$	$\rightleftarrows$	$RhCl_6^{3-}$
	$OsCl_5(H_2O)^{2-}$	$\rightleftarrows$	$OsCl_6^{3-}$		
	$IrCl_4(H_2O)$	$\rightleftarrows$	$IrCl_5(H_2O)^{2-}$	$\rightleftarrows$	$IrCl_6^{3-}$
	$IrCl_5(H_2O)^-$	$\rightleftarrows$	$IrCl_6^{2-}$		
Base metals	$MoCl_5(H_2O)^{2-}$	$\rightleftarrows$	$MoCl_6^{3-}$		
	$CdCl_3(H_2O)_x^-$	$\rightleftarrows$	$CdCl_4^{2-}$		
	$SbCl_5(OH)^-$	$\rightleftarrows$	$SbCl_6^-$		
	$PbCl_5(OH)^-$	$\rightleftarrows$	$PbCl_6^{2-}$		

The third class of ions form true chloro-complexes in concentrated acid and at intermediate acid concentrations. These are in equilibrium with either neutral or cationic complexes:

$FeCl_2(H_2O)_5^+$	$\rightleftarrows$	$FeCl_3(H_2O)_3$	$\rightleftarrows$	$FeCl_4^-$
$Co(H_2O)_6^{2+}$	$\rightleftarrows$	$CoCl(H_2O)_5^+$	$\rightleftarrows$	$CoCl_3(H_2O)^-$
$CuCl(H_2O)_3^+$	$\rightleftarrows$	$CuCl_2(H_2O)_2$	$\rightleftarrows$	$CuCl_4^{2-}$
$ZnCl(H_2O)_x^+$	$\rightleftarrows$	$ZnCl_3(H_2O)_y^-$	$\rightleftarrows$	$ZnCl_4^-$
$GaCl(H_2O)_5^{2+}$	$\rightleftarrows$	$GaCl_4^-$		

The classification of the chloride complexes of the transition metal series can be summarized in the following way:

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As
Y	Zn	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi

The transition metal ions of the first raw form weak anionic complexes. From the second and third raw transition elements, palladium, platinum, gold and mercury (in the solid box, first subgroup of the first class) form anionic complexes as the predominant species in solution. On the right stands the second subgroup (in the bracketed box) notably silver and copper, which are closely associated with the PGM. Those elements exist in the form of equilibrating anionic species and their extraction behaviour is hard to predict.

On the left, stands the second class elements, notably Ru, Os, Rh, Ir also called the secondary PGM (due to their rare occurrence in comparison to Pt and Pd). Those elements exist in an equilibrating mixture of true chloride and pseudochloride complexes.

From this classification the following conclusions are derived: (1) The so-called primary PGM, Pt and Pd, and also gold and mercury will be extracted as a group with highest binding constants; (2) the secondary PGM, Ru, Rh, Os, Ir will also be extracted as a group but with lower binding constants; (3) all the other metal ions appearing in the bracketed box are likely to interfere with the extraction of the secondary PGM.

3. Iso-Thiurea Resins

In 1956, Parrish has prepared polystyryl iso-thiourea by the reaction of chloromethylated polystyrene and thiourea[5]. He did not, however, characterize this resin which he followed to hydrolyze and yield polybenzyl mercaptan. Koster and Schmuckler[6a] took interest in the chelating properties of the isothiourea resin in an attempt to stabilize the d^8 oxidation state of the noble metals. They were the first to discover the potential of isothiourea resins in the recovery of PGM[6b].

Examining the published[6a,6b,6c] properties of Srafion NMRR (commercial trade name for isothiouronium 2% D.V.B. - polystyrene resin), the following points stand out:

(1) Exceedingly high capacity for monovalent $AuCl_4^-$, against very low capacity for divalent ($PdCl_4^=$) and trivalent ($IrCl_6^≡$) ions.

(2) Very strong dependency on hydrogen ion concentration in solution.

(3) The difficulty to break the bond between metal and functional group, makes elutriation difficult, and necessitates burning the resin to recover the metals[6b].

The practical disadvantages of those points are obvious. A PGM resin should have a high capacity for PGM and not only for gold. It should be able to bind the metal ions from highly acidic solutions, obtained after chlorination of ores in concentrated hydrochloric acid. Finally, the metals should be recoverable by elution and not by combustion.

From the fundamental aspect the following question stands up: could it be that the PGM bind to the isothiourea groups of Srafion by an ion exchange mechanism (suggested by the resin's high capacity for gold) and only later in the polymer-bound state, subsequent chelation with the strong sulfur or nitrogen ligands, converts the ion pairs into hard-to-elute coordination complexes? If this is so, it can be reasonably assumed that variations in resin matrix can strongly effect the overall mechanism of ion binding to isothiourea resins. The correct answer to this question has a fundamental and practical significance.

4. The synthesis of an anion exchanger incorporating 2-benzylisothiouronium functional groups

In a research programme designated to select a polymeric matrix which will allow the PGM to be bound predominantly by an exchange mechanism, several experimental and commercial[7] styrene-divinylbenzene copolymers were examined. It was concluded that flexible matrices which are free to stand volume changes during the introduction of the iso-thiouronium groups are to be elected[8a,8b]. Subsequently a resin with high capacity and specificity for the PGM and elutable, was synthesized[8c,d] from a commercial starting material, Amberlite XE-305[9]. The properties of this resin, designated the code name Monivex[10] are described hereafter.

5. Ion complexation properties of isothiouronium resins

The ion complexation studies were aimed to obtain information on:

(1) Fundamental and mechanistic properties of the resin.

(2) Application and process data.

The following subjects were investigated:

(1) Metal binding capacity in relation to solution parameters, e.g. acidity, ion composition and concentrations.

(2) Rate of metal binding and release.

(3) Resin specificity to PGM.

(4) Elution phenomena.

(5) Resin stability.

(6) Resin performance under real conditions, including cyclic tests on binding and release.

(7) Scanning electron microscope studies.

The integrated information from those studies will be useful for any separation process based on isothiouronium resins.

5.1 Solutions

The standard PGM solutions tested in this work were prepared by the staff of the analytical department of the National Institute for Metallurgy, by dissolution of the appropriate metal in aqua regia, chlorine/HCl or bromine/HCl. The solutions were evaporated to dryness to ensure removal of excess oxidizing agent, and made up to desired concentration by the addition of the right volume of an acid with known strength. Thus normally, unless otherwise mentioned, the sodium salts of Pt(II), Pd(II), Au(III), Rh(III), Ru(III), Ir(III) and Os(IV) chlorides were handled. Addition of slight excess of oxidizing agent converted Pt(II), Ru(III) and Ir(III) to Pt(IV), Ru(IV) and Ir(IV).

The dissolution of various PGM standards, and the analysis of various samples, solutions, resins are described in reference no. 11.

5.2 Metal binding capacity in relation to solution acidity[8]

The metal binding capacity for the individual PGM was determined by equilibrating resin samples in solutions of equivalent ion concentration in varying HCl concentration. In all cases, a large amount of metal ion retained in the solution after the resin was parted.

The binding capacity for Monivex is given in Table No. 1 and plotted in Fig. No. 1.

TABLE 1

Loading capacities for Monivex from different concentrations of hydrochloric acid

Conditions	Solutions:
Resin: 100 mg (air dry)	**5 ml, each containing one of the following:**
Time: 120 min	Au 90.3 mg, Pt 82.65 mg, Pd 96.70 mg Ru 17.50 mg, Rh 17.65 mg, Ir 15.54 mg

Acid normality N	metal per gram of dry resin, mg					
	Pt	Pd	Au	Ru	Rh	Ir
0.05	482.0	439.0	859.0	150.5	111.7	163.1
0.2	386.5	322.0	687.5	105.3		149.9
0.5	340.5	212.0	608.0	108.2	110.0	156.81
1.0	309.0	185.5	566.0	112.8	97.2	185.5
2.0	280.5	167.0	505.0	113.4	87.4	165.5
4.0	246.5	134.5	466.0	137.2	71.2	155.7
6.0	231.5	119.5	444.5	134.2	59.6	151.0

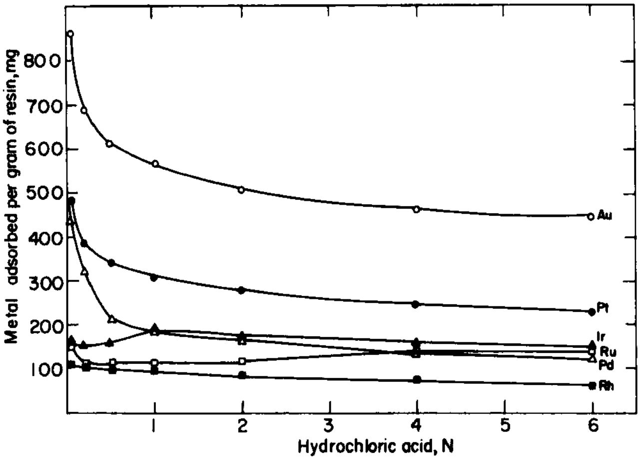


FIGURE 1

Monivex capacity for PGM ions in the acidity range 0-6 M HCl.

For comparison, the equivalent data for Srafion NMRR established under the same conditions[12] is given in Table No. 2.

The comparison between Srafion NMRR and Monivex shows that both resins have similar loading capacities from dilute acids (0.05 M HCl) which drops drastically for Srafion in 6M HCl, while for Monivex a long plateau remains. The metal binding capacities for Monivex from solutions containing approximately 3-4 gpl of Rh, Ru, Ir, and 20 gpl of Pt, Pd, Au, do not reach the theoretical exchange capacity for a fresh resin (4.13 mmole/g), except for gold which is loaded to the maximal capacity (4.3 mmol $AuCl_4^-$ per gram resin).

5.3 Equilibrium distribution factors[13]

Evidently, the high binding capacities reflect very high distribution factors. Equilibration of resin samples with individual PGM solutions at various concentrations, allowed the plotting of equilibrium distribution data. Figure 2 presents the distribution

TABLE 2

Loading capacities for Srafion*

Conditions	Solutions:
Resin: 100 mg (air dry)	5 ml, each containing one of the following:
Time: 120 min	Au 90.3 mg, Pt 82.65 mg, Pd 96.70 mg Ru 17.50 mg, Rh 17.65 mg, Ir 15.54 mg

Acid normality	Pt	Pd	Au	Ru	Rh	Ir
0.05**	488	218	1100		190	158
0.10	176	120	285	74	62	7
0.36	155	113	268	62	43	5
0.50	163	122	275	72	51	5
1.0	112	104	275	61	31	8
2.0	64	96	247	49	21	8
6.0	14	74	30	16	9	3

* Unpublished results, K. Dixon, Anal. Depart. NIM (ref. 8b).

** From ref. 6a.

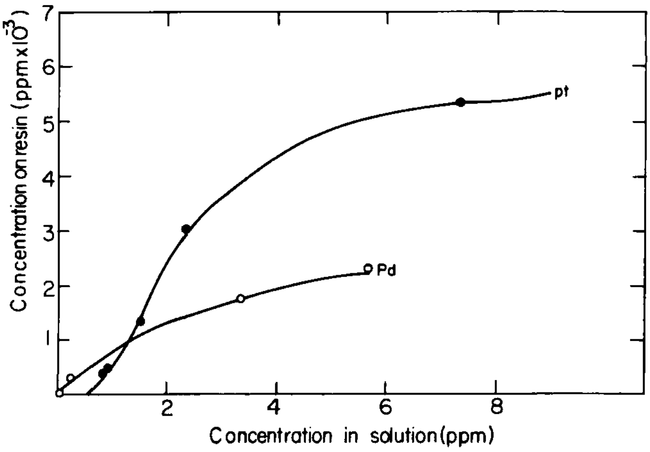


FIGURE 2

Distribution coefficients for Pt(IV) and Pd(II) from 0.5 M HCl. Ion concentrations (in ppm): Pd 0.04-52; Pt 0.12-120; Fe 1.12 10^5; Cu 3.12.10^4; Ni 2.94 10^3.

of Pt(IV) and Pd(II) from very dilute solutions (0.12-120 ppm Pt, 0.04-40 ppm Pd) in 0.5 M HCl), containing also the common base metals (BM) in 10^3-10^6 excess.

The distribution factors are in the order of 1000. Figure No. 3 shows the equilibrium distribution of the secondary PGM (rh(III), Ru(III), Ir(III) and Ir(IV)) from 4M HCl, through a wide range of their concentration. The equilibrium factors range between 50-150 and are relatively low in comparison to Pt and Pd. It is important to note that the change in oxidation state of Ir did not effect much its distribution factor. The effective range of PGM ion adsorption, by solid-liquid equilibration, starts at 0.1 ppm for Pd and Pt and only at 4 ppm for Rh, Ru, Ir. It is expected that this threshold will be reduced when column operation is used.

5.4 Selectivity factors

The selectivity factors for the PGM over five common base metals in the divalent and trivalent oxidation states were determined under conditions which allowed nearly maximal saturation of the resin sites, in order to simulate the condition which exist

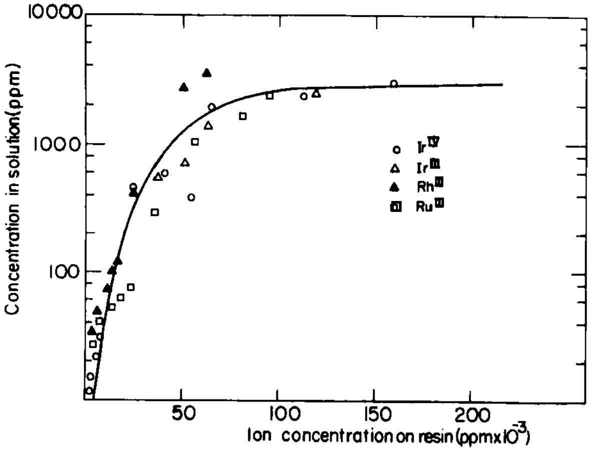


FIGURE 3

Distribution coefficients for Rh(III), Ru(III), Ir(III) and Ir(IV) from 4 M HCl.

during the normal operation of columns near the breakthrough point, in two different acidities 0.2 N, and 1.0 N HCl. The concentration of base metal was either 1 or 6 gpl. The results are shown in Table 3.

The selectivity factors for the PGM over the base metals (S^{M}_{BM}) were calculated from the concentration ratio of the resin-bound metals. It is clear that increasing the initial base metal concentration has an effect on the distribution factors, but only in the case of Fe(III) there is a considerable lowering of the selectivity factor due to ion exchange process. In the case of the other metals, physical adsorption causes the variations in selectivity factors. Again the selectivity factors for Pd and Pt are 10^1-10^2 higher than for Rh.

5.5 Rate of ion complexation

The rate of ion complexation by Monivex was determined from solutions of varying concentrations of metal ions. Since ion exchange processes in resins are usually controlled by diffusion within the resin particle, the dependence of the rate of complexation on solution concentration may relate to the mechanism of ion binding. The rate data was obtained by equilibrating a resin sample of 20-50 mesh size, with the appropriate solution, and following the change of the ion concentration in solution. The results obtained have only a comparative value, as for the calculation of rate parameters homogeneously sized resin beads must be taken.

The rate of metal complexation of the PGM and gold from 0.05M HCl is given in Table No. 4. Half approach to equilibrium values ($t_{\frac{1}{2}}$) is reached in all cases after less than 5 minutes.
The rate of Pt and Pd binding from 4M HCl solution and a wide range of ion concentrations is shown in Fig. 4 and Table 5. The $t_{\frac{1}{2}}$ for Pd and Pt from 4.10^{-5} gpl Pd and $1.2.10^{-4}$ gpl Pt is 30 minutes, but less than one minute from 14.5-50.3 gpl solutions. The faster rate of Pd binding from 4 M HCl compared to the rate of binding from 0.05 M HCl, is significant. In our opinion it shows that the rapid

TABLE 3

Selectivity factors

Base-metal (B.M.)	Acid (N)	Conc.(g/l) of B.M.	% Metal on resin		$S^{Pt}_{B.M.}$	% Metal on resin		$S^{Pd}_{B.M.}$	% Metal on resin		$S^{Ru}_{B.M.}$
			Pt	B.M.		Pd	B.M.		Ru	B.M.	
Fe^{3+}	1	1	25.08	0.119	*210.7*	21.13	0.023	*918.7*	-	-	-
	1	6	24.74	0.13	*190.3*	20.10	0.059	*340.6*	8.63	0.172	*50.2*
	0.2	1	31.78	0.167	*190.3*	27.45	0.0295	*930.5*	5.91	0.054	*109.4*
	0.2	6	31.27	0.171	*182.9*	23.42	0.0556	*418.2*	2.79	0.25	*11.1*
Cu^{2+}	1	1	26.15	0.0055	*4754*	20.18	0.0065	*3105*	7.28	0.039	*186.7*
	1	6	26.40	0.021	*1257*	20.60	0.0225	*915.5*	3.23	0.214	*15.1*
	0.2	1	30.7	0.07	*4386*	26.36	0.0159	*1658*	7.85	0.041	*191.4*
	0.2	6	29.9	0.022	*1359*	26.17	0.031	*843*	7.98	0.131	*60.9*
Ni^{2+}	1	1	30.4	0.008	*3800*	23.1	0.011	*2100*	5.69	0.028	*203.2*
	1	6	30.0	0.022	*1363*	23.6	0.059	*400*	7.53	0.094	*80.1*
	0.2	1	27.7	0.016	*1731*	27.6	0.021	*1314*	8.29	0.029	*285.8*
	0.2	6	25.2	0.040	*630*	28.8	0.057	*505.3*	7.60	0.139	*54.7*
Co^{2+}	1	1	31.9	0.012	*2658*	24.5	0.007	*3500*			
	1	6	26.5	0.063	*420.6*	20.7	0.030	*690*			
	0.2	1	24.0	0.006	*4000*	27.5	0.017	*1612*			
	0.2	6	32.9	0.05	*658*	31.8	0.042	*757*			
Cr^{3+}	1	1	31.0	0.007	*4428*	29.2	<0.0001	$2.9\ 10^5$			
	1	6	33.3	0.051	*652.9*	21.54	0.0001	$2.1\ 10^5$			
	0.2	1	28.7	0.007	*4100*	29.14	0.0001	$2.9\ 10^5$			
	0.2	6	30.4	0.033	*921.2*	25.51	0.0001	$2.5\ 10^5$			

Conditions:

Resin: 100 mg (air dry)
Time: 30 min

Solutions:

ca 20 mg of individual base metals per ml of 1 N or 0.2 N hydrochloric acid, diluted with precious-metal solutions (see Table 2) to give a solution containing ca 20 mg of precious metals and 1 and 6 mg of base metals per ml.

TABLE 4

Rate of adsorption from 0.05 M hydrochloric acid

Time min.	metal per gram of dry resin, mg					
	Pt	Pd	Au	Ru	Rh	Ir
5	444	388	797	99.6	96.2	128.9
10	448	382	795	104.2	106.5	131.8
20	473	422	862	124.4	-	166.2
30	480	454	880	124.4	110.5	174.5
45	488	462	889	131.4		174.1
60	491	474	902	129.1	125	174.6

Conditions

Resin: 100 mg

Time: 5 to 60 min.

Solutions: 5 ml, each containing one of the following:

Pt, Pd, Au ∿ 100 mg

Ru, Ir, Rh - 10 to 20 mg

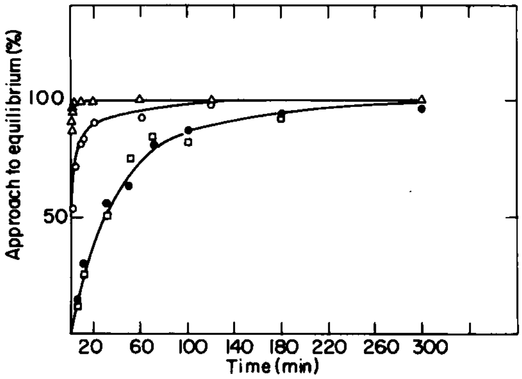


FIGURE 4

Rate of Pt(IV) and Pd(II) complexation on Monivex at 20°C from 4 M HCl (equilibrium values after 1000 min).

□——□ 0.12 ppm Pt ●——● 0.04 ppm Pd
○——○ 50.3 g/l Pt △——△ 14.5 g/l Pd

TABLE 5

Rate of loading of platinum and palladium from 4M hydrochloric acid

Time	Platinum on resin		Palladium on resin	
min.	mg/5 g	%	mg/5 g	%
0.5	850	53.22	722.3	99.7
1	778	48.71	722.3	
2	860	53.85	722.8	99.77
4	1137	71.19	722.8	
6	1132	-	723.2	
8	1300	81.40	722.9	
10	1321	82.71	723.3	99.84
20	1444	90.41	723.5	
40	1461	91.48	723.5	
60	1480	92.67	723.4	
120	1570	98.30	724.4	100.0
1000	1597	100	724.2	

Conditions of test:		
	Head soln	Pt 53.0 g/l Pd 14.5 g/l } in 4 M HCl
	Volume	50 ml
	Resin	5 g
	Method	1 ml aliquot withdrawn, diluted to 10 ml with 4M HCl.

uptake of $PdCl_4^=$ by the resin, in 0.05 M HCl is followed by slow coordination, and is responsible for the overall slowdown in the rate of palladium binding to the resin.

The combined capacity for Pd and Pt from 4 M HCl is 3.0 mmole/g which indicates the binding of HMX_4^- species, as the resin capacity for $MX_4^=$ ion is only 2.07 mmole/g.

5.6 Elution of the resin-bound metals

Careful consideration of the ion binding data presented so far - the very slight dependency on acid concentration (Fig. 1), the high distribution factors (Figs. 2, 3) and fast complexation rate (Fig. 4) all suggest that the reverse reaction, namely the elution of the resin with excess acid, is going to be difficult. This was confirmed by experiments in which Monivex resin, loaded with the PGM metals was equilibrated with large volume excess of hydrochloric acid of varying concentrations. The experiments were repeated with a Monivex sample loaded with the combined five metals. The results shown in Table No. 6, complement very well the complexation data shown in Fig. 1, and suggests that although the PGM may be eluted by an anion exchange reaction with Cl^- (as HCl), it is not a practical elution scheme, and an elution step based on

TABLE 6

Elution of precious metals with various hydrochloric acid solutions

Normality of acid	Metal eluted, %					
	Pt	Pd	Ru	Rh	Ir	Au
			Individual metals			
2	22.47	12.7	11.8	10.1	6.1	0.6
4	45.93	38.0	32.5	11.7	25.2	19.6
5	45.03	25.1	27.1	11.4	25.4	21.5
6	44.68	40.3	39.0	15.9	28.0	25.5
7		37.0	43.1	14.7	-	25.6
9	42.70	36.3	43.2	13.5	35.5	27.9
			Combined metals			
2	-	15.7	-	-	-	0.2
5	42.7	26.5	38.7	14.0	-	2.6
7	42.4	18.7	34.0	33.0	-	2.1
9	25.1	9.1	24.8	14.3	-	1.7

Loading conditions: Pt - 55 gpl; Pd - 21 gpl; Au - 1.5 gpl
Rh - 1.7 gpl; Ru - 0.44 gpl; Ir - 0.45 gpl
in 4M HCl

a stronger driving reaction must be chosen. Elution with thiourea as suggested for Srafion[6a] seemed appropriate.

The rate of elution at 20°C of a fully loaded (from 4M HCl) resin, by 5% thiourea in 0.05 M HCl, is described in Table No. 7. Although both Pd and Pt are eluted fast and quantitatively, the rate of elution is slower than the rate of ion binding.

The rate of elution of Rh, Ru (loaded unto the resin from 4 M HCl) is shown in Fig. 5. The rate of elution at 30°C is very slow, and complete elution at reasonable time (120 min.) is accomplished at 68°C.

TABLE 7

Rate of elution

Time min.	Platinum conc. in solution (g/l)	% elution	Palladium conc. in solution	% elution
0.5	0.775	18.90	0.28	17.39
1	0.97	23.66	0.352	21.86
2	1.27	30.97	0.48	29.81
4	1.66	40.48	0.612	38.01
6	1.90	46.34	0.741	46.02
8	3.08	75.12	1.17	72.67
10	3.44	83.90	1.225	76.09
20	-	-	1.535	95.34
60	4.07	99.25	-	-
120	-	-	1.53	95.34
1000	4.10	100	1.61	100

Conditions of test: Resin 5 g

Resin loading Pt 1597 mg/5g, Pd 724.4 mg/5g } in 4M HCl

Resin shaken with 100 ml of 5 per cent thiourea in 0.05 M HCl

1 ml samples withdrawn for analysis. 20°C

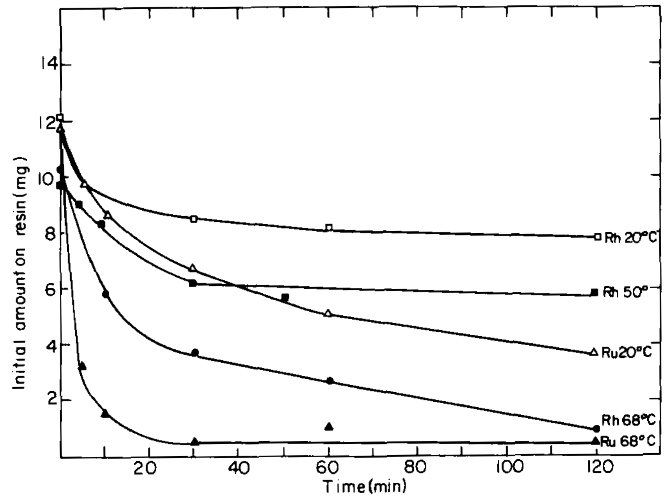


FIGURE 5

Elution of Rh(III), Ru(III) from Monivex: Dependency on temperature. Loading 4 M HCl: elution 410^{-2} M Tu in 0.1 M HCl.

The analysis of thiourea (Tu) solutions of the PGM, has imposed a considerable burden. Even small amounts of Tu or sulphate ions obtained after the oxidation of the samples, decreased significantly the flame response to the metal, and lower than-real results were recorded, The introduction of lanthanum or uranium as releasing agents into the samples to be determined by Atomic Absorption, has corrected the situation[11c,14]

5.7 Resin life test

The examination of the resin behaviour under alternating conditions for binding and elution, can point immediately to the suitability of the resin for continuous process application. Furthermore, it can give further support to the data obtained so far, analyzed under imposing conditions of varying mixtures and wide concentration range, and including interfering elements.

The so called "life tests" were divided into two series, Pt and Pd and the secondary PGM. This division, reflecting the differences in elution rates of the two subgroups, enabled a fast and reliable analysis of the experimental data generated.

The life tests were conducted at two acidities in order to differentiate between the two possible mechanistic pathways.

Life test no. 1: Pt, Pd adsorption from 0.5 M HCl

The resin was loaded with the metal ions by stirring a resin sample with 0.5 M HCl solution containing 38 gpl Pt and 17 gpl Pd, at 30°C. The loaded resin was washed with 0.05 M HCl and eluted with 5% Tu in 0.05 M HCl, by stirring at 30°C for 30 minutes. The Tu solutions were treated with 30% H_2O_2 in HCl at 80°C for one hour to allow complete oxidation of the thiourea, and then analyzed by atomic absorption. The results of life test no. 1, show that the elution of the resin is incomplete, and as a result the loading of the next cycle decreases considerably. After 10 cycles, the loading of Pt has decreased to half of its starting value. The beha-

TABLE 8

Life test no. 1: Loading from 0.5 M hydrochloric acid at 30°C

Cycle number	Platinum (mg per g of resin)		Palladium (mg per g of resin)	
	Loaded	Eluted	Loaded	Eluted
1	96.0	83.8	50.0	50.1
2	87.5	74.4	46.0	59.8
3	72.0	65.5	52.9	60.5
4	80.0	67.0	63.3	63.6
5	79.0	64.0	60.0	57.0
6	72.0	61.2	61.0	62.0
7	70	52.2	62.5	61.0
8	58.5	-	62.5	-
9	56.5	44.0	58.5	60.0
10	49.0	43.3	64.4	68.5

viour of palladium is different. It elutes quantitatively and is also picked up preferentially to platinum.

After 14 cycles the color of the resin turned to brown, indicating the presence of coordination complexes of thiourea, and the loading capacities fell further. The experiment was stopped.

Life test no. 2: Pt and Pd adsorption from 4 M HCl

This experiment was conducted as the test no. 1, except that loading was conducted from 4 M HCl at 50°C. During the first part of the test (50 cycles) the head solution contained only Pt and Pd in slight variations in concentration and metal ratios. The results of this experiment, shown in Table No. 9, prove the reversible behaviour of the resin under the test conditions.

In the second part of the test, the head solution was replaced by a 4 M HCl solution containing Pt and Pd and several other elements associated with platinoferrous ores (see Table 10). The addition of the large excess of base metals did not effect the

TABLE 9

Life test no. 2: Loading from 4 M HCl at 50°C

Cycle No.	Adsorption on resin mg		Head solution	Composition of head solution g/l
	Pt	Pd		
5	195.9	58.2	A	A =
10	198.2	64.0	"	Pt 44.0
20	192.5	66.3	"	
25	199.2	64.6	"	B
30	196.5	60.1	"	Pt 53.0
35	249.0	61.1	B	Pd 14.5
40	246.5	63.5	"	C
45	254.0	60.2	"	Pt 59.0
50	268.5	66.4	C	Pd 15.65

TABLE 10

Life test no. 2: Feed solution containing base metals*

Cycle No.	P.G.M.					Base Metals								
	Adsorbed (mg)		Eluted (mg)			Recovered in Solution (mg)								
	Pt	Pd	Pt	Pd	Fe	Cu	Ni	Sn	Pb	Zn	Co	Bi	Sb	Cr
Init. amount of metal	263	78.5	263	78.5	100	198	202	11.7	0.95	23.0	9.4	9.6	9.5	10
5	234.8	68.3	233	64.9	100	204	194	5.8	0.89	24.0	9.5	3.8	3.5	8.0
10	237.2	68.9	220	63.6	97	197	198	10.6	1.0	23.4	9.7	5.4	8.0	8.0
15	244.0	68.3	222	67.9	96.0	193	-	9.9	0.84	22.0	9.5	4.6	7.6	8.2
20	237.2	66.2	266	66.9	103.4	196	194	8.2	0.80	21.6	10.8	4.8	7.8	7.4
25	234.4	63.5	218	67.2	101.4	208	196	8.8	0.94	24.8	10.0	6.1	10.0	7.0
30	235.4	64.3	233	63.0	98.0	214	210	11.2	0.90	24.0	10.2	6.3	9.8	6.6
35	236.0	63.1	217	57.2	89.2	204	204	11.4	0.88	23.4	9.8	6.0	10.1	8.8
40	237.0	66.7	217	61.0		184	176	9.6	0.80	21.2	10.2	6.0	8.2	6.8

*Composition of the feed solution (g/1):

Pt(IV) 52.6; Pd(II) 15.7; Fe(III) 20.0; Cu(II) 39.60; Ni(II) 40.40; Zn(II) 4.6;
Cr(III) 2.0; Co(III) 1.88; Bi 1.93; Sb 1.89; Sn(IV) 2.33; Pb(II) 0.19, in 4 M HCl.

binding of either Pt or Pd, and from the transition metals, only bismuth and antimony showed signs of being adsorbed in some part by the resin.

After overall of 90 cycles the resin has retained its initial color (white) and showed the same adsorption properties as a freshly prepared resin sample. The elemental analysis of a resin sample after life test no. 2, is shown in Table 11.

From the two life tests it can be concluded, that loading of the resin from 0.5 M HCl, results in the partial formation of brown thiourea complexes and leads to resin failure in a very short time. Loading the resin from 4 M HCl produces a pale yellow resinate-PGM ion pair, completely elutable, and allows the continuous use of the resin. The presence of large concentration of base metals (115 gpl) does not interfere with the binding of the PGM. Bi and Sb do show some interaction with the resin.[15]

Life test no. 3: Rh, Ru, Ir from 4 M HCl

Incorporating the conclusions from life tests no. 1 and no. 2, and considering the slow elution of the secondary PGM, the life test was conducted from the following conditions: A mixture of Rh(III), Ru(III) and Ir(IV) in 4 M HCl, was loaded unto the resin by equilibration for one hour at 50°C. The loaded resin was washed with 0.5 M HCl and eluted at 85-95°C with 5% Tu in 0.1 M HCl. The

TABLE 11

Residual metals and nitrogen on the resin

Metal	Pt	Pd	Fe	Cu	Ni	Zn	Cr	Co	Bi	Sb	Sn	Pb
Resid. concn. ppm	392	53.2	178	42	20	37	ND	<10	2350	750	890	<10

Before % N	10.9 (3.89 mmole/g Tu groups)
After	8.7 (3.11 mmole/g Tu groups)

loaded resin acquired a brownish color, which changed to white after elution. The results for 10 cycles are presented in Table No. 12. The analysis of the solution showed good reproducibility for Rh and Ru, including good agreement between amounts loaded and eluted. The behaviour of iridium seemed erratic. Although loading was steady, very low recovery in the eluate was recorded. This comes from difficulties in the analysis of low concentrations of Ir in presence of thiourea or sulphate. Addition of Ir radiotracer, has confirmed the complete elution of Ir.

5.8 The adsorption of PGM on Monivex column[16]

At the completion of the evaluation of the basic properties of Monivex resin, column test work was conducted in order to obtain the information needed for stationary column operation. In the tests 75 ml of 20-50 mesh size beads were packed in a column. The solution passed was chosen to represent the typical composition of solutions from matte leach residues. During the loading stage the base metals Fe and Ni come out after 1 bed volume (Bv) but copper was initially retained on the resin (it was found later that this is due to precipitation of Cu^{2+} with free thiourea. This fact was later used as a test for the completion of thiourea washing from the resin). The PGM breakthrough capacity is reached after 6-8 Bv. The operational capacity for the PGM is 0.5 mmole/ml resin, under the conditions tested.

TABLE 12

Results of the cyclic tests for Ir, Ru, Rh

Metal loaded (mg)	Cycle No.					
	1	2	3	4	5	6
Ir	20.8	22.3	21.7	22.7	22.8	24.3
Ru	21.4	21.2	21.5	22.7	22.4	20.8
Rh	29.5	28.9	28.4	28.9	29.5	28.5

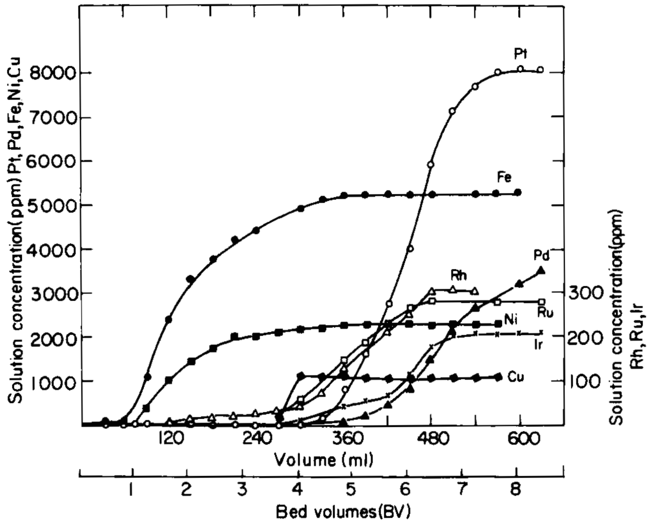


FIGURE 6

Column tests: Loading of PGM and other metals on Monivex from a metal mixture in 4M HCl. Ion concentrations (in ppm): Ir(III) - 194; Rh(III) - 260; Ru(III) - 255; Cu - 1050; Ni - 2280; Fe - 5163; Pd - 3607; Pt - 7792. temp. 20°C flow rate: 3 ml/min.

The resin washing with 0.5 M HCl is described in Fig. 7. Complete washing of adsorbed Fe, Ni, Cu (Fig. 7a) is achieved by 0.5 Bv of solution (the residual values of Ni and Cu are <1 ppm, and Fe 3.5 ppm).

The residual high levels of Pd and Pt (60 and 330 ppm) only point out to some elution process. The secondary PGM, Rh, Ru, Ir, are washed efficiently by IBV of 0.5 M HCl and are not eluted (Fig. 7b).

The thiourea elution of the loaded and washed resin was conducted in two steps. The cold elution (20°C) bringing out the majority Pd and Pt (98%) peaking at 2BV with some of the secondary metals peaking at 2.5-3 BV (Figs. 8a, circles, and 8b, triangles). The hot elution at 90°C brings out the residual Pt and Pd (2% of original value) and the majority of the secondary metals after ½ BV

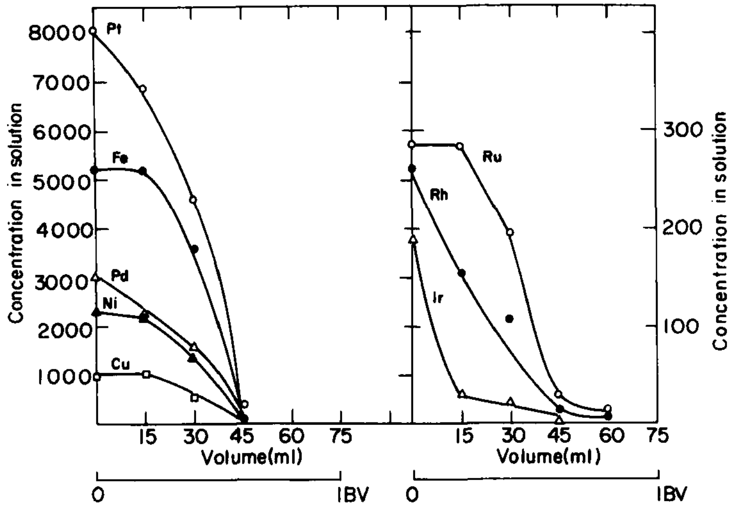


FIGURE 7

Column tests: washing with 0.5 M HCl. (a) Pt, Pd, Fe, Ni, Cu. (b) Ru, Rh, Ir. Residual values at 1 bed volume (ppm) Cu - 0.3; Ni <1; Fe - 3.5; Pd - 62; Pt - 334.

(Fig. 8a, triangles, 8b, circles). Two important conclusions may be drawn from the elution experiments; the cold elution allows very efficient recovery of Pd and Pt, which are concentrated by a factor of 2-3 in comparison to the starting loading solution. Also very good separation from secondary PGM: The first eluate has (Pt+Pd) to (Rh+Ru) ratio of 300:1. Secondly, the presence of base metals in the eluate was not detected, and this points to the very high efficiency of the washing step.

5.9 The oxidative conversion of the PGM-thiourea complexes into chloride complexes[17]

The thiourea complexes of the PGM are relatively little known, they are not well soluble and are not convenient for further refinement. The chloride complexes on the other hand, are well known, very well soluble in water and their behaviour in various

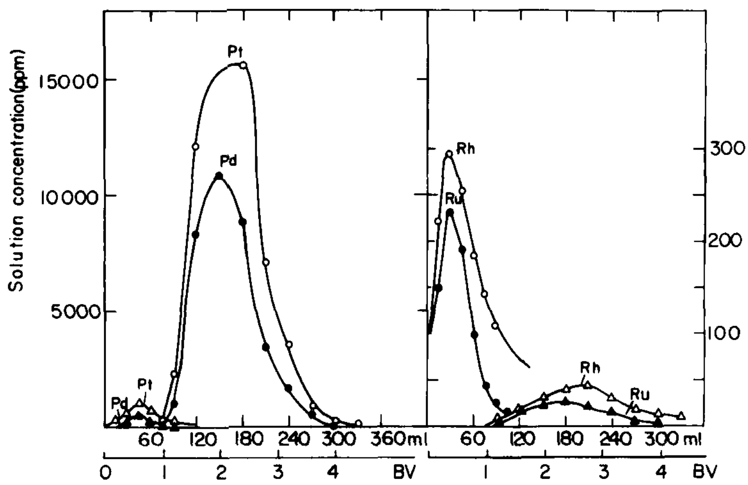


FIGURE 8

Column tests: elution with 5% thiourea in 0.05 M HCl.
(a) Pt, Pd ○—○ ●—● 20°C, △—△ ▲—▲ 90°C.
(b) Rh, Ru ○—○ ●—● 90°C, △—△ ▲—▲ 20°C.

extraction systems widely studied. For those reasons, an oxidative conversion procedure was developed.

Since the direct substitution of the thiourea ligand in a PGM-thiourea complex is extremely slow, the conversion was conducted in presence of an oxidant such as H_2O_2 or Cl_2, in hydrochloric acid. Under these conditions the thiourea ligand is converted to CO_2/N_2 gases, and is replaced by chloride ligands. The completion of the conversion procedure was tested by extracting a sample into a testing amine solvent (e.g. trioctylamine): The thiourea complex is completely insoluble in such a solvent while the chloride complexes are very well soluble. Under typical conversion conditions (one hour at 70°C, Cl_2/HCl) a solution containing: Pt 5.6 gpl, Pd - 2.1, Au - 0.18, Ru, Ir 0.05 gpl was converted with the following yields: Pt - 99.95%; Au - 99.5%; Ru, Ir > 90%.

A modification of this procedure[17b], making large scale conversion more convenient, is alkaline hydrolysis of the thiourea ligand at pH 11.5 at 100°C for one hour. This precipitates the sulfide complexes (having an average composition of PGM to S of 1:2), which are immediately oxidized in water slurry by Cl_2. The recoveries for the conversion procedures as determined many times on considerable quantities of metals are quantitative: Au, Ru, Rh, Ir - 99.95%; Pd, Pt - 99.997%.

6. Process flowsheet and pilot plant work[18]

The work described so far has demonstrated that a flowsheet using Monivex resin for the recovery of PGM is available. The flowsheet includes the following elements:

(1) Adsorption of the PGM from HCl solutions, in the concentration range of 3-5 M, preferably 4 M, containing PGM in wide compositions and concentrations, and in presence of large excess of base metals;

(2) Washing step - 0.5 M HCl;

(3) Cold elution with thiourea for the recovery of Pd, Pt;

(4) Hot elution - for the recovery of Ru, Rh, Ir.

(5) Conversion of the thiourea - PGM eluate into PGM chlorocomplexes.

(6) Continuation to separate the PGM from each other by any selected means.

Considering the information on the efficiency of Monivex operation under column conditions or solid-liquid distribution conditions, it was decided that the resin properties will be best shown in a continuous ion exchange operation based on solid-liquid distribution. A small continuous ion exchange pilot plant was erected: The results of this work[18] are beyond the scope of this paper and will be described elsewhere.

7. Electron microprobe studies[19]

Electron microprobe provide an excellent tool for the study of morphological and chemical transformations, taking place during consecutive chemical steps inside the resin bead.

In the preparation of the samples polished sections were prepared of the various resins, and those were studied in reflected light as well as with a stereo-microscope. In some cases fractured beads were studied directly.

New, unused Srafion NMRR consists of completely homogeneous transparent yellow spheres which turn honey-brown upon loading. The densely packed gel (Fig. 9, internal structure, X10300 magnifi-

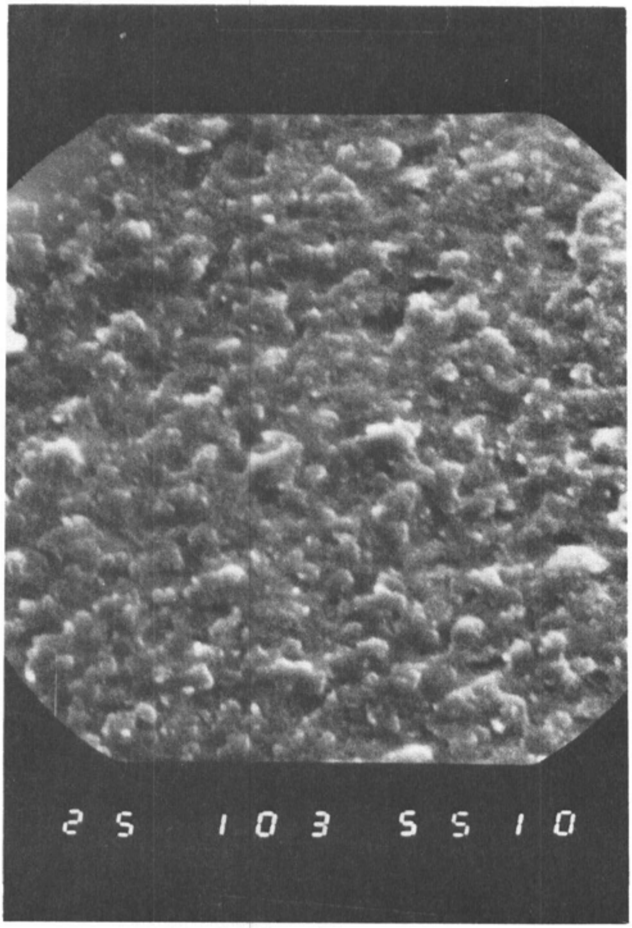


FIGURE 9
Internal structure of Srafion. X10300 magnification.

cation) turns into a stacked arrangement after Pt complexation from 4 M HCl (Fig. 10).

New unused Monivex resin consists of homogeneous white spheres. The internal structure of Monivex (Fig. 11) has the usual

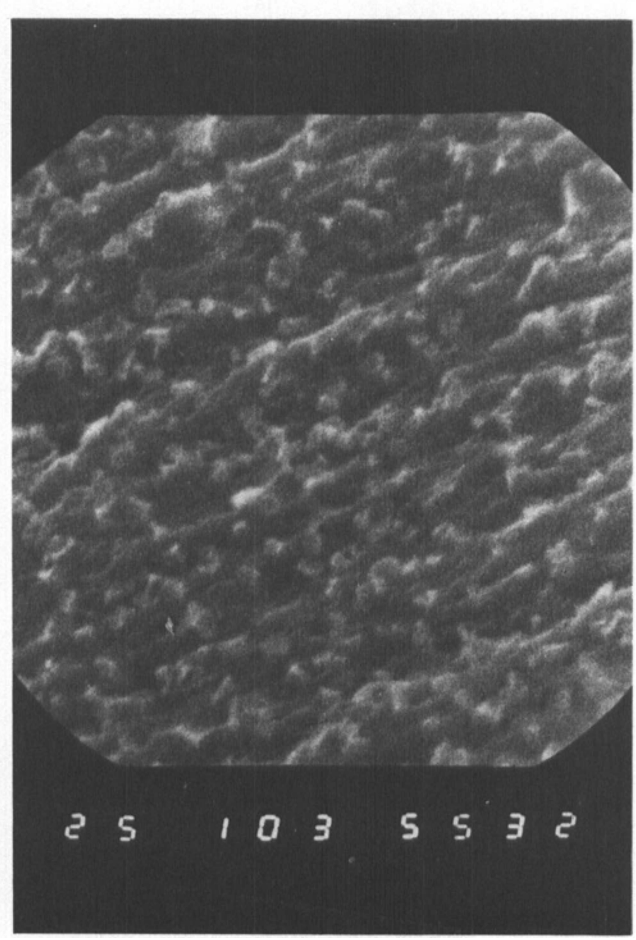


FIGURE 10

Internal structure of Srafion - Pt complex. X10300 magnification. Loading from 4M HCl.

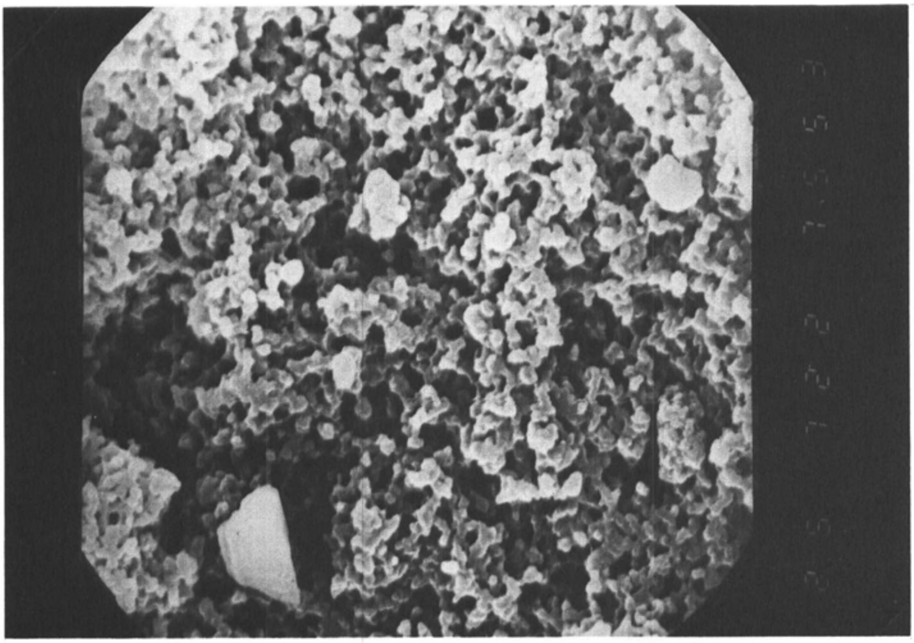


FIGURE 11

Internal structure of Monivex x 7220 magnification.

agglomerate appearance typical to macroporous resins and does not change upon Pt loading from 4 M HCl.

Table No. 13 shows the relative distribution of Pt for Monivex and Srafion NMRR, loaded under the same conditions.

Monivex resin loaded from 4 M HCl has an homogeneous appearance. The sulfur-to-platinum count ratio is quite steady throughout the cross-section of the bead. In contrast, a Monivex resin loaded from 0.05 M HCl, has a zoned appearance, and the concentration of platinum falls off gradually going from the outer zone into the core zone. The average concentration of Pt on Srafion resin loaded from 4 M HCl is 4-5 times lower in comparison to Monivex loaded from the same conditions. In addition the Pt concentration decreases five fold going from the outer zone to the core zone.

TABLE 13

Average relative count rates for platinum loaded Monivex and Srafion resins

	Cl	S	Pt
Loaded Monivex (unzoned)	42	54	32
Loaded Srafion	55	59	7
Loaded Monivex (zoned):			
core zone	61	3	0
intermediate zone	46	59	33
outer zone	37	55	39

This phenomenon is related to the size of the bead. Larger beads have lower platinum counts in the centre.

7.1 Examination of Monivex resin subjected to various treatments

Anticipating resin behaviour under various conditions is of interest for the following reasons:

(1) The chemical stability of polymer-bound isothiouronium group is not well known.

(2) Recovery of residual precious metals from poisoned resins is of significance.

Fresh Monivex samples were subjected to the following conditions (see Table 14):

(1) Alkaline hydrolysis (columns 2, 3).

(2) Oxidative acid hydrolysis (columns 4, 5, 6).

Used resin was subjected to the following:

(1) Standard elution (column 7).

(2) Various oxidation conditions, followed by standard elution (8, 9, 10).

It seems from the results presented in Table No. 14, that polymer-bound isothiourea groups undergo rapid alkaline hydrolysis at 75°C, but do not hydrolyze at 20°C. The resistance to acid hydrolysis, and to oxidizing conditions is remarkably high.

TABLE 14

Platinum loading from 4M HCl after various treatments

Treatment	Resin type	% activity in Pt binding
1) -	Fresh	100
2) 24 hrs 0.1N NaOH 20°C	Fresh	100
3) 6 hrs 0.1N NaOH 75°C	Fresh	10.2
4) 24 hrs 5% H_2O_2 - 1.0M HCl 20°C	Fresh	97.8
5) 6 hrs 5% H_2O_2 - 1M HCl, 75°C	Fresh	96.4
6) 24 hrs 10% NaOCL 1M HCl 20°C	Fresh	97.6
7) 5% Tu elution	Pilot Plant	46.5
8) 0.1N NaOH (1 hr, 20°C followed by 5% H_2O_2 - 1 hr, 70°C) 5% Tu elution	Pilot Plant	24.3
9) 5% H_2O_2 - 1M HCl (24 hrs, 20°C) then 5% Tu elution	Pilot Plant	46.5
10) Cl_2 - 70°C 1 hr then 5% Tu elution	Pilot Plant	30.9

The behaviour of a used resin is analogous to the behaviour of a fresh resin. The high stability to oxidative hydrolysis conditions allows recovery of residual bound metals, without any loss in subsequent binding activity (column 8, Table 14).

It is interesting to follow up by electron microprobe analysis the changes taking place in a resin subjected to cyclic treatments. A resin sample subjected in the laboratory to simulated plant conditions (namely, loading from a solution obtained by dissolution of matte-leach-residue (MLR) and adjusted to 4M HCl, then washing with 0.5 M HCl, and hot elution (90°C) with 5% thiourea) has the following properties: The resin suffered physical damage from the magnetic stirrer, the particles are covered with elemental sulfur, easily recoverable by washing with CS_2. Otherwise was in good condition, being homogeneous in appearance. No metal accumulation was found, except 0.1-1.0% of selenium (after 90 cycles).

The used pilot plant sample obtained for the electron microprobe study had a long (6-8 month) and varied use. Many times being subjected to unsuitable conditions, as long exposure to hydrolytic conditions.

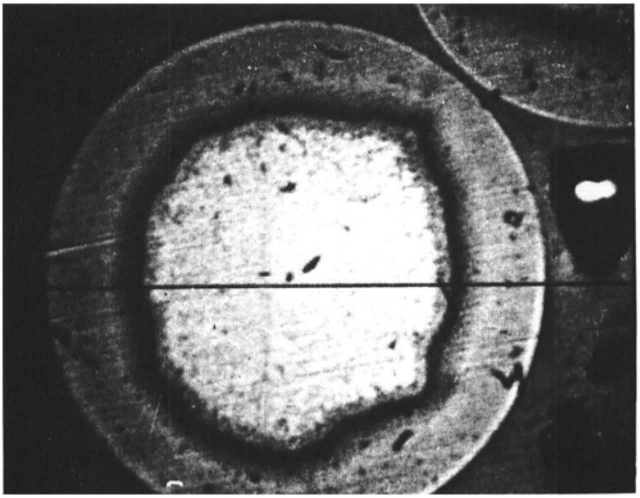
The optical examination showed the hydrolyzed pilot-plant samples to have, without exception, an outer translucent zone, which is either greenish or brownish in colour. This surrounds an inner core that is white where the outer zone is greenish and cream where the outer zone is brownish (see Fig. 12). The shape of the inner core is sometimes round concentric to the outer zone, sometimes irregular in shape, even transcending the outer zone up to the edge. Very occasionally a central core can be present.

The elemental distribution through the bead cross-section (Fig. 12) shows the dark zone area to have a maximum for sulfur and minimum for Pt. The inner core has significantly less sulfur and more Pt.

Some beads were caught in the transition from the zoned state to the homogeneous state. They have lost the strongly zoned area, which has expanded into a weakly developed outer-zone area, and a central bright core area. Again the dark zone has a higher sulfur-to-Pt count ratio, than the central core which has a very even distribution of both S and Pt (see Fig. 14).

In the samples treated for 24 hours a greenish or brownish translucent outer zone is present in spheres that have a cream core. The shape of the core can be round or irregular. Very occasionally multiple zoning with a completely transparent inner core can be seen. Most beads have been transferred into completely homogeneous S-to-Pt count ratio, and resemble the general appearance of a fresh Monivex resin (Fig. 15).

In some beads a very interesting phenomenon was observed. They possess a very narrow-ring dark zone of varying diameter (see



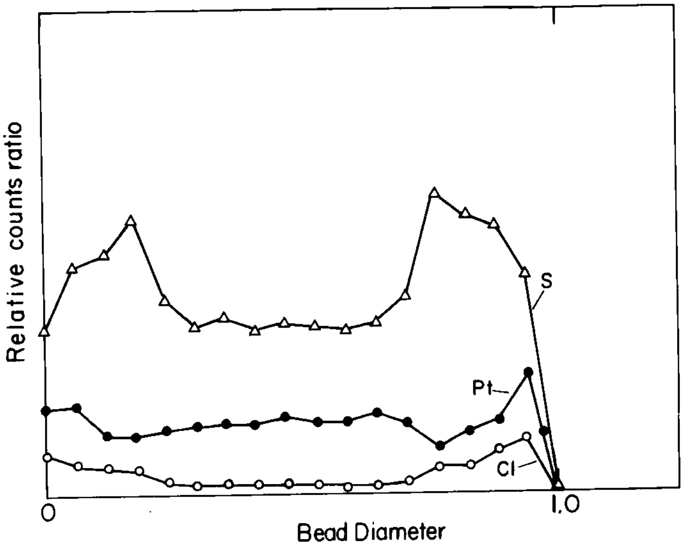


FIGURE 12

Dark zones in partially hydrolyzed Monivex samples. Resin loaded with Pt from 4M HCl. Pt, S, Cl profiles shown.

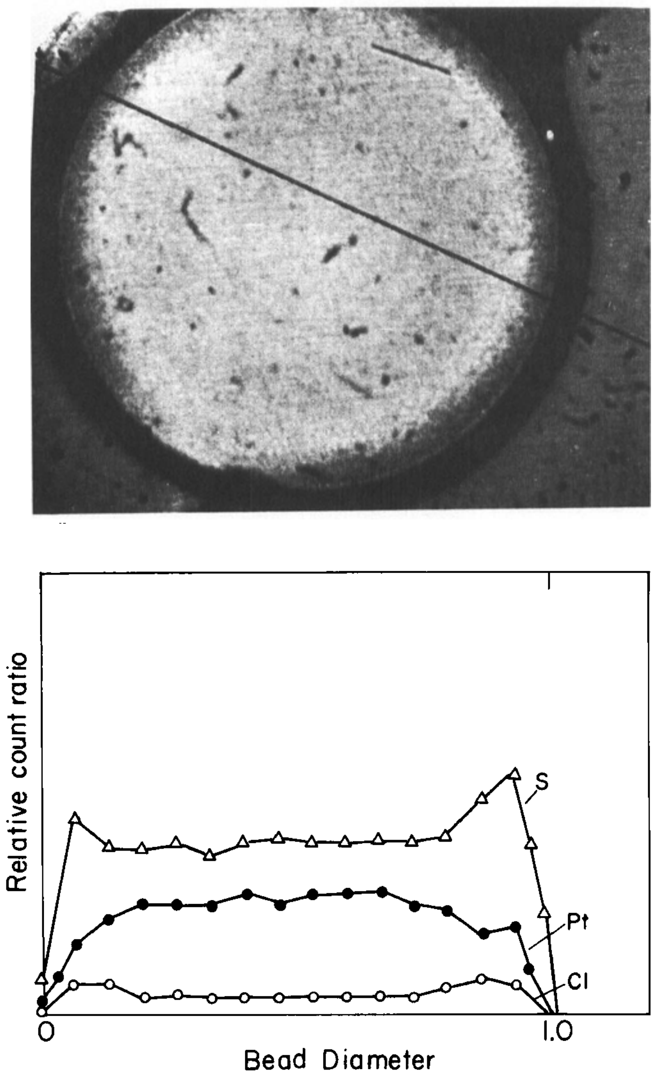
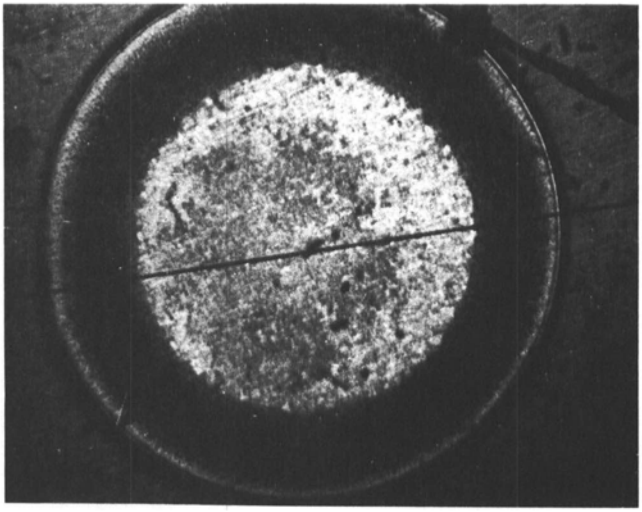


FIGURE 13

1 hour regenerated pilot plant samples (column 8, Table 14) and Pt, S, Cl profiles.



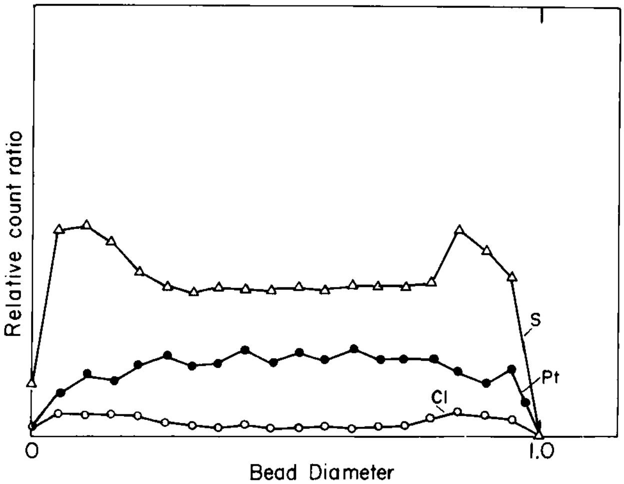


FIGURE 14

Partially regenerated sample. Central white core and darker outer zone.

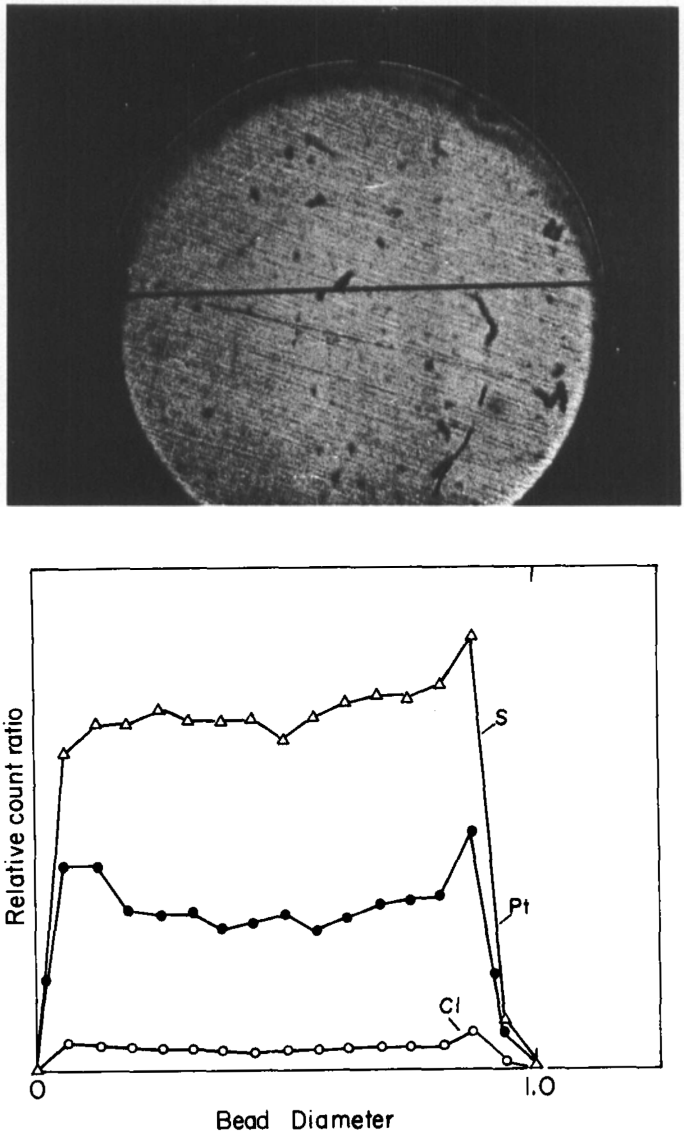


FIGURE 15

24 hour regenerated sample. Fully homogeneous appearance.

Figs. 16, 17). The inner core in these beads is completely void of sulfur and platinum, but has an extremely high chlorine concentration. This phenomenon can be explained by substitution of the isothiouronium group during the conversion procedure. There is however a possibility that those beads were carried through from the synthesis of Monivex (partial substitution during the reaction of chloromethylated intermediate with thiourea).

Following the regeneration procedure, the resin was analyzed. The results of the analysis from pilot plant resin, before and after regeneration are given in Table No. 15. The only metals accumulated on the resin are the PGM, and they can be substantially recovered by the regeneration procedure. The analysis of the residual elements on the resin prove again the suitability of the process step conditions for the correct handling of the resin, and particularly to the effectiveness of the washing and elution steps. Even elements like Bi, Sb, Fe, which were suspected to cause difficulties, were found in their detection levels.

8. Concluding remarks

In the application of isothiouronium resins in the refining of platinum group metals, there are three types of reactions which must be correctly applied[20].

(1) Ion binding to the resin ("loading")
(2) Ion release from the resin (elution)
(3) Oxidative conversion of the thiourea - PGM eluate into the chloride system.

We shall discuss points (1) and (2) (3) separately, and also consider the differences between the two isothiouronium resins.

8.1 Ion binding

The chemical behaviour of the isothiourea group bound to the resin determines the ion exchange mechanism (points 1, 2 above) and will be discussed first. The isothiourea (ITU) group exhibits the following acid-base equilibria:

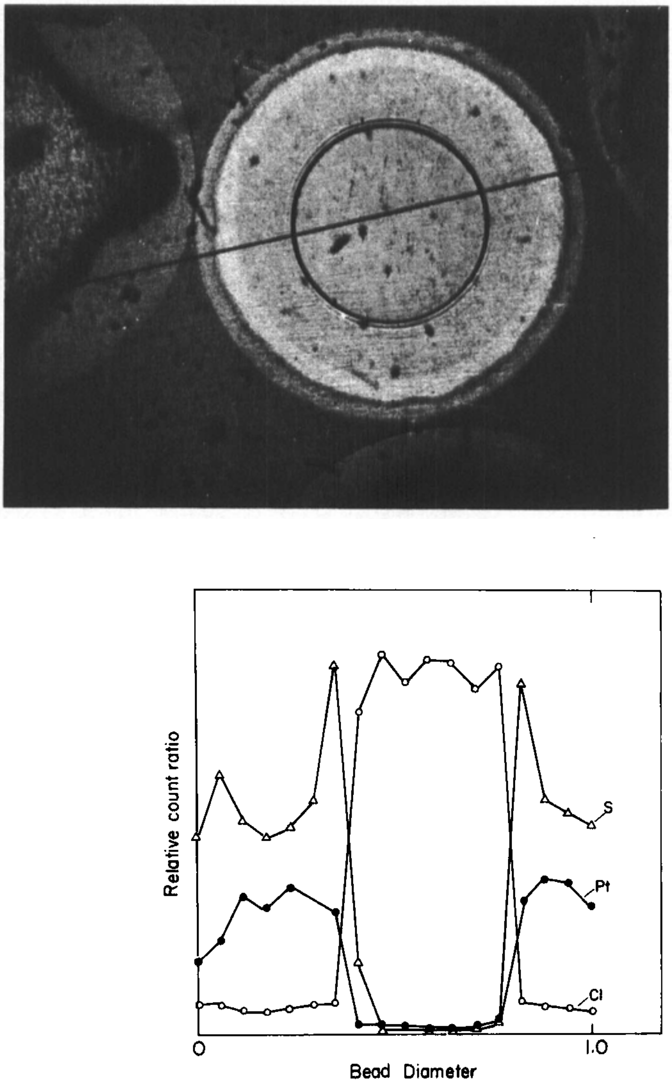
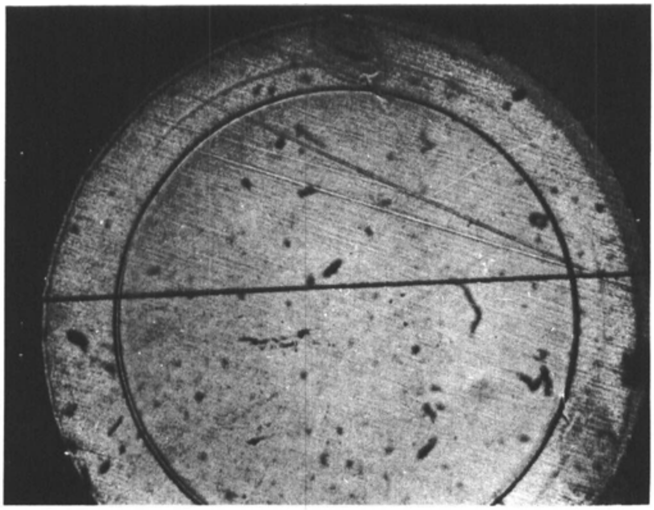


FIGURE 16

Resin bead no. 1 with inner core void of sulfur and platinum.



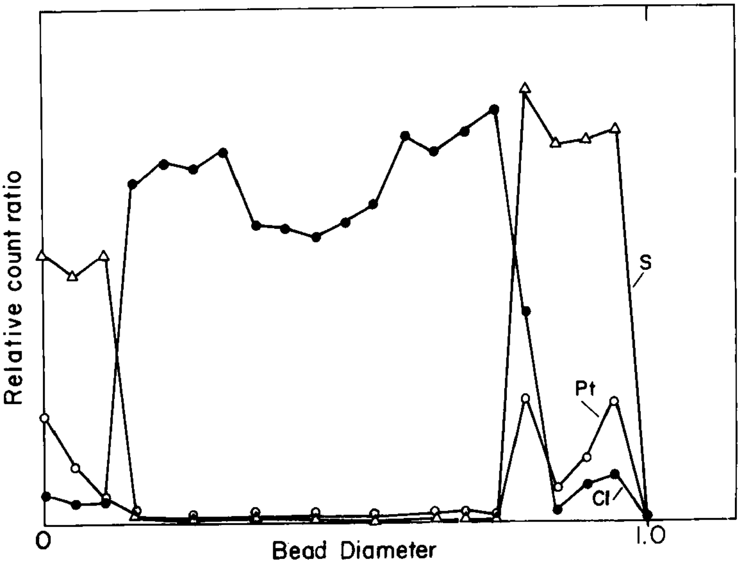


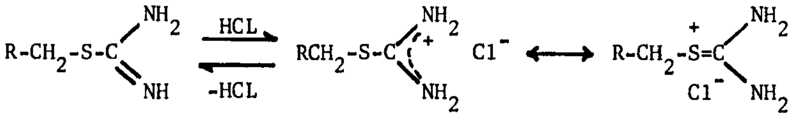
FIGURE 17

Resin bead no. 2 with inner core void of sulfur and platinum.

TABLE 15

Regeneration of used resin with 5% H_2O_2, followed by 5% thiourea elution

	Concentration on resin (ppm)		
	Before treatment	After treatment at 20°C	70°C
Ni	10.6	<1	<1
Fe	66	67	104
Bi	40	<1	<1
Sb	<1	<1	<1
As	-	<5	<5
Pt	983	739	563
Pd	649	413	166
Au	<12	<1	<1
Rh	323	208	90
Ru	621	271	83
Ir	-	510	330
Ag	-	<1	<1
Zn	8.1		
Cu	3.8	3.8	<0.2
$\%SiO_2$	<0.001		
%Ash	0.77	0.64	0.19



ITU HITU

Isothiourea compounds are stable as isothiouronium salts, but very sensitive to hydrolysis in the free base form. Thus, benzylisothiouronium chloride is stable in 2 M HCl and yields readily tetrachloroaurate and hexachloroplatinate salts[21a,c], but hydrolyzes rapidly in water, and with the addition of $NaAuCl_4$ or Na_2PtCl_6

yields only amorphous sulfides[6a,21c]. The same trends are evident for resin-bound isothiourea group, except that the hydrophobic matrix makes the functional group more resistant to hydrolysis. Thus 24 hours at 70°C in 0.1 N NaOH are needed to complete the base hydrolysis which in solution occurs spontaneously. Because of the instability of the isothiourea group in the neutral range of pH, the exact pKa for this group is hard to determine, and consequently the acidity at which the isothiourea is completely converted to the isothiouronium form is not known accurately. Nevertheless the ion binding properties of isothiourea resins may be explained by assuming three possible mechanistic pathways.

(1) Ion pair formation by exchange mechanism with the protonated form (HITU).

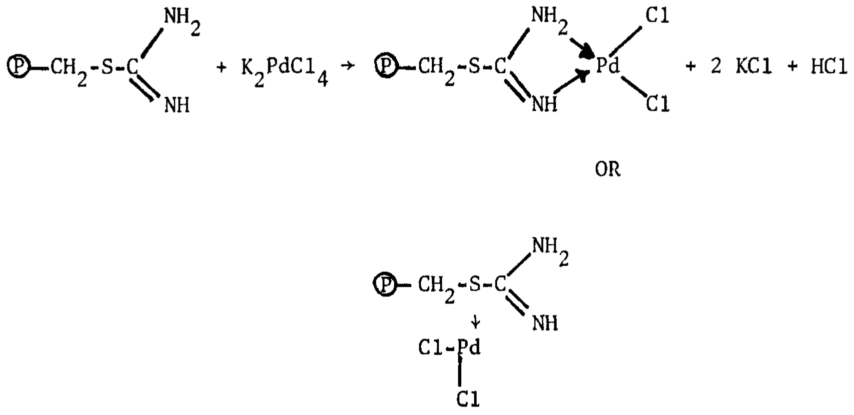
(2) Coordination by ligand exchange mechanism, via nitrogen or sulfur ligands, or both, with the unprotonated form (ITU).

(3) Ion pair binding, followed by slow ligand exchange. This combines both pathways 1 and 2 above.

The ion exchange mechanism is predominant in high acidity (see Fig. 1, and life test no. 2). To be on the safe side, a 4 M HCl concentration was chosen for the practical process use of Monivex, but binding in acidities which lie on the flat part of Fig. 1, is predicted to obey the ion exchange mechanism.

The coordination mechanism occurs through the range of acidities lying on the left side of Fig. 1, before the flat part. Throughout the range of acidities from pH = 2 (the highest pH before hydrolysis of the chlorocomplexes of the PGM starts), it is likely that type (1) and (2) mechanisms operate side by side. Conditions for type (2) mechanism above, do not exist, as the highest pH allowed is 2. Type (3) mechanism involves fast binding of the anionic complexes, followed by slow conversion in the resin-bound state to the coordination type complex. This mechanism is likely to start occurring whenever the metal loaded resin is subjected to low acidity conditions. For example in life test no. 2.

Further to the life test experiments, concerning large amounts of resin and metals, analytical data supporting the above conclusions were made by Schmuckler for Srafion[6a,6d] and by Boeyens for Monivex[21b]. Loading both resins from 0.01 N HCl liberates one equivalent of HCl by the following reaction:



Loading from 1 M HCl (Srafion, ref. 6d) or from 2 M HCl (Monivex, ref. 21b) releases an equivalent of Cl^- without an equivalent release of H^+.

Boeyens[21a,c] in an attempt to determine the structure of the resin analogue, has succeeded to show that benzylisothiouronium (BTU) complexes of Au(III) and Pt(IV), formed in 2 M HCl are ion pairs. Both $(BTUH)_2^+ \, PtCl_6^=$ and $(BTUH)^+AuCl_4^-$ exist in the crystalline state as ion pairs stabilized by a large number of hydrogen bonds between the nitrogen ligands and the chlorides of the platinum and gold chloro complexes. The important dimensions are: 15Å across one $BTUH.PCl_6.BTUH$ unit, and 20Å across one $BTUH.AuCl_4...BTUH$ unit, and the 5-5.5 Å separation of adjacent benzyl groups, in both $BTUH.AuCl_4$ and $PtCl_6(BTUH)_2$. The schematic structure for the $BTUH.AuCl_4$ salt is shown in Fig. 18.
Attempts to isolate crystalline BTU complexes of $AuCl_4^-$ or $PtCl_6^=$ from neutral conditions results only in amorphous precipitates suspected to be the sulfides[21c].

8.2 Ion release from the resin (elution)

As concluded earlier, when the loading of the resin is conducted from the right conditions e.g. 4 M HCl, the ion-binding

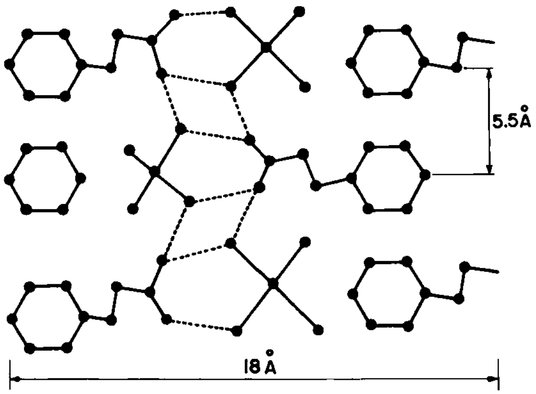
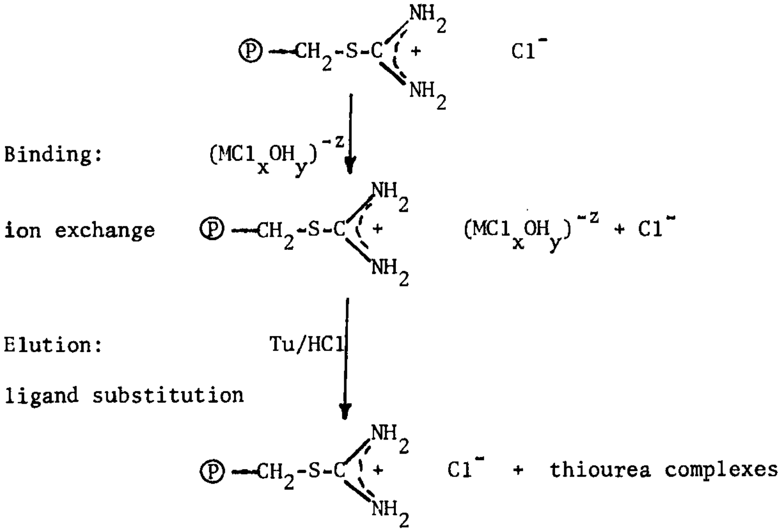


FIGURE 18

Structure of BTUH.$AuCl_4$ complex, after reference 21a, 21c.

reaction is reversible, and the bound PGM could be released by equilibration with hydrochloric acid solutions. However, the high equilibrium constants in the forward reaction, make elution with HCl impractical. A non-reversible ligand substitution-type elution with thiourea has been chosen to overcome this difficulty.

The binding and elution reactions are described for a general PGM anion of type $(MCl_x(OH)_y)^{-z}$:



The thiourea complexes of the PGM are described in Table No. 16. The substitution of the chloride ligands in a PGM chloride complex by thiourea ligands involves first anionic mixed-chloride-thiourea species, which are then converted to neutral and finally to fully

TABLE 16

Thiourea complexes of the PGM

Starting metal	Main reaction product in excess thiourea	Properties of main reaction product	Other products	Lit. reference
Pt(II) or Pt(IV)	$Pt(Tu)_4^{2+}$	Soluble in water precipitates with H_2SO_4 as $Pt(Tu)_4SO_4$	$Pt(Tu)Cl_3^-$ $Pt(Tu)\ Cl$ $PtCl_2.PtCl_4(Tu)_4$	22 22 22
Pd(II)	$Pd(Tu)_4^{2+}$	Precipitates in presence of hydrochloric acid as $Pd(Tu)_4Cl_2$	$Pd(Tu)_2Cl_2$	22 22
Rh(III)	$Rh(Tu)_6^{3+}$		$Rh(Tu)_5Cl^{2+}$ $Rh(Tu)_3Cl_3$	23 24,25
Ir(IV)	$Ir(Tu)_3Cl_3$ or $Ir(Tu)_6^{3+}$	Yellow	$Ir(Tu)_4Cl_2^+$ $Ir(Tu)_5Cl^{2+}$ $Ir(Tu)_6^{3+}$	23,24 23,24 23,24
Ir(III)	$Ir(Tu)_3Cl_3$	Golden yellow	$Ir(Tu)_2Cl_4^-$ (orange) $Ir(Tu)Cl_5^{2-}$ (orange)	24 26
Ru	-	Blue	-	26
Os(III) and Os(IV)	$Os(Tu)_6^{3+}$	Stable in strong acids (6N H_2SO_4 or 6N $HClO_4$)	$Os(Tu)_5Cl^{2+}$ $Os(Tu)_4Cl_2^+$	27-30 27-30
Os(VIII)	$OsO_4.(Tu)_4$	Exists as the insoluble sulphate $OsO_4.(Tu)_4SO_4$, in hydrochloric acid goes into $Os(Tu)_6^{3+}$		27,28
Au(III)	$Au(Tu)_2^+$	Decomposes to Au_2S		

substituted cationic PGM thiourea complexes. The full conversion, using excess thiourea, from anionic to cationic species, drives the elution reaction to completion and makes it an irreversible reaction. Under such conditions, some of the PGM-thiourea cationic species have a limited solubility and precipitate out as described in Table No. 16. For this reason a hot elution step is needed also for the elution of Pt and Pd if highly concentrated solutions are desired.

The rates of chloride substitution by thiourea ligands in solution were studied for several PGM complexes and are given in Table No. 17. A very rough division between square planar complexes and octahedral complexes can be made. The first group has rate constants in the order of 10^2-10^4 $M^{-1}s^{-1}$. The second group is several orders of magnitude lower. An exception is the octahedral Ir(IV) complex. The rate data presented in Table 17 explains very well the observed order of PGM elution from Monivex resin, and the good separation between the primary and secondary PGM in the column test work (Fig. 8).

The conversion of the thiourea PGM complexes by oxidative hydrolysis, under both variations, is needed to transfer the system into a form which can be further separated. The conversion is achieved with excellent yield and the PGM sulfide mixture contains only the precious metals.[18] (The base metal content is only 0.01%.)

Pilot plant samples regenerated according to the oxidative conversion procedure described in column 8 of Table 14, eluted with 5% thiourea and reloaded with Pt are described next. The sample treated for one hour, has been predominantly converted to homogeneous beads with almost even distribution of S and Pt (see Fig. 13).

8.3 Comparison between the various isothiouronium resins; the role of the matrix and preparative methods

The synthesis of Monivex was initiated on the hypothesis that variation in matrix structure can and will play an important role in determining the course of metal binding mechanism taking place

TABLE 17

Replacement of PGM chlorocomplexes by thiourea*

Reaction	Concentrations		Temp. °C	Rate constants
1. $PdCl_4^{2-}$ + Tu → $[PdCl_3Tu]^-$ + Cl^- (Medium 2.0 M hydrochloric acid)	[Tu] $8x10^{-3}$ $4x10^{-3}$ $2x10^{-3}$	$[Na_2PdCl_4]$ $1 x 10^{-4}$ $1 x 10^{-4}$ $1 x 10^{-4}$	25	$9 x10^3 M^{-1}s^{-1}$
	$8x10^{-3}$ $4x10^{-3}$ $2x10^{-3}$	$1 x 10^{-4}$ $1 x 10^{-4}$ $1 x 10^{-4}$	12.5	$5.6 x10^3 M^{-1}s^{-1}$
	$20x10^{-3}$ $10x10^{-3}$ $5x10^{-3}$	$1 x 10^{-4}$ $1 x 10^{-4}$ $1 x 10^{-4}$	4.3	$4.3 x10^3 M^{-1}s^{-1}$
2. $AuCl_4^{2-}$ + Tu → (Medium 2M hydrochloric acid) First reaction	[Tu] $100x10^{-3}$ $50x10^{-3}$ $25x10^{-3}$	$[AuCl_4^-]$ ca $1 x 10^{-4}$ ca $1 x 10^{-4}$ ca $1 x 10^{-4}$	3.7	$2.2 x10^4 M^{-1}s^{-1}$
Second reaction	$160x10^{-3}$ $80x10^{-3}$ $40x10^{-3}$	ca $1 x 10^{-4}$ ca $1 x 10^{-4}$ ca $1 x 10^{-4}$	3.6	$1.08x10^2 M^{-1}s^{-1}$
3. $PtCl_4^{2-}$ + Tu → (Medium 2M hydrochloric acid)	[Tu] $80x10^{-3}$ $40x10^{-3}$ $20x10^{-3}$ $10x10^{-3}$	$[PtCl_4]$ ca $1 x 10^{-4}$ ca $1 x 10^{-4}$ ca $1 x 10^{-4}$ ca $1 x 10^{-4}$	4.3	$8.1 x10^2 M^{-1}s^{-1}$
4. $(NH_4)_2OsCl_6$ + Tu → (Medium water)	[Tu] $1x10^{-1}$	$[OsCl_6^{2-}]$ $1 x 10^{-3}$	ca 20	$t^{½}$ = 17 h
5. K_3RhCl_6 + Tu → (Medium 0.2 M NaCl + 1 drop of hydrochloric acid)	[Tu] $1x10^{-1}$	$[RhCl_6^{3-}]$ $5 x 10^{-3}$	ca 20	$t^{½}$ = 14 h
6. $(NH_4)_2IrCl_6$ + Tu → (Medium 2M hydrochloric acid)	[Tu] $1x10^{-1}$	$[IrCl_6^{3-}]$ $1 x 10^{-3}$	ca 20	Too fast to be measured
7. $RuCl_3.xH_2O$ + Tu → (Medium 0.2 M NaCl + 1 drop of hydrochloric acid)	[Tu] 1 M $5x10^{-1}$ $1,25x10^{-1}$ $2,5 x10^{-1}$	$[RuCl_3.xH_2O]$ $1 x 10^{-3}$ $1 x 10^{-3}$ $1 x 10^{-3}$ $1 x 10^{-3}$	ca 20	$4 x 10^{-2} M^{-1}s^{-1}$

* This table was prepared by Dr. W. Robb, National Chemical Research Institute, C.S.I.R., Pretoria, South Africa.

within the macromolecular network. The experimental results of this work prove the validity of this assumption. Both resins (and other isothiourea resins prepared subsequently)[31] incorporate the same functional group in similar concentration, but show remarkable difference in ion binding properties. Those differences were born in the various stages of the resin preparation. First, the difference in the primary structure of gel and macroreticular resins, which is obtained through different polymerization conditions. Next, further transformations in structure, during the chloromethylation of the styrene-divinylbenzene copolymers. In a recent study,[33] we have estimated that up to 3 mmole/g of extra $-CH_2-$ groups are introduced by post-polymerization crosslinking even under very mild chloromethylation conditions. Namely, chloromethylether (CME) in large excess of chloroform as diluent at ambient temperature. Under the conditions of Monivex preparation, much more crosslinking is introduced by using CME as reagent and solvent at 45-55°C and a considerable amount of $SnCl_4$ catalyst.

Considerable morphological and structural transformations take place inside flexible copolymers. Under Friedel-Crafts condition Amberlite XE-305 can change its initial structure completely. In the presence of 5-chloromethyl-8-hydroxyquinoline hydrochloride and $AlCl_3$, in the dry impregnated state, a "twist" type of polymer results from the coordination of Al^{3+} ions during the Friedel-Crafts alkylation.[34] Under standard chloromethylation conditions, 1% 1.3.5-hexahydrotriacryloyltriazine-styrene copolymer, undergoes remarkable postpolymerization transformations.[33]

Chloromethylated XE-305 can be reacted with linear polyoxyethylene compounds to yield polymeric "pseudocrown" ether (PPCE)[35] which shows high binding of transition metal anions by an ion-pair mechanism. This effect is again obtained by adaption of the macromolecular network to the requirement of the incoming ligand. Other examples of interactions during polymerization and in swollen state have been reviewed recently.[36]

The distinct difference between the two resins in their preference to bind PGM ions by one mechanism or the other, is partially due to the fact that Monivex macroporous structure permits rapid diffusion of hydrochloric acid where Srafion does not. The swelling in HCl allows Monivex to maintain a constant chemical environment within the resin beads which is equivalent to the solution environment. Under those conditions, the resin can manifest its ion exchange properties. For Srafion, the chemical environment inside the resin is very different from the external environment.

The lower acidity in the resin prevents binding by anion exchange mechanism, or alternatively, the ion pairs are coordinated fast enough by the free base isothiourea groups present inside the resin beads. This explanation has been suggested from the observation that Pt concentration decreases going along the bead radius of Srafion, but is constant throughout the cross section of Monivex beads.

The high stability of the PGM anionic complexes as polymeric isothiouronium complexes, can be explained using the reasoning made by Boeyens[21b] for the BTU complexes, by the added hydrogen bonding in a semi-crystalline state. It is very interesting to note, in agreement with this explanation, that soluble isothiouronium extractants,[37] as N,N'-diphenyl-S-(1-decyl) isothiourea (DDTU), are able to transfer anionic PGM complexes into an organic solvent, but lack in this mobile state the ability to stabilize the ion pair. As a result DDTU is an anionic type extractant, non-selective for the PGM, and binds other anions, as $FeCl_4^-$.

Experimental

Polymers

Amberlite XE-305, XAD series, were obtained by courtesy of Rohm & Haas, South-Africa, Pty or Rohm & Haas, USA. Styrene-divinylbenzene copolymers of FP series were received by courtesy of Dow Chemical, Switzerland.

Platinum group metal salts

The platinum group metal salts were prepared at the analytical department of the National Institute for Metallurgy as described in ref. no. 11. A.R. grade metal was dissolved in HNO_3/HCl or Cl_2/HCl or Br_2/HCl mixture in sealed tubes. Standard solutions containing the individual metal salts of Pd(II), Pt(IV), Au(III), Rh(III), Rn(III) and Ir(IV) were obtained. Addition of a reducing agent, as hydroxyquinone 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.

Analysis of PGM solutions, solids, and resins[11,14]

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 Ru, Rh, Pd, Ag, the lighter elements, 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.

General Procedure for Isothiourea Resins

Preparation of Monivex

100 gr Amberlite XE-305, swollen in 660 ml of chlorodimethylether (B.D.H. technical grade) for 30 minutes. A solution of stannic chloride (26 ml) in chlorodimethylether (130 ml) was added (the ratio of $SnCl_4$-to-polymer is 3:5 by weight), and the mixture stirred for 18 hours at 45-50°C. After cooling the resin beads were washed with 10% hydrochloric acid and acetone-water (1:1), and finally with water and acetone. The resin was packed in a column and deionized water passed in a slow flow, until the effluent showed a negative test for Sn(IV).

The product, 164 g air-dry, has a chlorine analysis 20.20%. Performing the chloromethylation for 7½ hours gives a product with 20.10% Cl. 40 g of the chloromethylated XE-305 is added to a solution of 40 g thiourea in 400 ml water; the solution is heated to 85°C for 5 hours without stirring. The reaction is complete when the floating resin has settled down completely. After cooling, the resin is filtered and washed with water to a negative thiourea test (1% $CuSO_4$ reagent), usually placed in a column for slow washing of thiourea (24-48 hours), then washed with 1M HCl, water and finally acetone. The resin has an average analysis of 11.56% N (4.1 nmole isothiourea group/g resin). If the reaction is stopped after 2½ hours the heavy resin fraction accounts for 80% of the product and has 12.12% N, whereas the light fraction has only 7.66% N.

Metal distribution tests - general procedure

A known amount of resin was shaken for a definite time with a known volume of hydrochloric acid solution containing precious metals, after which the phases were separated by solid-liquid separation. The resin was then rinsed with a dilute hydrochloric acid solution, which was added to the original solution and diluted to known volume. Both solutions (before and after contact with the resin) were analyzed, and the amount of metal adsorbed was determined by subtraction. In many instances the resin (after contact with the solution) was burnt and the residual metals analyzed. Discrepancies between the results determined by the analysis of solutions and those obtained by analysis of the resin lies in the inaccuracy of the latter method, which always produces lower results.

In the case of distribution from very dilute solutions,[13a] the end-solutions were concentrated by extraction into trioctylamine in toluene, and analyzed in the organic solvent against standards prepared in the same way from a known solution containing higher concentration of metal, which was then diluted in the same solvent. In parallel the elution of the resin was done with 5% thiourea in a large solid:liquid volume ratio, and the metals were determined in the eluate by atomic absorption spectrophotometry against known standards in 5% thiourea.

Rate of metal complexation and elution - general procedure

1-5 gr of resin samples were stirred with 50-100 ml of a solution containing the individual or the admixture of the PGM. Aliquots were taken at the appropriate time, diluted to the concentration allowing reading by the AA instrument and analyzed against known standards.

In the rate of elution experiments, 1-5 gr of resin samples were loaded in parallel from a solution of known composition. The amount of metal on the resin was determined from residual solution analysis, and substraction. The resin samples were suspended and stirred in 5% thiourea in 0.05 M HCl. Aliquots were taken, oxidized by H_2O_2/HCl, diluted to appropriate volume and analyzed by AA spectroscopy against known standards, prepared from solutions containing the same amount of thiourea and treated by the same procedure. Introduction of lanthanum[11c] as a releasing agent in the determination of PGM in presence of sulphate (resulting from thiourea oxidation) has eliminated the need for the use of thiourea standards (which need to be freshly prepared).

Conversion of thiourea complexes into chloride complexes[17]

(a) Direct chlorination: A solution containing Pt (5.6 gpl), Pd (2.10), Au (0.18), Ru (0.05) and Ir (0.05) thiourea (1.5%) in 0.5 M HCl was sparged with Cl_2 at 70°C for one hour. The solution was cooled and then extracted three times with 5% Alamine-336 in toluene. The residual concentration of metals in aqueous solution was (in gpl): Pt: 0.028; Pd: 0.001; Au: 0.0007; Ru: 0.005; Ir: 0.002.

(b) Precipitation as sulfides followed by chlorination: The acidic thiourea solution is adjusted to pH $\geq$ 11.5, and the sulfides are precipitated by boiling at 100°C for one hour. Incomplete oxidation is indicated by the dark brown color of the solution. Further hydrolysis results in a clear solution. The composition of the precipitate is M_2S. The precipitate is slimy and hard to filter, but settles well and is easily parted from the mother liquor by decantation. The chlorination of the precipitate is achieved best in pure water at 90°C for 3 hours. Increase in HCl concentration reduces considerably the rate of conversion, to a complete halt at 1M HCl.

The completion of the conversion was tested as follows: $SO_4^=$ was determined by non-aqueous titration with $BaClO_4$ in alcohol. The conversion is complete when the concentration of sulphate reached the total sulfur concentration. This conversion was used on a 200 gr PGM scale, and resulted in 99.95% or better recoveries of Pt, Pd, Au, Rh, Ru, Ir.

Surface area[38]

The surface area was determined by nitrogen adsorption or krypton adsorption:

Amberlite XAD-2		(N_2):	328.5 mm^2/g
Amberlite XE-305		(Kr):	591 cm^2/g
Monivex		(Kr):	9564 cm^2/g
FP 4025	6% DVB	(Kr):	1325 cm^2/g
	8% DVB	(Kr):	4694 cm^2/g
	10% DVB	(Kr):	1613 cm^2/g
	12% DVB	(Kr):	50.67 m^2/g

Electron microscope

Most of the samples were handled by Mr. P. Mihalik, NIM. Figures 9, 10, 11 were prepared by the SEM Center, The Research and Development Authority, Ben-Gurion University, Beer-Sheba, Israel.

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