

Separation and Preconcentration Method for Palladium, Platinum and Gold from Some Heavy Metals Using Amberlite IRC 718 Chelating Resin

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The main object of the most of the researches on chelating resins, is preparation of insoluble functionalized polymers which can provide more flexible working conditions together with good stability and high capacity for certain metal ions.¹⁻⁵ The interest in this type of chelating resins are due to the rapid adsorption of metal ions, greater selectivity and less swelling compared to the analogous organic polymers. Comprehensive reviews have been written on the synthesis, properties and application of chelating resins.⁶⁻⁸ A number of chelating resins containing aminocarboxylic acid,⁹⁻¹² hexylthioglycolate¹³⁻¹⁵ and bicine¹⁶ groups have been prepared and investigated for their analytical properties.

Since the sorption characteristics of the metal ions together with the complexation properties of the reagent generally depend upon the size of the chelate ring and metal atom, number of donor atoms/bonding site on the reagent, type of donor atoms (hard or soft), oxidation state of the metal ion, nature of the solvent, pH of the solvent system etc.

In the previous work,¹⁷ the preconcentration and separation of metal ions by the use of Amberlite IRC 718 chelating resin have been extensively reported. Amberlite IRC 718 chelating resin bonded to the iminodiacetic acid functional groups, which has a high affinity for heavy metal ions. The very little evaluation has, however, been performed on this exchanger.

The purpose of the present work is to explore the possibility of separation of Au(III) ions from matrices by using a Amberlite IRC 718 chelating resin. The adsorption behaviour of Au(III), Pt(IV), Pd(II), Ti(IV), Ag(I), Zn(II), Co(II), Cu(II) and Fe(III) on the resin was investigated at different pH values. The separations are based on the affinity differences of these metal ions toward the chelating resin as a function of pH.

This paper describes the systematic investigation of column separation and preconcentration of Au(III) as their chloro complexes from acidic solutions on Amberlite IRC-718 chelating resin in a column. Au(III) retained was eluted with 0.25M thiourea solution. The method was used for the determination of platinum group elements (Au(III), Pt(IV) and Pd(II)) in PCBs sample.

Experimental Section

Apparatus and reagents. A Jobin Yvon JV-24 inductively coupled plasma spectrometer was used for metal ion

determination. A NOVA-310 digital pH-meter was used for pH measurement.

Amberlite IRC 718 chelating resin is a products of Aldrich. The metal ion stock solutions were prepared by diluting the 1000 ppm AAS standard solutions of Au(III), Pd(II) and Pt(IV) obtained from Junsei Chemical Co. The other chemicals were of analytical-reagent grade. The following buffered solutions were prepared: hydrochloric acid-potassium hydrogen phthalate (pH 1-3); acetic acid-sodium acetate (pH 3-6).

Experiment.

Optimum pH for metal ion adsorption: The adsorption behaviors of various metal ions were examined under batch equilibration technique. Excess amount of metal ion (50 mL, 20 $\mu\text{g/mL}$) was shaken with 0.2 g of resin for 24 hr. The pH of the metal ion solution was adjusted prior to equilibration over a range of 1-6 with buffer solutions. After the equilibrium, the concentration of the metal remaining in the solution was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES).

Concentration and separations of metal ions: The batch equilibration technique was used to concentration the metal ions. A sample solution (1000 mL) containing 0.1 $\mu\text{g mL}^{-1}$ metal ion was adjusted at optimum pH of adsorption with a buffer solution and shaken with 0.2 g of resin for 24 hr. The adsorbed metal ions were eluted with 0.25 M thiourea solution (20 mL) and the concentration of the metal ions in the eluent was determined by ICP-AES.

Separation of metal ions was carried out by a column method. A fixed volume of aqueous mixing solution of the metal ions was adjusted to pH 0.1 and percolated through the column (3.4 $\text{cm}^2 \times 7$ cm) at the flow rate of 1.0 ± 0.1 mL min^{-1} . Al(III), Fe(III), Cu(II) and Ni(II) was eluted with 1.0 M HCl, Au(III), Pt(IV) and Pd(II) with 0.25 M thiourea.

Result and Discussion

The effect of pH on adsorption of ten kinds of metals in pH 0.5-6.0 was examined by a batch method and the result is presented in Figure 1. Adsorption of platinum group elements (Au(III), Pt(IV), Ag(I) and Pd(II)) begins at lower pH and has the highest adsorption capacity at pH 1.0 compared with other metal ions. The adsorption of these metals slightly decreases beyond pH 5.0. Other metal ions shows gradual increase in adsorption with increasing pH and the

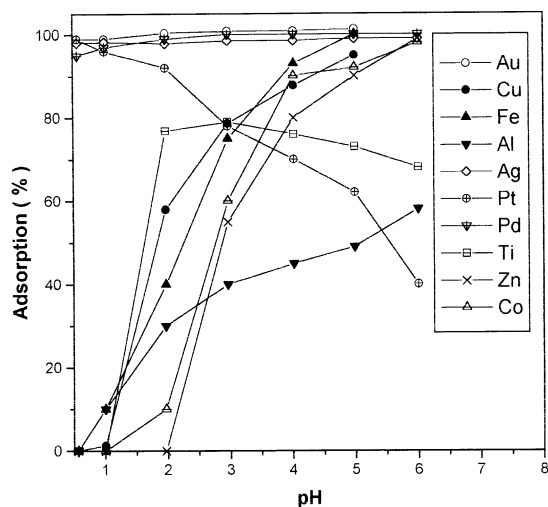


Figure 1. Sorption capacities of metal ions on Amberlite IRC-718 chelating resin according to pH change. Metal solution: 1.0 mg/50 mL, Resin taken: 0.2 g, Shaking time: 24 hr

optimum adsorption was observed in the higher pH region. From the results, It was found that the separation of platinum group elements (Au(III), Pt(IV) and Pd(II)) from the other metal ions was possible by varying only the pH of the solution.

The adsorption of Au(III), Pd(II) and Pt(IV) are almost complete in the range of 0.1–4.0 M HCl (1.0 mL min^{-1} flow-rate). Figure 2 shows the effect of the HCl concentration on the adsorption percentage of Au(III), Pd(II) and Pt(IV). The maximum adsorption of Au(III) is at about 1.0 M HCl, remained constant from 1.0 M to 2.0 M HCl and the adsorption percentage decreased slowly thereafter. Au(III) occurs in chloride solutions in the form of anions AuCl_4^- , which interact with functional groups of the chelating resin.

And, each of the flow-rate tested ($0.5\text{--}4.0 \text{ mL min}^{-1}$) has a almost complete adsorption of Au(III), Pt(IV) and Pd(II) (HCl concentration 1.0 M). Figure 3 shows the recoveries of Pt(IV), Pd(II) and Au(III) at different flow-rates. Obviously,

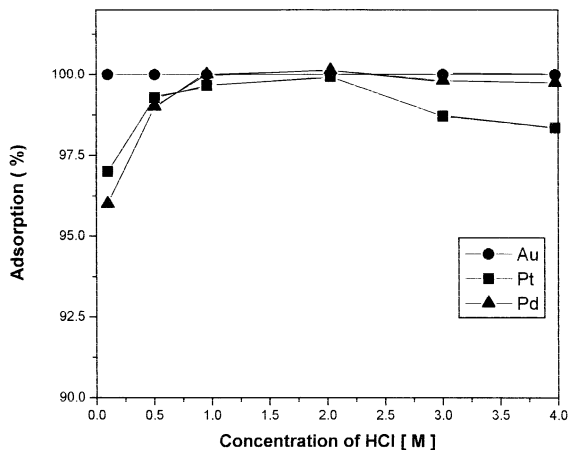


Figure 2. Effect of HCl concentration on Au(III), Pt(IV) and Pd(II) adsorption on Amberlite IRC-718 chelating resin. Metal solution: 1.0 mg/50 mL, Resin taken: 0.2 g, Shaking time: 24 hr

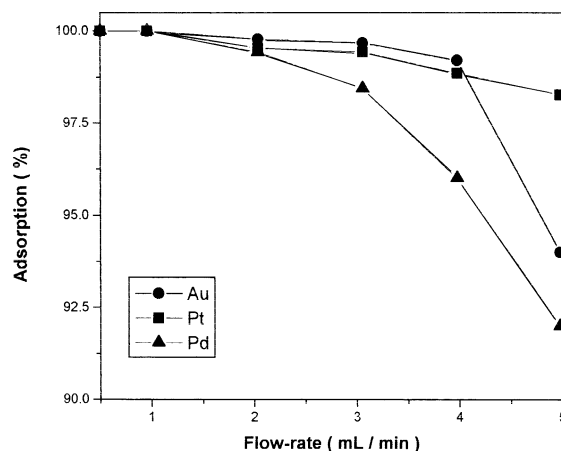


Figure 3. Effect of flow-rate on adsorption of Au(III), Pt(IV) and Pd(II) on Amberlite IRC-718 chelating resin.

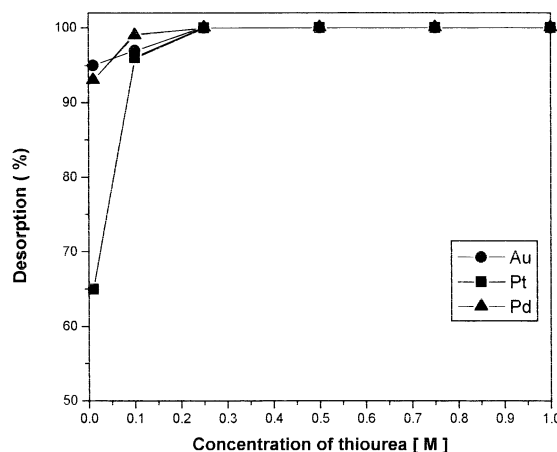


Figure 4. Effect of thiourea on desorption of Au(III), Pt(IV) and Pd(II) on Amberlite IRC-718 chelating resin.

Au(III), Pt(IV) and Pd(II) can be adsorbed quantitatively at a flow-rate of $\leq 2.0 \text{ mL min}^{-1}$.

Thiourea has long been known to form extractable complexes with both Au(III) and Pt(IV).¹⁸ The thiourea ligand can coordinate with either the 'hard' nitrogen atom, or 'soft' sulphur atom. It is quite different in the relative rates of complex formation each metal ions. The separation of metals by ion exchange resin was different from the formation of metal-thiourea complexes.

Figure 4 shows the recoveries of Au(III), Pt(IV) and Pd(II) desorbed with 20 mL different concentration of thiourea ($1.0 \pm 0.1 \text{ mL min}^{-1}$ flow-rate) from the column. Evidently, Au(III), Pt(IV) and Pd(II) can be desorbed quantitatively by 20 mL (0.25 M thiourea) and their recoveries are greater than 95% when 20 mL (0.1 M thiourea) is used as desorbent.

The metal capacity values (mmol g^{-1}) determined for the seven tested metal ion, namely Au(III), Pt(IV), Pd(II), Ti(IV), Fe(III), Cu(II) and Pb(II), by the Amberlite IRA 718 resin are compiled in Table 1. The values were determined in different buffer solutions to decide the optimum pH value for each metal ion adsorption and evaluate the effect of the pH value on the metal capacity. The most important thing is

Table 1. Metal sorption capacity values (mmol g⁻¹) of different metal ions in various buffer solution

pH	Pt(IV)	Au(III)	Pd(II)	Ti(IV)	Fe(III)	Cu(II)	Pb(II)
1.0	0.34	0.69	0.55	-	-	0.022	0.0048
2.0	0.32	0.69	0.50	0.35	-	0.25	0.048
3.0	0.31	0.65	0.50	0.31	0.18	0.26	0.068
4.0	0.28	0.68	0.49	0.29	0.29	0.29	0.074
5.0	0.26	0.65	0.49	0.25	0.32	0.32	0.086

the exceptionally high platinum group elements (Au(III), Pt(IV) and Pd(II)) capacity values demonstrated at low pH. The adsorption capacity was found as a 0.69 mmoles Au(III) per gram of dry resin at pH 1.0.

Preconcentration of the metal ions on the resin was carried out and the results are shown in Table 2. The preconcentration factors for Au(III), Pt(IV) and Pd(II) were found to be 60, 47 and 40, respectively. The results have been shown that the present resin can act as an effective adsorbent for preconcentration of the platinum group elements studied.

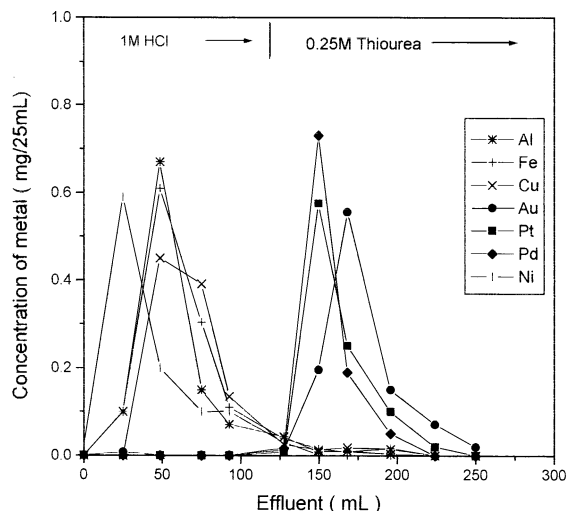
The separation of trace amount of Au(III), Pt(IV) and Pd(II) in the presence of diverse metal ions was examined by a column method (Fig. 5). As can be seen in Figure 5, 1.0 M HCl and 0.25 M thiourea solution have been considered as an eluent for the separation of the synthetic metal ion solution. Au(III), Pt(IV) and Pd(II) were able to separate from Al(III), Ni(II), Cu(II) and Fe(III) because they are not retained on the resin with 1.0 M HCl eluent. Au(III), Pt(IV) and Pd(II) retained on the resin were eluted with 0.25 M thiourea solution. Recovery is 96% and thus the separation is quite effective.

The proposed method has been applied to the separation and determination of Au(III) in a PCBs sample. A 100 g of sample of PCBs (whole computer board) was dissolved in a 50 mL of concentrated HCl and 20 mL of concentrated HNO₃ by heating on a water bath. After the residual plastic filtered through Whatman #2 paper and the solution evaporated to very small volume. The solution was cooled, filtered and diluted to 100 mL in a calibrated flask. A portion of sample was analysed in an aliquot metal ions by ICP-AES (without separation process). The 50 mL sample solution was loaded through the column (3.4 cm² × 7 cm) at a rate 1.0 mL onto the column. Ni(II), Pb(II), Fe(III), Al(III) and Cu(II) was eluted with 200 mL of 1.0 M HCl after loading with 50 mL of sample solution. Then 150 mL of 0.25 M thiourea solution was used to elute Au(III), Pt(IV) and Pd(II). The results shown in Table 3 was good agreement with those obtained by ICP-AES performed for comparison.

Table 2. Preconcentration factors for Au(III), Pt(III) and Pd(II)

Metal ion	Volume (mL)	Concentration (ppm)	pH	Desorption Solution	Recovery (%)	preconcentration factor*
Au (III)	1000	0.1	0.61	0.25 M Thiourea	98 ± 1.5	60
Pt (IV)	1000	0.1	0.5	0.25 M Thiourea	97 ± 2.1	47
Pd (II)	1000	0.1	0.8	0.25 M Thiourea	95 ± 3.7	40

*One liter sample solutions containing 0.1 mg metal ion were loaded on the column and eluted with 20 mL of 0.25 M Thiourea.

**Figure 5.** Elution curve of Al(III), Fe(III), Cu(II), Ni(II), Au(III), Pt(IV) and Pd(II). loading: 1.0 mg of Al(III), Fe(III), Cu(II), Ni(II), Au(III), Pt(IV) and Pd(II) in 10 mL, pH 0.1. elution: 1.0 M HCl and 0.25 M thiourea solution. flow rate: 1.0 ± 0.1 mL min⁻¹**Table 3.** Determination of Au(III) in PCBs sample

Contents of PCBs Sample (mg/50 mL)	This method		ICP
	Au(III) Recovered (mg/50 mL)	Recovery (%)	Au(III) found (mg/50 mL)
Pt(IV) 0.12			
Pd(II) 0.35			
Cu(II) 1412			
Al(III) 35.6			
Fe(III) 4.13	2.36	94 ± 0.5	2.51
Ni(II) 1.43			
Pb(II) 7.42			
Zr(IV) 0.01			
V(IV) 0.01			

Conclusion

These investigations indicate that the Amberlite IRC 718 chelating resin has good potential for the enrichment of platinum group elements (Au(III), Pt(IV) and Pd(II)) and their separation from other metal ions.

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