

# Paper VII



**RECOVERY AND SEPARATION OF PLATINUM GROUP METALS  
USING IMPREGNATED RESINS CONTAINING ALAMINE 336**

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**ABSTRACT**

The kinetics and equilibrium extraction of Pd(II), Pt(IV) and Rh(III) from hydrochloric acid media using impregnated resins containing Alamine 336 impregnated onto Amberlite XAD2 were studied and compared. While Rh(III) was hardly extracted, Pd(II) and Pt(IV) extraction could be explained by the formation of  $(R_3NH^+)_2MCl_n^{-2}$  complexes:  $n=4$  for Pd(II) and  $n=6$  for Pt(IV). Stripping and concentration of the extracted PGMs were assayed with HCl, HClO<sub>4</sub> and thiourea. Straightforward metal separations were designed on the basis of the results obtained in the single metal experiments, and selective co-extraction of Pd(II) and Pt(IV) from Rh(III) at low HCl concentrations, as well as partial separation between Pd(II) and Pt(IV) at high acid concentrations, were achieved.

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## INTRODUCTION

Platinum Group Metals (PGMs), namely Pt, Pd, Rh, Ir, Ru and Os, occur as minor components in ores and due to their specific properties are fundamental elements for production of new materials in fields such as electronics and autocatalysts.

Most PGM production is from natural ores. However, the recovery of these metals from scrapped materials has recently become a challenging problem in PGM refining. In this regard, it is noteworthy that automotive catalysts, for example, which use Pt, Pd and Rh to assist the oxidation and reduction of pollutants emitted by motor vehicles, usually contain a higher PGM concentration than the richest ore bodies (1).

There have been a number of studies on solvent extraction and separation of PGM with primary, secondary, tertiary and quaternary organic amines (2). Integrated solvent extraction and ion exchange (SX/IX), consisting of the use of liquid-liquid extraction with tertiary amines combined with ion exchange resins, may allow the extraction and separation of PGMs (3). Although processes based on ion exchange and solvent extraction have been published or patented, research into specific PGM strategies for separation and recovery based on impregnated resins is a field of development nowadays.

Impregnated resins in which a macroporous polymer matrix is impregnated by a suitable extraction reagent are already well established in the recovery and separation of metals. In recent years, the development of impregnated resins considered as a link between solvent extraction and ion-exchange technologies has been an important field of development in separation science (4). The use of impregnated resins or solvent impregnated resins in extraction and recovery processes dates back to the pioneering work in the early 1970s of Warshawsky (5), Grinstead (6) and Kroebe and Meyer (7).

Impregnated resins have been widely used in preconcentration procedures for metal analysis (8-11) as well as in technological applications in the nuclear industry (12, 13). Hydrometallurgical applications for the recovery of base metals (14-16), rare earth (17), gold from cyanide (18) and hydrochloric (19-21) solutions have been satisfactorily attained.

Until now, only a few studies have shown that impregnated resins combined with organic amines exhibit good efficiency in the extraction of PGMs. The sorption of Pd(II) from hydrochloric acid media with a macromolecular resin containing tri-n-octylamine (TOA) has been reported (22). Au(III), Pt(IV) and Pd(II) are also adsorbed onto macroreticular hydrophobic resins impregnated with TOA (23). In our previous works, resins impregnated with di-(2-ethylhexyl) thiophosphoric acid (DEHTPA) (24, 25) were characterized and performed selective extraction of Pd(II) over other metals, and also resins using Alamine 336, tertiary amine, impregnated onto Amberlite XAD2, have been prepared and applied to Pd(II) recovery in a fluidized bed column (26) as well as in batch operation (27).

The objective of this work is to complete the study of Pd(II) recovery with Alamine 336/XAD2 resins started in reference 27 and also to investigate the behavior of other PGMs such as Pt(IV) and Rh(III) with the above mentioned resins, paying special attention to the development of straightforward metal separations on the basis of differential extraction kinetics, differential extraction dependency on hydrochloric acid concentration or differential stripping.

## EXPERIMENTAL

### Reagents and Solutions

Alamine 336 was kindly supplied by Henkel and used as extractant without further purification. Its purity was determined elsewhere (27) and was

found to be 92.2%. Alamine 336 is a mixture of saturated and straight chain trialkylamines with carbon chains  $C_8$  and  $C_{10}$ , with the carbon chain  $C_8$  predominating by about 2 to 1.

Amberlite XAD2 (Rohm and Hass) with particle diameter between 0.3 and 0.9 mm, was used as a macroporous polymer adsorbent. To remove impurities, the resin was kept in contact with a 50% methanol-water solution containing HCl 4M for 12 hours; then the polymer was washed with water until chloride was not detected, and finally dried at 50°C.

Stock metal solutions were prepared by dissolving an appropriate amount of  $PdCl_2$ ,  $PtCl_4$  or  $RhCl_3 \cdot 3H_2O$  (Johnson Matthey) in hydrochloric acid medium, and were used to prepare the solutions employed in the extraction experiments. In the experiments with rhodium, 15-day aged solutions were used. Impregnated resins were prepared by using a dry impregnation method (4) mixing an appropriate amount of Alamine 336 dissolved in ethanol with dry XAD2 until total evaporation of the diluent was reached. The characterization of these resins was conducted by titration with  $HClO_4$  in glacial acetic acid and specific surface area measurements described in a previous work (27).

In this paper, Alamine 336 concentration in the resin phase is given in all cases as moles of extractant per kg of unimpregnated resin, and expressed in the text as “mol/kg dry XAD2 resin”.

#### Metal Extraction

The metal extraction experiments were carried out in batch experiments at room temperature. Samples of 0.1 g of impregnated resin, unless otherwise stated, were shaken vigorously with 20 ml of metal aqueous phase for different periods of time depending on the purpose of the experiment. After phase separation, metal concentrations in the aqueous phase were determined by ICP (Spectroflame of Spectro Analytical Instruments).

### Metal Stripping

Metal stripping tests were performed in batch experiments at room temperature. First of all, metal loading was conducted by contacting a Pd(II) or Pt(IV) solution as appropriate at 0.5 M HCl, with 0.1 g of 1.27 mol/kg dry XAD2 resin. Then, immediately after separating the liquid from the resin phase, 10 ml of stripping reagent was added to the loaded resin, and shaken vigorously for 24 hours. The metal concentrations after the extraction and stripping steps in the aqueous phases were determined by ICP (Spectroflame of Spectro Analytical Instruments).

The concentration of metal loaded on XAD2/Alamine 336 resins is given in this article as moles of metal per kg of impregnated resin and expressed in the text as “mol/kg dry impregnated resin”.

## RESULTS AND DISCUSSION

### Extraction Kinetics

In this section, the experimental work was performed by conducting separate tests for each metal.

The metal extraction ratio at various contacting times was calculated as follows:

$$E(\%) = 100 \frac{[M]_i - [M]_e}{[M]_i} \quad (1)$$

where  $[M]_i$  and  $[M]_e$  are the initial and the equilibrium concentration of metal in the aqueous phase respectively, expressed in M units.

As can be seen in Figure 1, the extraction rates of Pd(II) and Pt(IV) were similar in the range of conditions studied: fast for high loaded resins and very slow when low loaded resins were used. These phenomena could be interpreted by

taking into account the following assumptions: a) it has been reported that a large pore diameter in the resin bead allows a faster diffusion inside the resin (28), b) during the resin's impregnation the ligand molecules gradually fill the pore space from the smallest pores of the resin to pores with large diameters (24, 27, 29); therefore, in the case of resins with low Alamine 336 concentration, the extractant molecules predominantly occupy the smallest pores; thus low extraction rates can be observed (27).

A more detailed analysis of the kinetic data on the basis of the extraction half time,  $t_{1/2}$ , defined as the time necessary to achieve 50% of the resin's final extraction and shown in Table 1, demonstrates that the Pt(IV) extraction rate is lower than that of Pd(II), although from a practical criterion the time to reach the equilibrium is the same for both metals. In part, this seems to be in agreement with the order of solvent extraction reaction rates of chlorocomplexes of PGM with organic ligands reported in the literature and summarized in Table 2: Pd(II) is extracted "very fast" and Pt(IV) is extracted "slowly", but although in this work palladium is extracted faster than platinum, the latter is not extracted very slowly, as could be expected. It can be qualitatively interpreted by the fact that the diffusion inside the pores is the main kinetic limiting step, but in the case of Pt(IV) some contribution due to a very slow chemical reaction has to be taken into account. The different extraction rates of Pd(II) and Pt(IV) are justified on the basis that  $d^8$  electronic configurations are more labile than  $d^6$  configurations because of their highly inert electron system (2).

From these results it was concluded that there was no possibility of separation between Pd(II) and Pt(IV) from the kinetic viewpoint and also a contact time of 48 hours was established as necessary to reach equilibrium for the extraction experiments with different Alamine 336 and HCl concentrations.

The kinetic data obtained for Rh(III) are illustrated in Figure 2. By examining the half time extraction values it can be seen that for Rh(III) this



TABLE 1  
Half time dependency on Alamine 336 concentration  
in the resin. Experimental conditions as in Figures 1 and 2

$[R_3N]_{org}$ (mol/kg)	$t_{1/2}$ Pd (h)	$t_{1/2}$ Pt (h)	$t_{1/2}$ Rh (h)
0.19	3.6	5.0	-
0.37	2.3	2.6	-
0.94	0.4	0.6	0.5

TABLE 2  
Solvent extraction properties of Pd(II), Pt(IV) and Rh(III)  
chlorocomplexes with organic ligands  
(Based on data from Ref. 2, if not otherwise stated)

Metal	Electronic config.	Geometry	Metal complexes at >0.5 M HCl	Rate of extraction
Pd(II)	$d^8$	square planar	$PdCl_4^{-2}$ (30)	very fast
Pt(IV)	$d^6$	octahedral	$PtCl_6^{-2}$ (31)	slow
Rh(III)	$d^6$	octahedral	$RhCl_5(H_2O)^{-2}$ , $RhCl_6^{-3}$ (32)	slow

parameter was similar to those of palladium and platinum, the main conclusion to be drawn from this experiment being that a very low percent extraction was observed in comparison with the other metals investigated. This opens the door to a selective separation of Pd(II) and Pt(IV) from Rh(III) and will be treated extensively in the following sections.

#### Metal Extraction

Metal extraction at various concentrations of ligand as a function of HCl concentration was studied in single metal experiments for Pd(II) and Pt(IV), but not for Rh(III) since in the previous section Rh(III) extraction was found to be nearly zero.

The chemical reaction of Pd(II) extraction with XAD2/Alamine 336 resins

was investigated in our previous work and was found to be (27):



Figure 3 shows the percent extraction, E(%), for Pd(II) and Pt(IV), where it can be seen that both metals were effectively extracted by the resins. The metals showed a diminution in extraction ratio as HCl concentration was increased, the extraction being generally higher for Pt(IV). Platinum was very well extracted even at 8 M HCl, but in the case of palladium metal extraction clearly fell off as acid concentration was increased. In the case of low Alamine 336 concentration, 0.19 mol/kg dry XAD2 resin, the percent extraction was very low at 0.5 M HCl: 9% for palladium and 8% for platinum, and when [HCl] was increased the extraction was almost completely suppressed for the two metals, though the data are not shown in Figure 3. This kinetic effect, presumably could be involved with the location of the tertiary amine molecules in small-diameter resin pores in the case of low extractant concentrations as mentioned above, and related to steric effects which may influence the reaction between the metals and the ligand.

The extraction data for Pt(IV) were treated by the program LETAGROP-DISTR. (33). Pd(II) data treatment was made with the same program and was reported in a previous work (27). In the LETAGROP-DISTR. program, for a given model, the computer searches for the best set of stoichiometric equilibrium constants, which minimize the error squares sum defined by:

$$U = \sum (\log D_{exp} - \log D_{calc})^2 \quad (3)$$

where  $D_{exp}$  is the distribution coefficient determined experimentally and  $D_{calc}$  is the value calculated by the program. This program also calculates the standard deviation  $\sigma(\log D)$  defined by:

$$\sigma(\log D) = \sqrt{\frac{U}{N_p}} \quad (4)$$

where  $N_p$  is the number of experimental points.

The distribution coefficient corresponding to the extraction data is needed

to process the data using the program LETAGROP-DISTR. Analogously to solvent extraction, the distribution coefficient of the metal is defined as:

$$D = \frac{[M]_{\text{org}}}{[M]_{\text{aq}}} = \frac{([M]_i - [M]_{\text{aq}})V}{[M]_{\text{aq}} m} \quad (5)$$

where  $[M]_{\text{org}}$  and  $[M]_{\text{aq}}$  are the total equilibrium metal concentrations in the resin and aqueous phase expressed in mol/kg dry impregnated resin and mol/l respectively,  $[M]_i$  is the initial metal concentration in mol/l,  $V$  is the volume in the aqueous phase, and  $m$  is the mass of dry impregnated resin in kg.

With phase ratio conditions used in this work, 0.1 g impregnated resin/20 ml aqueous phase, the program LETAGROP-DISTR can only compute distribution data included in the range:  $0.30 < \log D < 4.30$ . Due to the high extraction of Pt(IV) exhibited by the resins, it was possible to compute the platinum extraction data only for hydrochloric acid concentrations over 4M, because over this concentration extraction decreased enough to make the distribution data processable for the program. The model which gave the best fitting of the data is expressed by the reaction:



Accordingly, the Pd(II) and Pt(IV) extraction with XAD2/Alamine 336 can be described with the following general ion-exchange reaction:



with  $n=4$  for Pd(II) and  $n=6$  for Pt(IV).

Furthermore, the stoichiometric equilibrium constant ( $K_{\text{ex}}$ ) for the reaction expressed in Equation 7 is defined as:

$$K_{\text{ex}} = \frac{[(R_3NH^+)_2MCl_n^{-2}]_{\text{org}} [Cl^-]_{\text{aq}}^2}{[R_3NH^+Cl^-]_{\text{org}}^2 [MCl_n^{-2}]_{\text{aq}}} \quad (8)$$

By treating the extraction data of Pt(IV) separately for each ionic strength with the program LETAGROP-DISTR the equilibrium extraction constants for

Pt(IV) were obtained at different HCl concentrations, which are listed in Table 3 and compared with those obtained with Pd(II). A stability constant corresponding to the hexahaloplatinate ion found in the literature (31) was used in the calculations. As can be seen, platinum equilibrium extraction constants are higher than palladium constants, probably due to the larger size of  $\text{PtCl}_6^{-2}$  which implies that the anion is more lipophilic and also favours the packing of large organic amine cations around the metal complex.

Rh(III) extraction with 0.94 mol/kg dry XAD2 resins was found to be around 7%, while 100% extraction was achieved for Pd(II) and Pt(IV) at 0.5 M HCl. Speciation and separation of Rh(III) from chloride solutions was reviewed by Benguerel et al. Extraction of rhodium by amines is favored at low acidity and low chloride concentrations, both of which favor the formation of mixed aquo-chloro complexes; therefore, significant extraction is found only at HCl 0.1 M, which explains the result observed in this article. It has been speculated that the rhodium complex extracted with amines is  $\text{RhCl}_5(\text{H}_2\text{O})^{-2}$ (32).

#### Metal stripping

Metal stripping experiments were performed as described in the experimental section. Before the described experiments, several preliminary experiments with palladium were conducted; because of their importance they will be explained and discussed here.

TABLE 3  
Stoichiometric equilibrium extraction constants for Pd(II) and Pt(IV) extraction by XAD2/Alamine 336 resins from hydrochloric acid solutions

[HCl](M)	$\log K_{\text{ex}}(\text{Pd})$	$\log K_{\text{ex}}(\text{Pt})$
5	4.54±0.07	5.78±0.04
6	4.28±0.07	5.66±0.03
8	3.8±0.1	5.11±0.2
Reference	(27)	This work

At first, the stripping Pd(II) experiments were carried out by using a stock palladium loaded resin for practical experimental reasons. The idea consisted in performing the metal extraction with a large mass of resin, 2g, in order to obtain a considerable amount of stock resin for use in several stripping experiences. When, after the metal extraction, the resin was washed with water and dried or kept in water, several days later, a change in the color of the resin, from orange to a dark color, was observed. The stripping kinetics with these resins was very slow, the time necessary to reach elution equilibrium being several days, and moreover the percentage of metal stripped was found to be low. From these results we decided to perform the experiments as described in the experimental section: conducting the stripping step immediately after the metal extraction. Preliminary tests showed that in this way the kinetics and the efficiency of the stripping were improved considerably. Therefore, this method was adopted, and a general contact time of 24 hours in all the stripping tests was used to simplify the experiments by avoiding kinetic back extraction factors. From these results, it could be concluded that when the method based on stock metal loaded resin solution was followed, a chemical change occurred in the palladium chlorocomplexes bonded to the tertiary amine in the resin. Since a dark color was observed in the resin, a kind of Pd oxide such as  $\text{PdO}_2 \cdot 2\text{H}_2\text{O}$ , which is dark red (34), was probably formed and precipitated on the resin because of the absence of acid in the solution and the basic media inside the bead resin due to the high content of Alamine 336. To avoid this problem, as mentioned before, the resin must be used immediately after the metal extraction. Oxide formations can probably also be prevented by keeping the loaded metal resins in strongly acidic media, but this has not been experimentally verified.

The percent stripping,  $S(\%)$ , was defined as the fraction of metal loaded in the resin which was back extracted, and was calculated as follows:

$$S(\%) = 100 \frac{V_s}{V_e} \frac{[Pd]_s}{([Pd]_i - [Pd]_e)} \quad (9)$$

where  $V_s$  and  $V_e$  are the volumes of aqueous solutions used in the stripping and extraction steps respectively,  $[Pd]_i$  and  $[Pd]_e$  are the initial and equilibrium palladium concentrations in the aqueous phases corresponding to the extraction step, and  $[Pd]_s$  is the metal concentration in the aqueous phase after the stripping.

Preliminary elution experiments with Pd(II) and HCl 10.2 M as a stripping reagent were conducted in order to study the effect of the concentration of metal loaded in the resin and the volume of the stripping aqueous phase solution in the percent elution. Results are listed in Tables 4 and 5 respectively. As can be seen, the Pd concentration in the resin did not affect the stripping efficiency, and a volume of 10 ml was found to be appropriate since it was the lowest volume which allowed almost complete stripping; in other words all the metal was recovered and moreover was concentrated, since the stripping volume was half that used for metal extraction. Although all these experiments were performed only with palladium and concentrated HCl as a stripping agent, the conclusions drawn from them were used to obtain a general idea of the experimental conditions to be used in the back extraction tests. For that reason 10 ml of stripping aqueous phase was used in all the tests, as described in the experimental section.

HCl, HClO<sub>4</sub> and thiourea were used as chemicals to re-complex the precious metals from the resin phase as a water-soluble complex compound. Figure 4 shows the percent stripping values for Pd(II) and Pt(IV) using HCl. At the highest HCl concentration, almost complete elution of Pd(II) was reached, whereas in the case of Pt(IV) more than half of the loaded metal remained in the organic phase. The elution was enhanced with increasing acidity since HCl displaced the extracted PGM species because the reverse of reaction 7 took place.

TABLE 4

Influence of the metal loading in the resin  $[Pd]_{i,org}$  (expressed in mol/kg impregnated resin) on the percent stripping.  
 Experimental conditions: mass of resin 0.1 g, volume of the stripping aqueous phase (HCl 10.2 M) 10 ml and shaking time 24 h.

$[Pd]_{i,org}$ (mol/kg)	S (%)
0.04	93
0.11	93
0.17	96
0.28	96

TABLE 5

Influence of the volume stripping aqueous solution (HCl 10.2 M) on the percent stripping. Experimental conditions: mass of resin 0.1g, initial metal concentration in the resin  $[Pd]_{i,org}=0.26$  mol/kg impregnated resin and shaking time 24 h.

Volume (ml)	S(%)
5	77
10	96
15	96
20	94

The reason why platinum cannot be quantitatively recovered can be related to the large size of  $PtCl_6^{-2}$ , which is more readily exchanged for chloride in the organic phase.

The data corresponding to PGM back extraction with  $HClO_4$  are reported in Figure 5. Efficient recovery was obtained for Pd(II) and Pt(IV) over  $HClO_4$  0.5 M. Stripping occurred through an anion exchange reaction, where the highly extractable perchlorate ion,  $ClO_4^-$ , replaced the PGM chlorocomplexes loaded in the resin. When  $HClO_4$  is used, the stripped organic then had to be scrubbed with alkali to remove  $ClO_4^-$  allowing the re-use of the resin, although this point has not been verified experimentally.

When thiourea (Tu) or  $\text{SC}(\text{NH}_2)_2$  was used as stripping reagent, complete elution for palladium and platinum was achieved in the studied range as can be seen in Figure 6. This time, the PGM species were converted to a different complex which is not extracted by the amine. For Pd(II), the labile  $d^8$  square-planar complex  $\text{PdCl}_4^{-2}$  was transferred to the aqueous phase by ligand replacement of chlorides with thiourea, which is a very strong nucleophilic ligand. The cationic thiourea complexes,  $\text{Pd}(\text{Tu})_4^{+2}$ , are non-extractable by amines and are inert to further ligand substitution (3). In the case of platinum, Pt(II) forms stable complexes with thiourea which had previously reduced Pt(IV) to Pt(II) (35). The chemical properties of thiourea can be predicted by Pearson's Hard and Soft Acids and Bases (HSAB) principle, and due to its soft acid character promoted by the presence of sulfur atoms, thiourea will tend to react with soft bases such as Pd(II) and Pt(II) (36).

Because no clear differences were observed in the stripping of the metals studied, metal separation schemes could not be designed from the results presented in this section. Thiocyanate, which like thiourea is a very strong nucleophilic ligand, may also be used as a good stripping agent for palladium and platinum, and by controlling the time of the stripping reaction, proper separation between platinum and palladium can be obtained in liquid-liquid extraction (3), but this reagent was not tested here because of the complexity of the stripping procedure since time control is required.

The conditions under which stripping experiments produced the best results are summarized in Table 6.

### Metal Separation

On the basis of the data presented so far from single-metal experiments, some straightforward metal separations from mixed metal solutions were attempted.



TABLE 6  
Stripping reagent ability for Pd(II) and Pt(IV) extracted by  
XAD2/Alamine 336 resins

Reagent	Stripping process	Pd	Pt
HCl 10.2 M	Chemical displacement	Quantitative	Qualitative
HClO <sub>4</sub> 1M	Anion-exchange	Quantitative	Quantitative
Tu 0.05M-HCl 1M	Complex formation	Quantitative	Quantitative

First, selective co-extraction of platinum and palladium from solutions containing rhodium was studied, since the single metal extraction tests showed a very high percent extraction for Pd(II) and Pt(IV) in comparison with Rh(III). Data showing the results are given in Table 7. A concentrated resin, 0.94 mol/kg dry XAD2 resin, was used for the experiments in order to ensure a fast extraction rate and reduce the contact time necessary to reach equilibrium. When only 0.1g of resin was used, Pt(IV) and Pd(II) extractions were lower than the values expected in the light of the single-metal experiments. At first, this was attributed to kinetic problems, but experiments with longer contact time, 8h, showed that the final extraction was hardly modified. When 0.2 g of impregnated resin was used in the tests, complete co-extraction of Pd(II) and Pt(IV) and good separation from Rh(III) were achieved at 0.5 M HCl. By increasing the HCl concentration, the extraction of all the metals was found to decrease. This result is in accordance with the previous data obtained for Pd(II) and Pt(IV), and with the literature in the case of Rh(III), since the extraction of the PGMs studied in this paper is favored at low acidity and low chloride concentrations, as discussed above.

The separation factor for one metal M1 with respect to another metal M2,  $\alpha(M1/M2)$ , is defined as:

$$\alpha(M1 / M2) = \frac{[M1]_{org} / [M1]_{aq}}{[M2]_{org} / [M2]_{aq}} = \frac{D_{M1}}{D_{M2}} \quad (10)$$

TABLE 7

Metal extraction ratios from a solution containing Pd(II), Pt(IV) and Rh(III).

Experimental conditions: volume of aqueous phase 20 ml,

initial metal concentrations  $[Pd]_i=[Pt]_i=[Rh]_i=4.7 \times 10^{-4}$  M,

Alamine 336 concentration 0.94 mol/kg dry XAD2 resin and contact time 4h

Resin mass (g)	0.1			0.2		
[HCl] (M)	E(%) Pd	E(%) Pt	E(%) Rh	E(%) Pd	E(%) Pt	E(%) Rh
0.5	29.3	80.9	3.0	99.2	10.0	4.2
3	20.2	79.6	0.9	77.4	98.5	1.8
5	11.5	67.2	0.8	49.6	96.0	1.4

TABLE 8

Separation factors for Pd(II) and Pt(IV) with respect to Rh(III)

Experimental conditions: as in Table 7

Resin mass (g)	0.1		0.2	
[HCl] (M)	$\alpha(Pd/Rh)$	$\alpha(Pt/Rh)$	$\alpha(Pd/Rh)$	$\alpha(Pt/Rh)$
0.5	13	137	2937	20620
3	27	423	183	3387
5	17	268	71	1716

TABLE 9

Metal extraction ratios from a solution containing Pd(II) and Pt(IV).

Experimental conditions: volume of aqueous phase 20ml,

initial metal concentrations  $[Pd]_i=[Pt]_i=4.7 \times 10^{-4}$  M,

Alamine 336 concentration 0.94 mol/kg dry XAD2 resin and contact time 4h

Resin mass (g)	0.1		0.2	
[HCl](M)	E(%) Pd	E(%) Pt	E(%) Pd	E(%) Pt
6	20.2	77.7	57.6	94.5
8	17.0	64.5	29.4	80.7

TABLE 10  
Separation factors for Pt(IV) with respect to Pd(II)  
Experimental conditions: as in Table 9

Resin mass (g)	0.1	0.2
[HCl](M)	$\alpha(\text{Pt/Pd})$	$\alpha(\text{Pt/Pd})$
6	13.8	12.6
8	8.9	10.0

Separation factors for Pt(IV) and Pd(II) with respect to Rh(III) are listed in Table 8. As can be seen, the highest separation factors for Pd(II) and Pt(IV) with respect to Rh(III) are found at 0.5 M HCl and using 0.2 g of impregnated resin.

Despite the similarity in the reaction extraction of palladium and platinum due to the resemblance of  $\text{PtCl}_6^{-2}$  and  $\text{PdCl}_4^{-2}$  chlorocomplexes, it can be observed in Figure 3 that there is a considerable difference in the extent of extraction for these metals in the range of high hydrochloric acid concentrations. Extraction experiments were performed with impregnated resins focusing on the selective recovery of Pt(IV) from solutions also containing Pd(II) with concentrated HCl. The results are listed in Tables 9 and 10, but unfortunately only partial separation between Pt(IV) and Pd(II) was achieved in the experimental conditions employed.

### CONCLUSIONS

Several conclusions can be drawn from the results of this study. Physical immobilization of Alamine 336 into Amberlite XAD2 provides highly effective impregnated resins for the recovery of Pd(II) and Pt(IV) and their separation from Rh(III).

The extraction kinetics of the metals investigated is similar from a practical viewpoint and does not allow the design of metal separation procedures.

Pt(IV) extraction increases at low HCl concentrations and when the extractant content in the resin is increased. Pt(IV) is extracted through an ion-exchange reaction by Alamine 336/XAD2 resins, as in case of Pd(II), whereas Rh(III) is almost not extracted.

Unlike Rh(III), Pd(II) and Pt(IV) show a very similar chemical behavior in hydrochloric acid media. This fact may be used to develop a selective co-extraction of palladium and platinum from rhodium at low hydrochloric acid concentrations. Moreover, despite the similarity of palladium and platinum chlorocomplexes, because of the higher affinity of Pt(IV) to form complexes with Alamine 336 in comparison with Pd(II), partial separation of Pt(IV) from Pd(II) in concentrated acid media is achieved.

HCl, HClO<sub>4</sub> and thiourea can be used as stripping agents to re-complex the precious metals from the resin phase as water soluble complex compounds, and with all these reagents optimum conditions for performing almost quantitative stripping were found, except for Pt(IV), which is not completely back extracted from the organic phase by using concentrated HCl.

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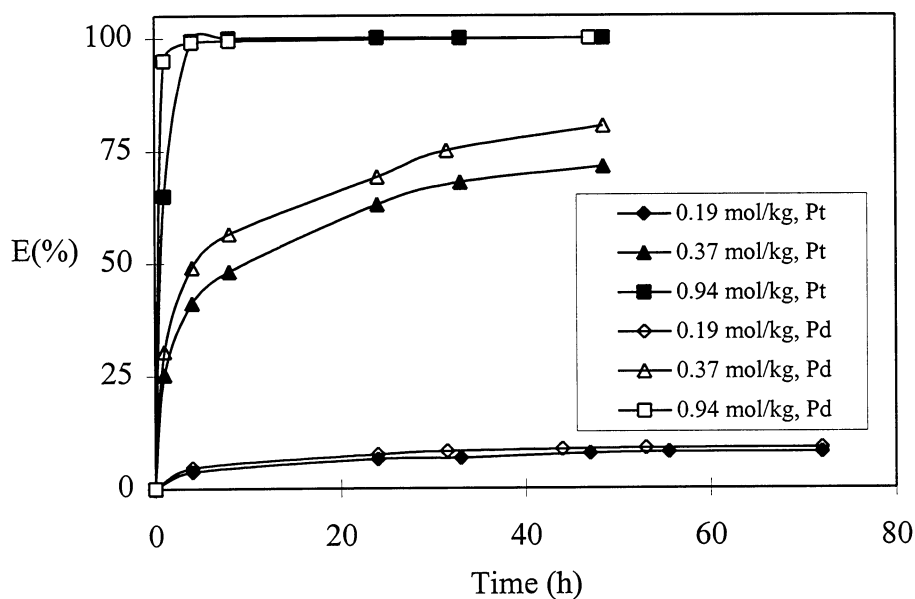


FIGURE 1. Effect of extractant content in the resin (expressed in mol/kg dry XAD2 resin) on extraction kinetics of Pd(II) and Pt(IV) by XAD2/Alamine 336 resins. Experimental conditions: mass of resin 0.1 g, volume of aqueous phase 20 ml, HCl 0.5 M and initial metal concentrations  $[Pd]_i=[Pt]_i=4.7 \times 10^{-4}$  M. Palladium data from Ref. 27.



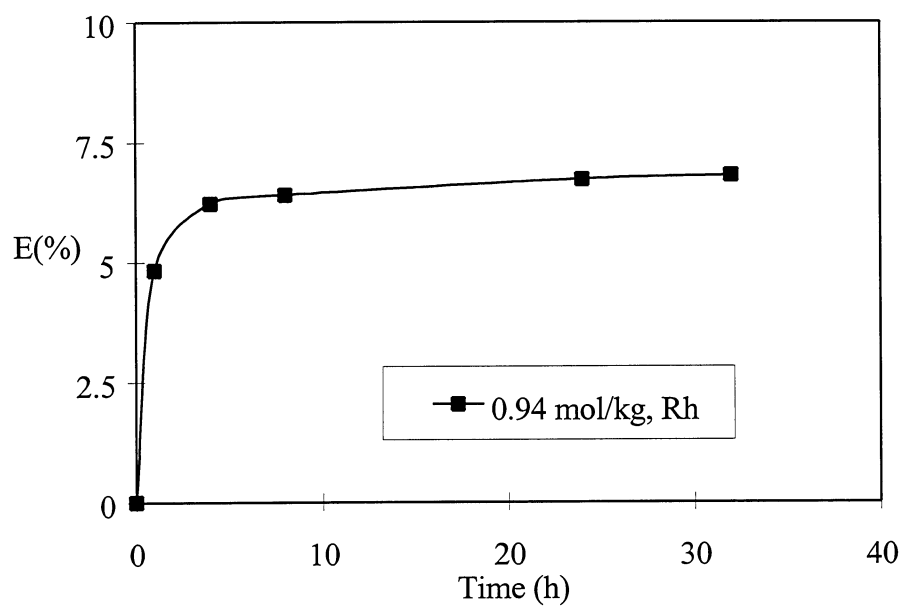


FIGURE 2. Extraction kinetics of Rh(III) by XAD2/Alamine 336 resins. Experimental conditions: mass of resin 0.1 g, volume of aqueous phase 20 ml, HCl 0.5 M and initial Rh(III) concentration  $4.7 \times 10^{-4}$  M.

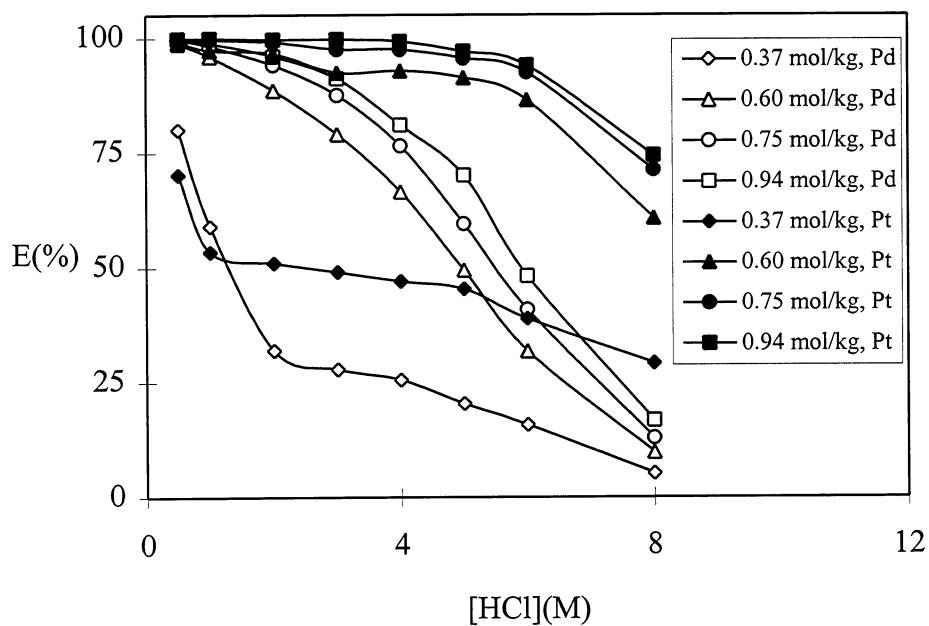


FIGURE 3. Effect of HCl concentration on the percent extraction of Pd(II) and Pt(IV) with XAD2/Alamine 336 resins. Experimental conditions: mass of resin 0.1 g, volume of aqueous phase 20 ml, initial metal concentrations  $[Pd]_i=[Pt]_i=4.7 \times 10^{-4}$  M, variable extractant content in the resins (expressed in mol/kg dry XAD2 resin) and shaking time 48 h. Palladium data from Ref. 27.

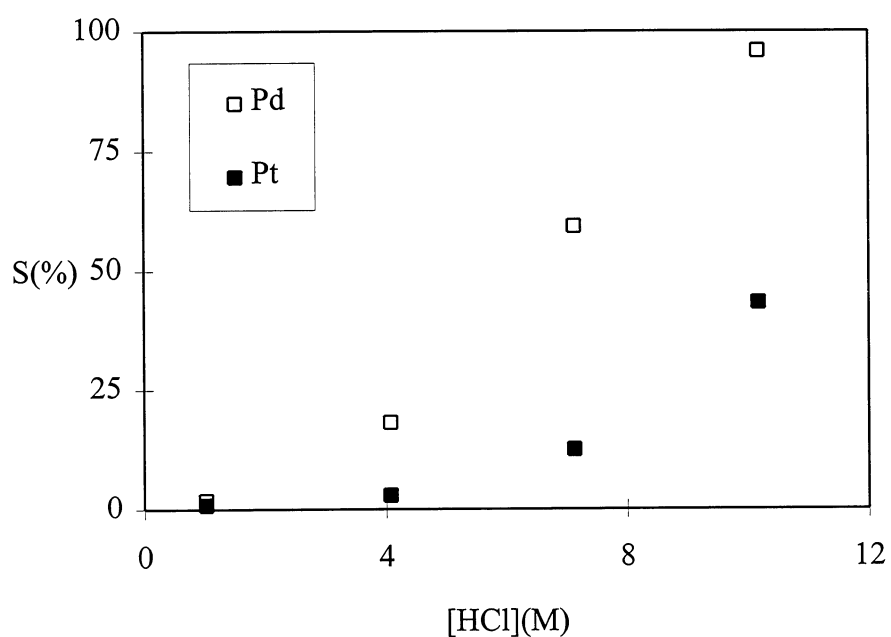


FIGURE 4. Effect of HCl concentration on the percent stripping of Pd(II) and Pt(IV) loaded onto XAD2/Alamine 336 resins. Experimental conditions: mass of resin 0.1 g, initial metal concentration in the resin  $[Pd]_{i,org}=[Pt]_{i,org}=0.18$  mol/kg dry impregnated resin, volume of the stripping aqueous phase 10 ml and shaking time 24 h.

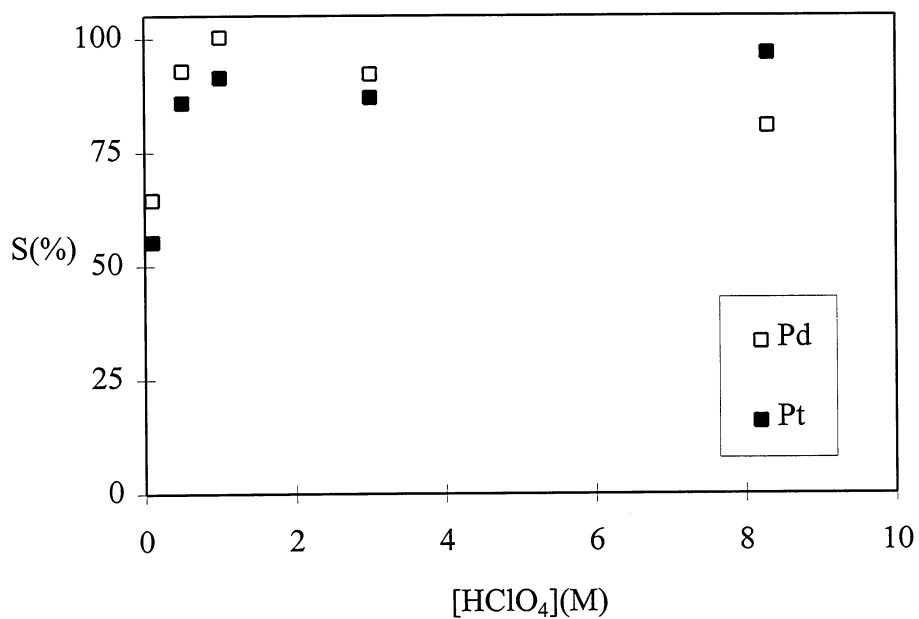


FIGURE 5. Effect of HClO<sub>4</sub> concentration on the percent stripping of Pd(II) and Pt(IV) loaded with XAD2/Alamine 336 resins. Experimental conditions: as in Figure 4.

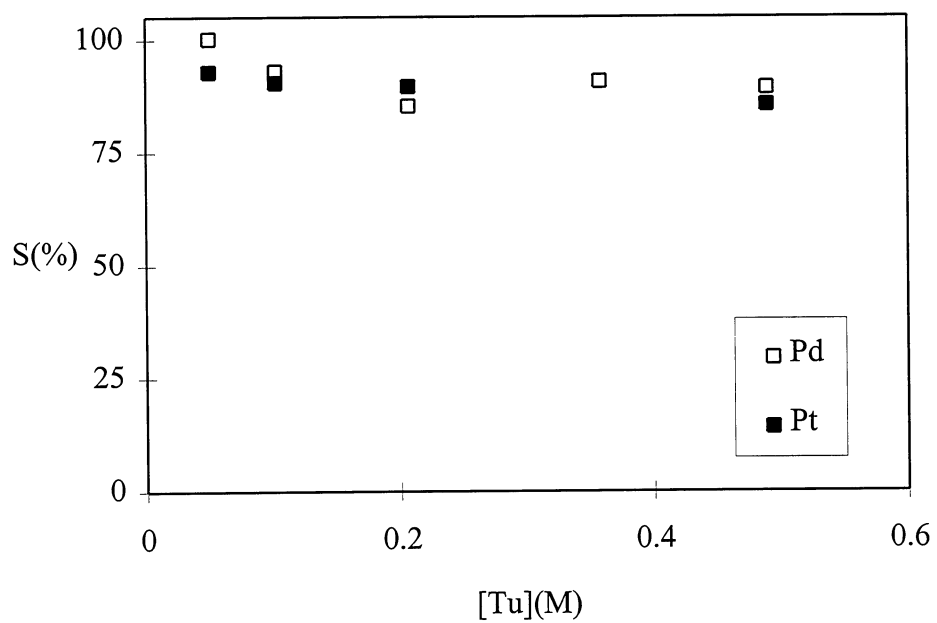


FIGURE 6. Effect of thiourea concentration in HCl 1 M medium on the percent stripping ratio of Pd(II) and Pt(IV) loaded with XAD2/Alamine 336 resins. Experimental conditions: as in Figure 4.

