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## **Application of Ion Exchange Methods in Recovery of Pd(II) Ions – a Review<sup>★</sup>**

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Literature data on sorption and separation of noble metal ions, especially Pd(II), on various modified chelating and commercially available ion exchangers have been reviewed.

Dokonano przeglądu literatury na temat sorpcji i rozdzielania metali szlachetnych, ze szczególnym uwzględnieniem Pd(II), na rozmaitych modyfikowanych jonitach chelatujących oraz na innych jonitach dostępnych w handlu.

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★ Dedicated to Professor Rajmund Dybczyński on the occasion of his 75th birthday.

Ion exchange chromatography has become a valuable or even irreplaceable method of noble metal ions separation in analytical chemistry and chemical technology. This has been accomplished owing to the common use of ion-exchange resin methods, which are indispensable in many fields of chemical industry, including analytical chemistry. Recently, ion exchange chromatography has developed largely as a result of availability of new types of commercially available ion exchangers, two types of which are widely applied: selective and modified ion exchangers on the one hand and liquid ion exchangers on the other hand.

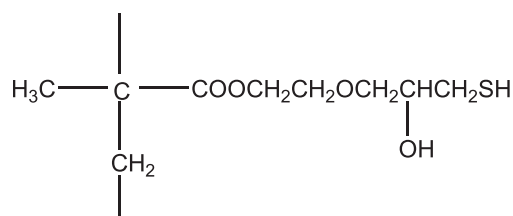
Separation of noble metal ions is extremely difficult due to the fact that precious metals occur as aggregates in nature forming isomorphous mixtures of the significant chemical affinity. Most of these metals occur at various oxidation states. Moreover, they easily form various complex compounds; the corresponding formation equilibria between aqua-complexes of different composition and charge are frequently complex. Platinum group metals (PGM) can also form polynuclear complexes and complexes with mixed ligands. The above facts make separation of these elements difficult. Moreover, the quality of separation depends on composition and origin of the solution. As a result, the relevant literature data are contradictory in some cases and separations reported in the literature are not fully quantitative [1]. Because of small amounts of platinum group metals in nature and impoverishment of their natural resources, physicochemical methods are of great importance for recovery of PGM from secondary sources *e.g.* used up three-way catalysts, dental alloys, industrial waste waters. One of these methods is ion exchange chromatography. Ion-exchange separations of palladium, platinum, rhodium, and iridium ions are most frequently based on the application of anion exchangers in chloride solutions making use of the change of valency till a proper distribution coefficient is reached. Recently, very good results in sorption and separation of trace and milligram amounts of noble metal ions using chelating ion exchangers have been obtained.

Based on hard and soft acids and bases theory (HSAB), ion exchangers with functional groups containing S or N donor atoms interact strongly with soft acids like precious metal ions. This condition is satisfied by Pd(II) ions. A wide range of chelating resins selective towards Pd(II) ions is known. These resins are characterized by diversified affinity and high selectivity for platinum metals. Their properties depend on the type of functional groups, and, to a lesser extent, on the grain size and physical properties. However, slow sorption kinetics is their undesired characteristics [2–4]. Bayer was the first who pointed out the importance of this type of ion exchangers based on the investigation of stability and chemical composition of chelate complexes [5]. Relative position of functional groups and their configuration affect sorption selectivity, while matrix properties are of smaller importance. Ion exchange capacity of these resins depends mainly on the number of functional groups and solution pH.

The most widespread chelating functional groups are: thiol, thiourea, isothiurea, thiosemicarbazide, dithiocarbamide, dithizone, and triisobutyl phosphine sulfide.

### Chelating ion exchangers with functional groups containing S, N and O donor atoms

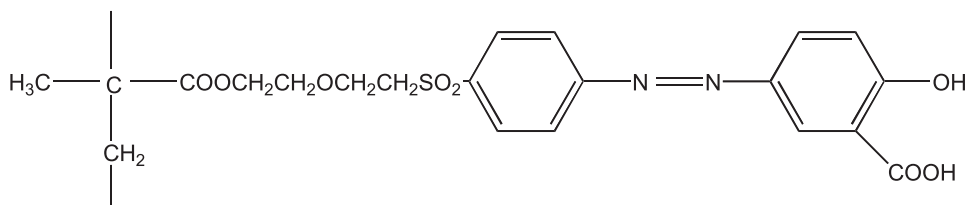
Commercially available ion exchangers with thiol groups, *e.g.* Duolite GT-73 and Spheron Thiol 1000 (ST 1000) exhibit high affinity towards Pd(II) and other PGM ions. Spheron Thiol (Fig. 1) is methylmethacrylate gel, which was synthesized by Smar• and Hradil [6]. Its sorption capacity is 2.01 mmol per 1 g of a resin. It is characterized by high selectivity for Pd(II) (0.949 mmol g<sup>-1</sup> resin) and Au(III) ions. Therefore, Spheron Thiol 1000 could be applied for their recovery from geological material and silicate rocks.



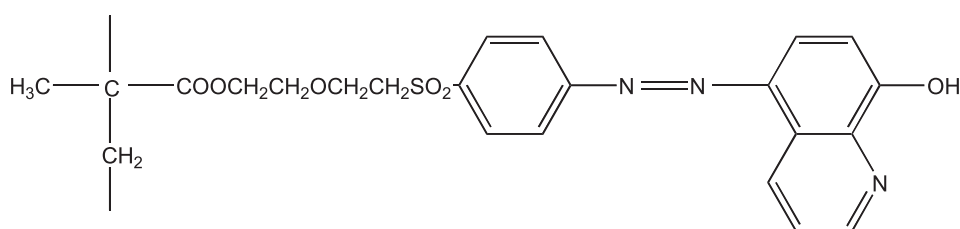
**Figure 1.** Spheron Thiol 1000

The abundance of gold and palladium in geological samples is normally so low that preconcentration is necessary prior to their determination. The samples need also treatment and digestion with 2 mol L<sup>-1</sup> HCl before preconcentration on ST 1000 chelating sorbent [7]. For desorption of Pd(II) ions from this ion exchanger, 0.5 mol L<sup>-1</sup> acidic solutions of thiourea and potassium thiocyanate were used. The 2:1 coordination stoichiometry of the formed S–Pd(II) complex was found.

Sorption of Pd(II) ions in the presence of Cu(II) ions onto Spheron Thiol 1000, Spheron Oxine 1000, and Spheron Salicyl 1000 was investigated [7, 8]. Spheron Salicyl 1000 (Fig. 2) and Spheron Oxine 1000 (Fig. 3) were formed by addition of salicyl and 8-hydroxyquinoline groups to the matrix of Spheron Thiol 1000 glycolmethacrylate gel [4, 9]. Ion exchange capacity of Spheron Oxine 1000 for Pd(II) ions equals to 0.57 mmol per 1 g of a resin. Taking into consideration the values of ion exchange capacities for Pd(II) ions, the following affinity series was found: Spheron Salicyl < Spheron Oxine < Spheron Thiol.



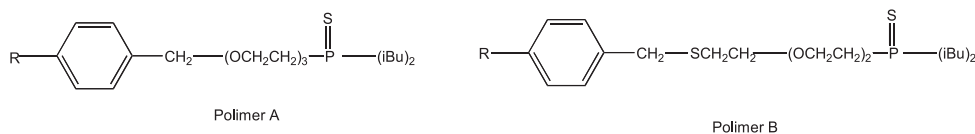
**Figure 2.** Spheron Salicyl (ion exchange capacity for Pd(II) ions 0.094 mmol g<sup>-1</sup> resin)



**Figure 3.** Spheron Oxine (ion exchange capacity for Pd(II) ions 0.57 mmol g<sup>-1</sup> resin)

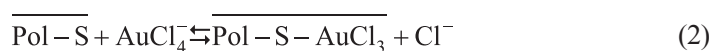
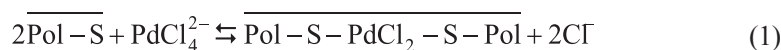
Iglesias *et al.* [10] used macroporous polystyrene resin Duolite GT-73 for recovery of Pd(II) and Au(III) ions from chloride solutions. High sorption capacities for Au(III) ions ( $0.58 \pm 0.03$  mmol g<sup>-1</sup> resin) and Pd(II) ions ( $0.262 \pm 0.015$  mmol g<sup>-1</sup> resin) were owed to the presence of thiol and sulfonic groups. As follows from the studies, the difference in sorption capacities resulted from the stoichiometry between gold and palladium ions and the functional groups of Duolite GT-73 (Au(III): —SH = 1:1, whereas for Pd(II): —SH = 1:2). Moreover, sorption of Pd(II) ions from 1 mol L<sup>-1</sup> HNO<sub>3</sub> resulted in 0.35 mmol g<sup>-1</sup> resin ion exchange capacity. Desorption yields of Pd(II) and Au(III) ions from the selective ion exchanger was achieved using acidic thiourea solution with the chemical yields of 80% and 60%, respectively.

The studies by Sánchez *et al.* [11,12] on modification of styrene–divinylbenzene copolymer by triisobutyl phosphine sulfide (TIBPS) (Fig. 4) in order to obtain the resin for concentration of precious metal ions are of significant importance. Donor O and S atoms present in the side chain of the modifier are responsible for selective separation of Au(III) and Pd(II) ions from chloride solution in the presence of Pt(IV), Rh(III), Ir(IV), Fe(III), Ni(II), Zn(II), and Cu(II) ions.



**Figure 4.** Structure of A and B polymers

Polymer B (Pol-B) containing S atoms in the side chain is characterized by higher ion exchange capacity ( $0.7 \pm 0.1$  mmol g<sup>-1</sup> polymer) towards Pd(II) ions than polymer A ( $0.5 \pm 0.1$  mmol g<sup>-1</sup> polymer), which contains O atoms. In this case, sorption mechanism can be described with the following equations 1 and 2:



The increasing sorption of Au(III) ions compared to that of Pd(II) ions with the increase of temperature from 298 to 333 K was observed. Sodium nitrate and thiourea were used as eluents. Sodium nitrate (2 mol L<sup>-1</sup>, pH 4.7) desorbed 75% of Pd(II) and did not elute Au(III), whereas thiourea (0.5 mol L<sup>-1</sup>, [H<sup>+</sup>] = 1.0 mol L<sup>-1</sup>) allowed for almost quantitative recovery of Au(III) containing trace amounts of Pd(II) ions.

Similar studies on the applicability of TIBPS-modified ion exchangers to sorption of small amounts of Pd(II) and Au(III) ions from aqueous and mixed aqueous-dioxane solutions containing Pb(II), Ni(II) and Cu(II) ions were carried out by Congost, Salvatierra, and others [13–16].

Microquantities of Pd(II) and Au(III) ions can be effectively recovered from geological samples using anion exchanger modified with chromeazurol S (CAS). Separation and enrichment of trace gold and palladium in geological samples can be carried out applying a reliable column procedure. This procedure is simple because most of base metals can not be enriched. Moreover, the procedure is characterized by low interference and, what is the most important, costs of gold and palladium analysis in geological samples is low. Due to the composition of geological samples, they need specific preparation. Firstly, organic compounds and sulfides must be eliminated. Then, the material is digested with *aqua regia* and concentrated HCl. Desorption of gold and palladium ions is possible using HCl, HNO<sub>3</sub>, and acidic NH<sub>2</sub>CSNH<sub>2</sub> solutions. The optimal concentration of thiourea for quantitative recovery of gold and palladium ions is 3% [17].

Chen Yi-Young *et al.* [18] synthesized a new polystyrene resin with piperazine groups (AEPZR) for concentration and recovery of Pd(II) ions. AEPZR resin (Fig. 5) is characterized by high selectivity and ion exchange capacity (2.78 mmol of func-

tional groups per 1 g of a resin). Ion exchange capacities of AEPZR resin for individual noble metal ions are: Au(III) – 5.38 mmol g<sup>-1</sup>, Pd(II) – 3.67 mmol g<sup>-1</sup>, Ru(III) – 3.46 mmol g<sup>-1</sup>, Os(VI) – 3.10 mmol g<sup>-1</sup>, Pt(IV) – 2.46 mmol g<sup>-1</sup>, Ir(IV) – 2.24 mmol g<sup>-1</sup>. 2% solution of thiourea in 0.1 mol L<sup>-1</sup> HCl solution is used for resin regeneration. This resin can find practical application in separation of Au(III) and Pd(II) ions from Fe(II), Cu(II) and Ni(II) ions [18, 19].

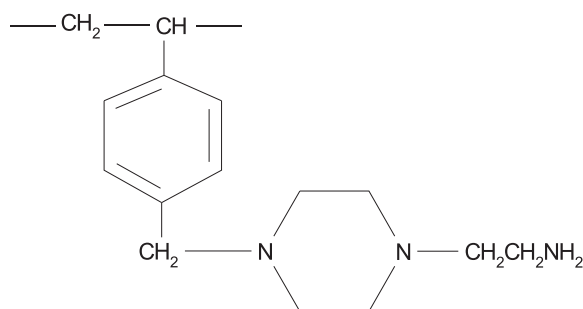
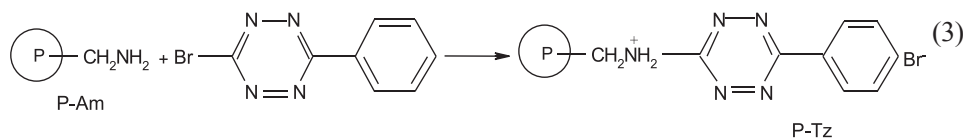


Figure 5. AEPZR resin

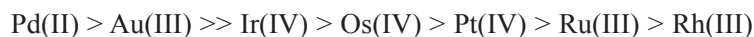
In many interesting studies 1,2,4,5-tetrazine was incorporated to macroporous styrene–divinylbenzene copolymer with primary amine groups (P-Am), according to the reaction (3):



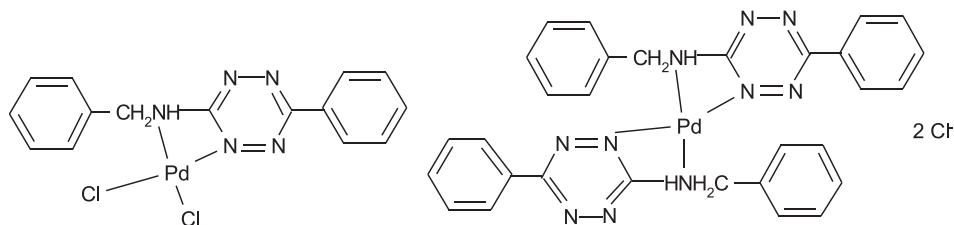
1,2,4,5-tetrazine resin (P-Tz) was used for concentration and separation of noble metal ions, each at the concentration of 0.001 mol L<sup>-1</sup>, in the presence of excess of Zn(II), Co(II), Cu(II), Fe(III), Ni(II) and Cd(II). The activity series for P-Tz and P-Am resins towards noble metal ions is:



whereas for the modified polymer (P-Tz) the series changes to:



High ion exchange capacity of P-Tz resin towards Pd(II) ions compared to that of P-Am resin has been explained by Grote and Topp [20] and assigned to the coordination reaction mechanism resulting in the 1:1 metal:ligand stoichiometry (Fig. 6) and to the increase in the resin hydrophobicity.



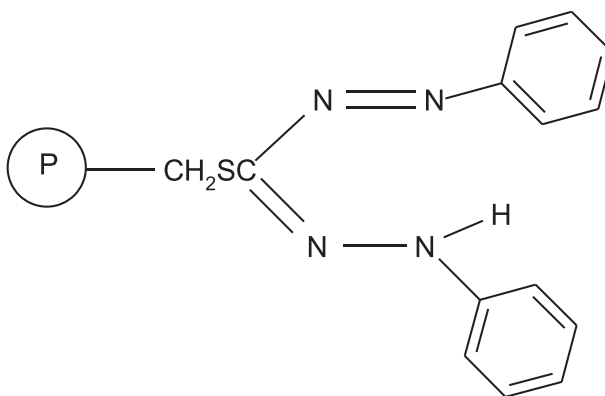
**Figure 6.** Pd(II) and 1,2,4,5-tetrazine complexes

Possibly Pd(II) ions are eluted with 2 mol L<sup>-1</sup> HClO<sub>4</sub> solution at 75% yield only from P-Am resin, which confirms retention mechanism with ion pair formation. Effective desorption of Pd(II) ions from P-Am and P-Tz can be carried out by passing acidified 5% thiourea solution through the column.

Many scientists have investigated sorption of noble metal ions onto the chelating ion exchangers with functional dithizone and dehydrodithizone groups. Polyvinylpyridine resins of this type exhibit good chemical and physical resistance (max. working temp. 473 K) as well as stable ion exchange capacity in the pH range 1–7.

Shah and Devi [21] preconcentrated Pd(II) and Pt(IV) in the presence of Ni(II) and Hg(II) in order to determine maximal ion exchange capacity for palladium (100 mg Pd(II) g<sup>-1</sup> resin) and platinum ions (250 mg Pt(IV) g<sup>-1</sup> resin). 0.2 mol L<sup>-1</sup> CH<sub>3</sub>COOH and 0.1 mol L<sup>-1</sup> HCl + 1% thiourea solutions were successively used to gradually elute Pd(II) ions from Ni(II) ions as well as Pd(II) and Pt(II) ions from Ni(II) ions.

Grote and Kettrup [22] investigated the usability of dithizone modified polymer (Fig. 7) in sorption and separation of 27 various elements including PGM and gold from HCl and HNO<sub>3</sub> solutions.

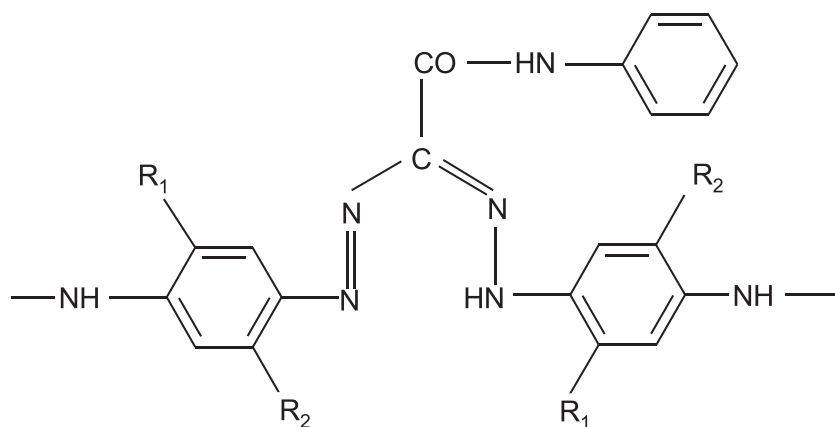


**Figure 7.** Dithizone resin

High values of distribution coefficients of noble metal ions (of the order of magnitude of  $10^4$ – $10^6$ ) and ion exchange capacities (0.74 mmol Au(III), 0.68 mmol Pd(II), 0.39 mmol Pt(II), 0.31 mmol Pt(IV), 0.12 mmol Os(IV), 0.14 mmol Ir(IV), 0.02 mmol Ir(III), 0.14 mmol Ru(III), 0.16 mmol Rh(III) per 1 g resin) indicate possible application of this polymer in separation of Pd(II), Pt(IV) and Au(III) ions from other ions.

Chwastowska *et al.* [23] obtained the sorbent selective for Pt(IV) and Pd(II) ions ( $0.16 \text{ mmol g}^{-1}$ ) by modification of the commercially available polyacrylic matrix of Diaion HP-2MG with dithizone. The obtained sorbent was found applicable in the recovery of the above mentioned ions from grass, dust, and soil samples collected near to the heavy traffic roads. Environmental samples were preliminarily cleaned and then digested using *aqua regia* and noble metals were separated on the dithizone sorbent. Desorption of palladium and platinum ions was possible using thiourea or concentrated nitric acid solutions. The major drawback of the sorbent used was its instability.

The research on the applicability of macroporous styrene–divinylbenzene, cellulose or methacrylate ion exchangers modified with formazan (Fig. 8) is of significant importance in sorption and recovery of noble metal ions [24–26]. Owing to the significant ion exchange capacity for noble metal ions, this sorbent is recommended for selective recovery and separation of Pd(II) ions from Ni(II) and Co(II) ions.

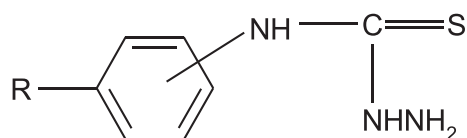


**Figure 8.** Formazane sorbent

The macroporous styrene–divinylbenzene ion exchanger with thiosemicarbazide functional groups (Fig. 9) is characterized by the largest ion exchange capacity for Pd(II) ions ( $0.78 \text{ mmol g}^{-1}$ ) in the presence of Pt(IV) ( $0.71 \text{ mmol g}^{-1}$ ), Ru(III) ( $0.685 \text{ mmol g}^{-1}$ ) and Rh(III) ( $0.615 \text{ mmol g}^{-1}$ ) ions. Effective separation ( $> 95.5\%$ ) of these

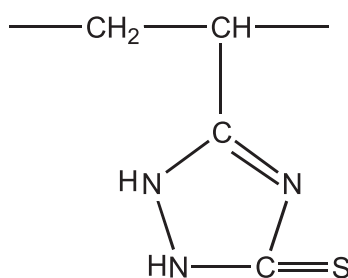


ions can be carried out using 4 mol L<sup>-1</sup> and 9 mol L<sup>-1</sup> HCl solutions. Ir(III), Cu(II), Bi(III), Hg(II), Fe(III), V(V) and Al(III) ions are not retained on this resin, while Au(III) and Os(VI) are reduced immediately after the contact with the polymer [27].



**Figure 9.** Thiosemicarbazide ion exchanger

Many interesting studies were performed using the polyacrylonitrile-thiosemicarbazide resin (PAN-TSC) of the structure shown in Figure 10. This resin was successfully applied in the recovery of Rh(III), Ru(III), Pd(II) and Ir(IV) ions. Ion exchange capacities for these ions were high and equalled respectively to 82.7, 239.9, 430.8 and 417 mg per 1 g of a resin; their distribution coefficients located in the range  $1.30 \times 10^4$ – $4.07 \times 10^5$  indicate the possibility of application of this resin in the recovery of PGM ions from acidic solutions (0.1–6 mol L<sup>-1</sup> HCl) [28].



**Figure 10.** PAN-TSC resin

Chelating resin containing isonicotinic acid hydrazone as functional group (P-NHZ) (Fig. 11), due to its remarkable selectivity, has been applied to recover Pd(II) and Pt(IV) ions from dust. Sorption of palladium and platinum ions can proceed from HCl, HNO<sub>3</sub>, HF and H<sub>3</sub>BO<sub>3</sub> solutions of the concentrations in the range 0.08–1.2 mol L<sup>-1</sup>. 0.1 mol L<sup>-1</sup> HCl solution containing 1% thiourea was used for desorption of these ions from the ion-exchange bed [29].

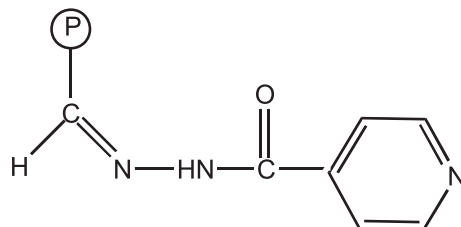


Figure 11. P-NHZ resin

Resins of the POLYORGS type (IV, V, VI) are worth considering in sorption of noble metal ions because of their high selectivity as well as chemical and thermal stability. POLYORGS resins are produced by modification of commercially available polyvinyle, polyacrylic and styrene-divinylbenzene matrices. They are widely applied in the recovery of some noble metal ions from ores, rocks, minerals, and waste waters.

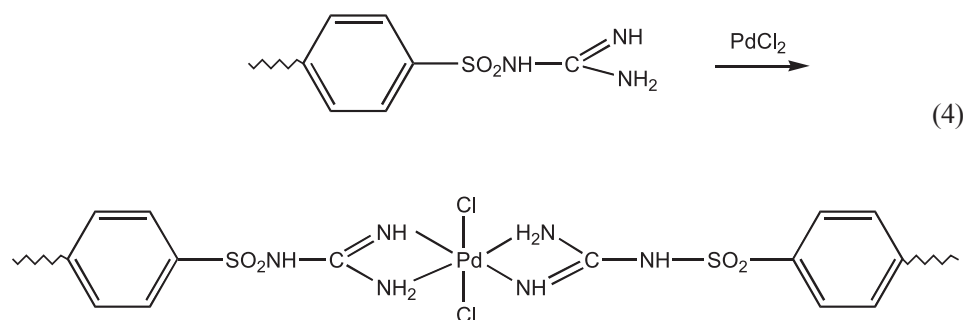
Table 1. Characteristics of POLYORGS chelating sorbents

Sorbent	Structure of chelate – forming groups	Polymer matrix, characteristic of sorbent	Sorption capacity, mg g <sup>-1</sup> *						
			Pt	Pd	Rh	Ir	Ru	Au	Ag
POLYORGS IV		macroporous, S-DVB, faint yellow	100	100	30	30	30	660	263
POLYORGS V		polystyrene, powder, dark red	—	18.4	12.5	12.5	—	340	107
POLYORGS VI		PVA, fibres, dark brown	25	48	—	30	—	219	80
POLYORGS VII		fibres, faint yellow	188	130	—	45	—	144	148
POLYORGS X		fibres, black	362	108	—	90	—	300	140
POLYORGS XI		macroporous, copolymer, beads, white	200	170	150	280	—	990	—

\* From 1–2 mg cm<sup>-3</sup> metal solution in 2 mol L<sup>-1</sup> HCl at 293 K.

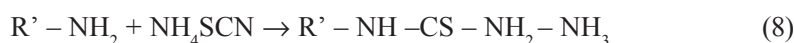
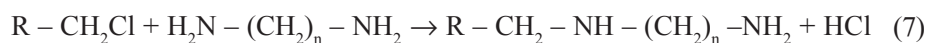
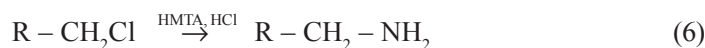
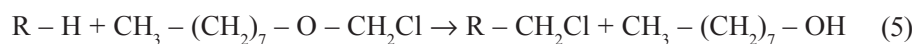
POLYORGS of types XI, VII and X(~IV) possess the highest ion exchange capacities for Pd(II) ions: 170, 130 and 100 mg per 1 g of resin, respectively. The detailed characteristics of these chelating sorbents are presented in Table 1 [26].

Complexing properties of ion exchangers containing sulphaguanidine (SG) functional groups, particularly in comparison to the properties of monomeric exchangers, are of significant practical importance, as investigated by Koster and Schmuckler [5]. They reported that the polystyrene–divinylbenzene sorbent with SG functional groups exhibits particularly high selectivity for Pd(II), Pt(IV) and Au(III) ions in the presence of Os(VI), Rh(III), Ir(IV), Ni(II), Cu(II) and Fe(III) in the acidic medium. The reaction between SG and Pd(II) ions proceeds *via* coordination to the amine group, according to reaction (4):



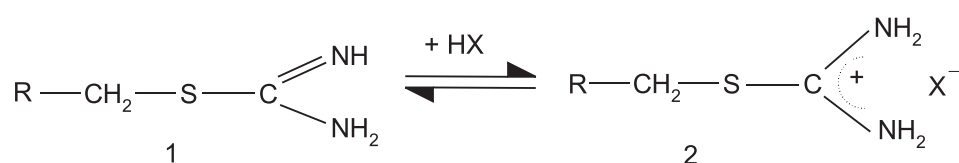
Maximal values of ion exchange capacities expressed in mmol per 1 g of dry resin were 2.05, 2.5 and 5.58 for Pd(II), Pt(IV) and Au(III) ions, respectively.

Resins containing thiourea or its derivatives incorporated into a matrix are widely used for separation of PGM ions from other ions. There are many commercially available ion exchangers with functional thiourea or isothioureia groups, *e.g.* Lewatit TP-214, Purolite S-920, or Srafion NMRR [5, 26, 30]. They are obtained by modification of a polymer matrix according to Eqs. 5–8:



where R is the polymer matrix, R' represents R-CH<sub>2</sub>- or R-CH<sub>2</sub>-NH-(CH<sub>2</sub>)<sub>n</sub>-, and HMTA denotes hexamethylenetetramine.

Depending on medium's pH and a form of the functional group (Fig. 12), Warshawsky [31] proposed the following retention mechanisms. When the groups occur in form (1), they create coordination bonds with metal ions. When the groups occur in form (2), platinum metal anion complexes are bonded according to the anion-exchange mechanism, *e.g.*  $[\text{PdCl}_4]^{2-}$ . To assure quantitative desorption of ions, they should be sorbed from acidic solutions in order to avoid hydrolysis of platinum inside the pores.



**Figure 12.** Forms of isothiurea groups

Using commercially available polystyrene matrices – Bonpor or Amberlite, Zuo and Muhammed [32] synthesized a large number of selective ion exchangers with functional thiourea groups (Tab. 2), similar to Koster and Schmuckler [5].

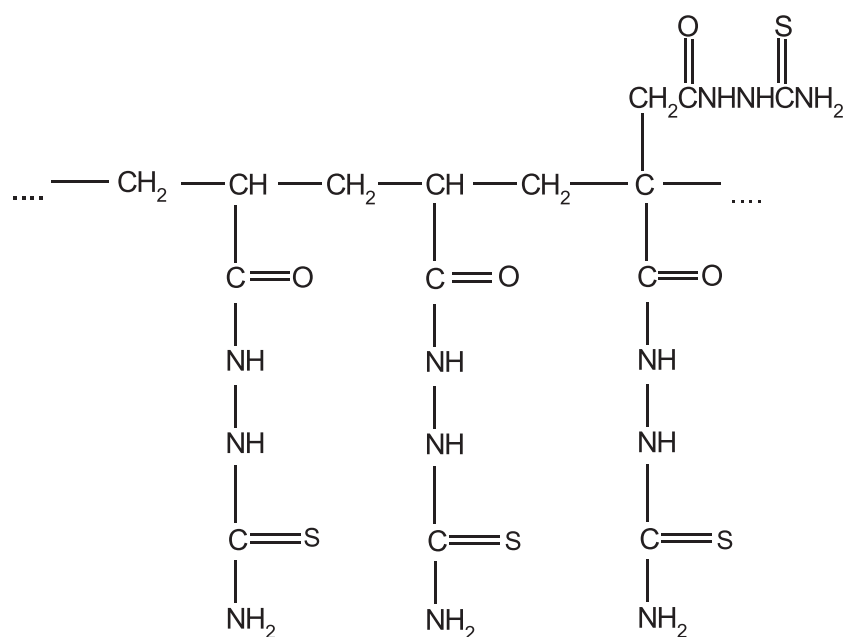
**Table 2.** Thiourea ion exchangers formed by modification of other resins; R denotes the polymer matrix

Starting polymer	Resin	Structure
Amberlite XAD-4	PTU-1	$\text{R}-\text{CH}_2-\text{NH}-\text{CS}-\text{NH}_2$
Amberlite XAD-2	PTU-2	
Amberlite IR-45	ITU	
Bonopore	BTUO-1	
Bonopore	BTUL-1	$\text{R}-\text{CH}_2-\text{NH}-(\text{CH}_2)_2-\text{NH}-\text{CS}-\text{NH}_2$
Bonopore	BTUL-2	$\text{R}-\text{CH}_2-\text{NH}-(\text{CH}_2)_3-\text{NH}-\text{CS}-\text{NH}_2$

Silica gel modified with thiourea and its derivatives is characterised by high affinity towards noble metal ions, too [33–36]. Silica gel modified with amidothiurea (ATuSG) was applied in the recovery of PGM ions from acidic solutions (0.1–6.0 mol L<sup>-1</sup> HNO<sub>3</sub> or HCl) in the microcolumn system [33]. The values of ion exchange capacity for Au(III) and Pd(II) ions: 0.277 mmol g<sup>-1</sup> and 0.141 mmol g<sup>-1</sup> resin, respectively were determined from the breakthrough curves. They do not reveal the expected

ted capacity increase compared to the values estimated for isothiourea ion exchanger, despite the presence of two functional groups (thiourea and amidyne).

Polyacrylacylaminothiourea chelating fibres (Fig. 13) were used for concentration and separation of trace amounts of Au(III), Pt(IV), Pd(IV) and Ir(IV) from aqueous solutions in the presence of Ca(II), Mg(II), Fe(III), Al(III), Zn(II), Cu(II), Mn(II), Ni(II), and Cd(II). Ion exchange capacities of these fibers equal to 2.8 mmol g<sup>-1</sup>, 1.75 mmol g<sup>-1</sup>, 1.56 mmol g<sup>-1</sup> and 1.15 mmol g<sup>-1</sup> for Au(III), Pt(IV), Pd(IV) and Ir(IV), respectively [37].



**Figure 13.** Polyacrylacylaminothiourea chelating fibres

Applicability of the polythioether resin with aminoisopropylmercaptan functional groups (YPA<sub>4</sub>) (Fig. 14) to the separation and preconcentration of noble metal ions from slimes, waste waters, and geological samples was examined [38]. This resin possesses high ion exchange capacities for platinum metal ions (67.2 mg Au(III) g<sup>-1</sup>, 64.8 mg Pd(II) g<sup>-1</sup>, 27.6 mg Pt(IV) g<sup>-1</sup>).

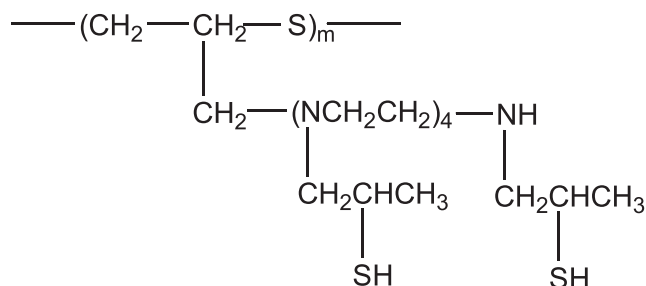


Figure 14. Structure of YPA<sub>4</sub>

The investigations performed by Chang *et al.* [39] on the applicability of epoxy-imidazole resin (Fig. 15) to the sorption of trace quantities (20 ng cm<sup>-3</sup>) of Au(III), Pd(IV), Ru(III) ions from the solutions containing Cu(II), Mn(II), Zn(II), Ni(II), Pb(II), Cd(II), Hg(II), Ga(III), Cr(III), Bi(III) and Al(III) ions are of significant importance. Quantitative sorption of noble metal ions depended on pH and proceeded in the acidity ranges pH 2–6, pH 4–6, pH 4–7 for gold, palladium and rhodium ions, respectively. Ion exchange capacities equalled to 81.6 mg Au(III) g<sup>-1</sup>, 64.7 mg Ru(III) g<sup>-1</sup> and 97.4 mg Pd(IV) g<sup>-1</sup> resin. 96% desorption could be achieved with 6 mol L<sup>-1</sup> HCl solution containing 0.2 g of thiourea. The sorbent with functional imidazole groups is characterized by fast sorption of Pd(II) ions [40].

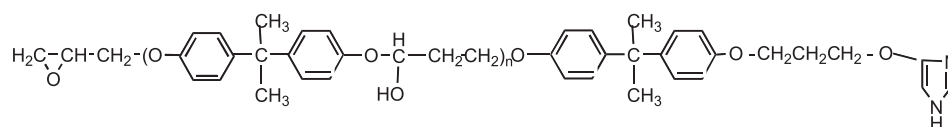
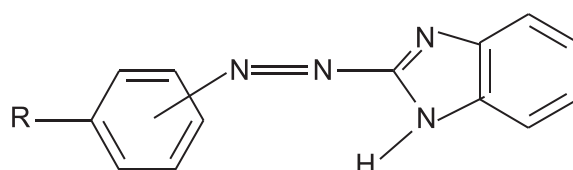


Figure 15. Epoxy-imidazole resin

Parodi *et al.* [41] used imidazol resin for Pd(II) and Pt(IV) recovery from chloride solutions. The sorbent exhibited stronger affinity towards Pd(II) at low concentration, while Pt(IV) was preferably sorbed at higher HCl concentration. The metals loaded onto the resin were recovered using 0.1 mol L<sup>-1</sup> thiourea solution. Desorption efficiency was 95% [41].

The sorbent with benzimidazolylazo functional groups incorporated into the styrene–divinylbenzene matrix (Fig. 16) is recommended for selective sorption of Pd(II), Hg(II) and Ag(I) ions (0.62 mmol Pd(II) g<sup>-1</sup>, 0.83 mmol Hg(II) g<sup>-1</sup> and 1.00 mmol Ag(I) g<sup>-1</sup> resin) from the solution of pH 4–6. 100% desorption of these ions from the bed is possible using acidic thiourea or concentrated HCl solutions. This sorbent has potential practical application in separation of Pd(II) ions from other noble metal ions since they do not sorb onto the resin, as well as in their recovery from dental

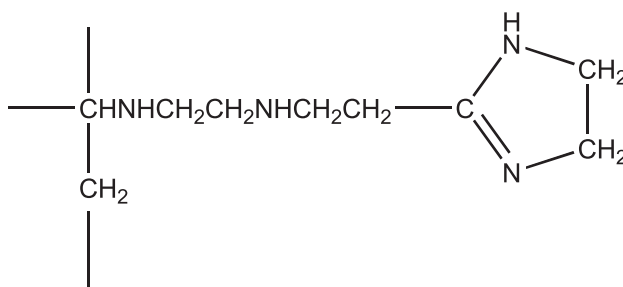
alloys, anodic slimes, and environmental and geological samples. Rock samples (from India, Calcutta) were digested with the mixture of three acids:  $\text{HNO}_3$  ( $15 \text{ mol L}^{-1}$ ),  $\text{HCl}$  (40%) and  $\text{HClO}_4$  (70%) combined at the ratio 1:1:1. Next, *aqua regia* was added and the volume of the solution was reduced by heating. Then, the solution was digested once again using  $\text{HCl}$  until it became clear.



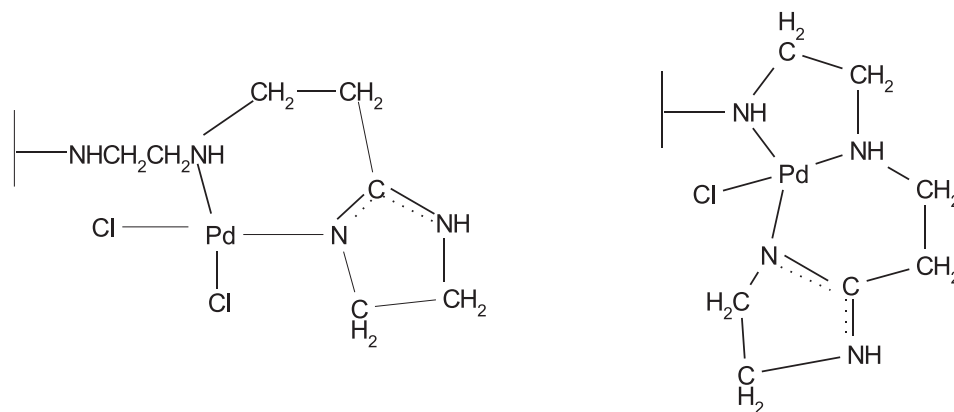
**Figure 16.** Benzimidazolylazo resin

Pd was also removed from the Pt wire by the consecutive treatment with *aqua regia* and  $12 \text{ mol L}^{-1}$   $\text{HCl}$ .

The resin with the functional imidazole (IEA) groups (Fig. 17) was used for pre-concentration of trace quantities of  $\text{Au(III)}$ ,  $\text{Pt(IV)}$ ,  $\text{Pd(II)}$  and  $\text{Ir(IV)}$  ions from the solution of  $\text{pH} < 4$ . The values of ion exchange capacities for the above mentioned ions equalled to 4.0, 1.57, 2.26 and 1.85  $\text{mmol g}^{-1}$  resin in  $2 \text{ mol L}^{-1}$   $\text{HCl}$  solution. The infrared absorption spectra of the  $\text{Pd(II)}$ –IEA complexes confirmed their structures shown in Figure 18. 4% thiourea and  $0.25 \text{ mol L}^{-1}$   $\text{H}_2\text{SO}_4$  solution were used for successful regeneration of the IEA resin. Good chemical stability of this sorbent enabled its multiple application in pre-concentration of trace amounts of  $\text{Pd(II)}$  and  $\text{Au(III)}$  ions [42].

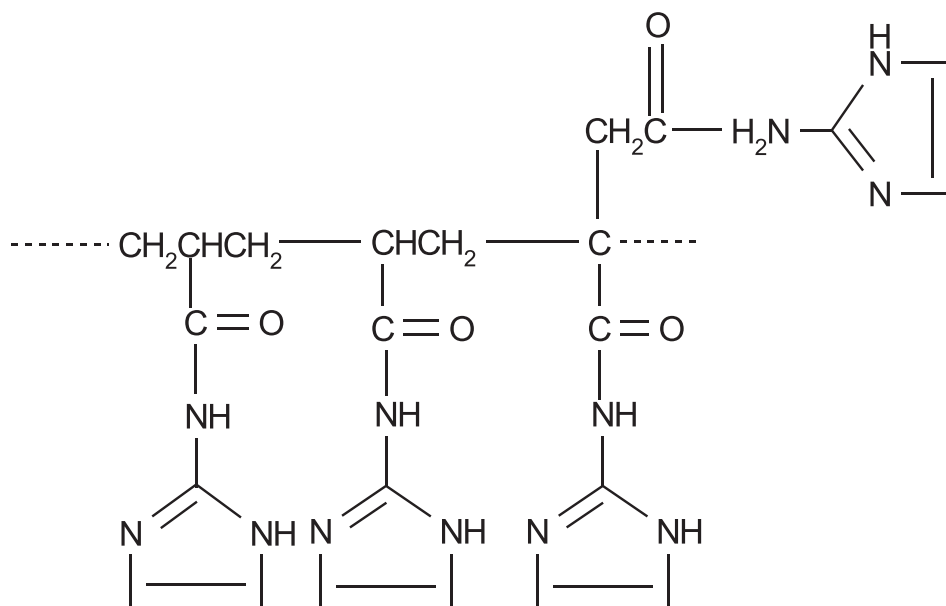


**Figure 17.** IEA resin



**Figure 18.** Structure of Pd(II)-IEA complexes

Similar research on the imidazole functional groups incorporated into nitrilon fibers was carried out by Gong [43]. The ion exchange capacity as well as desorption conditions ( $4 \text{ mol L}^{-1} \text{ HCl} + 3\% \text{ NH}_2\text{CSNH}_2$ ) were defined for Au(III), Hg(II) and Pd(IV) ions ( $2.92 \text{ mmol Au(III) g}^{-1}$ ,  $1.81 \text{ mmol Hg(II) g}^{-1}$ ,  $1.56 \text{ mmol Pd(IV) g}^{-1}$ ) in the column system. Because of high recovery factors of these ions (96.5–100%) during multiple application, the fibers (Fig. 19) can find practical application in their sorption.



**Figure 19.** Polyacrylaminoimidazole fibers



The polyacrylamidoxime chelating fibres were used in sorption of Pd(II) ions from acidic solutions. The ion exchange capacity for Pd(II) equaled  $1.50 \text{ mmol g}^{-1}$ . The  $[\text{PdCl}_4]^{2-}$ -AOPAN structure is shown in Figure 20 [44].

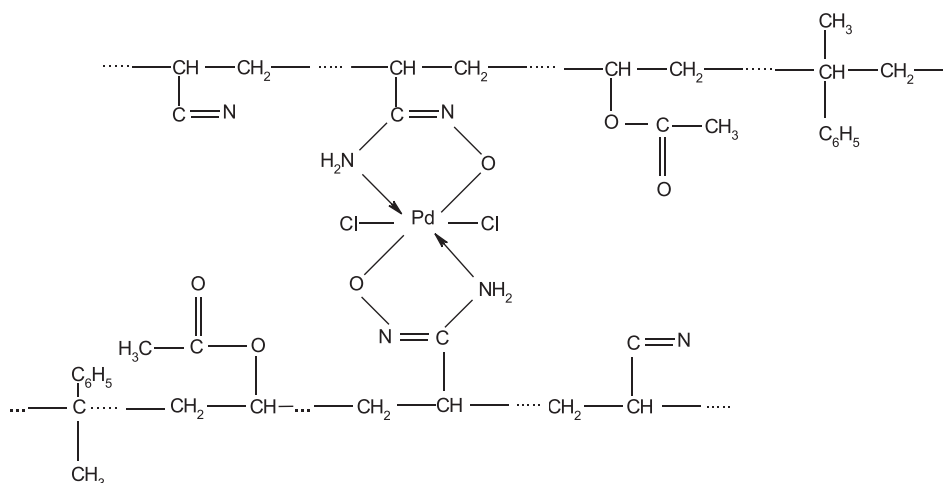


Figure 20.  $[\text{PdCl}_4]^{2-}$ -AOPAN structure

Ion-exchange procedure for recovery of trace amounts of Pd(II) ions from chloride ( $0.01$ – $10 \text{ mol L}^{-1}$ ), ammonium ( $0.05$ – $10 \text{ mol L}^{-1} \text{ NH}_4\text{OH}$  and  $0.01 \text{ mol L}^{-1} \text{ NH}_4\text{Cl}$ ) and mixed aqueous and non-aqueous ( $8 \text{ mol L}^{-1} \text{ NH}_4\text{OH}$  –  $0.01 \text{ mol L}^{-1} \text{ NH}_4\text{Cl}$  –  $\text{CH}_3\text{OH}$  and  $8 \text{ mol L}^{-1} \text{ NH}_4\text{OH}$  –  $0.01 \text{ mol L}^{-1} \text{ NH}_4\text{Cl}$  –  $\text{CH}_3\text{COCH}_3$ ) solutions using amphoteric ion exchangers: Duolite ES-346 and Chelex 100 with functional amidoxime and iminodiacetic groups was applied by Dybczyński *et al.* [45, 46]. This approach can find application in recovery and preconcentration of noble metal ions in the presence of other ions and also in case of geological and industrial materials due to large selectivity of the resins used.

The samples were digested in two steps. First, *aqua regia* and hydrofluoric acid were added. After the first step was finished, *aqua regia* and hydrogen peroxide were also added. Both mineralization cycles were carried out under high pressure.

Complexing agents like Alamine 336, TIBPS (Cyanex 471), dithiosemicarbazone and alkylamine (HMDA, ODETA, DDETA, OA, DA\*) were immobilized on Amberlite XAD-1, XAD-2, XAD-7, and XAD-8 in order to obtain selective sorbents for Pd ions [47–50]. The best results were obtained after incorporation of

\* HMDA –  $\text{NH}_2(\text{CH}_2)_6\text{NH}_2$ ; ODETA –  $\text{C}_8\text{H}_{17}\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_2$ ; DDETA –  $\text{C}_{10}\text{H}_{21}\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_2$ ; OA –  $\text{C}_8\text{H}_{17}\text{NH}_2$ ; DA –  $\text{C}_{10}\text{H}_{21}\text{NH}_2$ .

dimethylglyoxal bis(4-phenyl-3-thiosemicarbazone) (DMBS) (Fig. 21) into the Amberlite XAD-7 matrix [48].

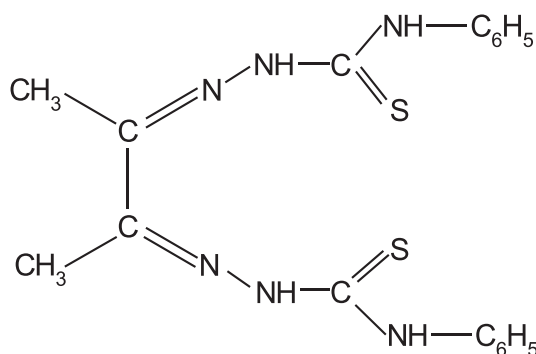


Figure 21. DMBS structure

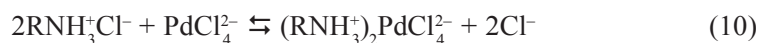
The platinum group metal ions were eluted with small volumes of *N,N*-dimethylformamide. Good results in preconcentration of microquantities of Pd(II) onto the modified Amberlite XAD-1 and XAD-16 were obtained.

Chitosan and its derivatives modified with glutaraldehyde, rubeanic acid, epichlorhydrin, and thiourea are of great interest [51–57]. Chitosan is the aminopolysaccharide obtained by deacylation of chitin. N donor atoms are responsible for sorption of many metal ions including PGM, depending on pH and concentration of the solution. Modification processes of chitosan are of great importance because of its good solubility in many acids. Cross-linking of chitosan with glutaraldehyde *via* the imine bond between the amine groups of biopolymer and the aldehyde groups of the modifier (Schiff reaction) leads to the selective sorbent (GCC) for Pd(II) ions of the ion exchange capacity of 180 mg g<sup>-1</sup> GCC (~2 mmol g<sup>-1</sup> GCC) [51].

Pd(II) sorption from chloride solutions depends not only on Cl<sup>-</sup> concentration but also on the type and concentration of palladium anion complexes.

Palladium may be also recovered by destructive procedure including burning or mineralization of chitosan with hydrogen peroxide after the acidic treatment.

Baba *et al.* [58] proposed the following reaction mechanism:

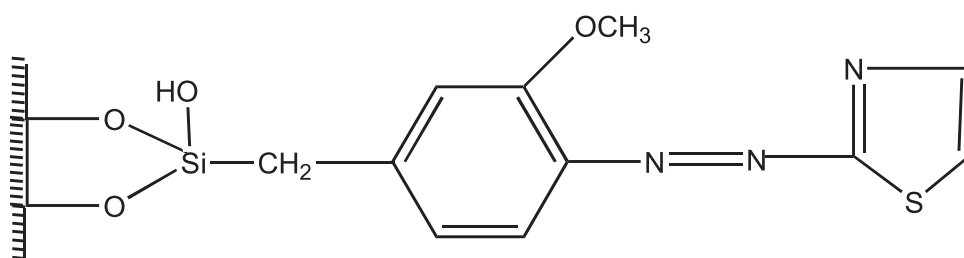


The affinity series of chitosan sorbents modified with rubeanic acid (RADC), thiourea (TGC), and glutaraldehyde (GCC) for Pd(II) ions is as follows:

## RADC &gt; TGC &gt; GCC

Significant sorption of trace amounts of palladium, platinum and rhodium ions (95% chemical yield) in the presence of Ni(II), Cu(II) and Fe(III) from refinery effluents using silicate ion exchangers with functional polyamine groups was observed. The samples were filtered and then digested by heating in concentrated  $\text{H}_2\text{SO}_4$ . Concentrated  $\text{HNO}_3$  was added until the solution became clear [59–61].

5-methylene-2-(2'-thiazolylazo)-anisoole [62] and dimethylglyoxime [63] were immobilized on silicate in order to obtain selective chelating sorbents (Fig. 22) for Pd(II) ions in the presence of Cu(II), Pt(IV), and Au(III) ions. The ion exchange capacities of these sorbents equaled  $0.07 \text{ mmol g}^{-1}$  and  $0.038 \text{ mmol g}^{-1}$ , respectively.



**Figure 22.** Silicate sorbent modified with 5-methylene-2-(2'-thioazolylazo)-anisoole

Brajter and Słonawska [64, 65] immobilized glycine, NTA, EDTA, and DPTA on Cellex T and Cellex D tcellulose ion exchangers. Glycine-modified sorbent can be used for separation of Pd(II) from Pt(IV) and Ir(III) ions, whereas DPTA sorbent can be utilized in column separation of Pd(II) from Pt(IV) ions as well as Rh(III) from Pd(II) ions.

Pd-Ir alloys were dissolved in *aqua regia* and after evaporation to dryness the residue was digested in  $0.1 \text{ mol L}^{-1}$  HCl solution.

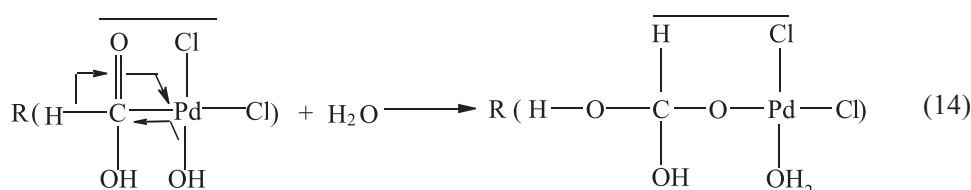
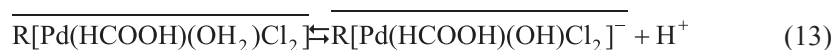
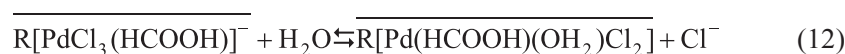
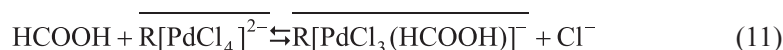
Modified and natural zeolites were employed in preconcentration of palladium ions. Clinoptilolites were modified with HCl,  $\text{HNO}_3$ ,  $\text{HClO}_4$ , and  $\text{H}_2\text{SO}_4$  acids. Clinoptilolite modified with concentrated HCl is characterized by higher sorption capacity for Pd(II) ions ( $11420 \mu\text{g g}^{-1}$ ) than natural clinoptilolite ( $635 \mu\text{g g}^{-1}$ ) because of complex formation on the zeolite surface.

Pd(II) solutions were prepared by dissolving pure metal in 1:1  $\text{HNO}_3$ - $\text{H}_2\text{O}_2$  mixture [66].

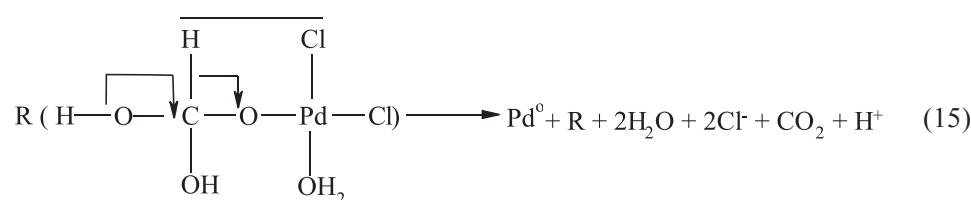
### Commercially available anion exchangers containing S, N and O donor atoms

Many interesting studies with commercial anion exchangers of various types were performed. Literature data [67, 68] on sorption and separation of noble metal ions on strongly basic anion exchangers are very important.

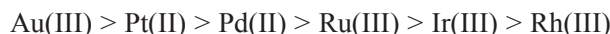
Amberlite IRA-900 and Amberlite IRA-410 with functional quaternary ammonium groups are used for separation of microquantities of Pd(II) ions from Ni(II), Sr(II), Rh(III), Fe(III), Al(III), Cr(III), Eu(III), Ce(III) and Cs(I) ions in nitric radioactive liquid wastes. Pd(II) adsorbed in the form of chloride complexes  $[\text{PdCl}_4]^{2-}$  was quantitatively washed by reduction with concentrated formic acid. The proposed reaction mechanism (11–15) is as follows:



finally leading to:



Based on the ion exchange capacities determined by Els *et al.* [69, 70], the affinity series for the strongly basic macroporous anion exchanger Amberlite IRA-900 is:



Lee and Chung [71] also examined the possibilities of selective removal of Pd(II) ions from nitric radioactive liquid wastes. They compared sorption characteristics of Pd(II), Rh(III) and Ru(III) ions onto anion exchangers with functional quaternary

ammonium groups (Amberlite IRN-78, Dowex 1X8) to these of anion exchangers with tertiary and quaternary benzoimidazole (AR-01) and dimethylamine (Amberlite IRA-93ZU) groups. It was found that Dowex 1X8 has higher selectivity for Pd(II) ions than Amberlite IRN-78 or Amberlite IRA-93ZU in nitric solutions. The best results were obtained for the ion exchanger of the AR-01 type (Fig. 23).

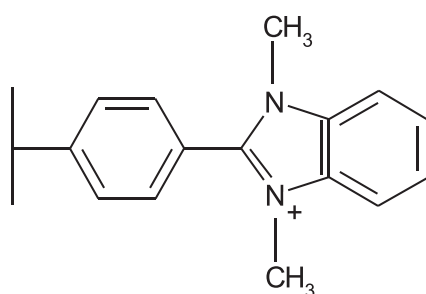


Figure 23. AR-01 ion exchanger structure

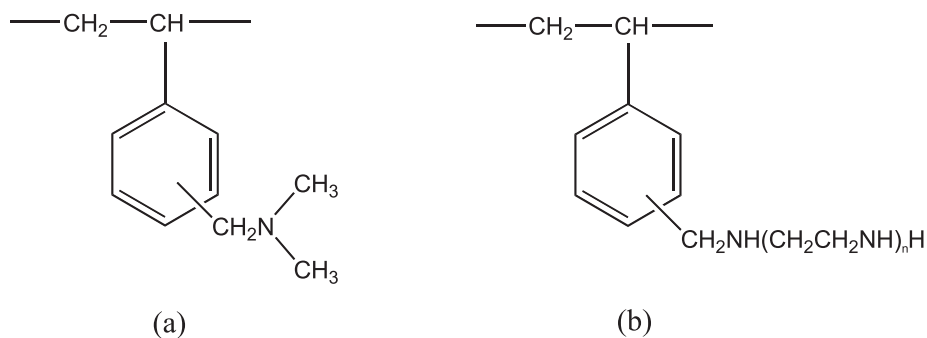
Strongly basic anion exchanger Bio-Rad AG1-X8 (100–200 mesh) exhibits high selectivity towards chloride complexes of noble metal ions. The values of distribution coefficients ( $10^6$  – Au(III),  $10^4$  – Pt(IV),  $10^3$  – Pd(II)) make it applicable in sorption of these ions from ores, rocks, and environmental samples (e.g. road dust) collected nearby the roads where concentrations of noble metals are high due to emission from automobile convertors. The samples should be mineralized using *aqua regia* [72].

Russian scientists [73] used vinylpyridyne amphoteric ion exchangers VP-14K and ANKF-5 as well as anion exchanger AN-251M in recovery of Pd(II) ions from chloride solutions obtained during leaching of spent TWC (three-way catalysts) by sodium chloride.

The above mentioned anion exchanger with  $-\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2$  functional groups and the ion exchanger ANKF-5 (total ion exchange capacity –  $5.4 \text{ mmol g}^{-1}$ ) are effective due to their high selectivity.

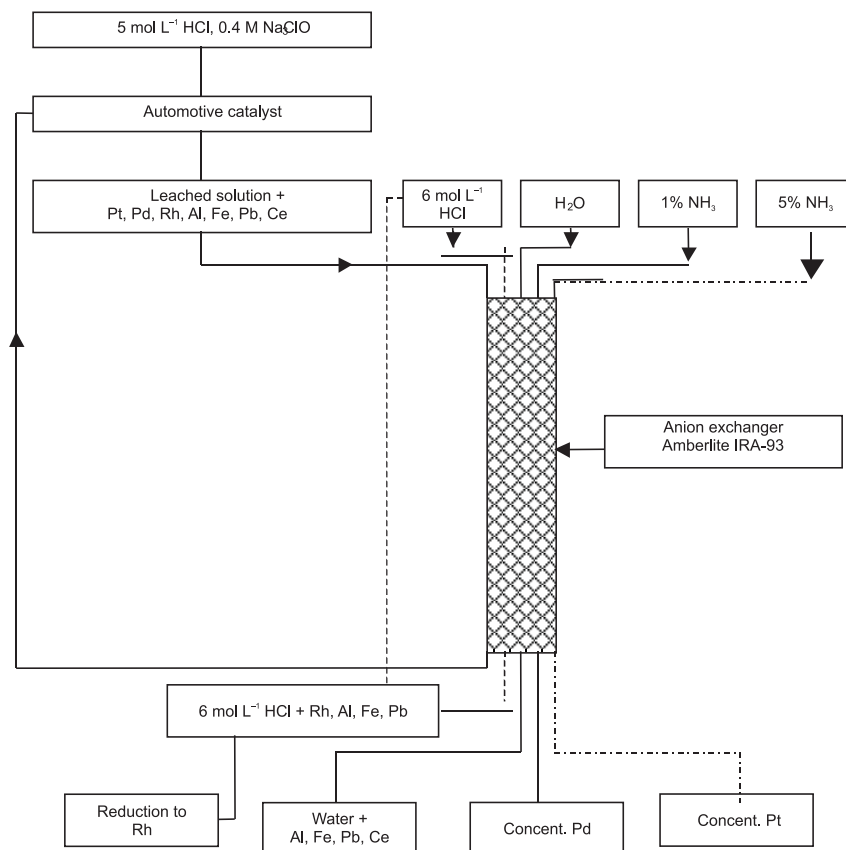
Matsubara *et al.* [74] examined adsorption and desorption behaviours of Au(III), Pd(II) and Pt(IV) in the chromatographic column systems using Amberlite IRA-35. The noble metals were strongly adsorbed on the anion exchange resin from diluted HCl, while most base metal ions like Ag(I), Al(III), Co(II), Cu(II), Fe(III), Mn(II), Ni(II), Pb(II), and Zn(II) did not show any remarkable adsorbability. The highest values of distribution coefficients of the order of magnitude of  $10^4$  were obtained for sorption from 0.05 and  $0.1 \text{ mol L}^{-1}$  HCl. Quantitative recovery of noble metals was commonly achieved by ignition of the resin or by elution with hot  $\text{HNO}_3$  or  $0.1 \text{ mol L}^{-1}$   $\text{NH}_2\text{CSNH}_2$  solution in ethanol. Two weakly basic anion exchangers (Fig. 24 a, b): Diaion WA-20 and WA-30 (polystyrene matrix, 20–50 mesh) of macroporous struc-

ture produced by Mitsubishi Co. Ltd. were investigated, too. Au(III), Pd(II) and Pt(IV) ions were eluted with  $0.1 \text{ mol L}^{-1} \text{ NH}_2\text{CSNH}_2$  solution in ethyl alcohol at 100% yield.



**Figure 24.** Structural formulas of Diaion WA-20 and Diaion WA-30

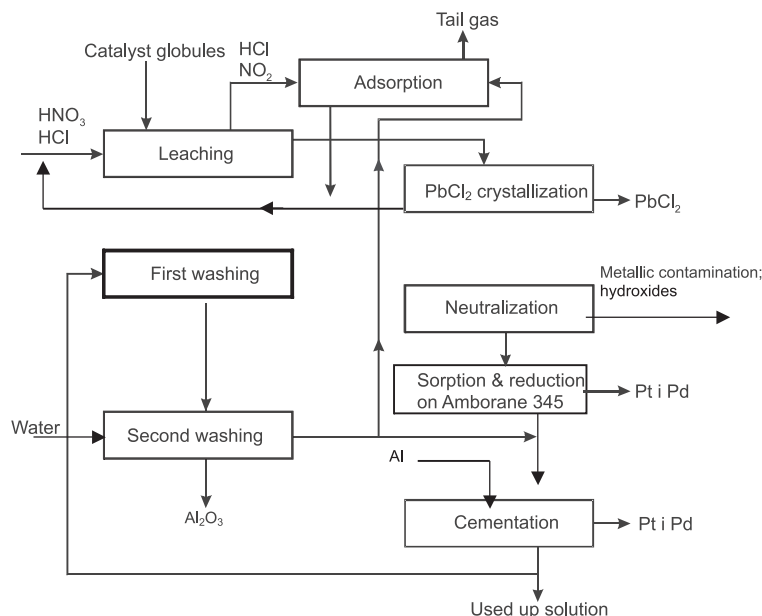
Amberlite IRA-93 is a weakly basic macroporous anion exchanger with functional dimethylamine groups and polystyrene-divinylbenzene matrix used in recovery of noble metal ions from the used automobile catalytic converters (Fig. 25). Rh(III) was desorbed from the anion exchanger bed as the first with  $6 \text{ mol L}^{-1} \text{ HCl}$  solution, while Pd(II) was eluted with 1% ammonia solution at the room temperatures. Pt(II) was eluted using 5% ammonia solution at elevated temperature. Separation of palladium from platinum can be achieved by reduction of Pd ions to the metallic state, or by precipitation of  $(\text{NH}_4)_2\text{PdCl}_4$  and  $(\text{NH}_4)_2\text{PtCl}_6$  with HCl solution. The presented ion exchange method with Amberlite IRA-93 for selective separation of palladium, platinum, and rhodium from acidic solutions obtained by leaching honeycomb-type catalytic converters can be regarded as the efficient technique for separation of these metals on the analytical scale and could be applied for large scale operations. Noteworthy, owing to nontoxicity, nonvolatility and nonflammability of the Amberlite IRA-93 resin, this method might be accompanied by fewer environmental hazards than the currently adopted solvent extraction and precipitation techniques [75].



**Figure 25.** Leaching of noble metals from automobile catalytic converters

Another way of PGM recovery from the used automobile catalytic converters is to apply the aminoborane resin of Amborane 345 type (Fig. 26). The catalysts recycled in this process are in the form of aluminum oxide globules containing  $300\text{--}350\ \mu\text{g cm}^{-3}$  Pt and  $100\text{--}200\ \mu\text{g cm}^{-3}$  Pd, or in the form of porous silicate „honey slice” covered with aluminum oxide containing  $800\text{--}1500\ \mu\text{g cm}^{-3}$  Pt and  $100\text{--}350\ \mu\text{g cm}^{-3}$  Pd. Recovery of noble metals from large amounts of these materials is of great importance. Wet method, assuming selective leaching, can be carried out in two ways: matrix leaching with  $\text{H}_2\text{SO}_4$  and leaving the metals in the sediment, or selective metal leaching with HCl. Metal leaching with HCl in the presence of  $\text{HNO}_3$  as the oxidizer proceeds as follows:





**Figure 26.** Recovery of platinum and palladium from used up TWC

In order to decrease digestion extent of  $\text{Al}_2\text{O}_3$  HCl can be partially replaced with  $\text{AlCl}_3$ . Leaching can be accomplished in the column packed with the used catalyst converters, through which the leaching solution of 368 K flows continuously.  $\text{PbCl}_2$  is crystallized from the saturated solutions by cooling; afterwards, the solution is partially returned to the leaching process. The remaining part is neutralized with NaOH to pH about 3.5 and the contaminants are precipitated in the form of hydroxides. After separation of hydroxides, platinum and palladium can be recovered by sorption and reduction on the Amborane 345 resin by cementation with aluminum, or in the electrolytic way [30].

## CONCLUSION

Determination of noble metals in various materials usually requires their preconcentration and often separation from other elements. Several methods are available for this purpose. Sorption methods utilizing chelating ion exchangers are widely used and the most effective.

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