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CHELATE SORBENTS FOR CONCENTRATION AND SEPARATION OF NOBLE METALS

S. B. SAVVIN, I. I. ANTOKOLSKAJA, G. V. MYASOEDOVA, L. I. BOLSHAKOVA and O. P. SHVOEVA

V.I. Vernadsky Institute of Geochemistry and Analytical Chemistry, U.S.S.R. Academy of Sciences, Moscow (U.S.S.R.)

SUMMARY

Chelate sorbents based on aminopolystyrene and chloromethylated and amino derivatives of styrene-divinylbenzene copolymers have been synthesized. The sorbents are of interest for the selective concentration of platinum-group elements. The sorption of the microgram amounts of Pd, Pt, Rh, Ir and Au has been investigated. The sorption of chloro-containing complexes of Pd(II), Pt(II), Pt(IV), Rh(III) and Ir(III) on sorbents with 8-aminoquinoline groups was studied. The difference in sorption may be explained by the formation of strong cyclic complexes of Pd and Pt with chelate groups of the resin. The sorbent can be used for the separation of milligram amounts of Pd, Pt and Au from microgram amounts of Rh and Ir and also for the selective concentration of Pd, Pt and Au from strongly acidic solutions containing large amounts of Cu, Fe, Ni and Co.

INTRODUCTION

Noble metals are usually found in natural materials in very low concentrations and, for their determination, a preliminary concentration for their separation from large amounts of other elements is required. For this purpose, the use of chelate sorbents is a promising technique¹.

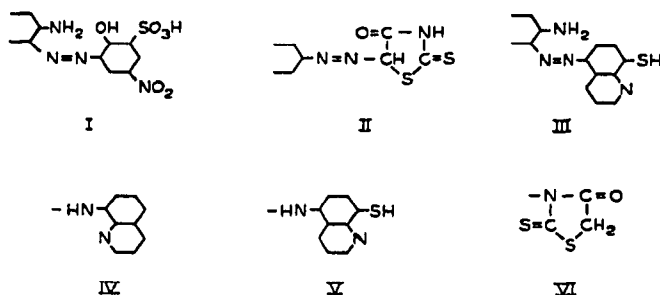
The selective properties of chelate sorbents depend on the nature of the functional groups that they contain. The sorbents with donor N and S atoms in the functional group are most significant for the noble metals^{2,3}. These groups form stable cyclic complexes with ions of the noble metals⁴.

New chelate sorbents for the concentration and separation of the noble metals have been synthesized in this laboratory in the light of known data about the formation of complexes of these metals with monomeric organic reagents.

EXPERIMENTAL

Aminopolystyrene and chloromethylated and amino derivatives of styrene-divinylbenzene macroporous copolymers have been used as polymer matrices for the

syntheses of these sorbents. The sorbents synthesized contain the following functional groups:



The sorbents were synthesized by known polymer transformation methods⁵. The sorbents are powdery or spherical granulated materials coloured yellow, brown or black; they are stable when heated in a strongly acidic solution.

The sorption of the noble metals was studied under static conditions from 0.5–10 *N* HCl, H₂SO₄ and HClO₄. Standard chloride complexes of the noble metals and their aquohydroxychlorides were prepared according to previous work^{6–9}. The experimental technique was described by Myasoedova *et al.*³.

RESULTS AND DISCUSSION

The investigation of the sorption properties of the chelate resins has shown that all of the sorbents synthesized can be used for the concentration of microgram amounts of Au and Pd from strongly acidic solutions. The sorption of Pt is most complete from hydrochloric acid solution. The sorption of Rh and Ir is effective on heating with resins with chelate groups III and V (Table I). Table I gives results for the extent of sorption of noble metals from 1 *N* HCl by resins synthesized on the basis of styrene–divinylbenzene copolymers.

The sorbents with III and V functional groups are the most interesting for the concentration of the noble metals. These sorbents have high selectivity for Al, Ca, Mg, Co, Ni, Fe and Cu. For instance, the extent of sorption of Ir is independent of

TABLE I

EXTENT OF SORPTION (%) OF PLATINUM-GROUP METALS

100 μ g of metals; 50 mg of resin; 10 ml of 1 *N* HCl; 2 h contact.

Chelate group	At room temperature (20°)					With heating (100°)	
	Au	Pd	Pt	Rh	Ir	Rh	Ir
I	90	100	25	20	—	—	—
II	100	100	40	26	15	69	—
III	100	100	96	39	40	88	95
IV	100	96	100	10	16	60	60
V	100	100	88	34	40	94	87
VI	100	92	50	—	—	83	46

the presence of Cu and Fe (10 mg/ml), Al (25 mg/ml) and Ca, Mg, Ni and Co (50 mg/ml) (Fig. 1). This result permits sorbents with III and V groups to be used for the concentration of the noble metals from complicated salt solutions. A considerable difference in the extent of sorption of the noble metals by sorbents with I and IV groups can be used for their separation. In this connection, the sorption properties of the above two sorbents have been thoroughly investigated and optimal conditions for the separation of Pd and Pt from Rh and Ir have been found. A sorbent based on aminopolystyrene with I groups was described by Dedkov *et al.*¹⁰.

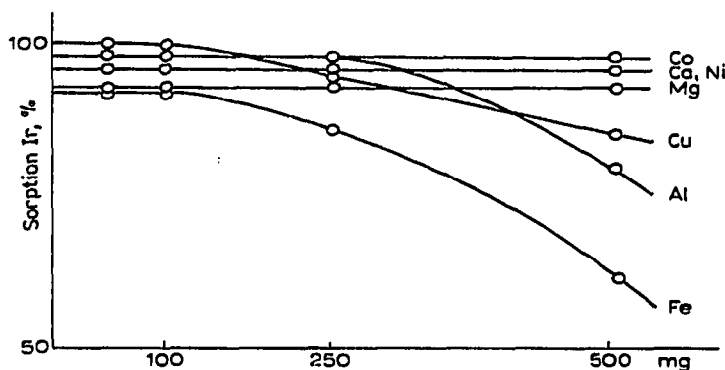


Fig. 1. Sorption of Ir in the presence of non-noble metals: 100 μ g of Ir; 20 mg of resin; 10 ml of 1 N HCl; 2 h contact; temperature *ca.* 100°.

Results are given here of the investigation of the sorption of chloro complexes of Pd, Pt, Rh and Ir by a resin containing IV groups (Table II). This sorbent was synthesized by aminating a chloromethylated styrene-divinylbenzene copolymer with 8-aminoquinoline. The presence of -NH groups in the 8-position and a heterocyclic nitrogen atom (-N \leq) favour the formation of cyclic complexes with the noble metals. The chloro complexes $[\text{PdCl}_4]^{2-}$, $[\text{Pt(II)Cl}_3\text{H}_2\text{O}]^-$ and $[\text{PtCl}_4]^{2-}$ are completely adsorbed by the resin, independent of the nature of the acids, but the Pt(IV) complexes $[\text{PtCl}_6]^{2-}$ and $[\text{PtCl}_5\text{OH}]^{2-}$ are adsorbed completely only from hydrochloric and sulphuric acids. The sorption of Pt from perchlorate solutions is slight. A

TABLE II

EXTENT OF SORPTION (%) BY RESIN WITH IV GROUPS USING DIFFERENT ACIDS
100 μ g of metals; 50 mg of resin; 10 ml of solution; 2 h contact; temperature *ca.* 20°.

Metal	State in solution	1 N HCl	0.5 N H ₂ SO ₄	1 N HClO ₄
Pd(II)	$[\text{PdCl}_4]^{2-}$	100	100	100
Pt(IV)	$[\text{PtCl}_6]^{2-}$	99	88	15
	$[\text{PtCl}_5\text{OH}]^{2-}$	100	100	28
Pt(II)	$[\text{PtCl}_3\text{H}_2\text{O}]^-$	100	100	100
Rh(III)	$[\text{RhCl}_6]^{3-}$	—	—	—
	$[\text{RhCl}_5\text{H}_2\text{O}]^{2-}$	10	—	—
	$[\text{RhCl}_3(\text{H}_2\text{O})_3]$	0	0	0
Ir(III)	$[\text{IrCl}_5\text{H}_2\text{O}]^{2-}$	15	15	0

comparison of the results obtained with those reported in the literature permits the possibility of reducing Pt(IV) to Pt(II) during the sorption from hydrochloric and sulphuric acids, while in perchloric acid Pt(IV) is not reduced. This explains the low extent of sorption. In the context of previous results^{8,11-13}, a greater extent of sorption of Rh and Ir may be expected than actually occurs (Table I). This result can probably be explained by the fact that under the experimental conditions used, Rh(III) and Ir(III) complexes retain an octahedral configuration. The sorption of these complexes is hindered because of steric factors that result from the interaction between these complexes and chelate groups of the resins.

Hence the difference in the sorption of noble metals is due to a dissimilar ability of the metals to give stable cyclic chelate complexes with functional groups of the resin, depending on the composition and electronic structure of the complexes.

It is the difference in the sorption abilities of these elements that enabled us to devise a method for the separation of milligram amounts of Pd, Pt and Au from microgram amounts of Rh and Ir. The separation is achieved by passing a solution of the noble metals in 3 *N* HCl through a sorbent-filled column. For the regeneration of the sorbent, a hot solution of thiourea in 0.1 *N* HCl is suitable. The dynamic capacity of the sorbent for Pt is 20 mg/g, and for Au 100 mg/g.

Separation of Rh from Pd, Pt and Au

A column of 0.5 cm diameter and 10 cm height packed with resin (*ca.* 1 g, the particle size being 0.25–0.5 mm) is washed with 3 *N* HCl. Then 1–5 ml of a solution containing the noble metals in 3 *N* HCl is passed through the sorbent layer at the rate of 0.5 ml/min. The column is then washed with 50 ml of 3 *N* HCl. The eluate is evaporated to dryness, 1–2 ml of a 1:2 mixture of concentrated HClO₄ and HNO₃ is added and the mixture is evaporated to dryness in order to decompose the organic material. The residue is treated with 2 ml of aqua regia and then twice with concentrated HCl. After evaporation to dryness, the residue is dissolved in 2 ml of 1 *N* HCl and Rh is determined.

This method of separation of Rh from Pd and Pt was checked on an artificial mixture of these elements and in the determination of Rh in some alloys. The Rh is determined by a spectrophotometric method with the new organic reagent 5-sulphoallthiox (allyl ester of 5-sulpho-8-mercaptoquinoline)^{14,15}.

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