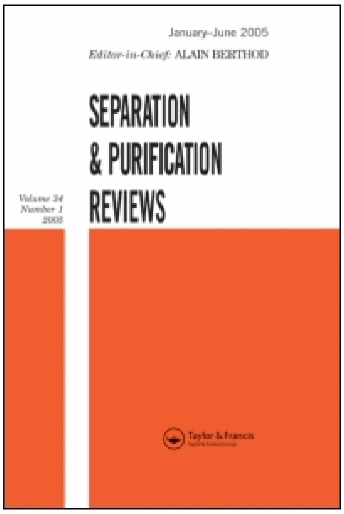

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Extraction of Platinum Grop With Teriary Amines and Controlled Separation by Strippling With Nucleophilic Ligangs

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EXTRACTION OF PLATINUM GROUP METALS WITH TERIARY AMINES AND CONTROLLED SEPARATION BY STRIPPING WITH NUCLEOPHILIC LIGANDS.

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Abstract

A liquid-liquid extraction process of platinum group metals, from two sources: (a) Cl_2/HCl leaching of PGM ores or concentrates (b) a converted thiourea eluate from a PGM-selective isothiouronium resin, by high molecular weight teriary amines, is presented.

In the first step, separation of platinum and palladium (primary PM) from secondary PM (Rh, Ir, Ru, Os) and other transition metal ions, is achieved by conditioning the aqueous feed, to obtain the right ionic forms, and extraction from dilute HCl. Platinum is then stripped selectively from the organic phase with sodium thiocyanate solution, followed by a selective strip of palladium with a thiourea solution.

The mechanism of both reactions, is related to the high lability of the d^8 ions (e.g. Pd, Au) in ligand substitution

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reactions. In the thiourea stripping reaction, cationic non-extractable $Pd(Tu)_4^{2+}$ is formed. In the thiocyanate strip, the thiocyanate displaces from the amine solvent $PtCl_6^{2-}$, and $PdCl_4^{2-}$. Which are transfered to the aqueous phase where $PdCl_4^{2-}$ is rapidly converted to the thiocyanate complex and reextracted.

1. Introduction.

The behaviour of amines as extractants for platinum group metals (PGM) has been known from early studies on such systems [2]. Considerable efforts to develop industrial processes were made by Russian researchers, notably by L.M. Gindin [3-7].

First they studied the extraction of PGM from solutions of anode slimes, which resulted from the chlorination of PGM in sulphuric acid by primary amines known as ANP collectors. These collectors are made from nitroparaffins, and are mixtures of both primary and secondary amines with varying numbers of carbons. The use of ANP collectors enabled the extraction of over 99 per cent of the platinum, palladium, and iridium, [3,4]. The structure of the extracted complexes were:

$$(AmH)_2PtCl_6, \text{ and } (AmH)_3IrCl_6$$

In later experiments, difficulties were experienced in bringing the extraction of rhodium and iridium to completion, and there was a change of opinion about the extraction mechanism, first considered an ion exchange mechanism [3], then a substitution mechanism [5] and, finaly, both substitution and ion-exchange [6].

It seems that the difficulties in the use of primary amines arose from their impure nature, their tendency to form coordination complexes with the PGM, and also to extract the anionic complexes of other transition metal ions.

In view of these results, further research was directed to the investigation of teriary and quaternary amines. Teriary amines [8-13] extract platinum and palladium, do not extract rhodium (III), extract iridium (III) poorly [9] and extract ruthenium, depending on its state of aging [11].

Extraction with quaternary amines [12], which can proceed only by an anion exchange mechanism, was supposed to simplify the extraction process. Yet, the extracted species were binuclear complexes, such as $(R_4N)_2Pd_2Cl_6$, $(R_4N)_3Rh_2Cl_9$, $(R_4N)_3Ru_2\ Cl_9$, and $(R_4N)_3Ru_2O(H_2O)Cl_9$, and not the expected simple anionic chlorocomplexes [13]. A comprehensive review on this work was recently written by Gindin [14].

2. Objects of the liquid-liquid extraction process.

The present work aims at a separation process to achieve the following objects:

(1) Separation of precious metals from base and other metals.

(2) Quantitative recovery of platinum, palladium and gold.

(3) Separation of platinum, palladim and gold from rhodium, ruthenium and iridium.

(4) Separation of platinum from palladium.

3. Conditioning of the feed solution by oxidative hydrolysis [15].

In a previous paper in this series [16], an ion exchange method separating the PGM from base metals has been described. Consequently the feed to the liquid-liquid extraction process, may come from the direct dissolution of a PGM concentrate or ore, or from an anion exchange eluate. In order to homogenize the chemical composition of the feed, and "condition" the various PGM ions to definite and consistently reproducoable chemical forms, an oxidative hydrolysis procedure [15], which converts Pt, Pd and Au (known as Primary PGM [17]) into extractable MCl_4^{-2}or MCl_6^{-2} complexes, and Rh,Ir,Ru,Os (secondary PGM, [17]) into non-extractable aqua-chloro complexes of the type $[M^nCl_x(H_2O)_y]^{(n-x)}$ (X+Y=6), was developed.

4. Extraction from chloride solutions; preliminary studies.

Preliminary studies were aimed at the selection of the right solvent system, i.e., the right extractant in the right diluent. Two solvents representing teriary amines (Alamine-336) and quaternary amines (Aliquat-336) were chosen. These were diluted to 5% strength in three diluents: paraffin containing 2% isodecanol, Solvesso-150 and methyl isobutyl ketone (MIBK).

The determined distribution coefficients showed all six solvents suitable for the extraction of precious metals, but 5% Alamine-336 in Solvesso-150 is the solvent of choice because it permits the rejection of the secondary platinum group metals and base metals,

and does not form emulsions as some of the other solvents do. The results of this work are not reported in detail here.

A suitable ratio of aqueous-to-organic phases was sought for all the solvents. Yet, this ratio is not critical, conveniently an aqueous-to-organic ratio of 1 to 1 was adapted for further test work.

5. Extraction of individual and mixed PGM ions

The extraction capacity of 5% Alamine-336 in Solvesso-150, for the individual PGM ions, in different aqueous concentrations is shown in Table 1. The distribution factors for the "primary" PGM ions (Au,Pt,Pd) are very high in the order: $D_{Au} > D_{Pt} > D_{Pd}$ and much higher than the corresponding factors for the "secondary" PGM (Ir,Ru).

Next, the distribution factors for the coextraction of combined PGM in solutions of different hydrochloric acid conentrations were determined. The composition of the PGM ions in those solutions resembles the composition of an anion exchange eluate [16].

The distribution factors are affected by (Table 2):

(a) The hydrochloric acid concentration.

(b) The composition of the PGM ions.

Decrease in hydrochloric acid concentration generally causes

Table 1: Extraction of individual precious metals.

Metal	Metals in starting solution mg/ml	Metals extracted		$D_{O/A}$*
		in aqueous phase mg/ml	in organic phase mg/ml	
Pt	1,76	0,002	1,76	880
	2,64	0,002	2,64	1320
	3,52	0,004	3,52	880
	4,40	0,006	4,39	732
Pd	1,96	0,003	1,96	653
	2,94	0,01	2,93	293
	3,92	0.028	3,89	139
	4.90	0,10	4,80	48
Au	1,968	0,0002	1,968	9840
	2,952	0,0002	2,952	14760
	3,936	0,0002	3,936	25252
	4,920	0,0002	4,920	24600
Ir	1,11	0,038	1,072	28,2
	2,22	0,075	2,145	28,6
	4,44	0,170	4,27	25,1
	6,66	0,310	6,35	20,4
	8,88	1,45	7,43	5,1
Ru	0,604	0,034	0,569	16,7
	1,207	0,080	1,127	14,1
	2,415	0,203	2,120	10,4
	3,622	0,4500	3,175	7,1
	4,830	0,935	3,895	4,2

*Distribution factor $D_{O/A} = \frac{\text{concentration in org. phase}}{\text{concentration in aqueous phase}}$

Conditions: aqueous phase : 1 N hydrochloric acid
solvent : 5% Alamine 336 in Solvesso 150
organic to aqueous ratio : 1 to 1

Table 2: Extraction of mixed precious metals solutions (at one concentration).

Distribution factors ($D_{O/A}$) at varying HCl concentrations

Metal	1 N	2 N	4 N	6 N	8 N
Pt	29.3	19.9	15.9	15.0	8.3
Au	9.85	10.9	9.85	11.3	10.9
Pd	8.7	4.9	2.8	2.05	1.15
Rh	0.11	0.08	0.11	0.12	0.14
Ru	0.21	0.14	<0.01	<0.01	<0.01
Ir	1.9	2.66	2.66	1.75	0.6

Standard conditions:
aqueous solution, mg/ml : Pt 5.600
Pd 2.100
Rh 0.151
Ru 0.048
Ir 0.055
Au 0.179
Solvent : 5% Alamine 336 in Solvesso 150
Organic to aqueous ratio : 1 to 1

increase in the distribution factors, whereas competition between the various PGM ions, causes the distribution factors to be strongly dependent on the identity and concentration of the competing elements. Calculations of distribution factors for a combined PGM system, from data for individual metal ions, is very inaccurate. Consequently the distribution factors for six compositions of PGM ions from an optimal acid concentration (0.1N HCl), were determined. The data in Table 3 includes both solvent-

Table 3: Coextraction of mixed precious metals of varying concentrations from 0.1 N HCl

Metal	Solution	Concentration mg/ml	Metals extracted in aqueous phase mg/ml	in organic phase mg/ml	$D_{O/A}$
Pt	A	1.380	<0.1	1.206	12.06
	B	2.760	0.0375	2.5625	68.3
	C	5.52	0.2125	5.125	24.1
	D	11.04	4.375	6.625	1.51
	E	16.56	11.625	5.510	0.47
	F	22.08	17.1875	4.40	0.26
Pd	A	0.525	0.003	0.485	161.7
	B	1.05	0.005375	0.95	176.7
	C	2.10	0.0095	2.00	210.5
	D	4.20	0.825	3.05	3.7
	E	6.30	2.10	3.65	1.7
	F	8.40	3.00	4.65	1.55
Rh	A	0.0425	0.03125	0.0075	0.24
	B	0.0850	0.0775	0.005	0.07
	C	0.170	0.160	0.002	0.012
	D	0.340	0.3375	<0.01	<0.01
	E	0.510	0.5125	<0.01	<0.01
	F	0.680	0.6875	<0.01	<0.01
Ru	A	0.01105	0.0095	0.006	0.66
	B	0.02210	0.0165	0.0120	0.73
	C	0.0442	0.0420	<0.01	<0.23
	D	0.0884	0.0950	<0.01	<0.10
	E	0.1326	0.1210	<0.01	<0.10
	F	0.1768	0.175	<0.01	<0.10
Ir	A	0.0113	0.00475	0.0095	2.0
	B	0.0226	0.0095	0.0095	1.0
	C	0.0452	0.032	0.019	0.59
	D	0.0904	0.073	0.019	0.26
	E	0.1356	0.110	0.019	0.17
	F	0.1808	0.150	0.019	0.13

Conditions:

Aqueous phase :0.1 N hydrochloric acid
Solvent :5% Alamine 336 in Solvesso 150
Organic to aqueous ratio: 1 to 1.

loading data and distribution coefficients for a variety of metal concentrations.

6. Back extraction (stripping) from the organic phase (Table 4).

The back extraction into various acids has shown the anion to have a significant role. Perchloric acid, is the most efficient strippant for the PGM ions. Further results on this system are presented later.

Table 4: The stripping of precious metals from 5% Alamine in Solvesso 150 by different acids.

	concentration in aqueous phase (mg/l)					
	Pt	Pd	Au	Ru	Rh	Ir
HCl, 1N	2	4	0.4	-	-	-
HCl, 6N	-	-	-	220	65	-
H_2SO_4, 1N	2	1	0.4	19	-	2
HNO_3 1N	70	160	0.8	513	-	16
$HClO_4$ 1N	510	2000	17	720	140	450
H_3PO_4 1N	7	1	0.4	Emu.	-	Emu.
H_2O	2	1	0.4	-	-	-
HF, 1N	0	0	0.4	-	-	-

Conditions:

Organic-to-aqueous ratio : 1 to 1.

Metal concentration in solvent (mg/l): Pt-540; Pd-2250; Au-2380; Ru-779; Rh-150; Ir-429.

Table 5: Extraction and stripping of base metals.

Metal	no.	Solution conc. mg/ml	Extracted into solvent mg/ml	%	Stripped with A %	B %	C %
Fe^{2+}	1		0.08	22.9	5.0	19.0	2.2
	2	0.725	0.065	8.9	7.7	45.8	2.7
	3	1.40	0.06	4.3	16.3	96.7	2.9
	4	3.55	0.23	6.5	4.3	78.2	2.2
	5	7.5	0.80	10.7	1.1	53.1	2.9
Cu^{2+}	1	1.0	0.06	6.0	0.84	0.17	0.82
	2	2.04	0.05	2.5	1.0	03	1.2
	3	4.06	0.006	1.5	1.3	0.5	1.7
	4	10.10	0.22	2.2	1.0	0.36	0.9
	5	20.20	0.20	1.0	1.6	0.5	1.6
Ni^{2+}	1	0.252	0.01	<0.1	-	-	-
	2	0.506	0.06	-	<0.1	0.3	3.3
	3	1.012	0.002	0.2	0.0	10.0	99.0
	4	2.53	0.03	1.2	0.7	0.7	6.7
	5	5.02	0.02	0.4	2.1	1.0	10.0
Zn^{2+}	1	0.096	0.044	45.8	9.1	30.5	9.5
	2	0.199	0.096	48.2	8.5	59.0	8.5
	3	0.386	0.172	44.6	10.2	62.4	14.0
	4	0.97	0.46	47.4	9.7	54.0	9.8
	5	1.95	0.61	31.3	13.6	69.8	13.9
Co^{2+}	1	0.098	0.01	<0.1	-	-	-
	2	0.20	0.01	<0.1	-	-	-
	3	0.40	0.002	0.5	<0.1	9.0	100.0
	4	0.984	0.003	0.3	<0.1	7.0	68.0
	5	2.0	0.01	<0.1	-	-	-

Conditions:
Solvent : 5% Alamine in Solvesso 150 ($HClO_4$ form)
Organic to aqueous ratio: 1 to 1
Stripping media A : Hydrochloric acid 6 M
(organic to aqueous B : Sulphuric acid 1 M
ratio 1 to 1) C : 2 M NaCl in 2 M hydrochloric acid

7. Extraction and stripping of several base metals (Table 5).[18]

The extraction of $[MCl_4]^{2-}$ or $[MCl_6]^{2-}$ complexes of the transition metals by amines is related to the chloride concentration in solution. In solutions of low HCl concentrations, the degree of extraction is very low, and under suitable conditions, where the amine is totaly loaded with the PGM anions, little interference from the transition metal ions may be expected. Table 6 describes an experiment in which a solution of 5% Alamine-336 (in $HClO_4$ form) in Solvesso-150 was equilibrated with a series of five aqueous solutions (1 to 5) containing various concentrations of Fe^{3+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, and Co^{2+}, in 4 M HCl. The loaded solvent was then equilibrated with solutions of different stripping agents as follows: 6M HCl (A); 1M H_2SO_4 (B) and 2M NaCl + 2M HCl (C). The results indicate that only Fe^{3+} and Zn^{2+}, are extracted by the solvent, and they can be removed efficiently by a wash with 1M H_2SO_4

8. Coextraction of platinum and palladium under counter-current extraction conditions (Table 6).

Several experiments were conducted to determine the best conditions for quantitative extraction of Pt and Pd, from an aqueous feed solution containing in addition to the PGM ions also the following ions: Cu, Ni, Fe, Al, Mg, Ca, Co, Ag, Cr, Sn, As, Se, Te, Sb, Bi, Pb, and Mn. These elements were probably in their higher oxidation states as they had been dissolved under oxidizing

Table 6: Coextraction of Pt and Pd under counter-current extraction conditions

Metal	Cell no. 1		Cell no. 2		Cell no. 3		Cell no. 4		Cell no. 5		Cell no. 6	
	Aqu. mg/ml	Org. mg/ml	Aqu. mg/ml	Org. mg/ml	Aqu. mg/ml	Org. mg/ml	Aqu. mg/ml	Org. mg/ml	Aqu. mg/ml	Org. mg/ml	Aqu. mg/ml	Org. mg/ml
Pt	ND	0.00083	0.0043	0.237	0.187	6.083	0.012	6.083	0.012	6.083	0.012	6.083
Pd	ND	0.0005	0.00167	0.132	0.1133	2.275	0.012	2.275	0.011	2.275	0.008	2.275
Ru	0.0107	0.00035	0.0167	0.0102	0.113	0.0128	0.043	0.0122	0.022	0.004	0.005	0.00125
Rh	0.033	0.0115	0.0425	0.0264	0.05	0.00687	0.007	0.0066	0.006	0.0064	0.004	0.0062
Ir	0.00133	0.0016	0.00233	0.00125	0.01266	0.0358	ND	0.0347	ND	0.0333	ND	0.0321
Cu	0.5375	ND	0.5375	ND	0.5375	ND	ND	ND	ND	ND	ND	ND
Ni	0.290	ND	0,290	ND	0.290	ND	ND	ND	ND	ND	ND	ND
Zn	0.00875	0.222	0.05375	0.133	0.350	0.00533	ND	0.00177	Trace	0.00107	ND	0.0009
Fe^{3+}	0.0074	ND	0.008	ND	0.0074	ND	ND	ND	ND	ND	ND	ND
Al	0.042	-	0.043	ND	0.042	ND	ND	ND	ND	ND	ND	ND
Mg	0.024	0.00066	0.024	0.0006	0.022	0.0006	0.001	0.0006	0.001	0.0006	0.001	0.002
Ca	0.004	0.0013	0.003	0.0026	0.0035	0.0026	0.001	0.0026	0.001	0.0033	ND	0.005
Co	0.010	ND	0.0064	ND	0.0064	ND	ND	ND	ND	ND	ND	ND
Ag	ND	0.00025	ND	0.00007	ND	0.000177	ND	0.000147	ND	0.000126	ND	0.00011
Cr	0.0035	0.0016	0.006	ND	0.006	ND	0.0025	ND	0.0025	0.000126	0.0025	ND
Sn	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.000126	ND	ND
As	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.000126	ND	ND
Se	0.012	ND	0.020	0.020	0.024	0.006	ND	ND	ND	0.016	ND	0.008
Te	0.045	ND	0.050	ND	0.050	ND	ND	ND	ND	ND	ND	ND
Sb	0.013	ND	0.014	ND	0.012	ND	ND	ND	ND	ND	ND	ND
Bi	0.003	ND	0.005	0.007	0.002	0.025	0.022	0.022	ND	0.015	ND	0.012
Pb	0.023	0.058	0.066	0.185	0.161	0.0056	0.018	ND	0.0034	ND	ND	ND
Mn	0.012	ND	0.012	ND	0.012	ND	ND	ND	ND	ND	ND	ND

ND = not detected

<u>Conditions:</u>

Feed concentration)in 0.05 N hydrochloric acid after filtration

	g/l		g/l
Pt	6.00	Ca	0.0078
Pd	2.08	Co	0.010
Ru	0.0422	Ag	ND
Rh	0.0374	Cr	0.0035
Ir	0.0354	Sn	ND
Cu	0.590	As	ND
Ni	0.297	Se	0.024
Zn	0.051	Te	0.065
Fe	0.01	Sb	0.013
Al	0.017	Bi	0.021
Mg	0.024	Pb	0.046
		Mn	0.014

Organic phase: 18 ml of 5% Alamine-336 in Solvesso-150

Aqueous phase - scrubbing soln : 4 ml of 0.01 N hydrochloric acid
feed : 20 ml of 0.05 N hydrochloric acid

conditions.

Under the given conditions, the quantitative extraction of Pt and Pd, and their separation from Rh, Ru and base metals is achieved. Ir (IV) follows with Pt and Pd in the solvent, but this problem can be solved if Ir (IV) is reduced to Ir (III) in the feed conditioning step. Amongst the base metals, Bi seems to be the major contaminant and is not efficiently scrubbed out.

9. Stripping of Pt, Pd and Au by $HClO_4$ and $NaClO_4$ (Tables 7,8). [19].

The stripping data presented in Table 4, shows $HClO_4$ to be the best stripping agent for all the PGM ions. Further distribution data for this system, is of interest for two reasons:

(1) The perchlorate anion is known to have a great affinity for the alkylammonium cation.

(2) The possibility of using $HClO_4$ or $NaClO_4$ as a selective stripping system to separate Pd from Pt.

The distribution factors (from organic-to-aqaeous, $D_{A/O}$) for both the perchloric acid (Table 7) and sodium perchlorate (Table 8) were determined for different concentrations of Alamine-336 (5-30%) in Solvesso-150, and different concentrations of sodium perchlorate (0.1-4.0 M). The distribution factors are strongly dependent on ClO_4^- concentration (under acidic or neutral

Table 7: Distribution factors ($D_{O/A}$) for stripping of Pt and Pd from Alamine 336 in Solvesso 150 into $HClO_4$ solutions

	5% Alamine			7.5% Alamine		10% Alamine		20% Alamine		30% Alamine	
$HClO_4$(M)	Pt	Pd	Au	Pt	Pd	Pt	Pd	Pt	Pd	Pt	Pd
0.2	-	-	-	0,17	0,14	0,008	0,006	-	-	-	-
0.3	2,91	0,865	0,0002	-	-	-	-	-	-	-	-
0.4	-	-	-	1,86	1,03	0,43	0,56	-	-	-	-
0.5	9,17	1,27	0,021	-	-	-	-	1,22	0,47	1,018	0,24
0.8	-	-	-	9,45	3,43	3,95	3,12	-	-	-	-
1.0	52,49	2,71	0,053	16,26	6,0	7,17	8,10	4,61	1,09	3,37	0,48
2.0	154,9	4,25	0,096	88,5	20,85	33,6	20,85	197,1	3,80	8,87	0,90
4.0	-	6,77	0,202	88,5	20,85	-	132,00	-	-	-	-
Initial conc. in organic phase (g/l)	5,75	2,14	0,15	6,10	2,25	6,10	2,25	13,87	3,90	26,26	15,55
phase ratio A : O		1:4,5		1:3		1:3		1:1		1:1	

Table 8: Distribution factors ($D_{A/O}$)* for Pt and Pd from Alamine-336(as hydrochloride) in Solvesso-150, into $NaClO_4$ solutions (phase ratio 1:1)
approximate Pt : Pd ratio : A 2.5 : 1
B 10 : 1
C 1 : 10

Solvent	5% Alamine						10% Alamine					
Designation	5A		5B		5C		10A		10B		10C	
$NaClO_4$	Pt	Pd	Pt	Pd	Pt	Pd	Pt	Pd	Pt	Pd	Pt	Pd
0.1	1.12	0.36	0.66	0.19	0.135	0.03	0.16	0.19	0.12	0.13	0.16	-
0.5	13.16	0.59	1.72	0.48	3.11	0.50	1.75	0.81	1.78	0.48	2.04	0.37
1.0	41.67	1.45	6.80	0.53	4.40	2.12	16.66	1.45	9.80	0.73	13.16	1.03
2.0	52.63	1.75	14.92	0.59	12.50	2.56	34.48	2.50	25.00	0.79	25.00	1.38
4.0	83.33	1.99	28.72	0.59	-	2.63	62.50	2.94	26.31	0.79	25.00	1.64
Initial metal concentration in organic phase g/l	2.76	1.05	2.75	0.25	0.105	1.05	5.52	2.10	5.50	0.50		2.10

$$^{*}D_{A/O} = \frac{1}{D_{O/A}}$$

conditions), and almost independent of the ratio of Pt-to-Pd (which varied from 10:1 to 1:10, see Table 8). The differences between the distribution factors for Pt and for Pd, promised an excellent possibility for separating the two elements. However, separation experiments under continuous counter-current separation conditions failed to provide this target. This failure is explained after considering the following:

(1) The extraction of Pd^{2+} by neutral Alamine-336 in Solvesso-150 (preequilibrated with 1M NaOH) proceeds well, in comparison to Pt^{2+}, which is not extracted [20].

(2) Pd^{2+} is <u>not</u> extracted into $[\text{Aliquat-336}]^+ \ ClO_4^-$ (Aliquat-336 is a quaternized Alamine-336).

(3) $Pd(Cl_2)Am_2$ is formed in the organic phase following extraction from neutral aqueous solution, and is not stripped by $HClO_4$

(4) $PdCl_4^{2-}$ hydrolyzes readily in $HClO_4$ or $NaClO_4$ solutions.

From the above it is readily concluded, that the labile d^8, square planar palladium complexes show a non-reversible behaviour in both phases, and this makes absolute separation of Pt and Pd in perchloric acid system, a very difficult or even impossible task.

10. Selective stripping of palladium by ligand substitution from the organic phase with thiourea [21].

The observation that the Alamine-336 tetrachloro palladate complex is interconverted in the organic phase by ligand - substitution reaction with the free amine, to $PdCl_2(Am)_2$, has suggested that an effective way of separating palladium from platinum could be stripping with a water-soluble ligand. Examination of the available rate data for substitution of chloride groups by thiourea in PGM complexes, [summarized in Table 17, ref. 14], shows the following order:

$$Ir > Au > Pd > Pt \gg Ru > Rh > Os$$

The place of Ir at the head of this series, is most certainly due to the fact that Ir (IV) is reduced with thiourea to Ir (III) and the measured rate constant relates to the reduction reaction.

The same order of rate constants is observed in the stripping of Pd and Au from their alamine-336 in Solvesso-150 solution, as shown in Table 9. The stripping reaction, a ligand substitution reaction taking place on the interphase-proceeds very fast with the labile d^8 square-planar complexes of Pd (II), Au (III) but very slow with the octahedral d^6 complexes of Pt (IV). The stripping reaction is complete and irreversible, as indicated from the high distribution factor ($D_{A/O}$) for the stripping and the low distribution factor for reextraction ($D_{A/O}$)

An integrated process using the thiourea stripping reaction for the separation of Pt and Pd is described in ref. 22.

11. Selective stripping of platinum and iridium by ligand substitution with thiocyanate [23-25].

Measurements of the rate of the stripping reaction for Pt(IV) from loaded Alamine-336 at 0°C and 20°C show that, (Table 10):

Table 9: Stripping of Pd and Au from Alamine-336 (in Solvesso-150) by ligand substitution with 5% thiourea in 0.5 N HCl (phase ratio 1:1) [ref. 21].

Metal concentraion in organic phase (g/l)	3% Alamine			5% Alamine		
	Pt	Pd	Au	Pt	Pd	Au
A. Initial	4.02	1.66	0.156	4.00	2.50	4.50
B. After strip	4.00	0.0011	0.2	3.89	<0.0001	0.02
C. After reextraction from strip solution	-	-	-	3.93	0.0003	-
Distribution factor for stripping ($D_{A/O}$)	0.0057	1640	735	0.029	-	224
Distribution factor for reextraction ($D_{O/A}$)	-	-	-	-	0.00014	0.0058

The stripping reaction is very fast, yet the time of the stripping must be carefully controlled to stop reextraction. This phenomena is explained by several different reactions takeing place simulatenously: First the stripping reaction, in which the amine is converted into the thiocyanate form (a fast reaction) and second, the stripped $[Pt(Cl_6)]^{2-}$ anion is converted (a slow reaction) in the aqueous phase into $[Pt(SCN)_6]^{2-}$ and reextracted.

Table 10: Effect of temperature and contact time on the stripping of Pt from 5% Alamine 336 in Solvesso-150 with 0,25 M NaSCN

Initial concentration - 3,45 g/l A/O=1

Time	% stripped	
(min.)	0°C	20°C
0	0	0
2	76,0	82,61
5	76,0	74,5
10	37,7	71,3
30	-	40,0
60	-	34,5

Further examination of this reaction (see Table 11) show that control of the pH during the stripping reaction is also very important. At pH=4, some 3% of the platinum is retained in the organic phase, whereas at pH 8, as a result of conversion of the amine into the free-base form, a considerable amount of Pd(II) is stripped. Consequently, the pH of the stripping reaction must be controlled and kept between 4-6.

The usefulness of the thiocyanate stripping reaction to the separation of platinum from palladium was demonstrated in contineous counter-current separation, as shown in Table 12. The composition of the aqueous compartment of cell no. 1, shows

Table 11: The pH dependence of the platinum stripping reaction from 5% Alamine-310 in Solvesso-150, with 0.37 M NaSCN

	pH=4		pH=6		pH=8		pH=10	
Step	Pt	Pd	Pt	Pd	Pt	Pd	Pt	Pd
Strip no. 1	2125	2.7	1638	3.0	1675	26.5	1338	725
Reextraction	2150	N.D.	1675	2.5	1515	-	1340	520
Strip no. 2	195	0.20	160	2.5	98	31	5	278
Strip no. 3	15	2.0	15	2.5	75	195	5	29
Concentration in organic phase after strip no. 3	88	1100	48	1063	4	244	3	356

A:O=1; Time=5 min.; Initial concentrations in organic phase (p.p.m.) Pt=2763; Pd=1156.

Concentration in aqeous phase (p.p.m.) after corresponding step.

complete separation between Pt and Pd, iridium is also completly removed from the organic phase. Under more controlled conditions (0.1 M NaCNS) separation between Ir and Pt is obtained [24]. (In the experiment described in Table 12, the aqueous phase is kept acidic, and consequently the Pt concentration in the organic compartment of cell no. 5 is still high).

Table 12: Counter current Pt-Pd separation using 0.2 M NaCNS (loaded solvent - HCl form).

	Concentration in cell no.(p.p.m.)									
Metal	1		2		3		4		5	
	A	O	A	O	A	O	A	O	A	O
Pt	2190	830	2810	1067	3190	640	1380	215	290	112
Pd	N.D.	<0.2	N.D.	19.8	N.D.	1010	N.D.	1010	1010	1010
Ir	15.6	N.D.	15.6	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Ru	3.1	N.D.	3.1	N.D.	3.1	N.D.	N.D.	N.D.	N.D.	N.D.

Conditions:

5 cells, 2 min. contact, 12 cycles completed.

No. 1: 5 ml of 5% Alamine-336 in Solvesso-150 (thiocyanate form).

No. 3: 5 ml of loaded solvent (from HCl solutions), containing: Pt-5814; Pd-1773, Ir-31; Ru-8.5, p.p.m.

No. 5: 10 ml of (0.2 M NaSCN + 0.2 M H_2SO_4)

A=Aqeous compartment: O=Organic compartemnt; N.D.=Not detected.

12. Discussion. [25]

12.1 Extraction from hydrochloric acid solutions.

The objects of the process presented in this work are the separation of platinum group metals from base metals and then from each other, by exploiting differences in chemical reactivity in both phases or on the interphase.

The separation of the d^8 ions (Pt, Pd, Au) from the d^6 ions (Ru, Os, Rh, Ir) and other transitions metal ions, is based on the fact that the first group (also called primary PGM ions) forms MCl_4^{2-} or MCl_6^{2-} anions, which are extracted as ion pairs:

(1) Extraction by anion exchange:

$$2HCl+\overline{2Am} \rightleftharpoons \overline{2Am\ HCl} \xrightarrow{MCl_4^{2-}} \overline{[2AmH^+][MCl_4]^{2-}}$$

where Am=Amine;

where bars indicate species in the organic phase;

The extraction of d^8 ions is best at low HCl concentration, but still very good at 1 molar HCl. The d^6 ions, form true halide complexes only in high HCl concentrations, and at very dilute HCl solutions, form only mixed aqua-chloride complexes (pseudohalide complexes) which are poorly extracted. The behaviour of the transition metals; Zn^{2+}, Cu^{2+}, Fe^{2+}, Fe^{3+} is similar, but they form halide complexes only if $[HCl] \geq 2M$.

Thus, good separation between Pt, Pd, Au and the rest is achieved readily after the loaded organic phase is washed (scrubbed) with dilute acid, to remove entrained metal impurities. Only Ir(IV) causes difficulties and must be reduced to Ir(III) or complexed by a water soluble ligand.

Our work on extraction from neutral solutions[20], has shown that a second extraction mechanism exists:

(2) extraction by ligand substitution:

$$\overline{2Am} + MCl_4^{2-} \rightleftharpoons \overline{M(Am)_2Cl_2} + 2Cl^-$$

The presence of complexes of the type $M(Am)_2Cl_2$ in the organic phase, is significant, when separation between Pt and Pd is contemplated in the extraction step, or by chemical stripping reactions from the organic phase, thus, Pd can be almost exclusively extracted (in presence of Pt) under neutral conditions by ligand substitution mechanism [25].

12.2 Stripping with perchloric acid.

The stripping of the PGM-amine complexes by perchloric acid is driven by theromdynamically favoured reactions, but complicated by several side-reactions.

$$\text{(3): } \overline{[2\ AmH]^{+}[MCl_4]}^{2-} \xrightarrow{HClO_4} \overline{[2\ AmH]^{+}[ClO_4]}^{-} + MCl_4{}^{2-}$$

$$\text{(4): } \overline{[2\ AmH]^{+}[MCl_6]}^{2-} \xrightarrow{HClO_4} \overline{[2\ AmH^{+}][ClO_4]}^{-} + MCl_6{}^{2-}$$

$$\text{(5): } \overline{M(Am)_2Cl_2} \xrightarrow{HClO_4} \overline{[2\ AmH^{+}][ClO_4]}^{-} + MCl_2(ClO_4)_2$$

The stripping of ionic PGM complexes, reaction (3) for square planar complexes and reaction (4), for octahedral complexes, proceeds by an anion exchange mechanism; the driving force for those reactions is the affinity of the alkylammonium cation for the "soft" perchlorate anion. Reaction (5), the stripping by ligand substitution of chloride by perchlorate is thermodynamically unfavoured.

The results abtained in this work, show both reactions (3) and (4) to proceed well. Consequently $HClO_4$ (or $NaClO_4$) are effective strippants for the whole PGM group.

Yet, under controlled conditions, a separation scheme between Pt and Au and Pd based on a combination of the following factors, is feasible:

(1) The equilibrium constants for reactions 3 (Pd^{2+}) and reaction 4 (Pt^{4+}) are different.

(2) Au and Pd exist in the organic phase mainly as $M(Am)_2Cl_2$ complexes.

(3) Reaction 5 does not proceed.

The incomplete separations, between Pt and Pd are attributed to the following reasons:

(1) $PdCl_4^{2-}$ is rapidly hydrolyzed in perchorate solutions, to non-extractable mixed aqua-chloro complexes.

(2) Pd(II) is oxidized by perchlorate in the aqueous phase to Pd(IV), which behaves like Pt(IV), and stays in the aqueous phase.

For the above limitations, separations based on thermodynamic principles alone, must be ruled out. The chemical inertness of the perchlorate ligand, and the ease of reduction of PGM salts to metals in that system, remains the major attraction of the perchlorate stripping step.

12.3 Stripping with thiourea.

In the thiourea system, the separation is simplified by the fact that the two major reactions lead to a common product.

$$(6)\quad \overline{[2\ AmH^+]\ [MCl_4]}^{2-} \xrightarrow{Tu/HCl} \overline{2Am\cdot HCl} + M(Tu)_4^{2+} + 4Cl^-$$

$$(7)\quad \overline{M(Am)_2Cl_2} \xrightarrow{Tu/HCl} \overline{2Am\cdot HCl} + M(Tu)_4^{2+} + 2Cl^-$$

Reactions 6 and 7 both result in cationic thiourea complexes which are no more extractable by amines. The separation of Pt and Pd in that case is based only on differences in the rate of the substitution reaction of the chloride ligands by thiourea taking place on the interphase. [27].

Although large separation factors between Pd and Pt were obtained, the slight amount of $Pt(Tu)_6^{2+}$ that is found in the palladium strip, can not be recovered by reextraction, and must be removed at a later stage. (For example, after selective reduction of Pd with ethylene) [21].

12.4 Stripping with thiocyanate

The chemistry of PGM-thiocyanate complexes, especially their structure and question of linkage isomerism, has been adressed in several publications [29-35]. Extraction of mixed halide-thiocyanate complexes of the PGM, has been described for several analytical separations [36].

The reactions which concern our extraction process are as follows:

Equilibration between chloride form and thiocyanate form (reaction 8):

(8) $\overline{Am\cdot HCl} + SCN^- \longrightarrow \overline{Am\cdot HSCN} + Cl^-$

Ligand substitution in solvent (reactions 9, 10, 11):

(9) $\overline{[2AmH^+][MCl_4]}^{2-} \xrightarrow{4SCN^-} \overline{[2AmH^+]\ [M(SCN)_4]}^{2-} + 4Cl^-$

(10) $\overline{[2AmH^+][MCl_6]}^{2-} \xrightarrow{2SCN^-} \overline{[2AmH^+]\ [M(SCN)_6]}^{2-} + 6Cl^-$

(11) $\overline{M(Am)_2Cl_2} \xrightarrow{2SCN^-} \overline{M(Am)_2(SCN)_2} + 2Cl^-$

The stripping reactions (12) and (13):

(12) $\overline{[2AmH^+][MCl_6]}^{2-} \xrightarrow{2SCN^-} 2\overline{[Am \cdot HSCN]} + MCl_6^{2-}$

for octahedral complexes e.g. Pt^{4+}, Pt^{2+}

(13) $\overline{[2AmH^+][MCl_4]}^{2-} \xrightarrow{2SCN^-} \overline{2Am \cdot HSCN} + MCl_4^{2-}$

for square planar complexes, e.g. Pd^{2+}

Ligand substitution in aqueous phase:

(14) $MX_4^{2-} + 4SCN^- \longrightarrow [M(SCN)_4]^{2-} + 4X^-$

(15) $MX_6^{2-} + 6SCN^- \longrightarrow [M(SCN)_6]^{2-} + 6X^-$

Reextraction of thiocyanate complexes:

(16) $\overline{2Am \cdot HSCN} + [M(SCN)_4]^{2-} \longrightarrow \overline{[2AmH^+]\ [M(SCN)_4]}^{2-} + 2SCN^-$

for square planar complexes:

(17) $\overline{2Am \cdot HSCN} + [M(SCN)_6]^{2-} \longrightarrow \overline{[2AmH^+]\ [M(SCN)_6]}^{2-} + 2SCN^-$

for octahedral complexes.

The following reactions show favourable equilibrium constants:

(a) Conversion of the amine solvent into the thiocyanate form (reaction 8).

(b) Ligand substitution of square planar d^8 complexes (particularly Au,Pd), in the organic phase (reaction 9).

(c) The stripping reactions 12 and 13.

(d) Ligand substitution of square planar d^8 complexes (particularly Au,Pd), in the aqueous phase (reaction 14).

(e) The reextraction of square-planar thiocyanate complexes (reaction 16).

The ligand substitution reaction (15), for octahedral MX_6^{2-} complexes, is slow, yet once the $M(SCN)_6^{2-}$ complexes have formed, they are extracted to some degree (reaction 17). Not much is known about reaction 11, the ligand substitution of $M(Am)_2Cl_2$ complexes in the organic phase, since this reaction does not involve metal transfer from phase to phase.

To summarize, the key steps in the platinum-thiocyanate stripping are reactions 12,15 and 17, involving the transfer of Pt from and then back into the organic phase. Setting the phase contact time, controls reaction 15 and eventually controls the separation of Pt from Pd and Au, since all the reactions of Pd and Au are fast and all the equilibrium constants favour transfer to the organic phase.

Consideration must be given to the sequence of performing the stripping reactions, namely, the following alternatives:

(A) First thiourea then thiocyanate

(B) First thiocyanate, then thiourea.

Considering that in both cases Pd(II) [and not Pt(II)], is the reactive species in the ligand substitution reaction. The single major difference between routes (A) and (B) is that in the thiourea substitution reaction via route (A) the leaving group is Cl^-, whereas in route (B) the more nucleophilic SCN^- group. Experimental tests (ref. 24) show both sequences are feasible but alternative (B) is prefered.

EXPERIMENTAL

Materials.

Alamine-336, Alamine-310 are mixtures of triheptyl amine, trioctylamine and triundecylamine, sold by General Mills Company, U.S.A. Aliquat-336 is Alamine-336 quaternized with methylchloride. Solvesso-150 is an aromatic diluent sold by Shell Co.

Counter-current extraction experiments (Table 6).

The counter-current extraction experiments were carried out in 60 ml cylindrical separating funnels having fast rotating glass stirrers. The extraction was continued usually for 20 cycles, after which the phases were separated, filtered through Whatman phase-separating paper. The metals in the aqueous phase were analyzed directly, or after suitable adjustments were made. The organic phase was quantitatively stripped with 1 M perchloric acid, and then analyzed. In some cases, direct analysis in the organic phase by atomic absorption spectrophotometry, using organic standards, was performed.

Radiochemical analysis of thiocyanate solutions [37].

Since the atomic absorption analysis in thiocyanate solution is subject to large interferences, radio tracer analysis was used to control and standartize the AA results.

^{192}Ir (468 Kev), ^{185}Os (646 Kev) and ^{103}Ru (497 Kev) were obtained from Amersham. ^{198}Au (411.8 Kev) was obtained from

Pelindoba, South Africa. The activity was counted with a lithium-germanium detector coupled to an "Inertechnique" 4000-channel analyzer.

Reduction by ethylene

A stream of ethylene was sparged for one hour through 100 ml of a solution containing 4.35 g/l Pt and 0.237 g/l Pd, at 20°C. The precipitation of the palladium as black sponge was immediate. After one hour, the Pt concentration in solution remained unchanged, the Pd concentration was reduced to 0.012 g/l. After further reduction with ethylene for 1 hour at 80°C, the platinum concentration remained unchanged.

To precipitate the platinum, H_2 was passed at 80°C for 45 minutes. The final solution was analyzed, and found to contain 0.001 g/l Pd and <0.0001 g/l Pt.

Extraction from neutral conditions.

A solution containing 8.3 g/l Pt and 4.6 g/l Pd as chloride complexes, was adjusted to a pH value of 3.5. The solution was extracted into preneutralized 5% Alamine-336 in Solvesso 150 at an aqueous-to-organic phase ratio of 1 to 2, and the emulsion was centrifuged at 1560 rev/min for 30 minutes. The solvent was then stripped with 1 M $HClO_4$ at A/O ratio of 1. The organic phase was found to contain 0.05 g/l Pt (0.61% extraction) and 1.25 g/l Pd (54.3% extraction).

The formation of thiocyanate complexes in chloride solutions.

Solutions containing 0.100 g/l of the chloride complexes of Pd(II), Pt(IV), Rh(III), Ir(III), Ir(IV) and Os(IV) adjusted to pH=3 were reacted with NaCNS (5 g/l) at 20°C and 94°C. The reaction was followed by recording the U.V. spectra on a Hitachi-Perkin Elmer Coleman 124 double beam spectrophotometer.

At room temperature, platinum and palladium thiocyanates form rapidly. The rhodium complex forms very slowly (the conversion is only 20 per cent after 72 hours). Osmium does not form a complex at this temperature, and iridium is difficult to follow, perhaps because the ultraviolet maxima are masked by the ligand absorption bands. Ruthenium, which is also difficult to follow, undergoes fast hydrolysis reactions of its chloride complex.

At 94°C, platinum, palladium, rhodium, and even osmium form complexes fairly rapidly, 5 hours being required for complete formation of the osmium complex.

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k_3 ($AuCl_4^-$) : k_3($PdBr_4^{2-}$) : k_3($PdCl_4^{2-}$) : k_3($PtCl_4^{2-}$)
= 30 : 10 : 5 : 1

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