

## Recovery of platinum, tin and indium from spent catalysts in chloride medium using strong basic anion exchange resins

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### ABSTRACT

This work describes a route for platinum recovery from spent commercial Pt and PtSnIn/Al<sub>2</sub>O<sub>3</sub> catalysts using strong basic mesoporous and macroporous anion exchange resins (Cl<sup>-</sup> form). The catalysts were leached with aqua regia (75 °C, 20–25 min). Platinum adsorption was influenced by the presence of other metals which form chlorocomplexes (tin, indium) and also base metals (aluminum). However, it was possible to overcome this fact by a sequential desorption procedure. Aluminum was selectively removed from the resins by elution with 3 mol L<sup>-1</sup> HCl. Platinum was desorbed passing 1 mol L<sup>-1</sup> Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (pH 9). Tin was removed by elution with 0.1 mol L<sup>-1</sup> ascorbic acid. Indium was removed using 0.1 mol L<sup>-1</sup> EDTA as eluent. Desorption efficiency exceeded 99% for all metals. Metals were recovered in high yields (>98 wt%).

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### 1. Introduction

Platinum-group metals (PGM) are used widely in many fields such as catalysts in many chemical processes, electrical and electronic industries, corrosion resistant materials and jewellery [1]. Their excellent selectivity and activity towards reactants and resistance to oxidation at high temperatures make them very effective catalysts. For instance, platinum is a common active phase of petroleum cracking, dehydrogenation, reforming, and hydrogenation catalysts, which are extensively used in refining and petrochemical industries.

The demand for PGM has not been balanced by supply due to limited resources [2]. The cost of production from naturally occurring supplies is very high [3]. The worldwide reserves are concentrated in only two regions, Siberia and South Africa. Although the amount of this metal in a commercial catalyst is approximately 1 wt%, it corresponds to the main cost of this product [4,5]. The deactivated (spent) catalysts are replaced periodically by fresh ones. Even if these catalysts can be regenerated, their lifetime is limited [3]. The petroleum and petrochemical industries produce

considerable amounts of spent catalysts containing platinum and other precious and rare metals annually. Spent catalysts are classified by the North-American Environmental Protection Agency (EPA) as a hazardous waste since they commonly contain contaminants such as coke, vanadium and nickel [3]. As most of their rich natural deposits are getting exhausted, the production of PGM from secondary sources (spent catalysts, electronic scrap, etc.) has become an important issue [6,7]. Recovery of PGM from spent catalysts (including automotive ones) is an attractive way to lower the catalyst cost [6] and is nowadays a viable and cost effective alternative [3].

Pyro and hydrometallurgical processes have been investigated during recent decades for recovering precious and strategic metals from wastes (spent catalysts, electronic devices, etc.) [2]. In hydrometallurgical routes, the waste is generally subjected to strong acidic oxidative leaching (particularly aqua regia). Acidic leachates are formed containing a wide diversity of leached metals, including PGM and also the so-called base metals (BM) [2,7]. The ionic state of platinum in chloride solutions depends on medium acidity, concentration of chloride ions [8] and temperature. Hexachloroplatinate ions (PtCl<sub>6</sub><sup>2-</sup>) predominate in strong acidic solutions (HCl ≥ 3 mol L<sup>-1</sup>). Under reduction of the free acidity (increase in pH value) aquation and hydrolysis take place. Aquachloro- and aquahydroxo-complexes of Pt(II) and Pt(IV) are

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**Table 1**  
Chemical analysis (wt.%, dry basis) of the spent catalysts.

	Pt	Sn	In	Al	Fe	C
Pt/Al <sub>2</sub> O <sub>3</sub>	0.35	–	–	52.80	0.02	3.5
PtSnIn/Al <sub>2</sub> O <sub>3</sub>	0.39	0.42	0.28	50.82	0.03	5.0

formed [7,8]. Binuclear complexes can also be present in these systems, and this fact should be taken into account for a study of platinum recovery from these solutions [7–9].

Solvent extraction is a powerful technique for recovery and separation of many metals [2], and has been widely used for separation of PGM from aqueous solutions [10]. The prerequisite for this process is that the concentration of PGM in these solutions must be over several hundreds of ppm. On the other hand, its efficiency decreases for the treatment of less concentrated solutions [2].

Sorbents, including ion exchange and chelating resins, may be an alternative to solvent extraction processes. Ion exchange has been recognized as a powerful tool for selective recovery of small amounts of PGM ions from solutions containing high amounts of BM, particularly aluminum [2,8,11,12]. This method is quick and offers separation of noble metal ions from variety of other ions [11,13]. Strongly basic anion exchange resins of styrene and acrylic structures, particularly those containing nitrogen-heterocycle groups [8], have found wide application in the recovery and concentration processes of PGM metal ions. These resins display high selectivity towards noble metal ions [14]. Among PGM platinum [1,3,7,8,15–19] and palladium [1,2,9,12,14–16,20,21] are by far the most employed in these studies. Rhodium has also received many attention in recent years [11,16,19]. Some of these studies employ spent automotive [14,16] or refinery catalysts [3,17]; the others have employed model solutions of PGM.

Adsorption of PGM is not a difficult step since high selectivity and high adsorption rates are commonly reported. The ion exchange resins used in removal of PGM ions have usually large ion exchange capacities, which allow to concentrate such metals [10]. The desorption step (thus allowing recycling of the resin) is the key to the implementation of the ion exchange system. Several media have been tested for the recovery of the metals loaded on the sorbent. Many acids at different concentrations [15] have been employed but the behavior is very dependent on the experimental conditions employed. Some studies employ thiourea (a ligand that displays high affinity for precious metals due to the presence of both amine and sulfur groups) in aqueous HCl, which can desorb fully [15], or partially [7] platinum from the resin. Aqueous ammonia has also been reported as a possible desorbent for platinum [16] at moderate temperatures. On the other hand other studies show that the noble metal keeps adsorbed [1,17]. In these circumstances the final decision is to calcine the resin [3,14,17] leaving platinum as an ash residue.

As a conclusion, PGM recovery using ion exchange resins is worth exploring. The presence of other possible interfering metals and the influence of parameters such as acidity, chloride concentration, time, flow rate and temperature may play an important role on the behavior of the sorption process. Also desorption requires further studies to be better understood. This work presents a route for recovering platinum from the acidic leachate of spent catalysts leached with aqua regia [22] using anionic ion exchange resins. The

**Table 2**  
Elements concentration in the leachates.

Catalyst	Free acidity (mol L <sup>-1</sup> )	Pt (g L <sup>-1</sup> )	Cl <sup>-</sup> (mol L <sup>-1</sup> )	In (g L <sup>-1</sup> )	Sn (g L <sup>-1</sup> )
Pt/Al <sub>2</sub> O <sub>3</sub>	3.44	1.04	1.40	–	–
PtSnIn/Al <sub>2</sub> O <sub>3</sub>	1.19	0.73	0.49	0.66	0.30

route presented in this work was compared to those found in the literature for platinum recovery using the same strategy.

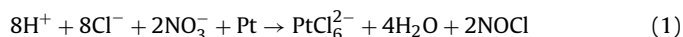
## 2. Experimental

### 2.1. Catalysts

Two commercial spent catalysts were employed in this study: a monometallic Pt/Al<sub>2</sub>O<sub>3</sub> and a multimetallic PtSnIn/Al<sub>2</sub>O<sub>3</sub>. Both were kept in their original forms (spheres  $d = 1.5$  mm). Both samples were used in catalytic reforming units. Spent samples were oxidized in a furnace (500 °C, 1 atm, 5 h, 1 °C min<sup>-1</sup>) to eliminate coke and water. Chemical analysis data of the spent catalysts are presented in Table 1.

### 2.2. Leaching procedure

Aqua-regia was used as the leaching agent. It oxidizes platinum according to the following reaction:



The volume of aqua-regia employed was 4 mL g<sup>-1</sup> sample (liquid/solid ratio = 4), which was the minimum amount to cover all catalyst. The experiments were run at 75 °C for 20 min (Pt/Al<sub>2</sub>O<sub>3</sub> catalyst) or 25 min (PtSnIn/Al<sub>2</sub>O<sub>3</sub> catalyst) in order to dissolve all platinum with limited aluminum leaching under magnetic stirring (50 rpm). These are the optimum conditions found in a previous study [22]. After the experiments, the insoluble matter was separated from the liquid phase by filtration and washed with water (10 mL g<sup>-1</sup> Pt/Al<sub>2</sub>O<sub>3</sub>; 20 mL g<sup>-1</sup> PtSnIn/Al<sub>2</sub>O<sub>3</sub>). Washing waters were added to the leachate. All experiments were run in triplicate, and data obtained were within ±3%. Table 2 presents some features of the leachates after addition of washing waters.

### 2.3. Anion exchange resins

Four strongly basic anion exchange resins (type-I) were employed in platinum adsorption from the leachate: Amberlite IRA-400AR (Carlo Erba), Amberlite IRA 420 (Carlo Erba), Dowex 1 (Dow Chemicals) and Amberjet 4200 Cl (Rohm & Hass). The main properties of these resins are presented in Table 3.

### 2.4. Metals adsorption and desorption

The dynamic method was applied to this study. Glass columns (diameter  $d = 10$  mm) were packed with a slurry of the resin until the settled resin bed attained the established height ( $L = 10$  cm). Therefore,  $L/d$  ratio was 10 in all experiments. The resins were previously equilibrated with 1 mol L<sup>-1</sup> HCl for 2 h. The leachate was passed through the columns (2.0 mL min<sup>-1</sup>) at 25 °C. The eluate was collected for metal analysis. The capacity of the resins to retain platinum, tin and indium was estimated from a breakthrough study. For

**Table 3**  
Anion exchange resins characteristics.

Description	Amberlite IRA-400AR	Amberlite IRA 420	Dowex 1	Amberjet 4200 Cl
Matrix	Styrene-divinylbenzene	Styrene-divinylbenzene	Styrene-divinylbenzene	Styrene-divinylbenzene
Functional group	Quaternary ammonium	Quaternary ammonium	Quaternary ammonium	Quaternary ammonium
Structure	Mesoporous	Macroporous	Macroporous	Macroporous
Ionic form	Cl <sup>-</sup>	Cl <sup>-</sup>	Cl <sup>-</sup>	Cl <sup>-</sup>
Apparent density	730 g L <sup>-1</sup>	650 g L <sup>-1</sup>	705 g L <sup>-1</sup>	670 g L <sup>-1</sup>
Exchange capacity	2.0 eq L <sup>-1</sup>	1.3 eq L <sup>-1</sup>	1.4 eq L <sup>-1</sup>	1.3 eq L <sup>-1</sup>
Grain size	0.125–0.150 mm	0.125–0.177 mm	0.30–1.20 mm	0.60–0.80 mm
Operating pH range	0–14	0–14	0–14	0–14
Moisture retention capacity (%)	45	50–55	43–48	49–55

**Table 4**  
Platinum, indium and tin uptake (mmol g<sup>-1</sup>) of the anion-exchange resins tested in this work.

Catalyst or standard Pt solution	PtSnIn/Al <sub>2</sub> O <sub>3</sub>	Pt/Al <sub>2</sub> O <sub>3</sub>	1 g L <sup>-1</sup> Pt
<b>Platinum</b>			
Amberlite IRA-400AR	0.085	0.154	0.260
Amberlite IRA 420	0.186	0.398	0.586
Dowex 1	0.182	0.385	0.573
Amberjet 4200 Cl	0.213	0.432	0.660
<b>Tin</b>			
Amberlite IRA-400AR	0.057	Absent	–
Amberlite IRA 420	0.126	Absent	–
Dowex 1	0.118	Absent	–
Amberjet 4200 Cl	0.130	Absent	–
<b>Indium</b>			
Amberlite IRA-400AR	0.130	Absent	–
Amberlite IRA 420	0.286	Absent	–
Dowex 1	0.270	Absent	–
Amberjet 4200 Cl	0.320	Absent	–

this purpose the leachates and a standard platinum solution (1 g L<sup>-1</sup> Pt as H<sub>2</sub>PtCl<sub>6</sub> in HCl, free acidity 1.0 mol L<sup>-1</sup>) were employed. Flow rate was 2.0 mL min<sup>-1</sup> and the experiments were performed at 25 °C.

Metals desorption from the resins was tested using the following solutions NH<sub>4</sub>OH (1–6 mol L<sup>-1</sup>); HCl (1–6 mol L<sup>-1</sup>); HNO<sub>3</sub> (1–6 mol L<sup>-1</sup>); H<sub>2</sub>SO<sub>4</sub> (1–6 mol L<sup>-1</sup>); (N<sub>2</sub>H<sub>5</sub>)<sub>2</sub>SO<sub>4</sub> (1% in 1 mol L<sup>-1</sup> HCl); thiourea (1% in 1 mol L<sup>-1</sup> HCl); Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (0.5–1 mol L<sup>-1</sup>). pH was adjusted to 9 by adding 6 mol L<sup>-1</sup> NaOH); ascorbic acid (0.1 mol L<sup>-1</sup>); EDTA (0.1 mol L<sup>-1</sup>). In the experiments with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, the resins were previously equilibrated with NaHCO<sub>3</sub>/Na<sub>2</sub>CO<sub>3</sub> buffer (pH 9) for 1 h prior to elution. Before elution with ascorbic acid or EDTA, the resins were washed with water (final pH 7). Flow rate was fixed at 1 mL min<sup>-1</sup> and experiments were run at 25 °C. The eluate was collected for metal analysis. All experiments in this section were run in triplicate and data obtained were within ±5%.

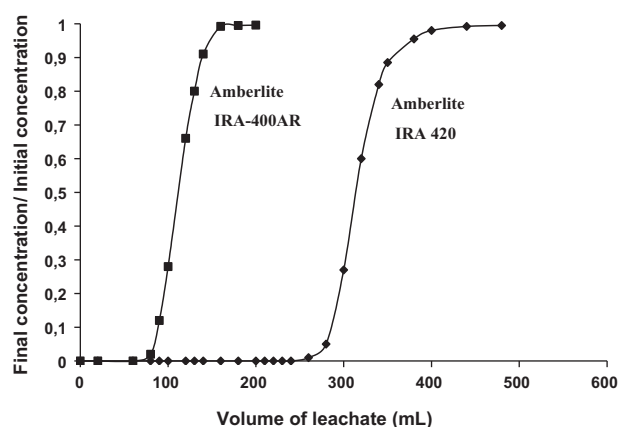
### 2.5. Analytical methods

Metal concentrations in the aqueous phases were determined by atomic absorption spectrometry (Perkin Elmer AAS 3300). The following wavelengths were employed: platinum, 265.9 nm; tin, 286.3 nm; indium, 303.9 nm; aluminum, 396.2 nm. The following detection limits were determined experimentally: 1 mg L<sup>-1</sup> (aluminum and tin), 0.5 mg L<sup>-1</sup> (indium and platinum). Acidity was determined by potentiometry using an Ag/AgCl reference electrode (Orion 2A13-JG). Chloride concentration was determined by an ion-selective electrode (Orion 9417-BN).

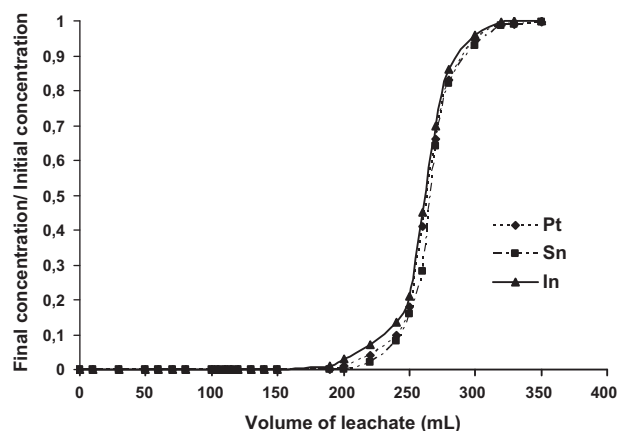
## 3. Results and discussion

### 3.1. Capacity of resins for metals uptake

Table 4 presents the platinum, tin and indium uptakes for the resins used in this work. Figs. 1–3 present the breakthrough curves



**Fig. 1.** Breakthrough curves for platinum present in the leachates of the Pt/Al<sub>2</sub>O<sub>3</sub> catalyst on Amberlite IRA-400AR and Amberlite IRA 420 resins.



**Fig. 2.** Breakthrough curves for platinum, tin and indium present in the leachate of the PtSnIn/Al<sub>2</sub>O<sub>3</sub> catalyst on Amberlite IRA-400AR resins.

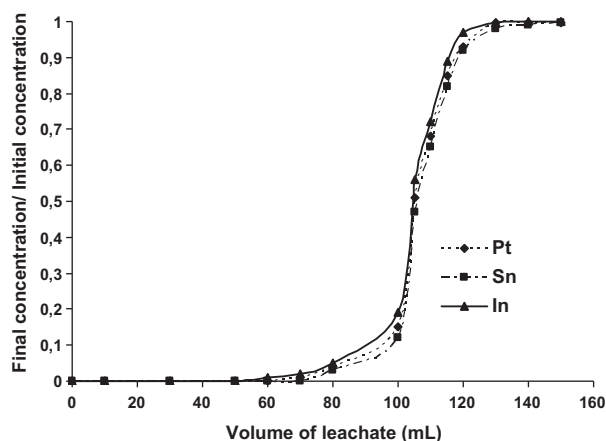


Fig. 3. Breakthrough curves for platinum, tin and indium present in the leachate of the PtSnIn/Al<sub>2</sub>O<sub>3</sub> catalyst on Amberlite IRA 420 resins.

for these metals on Amberlite IRA 420 and Amberlite IRA-400AR resins.

Indium sorption was the strongest for all resins, followed by platinum and tin. The platinum sorption order found in all resins was: standard platinum solution > Pt/Al<sub>2</sub>O<sub>3</sub> leachate > PtSnIn/Al<sub>2</sub>O<sub>3</sub> leachate. In the experiments with the multimetallic catalyst, aluminum was also somewhat adsorbed (0.02–0.03 mmol g<sup>-1</sup> resin). The sum of the three capacities (Pt+Sn+In) is approximately equal to the capacity for platinum using its standard solution. The acidities of this solution (1 mol L<sup>-1</sup>) and the leachate of the PtSnIn/Al<sub>2</sub>O<sub>3</sub> catalyst (1.19 mol L<sup>-1</sup>) are comparable, and the breakthrough curves for Pt, Sn and In (Figs. 2 and 3) are superimposed. As a conclusion, platinum sorption was affected by the presence of other elements that also form chlorocomplexes (InCl<sub>4</sub><sup>-</sup>, SnCl<sub>6</sub><sup>2-</sup>). Literature has already demonstrated that when leachates from processing multicomponent spent materials and model solutions are eluted through ion exchange resins, many metals can be adsorbed in some extent together with PGM [3,16,17]. It is also known that the increase of acidity (HCl concentration) reduces the exchange capacity for platinum [8,12]. The acidity of the leachate of the Pt/Al<sub>2</sub>O<sub>3</sub> sample is the highest (3.44 mol L<sup>-1</sup>, Table 4). This explains the lower platinum uptake for this leachate when compared to its standard solution (acidity 1 mol L<sup>-1</sup>).

Platinum uptake in the mesoporous resin was the lowest. This result possibly justifies the wide use of macroporous resins for PGM uptake from aqueous media [2,7]. Some of the exchange centers of the mesoporous resin may not be accessible to PtCl<sub>6</sub><sup>2-</sup> ions (ionic radius 259 pm [23]), which are greater than the Cl<sup>-</sup> anion (ionic radius 167 pm) and Al<sup>3+</sup> (ionic radius 53 pm) ions [24]. However, mesoporous resins typically present pore diameter between 20 and 500 Å (2000 and 50,000 pm) [25]. Perhaps diffusion of the leachate through the structure of the mesoporous resin under our experimental conditions was more difficult than in the macroporous one [25].

### 3.2. Metals desorption

Literature data indicate that when sorption is performed at HCl concentration up to 2 mol L<sup>-1</sup> under high sorption capacity resins it is expected that acidic solutions are not appropriate for the desorption of metals from these resins [15]. In fact, HCl, HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> were ineffective for platinum, tin and indium desorption in the concentration range tested (1–6 mol L<sup>-1</sup>). However, washing with 3 mol L<sup>-1</sup> HCl quickly removed aluminum from the resins (~10 mL). This procedure is suitable as a previous step in the noble metal recovery from the PtSnIn/Al<sub>2</sub>O<sub>3</sub> catalyst, but is not necessary

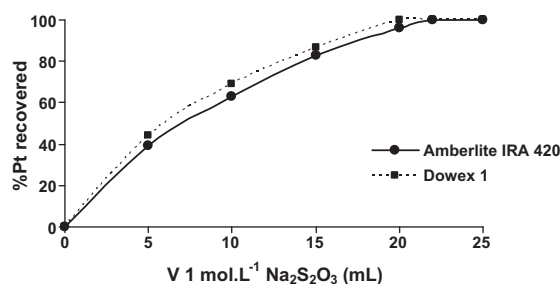


Fig. 4. Platinum recovery from PtSnIn/Al<sub>2</sub>O<sub>3</sub> catalyst after desorption using 1 mol L<sup>-1</sup> Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> on Amberlite IRA 420 and Dowex 1 resins.

for the Pt/Al<sub>2</sub>O<sub>3</sub> sample since its acidity (Table 2) is high enough to avoid aluminum adsorption by the resins. NH<sub>4</sub>OH was ineffective for metals desorption in the concentration range tested. This result agrees with literature data for platinum [16], where desorption with 5% NH<sub>4</sub>OH at 25 °C also showed poor results (<10% desorption).

Hydrazine sulfate and thiourea (in HCl) did not remove platinum, tin and indium significantly (<1%). This result was not modified when HCl or reducing agent concentration was varied. It is interesting to remark that the successful use of thiourea for platinum desorption was apparently verified in aqueous medium containing only chloride ions [4,7].

#### 3.2.1. Platinum desorption

Sodium thiosulfate had no effect on tin and indium desorption. Although reduction of Sn(IV) to Sn(II) is possible, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> appears not to behave as a reducing agent for Sn(IV) under our experimental conditions. However, S<sub>2</sub>O<sub>3</sub><sup>2-</sup> ions readily removed platinum from the resins. The eluate presented a greenish color, thus suggesting that desorption occurred via the following reaction [22]:

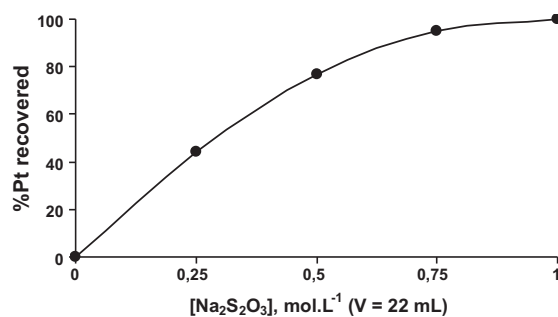
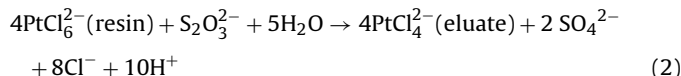


Fig. 5. Influence of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> concentration on platinum desorption from Amberjet 4200 CI resin (V=22 mL, PtSnIn/Al<sub>2</sub>O<sub>3</sub> catalyst). Data for other macroporous resins are similar.

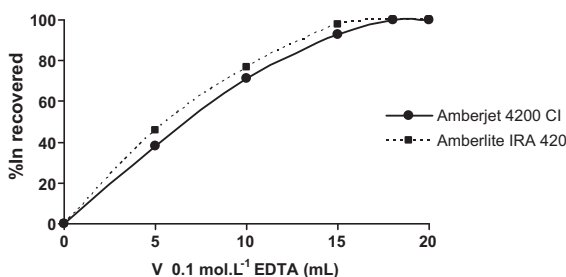


Fig. 6. Indium recovery from PtSnIn/Al<sub>2</sub>O<sub>3</sub> catalyst after desorption using 0.1 mol L<sup>-1</sup> EDTA on Amberlite IRA 420 and Amberjet 4200 CI resins.

**Table 5**

Metals concentration ( $\text{g L}^{-1}$ ) in the eluates after desorption (99.5 wt%) of the saturated resins with  $1 \text{ mol L}^{-1} \text{ Na}_2\text{S}_2\text{O}_3$  (Pt),  $0.1 \text{ mol L}^{-1}$  ascorbic acid (Sn) or  $0.1 \text{ mol L}^{-1}$  EDTA (In).

Resin	Catalyst	Pt <sup>a</sup>	Enriching factor	Sn <sup>a</sup>	Enriching factor	In <sup>a</sup>	Enriching factor
Amberlite IRA-400AR	Pt/Al <sub>2</sub> O <sub>3</sub>	9.5	9.1	–	–	–	–
	PtSnIn/Al <sub>2</sub> O <sub>3</sub>	9.5	12.9	1.1	3.7	8.6	13.1
Amberlite IRA 420	Pt/Al <sub>2</sub> O <sub>3</sub>	9.5	9.1	–	–	–	–
	PtSnIn/Al <sub>2</sub> O <sub>3</sub>	8.7	11.9	1.8	6.0	12.8	19.4
Dowex 1	Pt/Al <sub>2</sub> O <sub>3</sub>	9.2	8.8	–	–	–	–
	PtSnIn/Al <sub>2</sub> O <sub>3</sub>	8.9	12.2	1.8	6.0	13.6	20.6
Amberjet 4200 Cl	Pt/Al <sub>2</sub> O <sub>3</sub>	9.4	9.0	–	–	–	–
	PtSnIn/Al <sub>2</sub> O <sub>3</sub>	8.8	12.1	1.8	6.0	11.6	17.6

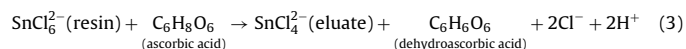
<sup>a</sup> Original values: see Table 2.

The above reaction also explains platinum stripping from the organic phase loaded with Aliquat 336 [22]. The pH of the eluate containing platinum decreased from 9 to around 7.5. The increase of the acidity is explained by the equation above.

For the SnIn/Al<sub>2</sub>O<sub>3</sub> catalyst 25–30 mL of  $1 \text{ mol L}^{-1} \text{ Na}_2\text{S}_2\text{O}_3$  were necessary to remove more than 99.5 wt% of adsorbed platinum from the macroporous resins (10 mL for the mesoporous one), as seen in Fig. 4. The corresponding volumes for the Pt/Al<sub>2</sub>O<sub>3</sub> catalyst were 55–60 mL and 18 mL, respectively. When  $\text{Na}_2\text{S}_2\text{O}_3$  concentration was below  $1 \text{ mol L}^{-1}$ , the amount of platinum removed markedly decreased in all cases (Fig. 5). This result demonstrates that PGM (and other elements) tend to be strongly adsorbed on the exchange centers of the strong basic anion exchange resins (type I) [7,12,14] and explains why in some studies the saturated resins are calcined for PGM recovery as an ash residue [3,14,17].

### 3.2.2. Tin desorption

EDTA removed both tin and indium, being not adequate for selective tin desorption. Since Sn(IV) may be reduced to Sn(II) by a strong reducing agent [26],  $0.1 \text{ mol L}^{-1}$  ascorbic acid (pH 4) successfully removed tin from the resins without affecting indium. The best technique was to wash previously the resins with water (after platinum desorption) in order to remove thiosulfate ions and to set pH around 7. This procedure reduces consumption of ascorbic acid during tin desorption. More than 99.5 wt% of this element was desorbed from the macroporous resins after elution with 50–55 mL (35 mL for the mesoporous one). The eluate was colorless and pH was around 3. Reduction of Sn(IV) by ascorbic acid may be expressed by the following equation:



This reaction explains the slight increase of the acidity after tin desorption from the resins.

Co-adsorption of tin and platinum from a spent dehydrogenation catalyst on a type-I anion exchange resin (Cl<sup>−</sup> form) has already been reported [17], and the strategy adopted was to convert the resin to the OH<sup>−</sup> form. Tin was no longer adsorbed on the resin.

### 3.2.3. Indium desorption

After tin removal, the resins were washed with water to remove ascorbic acid and increase pH to 7. Complexation was the choice to remove indium from the resins. EDTA forms a very stable complex with In<sup>3+</sup> [26]. Elution with  $0.1 \text{ mol L}^{-1}$  EDTA readily removed indium from the resins. Only 15–18 mL were necessary to remove more than 99.5% of this element (Fig. 6) from the macroporous resins (10 mL for the mesoporous one).

After metals desorption, the resins were washed with  $1 \text{ mol L}^{-1}$  HCl followed by equilibration with  $1 \text{ mol L}^{-1}$  HCl for 2 h. Three

adsorption–desorption cycles were performed. Platinum, tin and indium adsorption and desorption remained unchanged.

### 3.2.4. Metals concentration in the eluates after sequential desorption

Taking into account the volume of leachate necessary to reach resin saturation (Figs. 1–3) and the amount of eluent employed (see previous sections) the  $V_{\text{leachate}}/V_{\text{eluent}}$  ratio was calculated. Data are presented in Table 5. Platinum concentration in its eluate was greatly increased. The general order is In > Pt ≫ Sn. This indicates that tin desorption via reduction with ascorbic acid was the most difficult step.

### 3.2.5. Metals recovery

Platinum was isolated as a black powder by treating its eluate with ascorbic acid [22]. For this reason  $0.1 \text{ mol L}^{-1}$  ascorbic acid is not adequate to remove platinum from the resins because it will be reduced to metal, being deposited along the bed resin. Tin was recovered from its eluate via addition dropwise of  $2 \text{ mol L}^{-1} \text{ Na}_2\text{S}$  at 80 °C. A dark-brown precipitate (SnS) was quickly formed, thus confirming that tin was reduced during the desorption step. Indium was isolated from its eluate by adding dropwise  $2 \text{ mol L}^{-1} \text{ Na}_2\text{S}$  at 80 °C. The sulfide (In<sub>2</sub>S<sub>3</sub>) quickly precipitated as a brown–yellowish solid.

The final platinum, tin and indium products were dissolved in aqua regia and analyzed for metals (Section 2.5). The purity of all solids is very high (>99 wt%) and they contain more than 98 wt% of the corresponding element present in the original leachates (Table 2).

## 4. Conclusions

Strong basic anion exchange resins removed platinum from acidic leachates under appropriate experimental conditions. The macroporous resins presented about the same behavior and were better in terms of platinum uptake than the mesoporous sample studied. Adsorption is sensitive to the presence of other metals that form chlorocomplexes, as well as base metals, but the influence of these latter on platinum uptake was much less important. Despite the relatively low selective of the resins for platinum, it was possible to overcome this problem by a sequential desorption procedure based on the chemical behavior of the adsorbed metals. If present, aluminum was firstly removed by washing the resins with  $3 \text{ mol L}^{-1}$  HCl. Platinum was desorbed by elution with a moderate reducing agent ( $\text{Na}_2\text{S}_2\text{O}_3$  at pH 9) in order to avoid co-reduction of tin. This latter was desorbed by elution with ascorbic acid, a strong reducing agent. Indium was removed by complexation with EDTA. More than 99 wt% of the adsorbed elements was desorbed from the resins. The resins can be regenerated and reused at least three times.

Although the presence of other metals in the active phase (tin, indium) adversely affected platinum uptake of the resins, the pos-

sibility of selective desorption and recovery of these metals makes this technique an interesting way to separate them from the acidic leachates.

Taking into account our data and previous literature results, more research is necessary to better understand the adsorption and desorption of precious metals such as platinum in strong basic anion-exchange resins. The nature and composition of the sample as well as leaching procedure and resin properties seem to affect the feasibility of noble metals recovery from secondary sources by ion exchange techniques.

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