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APPLICATION OF LIGANDS WITH SULPHONIC GROUPS TO THE SEPARATION OF METAL IONS ON STRONGLY BASIC ANION EXCHANGERS

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SUMMARY

The possibility of using bromopyrogallol red, chromotropic acid and alizarin red S as complexing agents for the selective separation of Ti and Zr from the other metal ions was investigated. Bromopyrogallol red was used for the separation of titanium(IV) from Co(II), Cu(II), Cr(III) and Fe(III), chromotropic acid for the separation of titanium from Ni, Cu and Fe, and alizarin red S for the separation of zirconium from Cu, Ni and Al.

Using chromotropic acid it is possible to separate titanium(IV) from large excess of metal ions giving weak complexes. By elution of metal ions which formed less stable complexes with the complexing agent no evidence of ligand in the eluate was discovered. This proves that very strong binding of ligand on anion-exchange resin occurs. It was found that for separation of Ti, chromotropic acid is more suitable than bromopyrogallol red.

INTRODUCTION

The selectivity of ion-exchange resins for metal ions can be increased by a suitable choice of the complexing agent. Aromatic complexing agents with sulphonic groups are very useful for the separation of metal ions on strongly basic anion-exchange resins, as was shown in previous papers^{1,2}. These compounds and their complexes with metal ions, owing to their aromatic character and the presence of sulphonic groups, have a great affinity for anion-exchange resins. When such a complexing agent is immobilized on the resin, it is transformed into a kind of specific resin preferring one (or a few) counter ion species much more strongly than any others according to its complexing ability.

This paper describes the possibility of using bromopyrogallol red (BPR), alizarin S and chromotropic acid as complexing agents for the separation of metal ions on strongly basic anion exchangers. The aim was to establish conditions for the separation of titanium and zirconium from other metal ions using the most selective complexing agent for these metal ions.

EXPERIMENTAL

The strongly basic anion exchangers Amberlite IRA 400 (capacity 3.55

mequiv./g), and Amberlite IRA 410 (capacity 3.0 mequiv./g) for alizarin S only, were used.

All the reagents used were of analytical grade. Solutions of metal ions were prepared from appropriate salts. Metal ions were determined by colorimetric methods.

Bromopyrogallol red (BPR) (dibromopyrogallolsulphonphthalein) as complexing agent

According to the literature^{3,4}, optimum conditions for the reaction of titanium with BPR occur at pH 2.2, for Cu^{2+} at pH 5, and for Co^{2+} above pH 5 (no stability constants for these metals are available). For Fe^{3+} , it was stated that the optimum conditions are close to pH 3. Those data show that it may be possible to separate titanium from Co^{2+} , Cu^{2+} and probably Fe^{3+} . No information was found in the literature about complexes with Cr^{3+} . Cr^{3+} was also used in this experiment because of its inert character.

In batch measurements, the correlation between the uptake of metal ions and the concentration of the ligand at pH values of 2.2 and 3.6 for Cu^{2+} , Co^{2+} and Cr^{3+} and for Fe^{3+} and TiO^{2+} also at pH 5.5 was established, using 200 mg of resin in the CH_3COO^- form and 20 ml of external solution. After equilibration, the external solutions were measured spectrophotometrically. In the external solution at pH 2.2 and 3.6, only free metal ions were present and the ligand was bound to the resin. However, at pH 5.5 it was noted that in the external solution BPR complexes with Fe^{3+} and TiO^{2+} ions exist.

At pH 2.2 and 3.6, Fe^{3+} ions starting from the ratio $\text{Fe}^{3+}:\text{ligand} = 1:2$ were bound to the resin to the extent of 90%. An increase in ligand concentration at these pH values does not change the uptake of Fe^{3+} . TiO^{2+} ions were bound quantitatively, starting from the ratio $\text{TiO}^{2+}:\text{ligand} = 1:2$ (Figs. 1 and 2). Co^{2+} , Cu^{2+} and Cr^{3+} are not bound.

The column conditions were as follows: height of packing, 17 cm; diameter, 1 cm; volumes of feed solutions, 10 ml. The solutions consisted of a mixture of TiO^{2+} ions with BPR; or Cu^{2+} , Cr^{3+} , Co^{2+} or Fe^{3+} ions with BPR or a pair of these ions with BPR (for instance, TiO^{2+} and Cu^{2+} ions); metal ion:BPR = 1:2.5; pH of solutions = 2.2.

The aim of these experiments was to check whether, under conditions given by both measurements, the separation of titanium from the other metal ions in column experiments would be possible.

The column experiments showed that at pH 2.2 titanium was bound quantita-

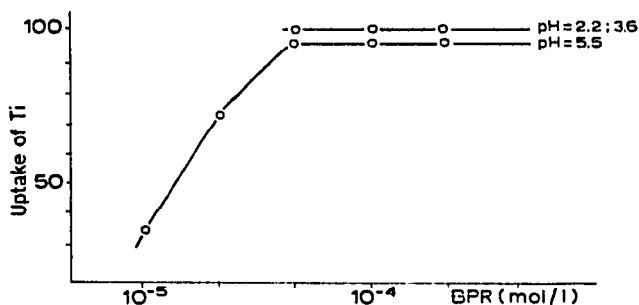


Fig. 1. Correlation between uptake of Ti and concentration of BPR at pH 2.2, 3.6 and 5.5.

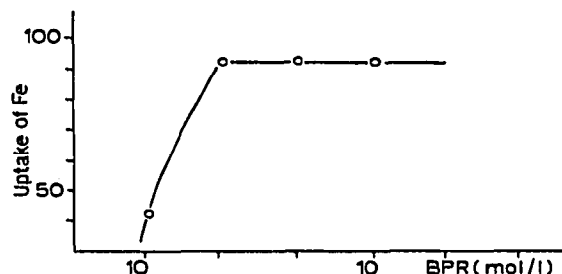


Fig. 2. Correlation between uptake of Fe and concentration of BPR at pH 2.2.

tively. Quantitative elution was obtained with 2 *N* hydrochloric acid (in order to elute 0.1 mg of titanium, 50 ml of acid are necessary). Cu^{2+} , Co^{2+} and Cr^{3+} , under conditions with which TiO^{2+} ions remained bound, passed to the effluent (found quantitatively in the effluent after washing the column with 50 ml of very dilute hydrochloric acid). But Fe^{3+} ions were partially bound to the resin under these conditions; Fe^{3+} ions passed to the effluent when 0.5 *N* hydrochloric acid was used. The results are summarized in Table I.

Chromotropic acid (ChH₄) (1,1-dihydroxynaphthalene-3,6-disulphonic acid) as complexing agent

ChH_4 is very convenient as a complexing agent for the separation of metal ions, because in a strongly acidic solution it gives complexes only with a limited number of metal ions, especially TiO^{2+} ions^{5,6,17}. Fe^{3+} ions^{7,8} also give complexes with ChH_4 in acidic solution, but not so strongly as TiO^{2+} ions. According to the literature⁹, Cu^{2+} ions give weak complexes with ChH_4 , while Ni^{2+} does not form such complexes¹⁰.

The conditions for the separation of TiO^{2+} ions from Fe^{3+} , Cu^{2+} and Ni^{2+} ions were investigated in batch and column experiments. These metal ions were chosen because of the different stabilities¹⁷ of their complexes with ChH_4 .

In batch measurements, it was noted that with a metal ion: ChH_4 ratio of 1:4 at pH 2 with anion exchangers in the acetate form (20 ml of solution, 200 mg of resin), TiO^{2+} ions were quantitatively bound to the anion exchangers.

There was no absorption of Ni^{2+} and Cu^{2+} ions under the above conditions. The absorption of TiO^{2+} , Cu^{2+} , Fe^{3+} and Ni^{2+} ions under these conditions of pH and metal ion: ChH_4 ratio was checked in column experiments.

TABLE I
SEPARATION OF Ti FROM Co, Cu, Cr AND Fe

Element	Amount of Ti (mg)	Amount of element (mg)	No. of determinations	Amount of Ti in effluent (mg)	Standard deviation
Cu	0.1	100	6	0.099	$7.0 \cdot 10^{-3}$
Co	0.1	100	6	0.099	$1.7 \cdot 10^{-3}$
Cr	0.1	100	6	0.098	$1.7 \cdot 10^{-3}$
Fe	0.1	0.5	3	0.098	

TABLE II

RESULTS OF ELUTION OF Ni²⁺, Cu²⁺ AND Fe³⁺ USING CHROMOTROPIC ACID AS COMPLEXING AGENT

Element	Taken (mg)	Found (mg)	Column height (cm)	pH of solution	Excess of ChH ₄	No. of determinations
Ni	0.50	0.52	13	2	6-fold	3
Cu	0.50	0.48	13	2	6-fold	3
Fe	0.50	0.49	13	2	6-fold	3

Column experiments. In column experiments, the absorption of single metal ions and the separation of mixtures of metal ions in different ratios were studied.

The feed solution equals 10 ml at equivalent metal ions ratio, at not equivalent larger ratio (Ti:Cu = 1:16 000 about 70 ml); metal ion:ChH₄ ratio = 1:3 1:4, 1:6, 1:60 or 1:80; pH = 2.0. The heights of the columns were 13, 15, 21 and 30 cm.

TiO²⁺ ions were quantitatively bound to the resin; 1.0 or 0.5 *N* perchloric acid was used to elute the TiO²⁺ ions. In order to elute Fe³⁺ ions, 0.2 *N* hydrochloric acid was used. Cu²⁺ and Ni²⁺ passed through the column without being bound, and for their quantitative elution very dilute hydrochloric acid was used.

The results of these experiments are summarized in Tables II and III.

TABLE III

SEPARATION OF Ti FROM Cu, Ni AND Fe USING CHROMOTROPIC ACID AS COMPLEXING AGENT

Element	Amount (mg)		Amount in effluent (mg)		Column height of packing (cm)	ChH ₄ :Metal ion ratio	No. of determinations
	Element	Ti	Element	Ti			
Ni	0.5	0.5	0.48	0.51	15	6	3
Ni*	500	0.5	—	0.50	21	(Ti) 80	2
Ni**	2000	0.5	—	0.50	30	(Ti) 80	3
Ni**	8000	0.5	—	0.50	30	(Ti) 80	1
Cu	0.5	0.5	0.48	0.51	15	6	3
Cu***	530	0.5	—	0.50	30	(Ti) 60	1
Cu [§]	2000	0.5	—	0.50	30	(Ti) 60	1
Cu [§]	8000	0.5	—	0.50	30	(Ti) 60	2
Fe*	12	0.25	—	0.26	21	3	3
Fe*	25	0.25	—	0.26	21	3	3
Fe [¶]	50	0.25	—	0.26	30	4	4

* Ni²⁺ was eluted with 200 ml of very dilute HCl, pH 3–4. Ti⁴⁺ was eluted with 100 ml of 0.5 *N* HClO₄.

** Ni²⁺ was eluted with 200 ml of very dilute HCl, pH 3–4. Ti⁴⁺ was eluted with 200 ml of 0.5 *N* HClO₄.

*** Cu²⁺ was eluted with 200 ml of very dilute HCl, pH 3–4. Ti⁴⁺ was eluted with 200 ml of 0.5 *N* HClO₄.

§ Cu²⁺ was eluted with 300 ml of very dilute HCl, pH 3–4. Ti⁴⁺ was eluted with 200 ml of 0.5 *N* HClO₄ (in cases not listed in these footnotes, Ti⁴⁺ was eluted with 50 ml of 1.0 *N* HClO₄).

¶ Fe³⁺ was eluted with 150 ml of 0.2 *N* HClO₄.

Alizarin red S as complexing agent

Alizarin S gives, in strongly acidic solution, very strong complexes with zirconyl ions^{11,12}. Other metal ions, such as Al^{13,14}, also give comparatively strong complexes, but not as strong as those with Zr, and not as stable in acidic solution.

In this work, the conditions for the separation of Zr from Al, Cu^{15,16} and Ni were investigated. In batch measurements it was found that on Amberlite IRA 410 (Cl⁻) at a Zr:alizarin red S ratio of 1:5 (200 mg of resin, 20 ml of external solution), in 0.2 N hydrochloric acid Zr⁴⁺ is bound quantitatively, and in 2 N perchloric acid Zr⁴⁺ is not bound.

Column experiments. The height of the column was 17 cm and the Zr-alizarin S ratio was 1:5. The feed solution contained 0.2 mg of Zr in a volume of 10 ml (pH 1.0). It was found that 0.2 N perchloric acid does not elute Zr⁴⁺, 0.5–1.0 N perchloric acid partly elutes Zr⁴⁺ and 2 M hydrochloric acid elutes Zr⁴⁺ quantitatively. In order to elute 0.20 mg of Zr, 50 ml of 2 N perchloric acid were used; the amount found was also 0.20 mg with an error of 0% in four determinations.

Ni²⁺ and Cu²⁺ passed quantitatively through the column if the column was washed with very dilute hydrochloric acid. Al³⁺ was eluted with 30 ml of 5.0 · 10⁻³ N hydrochloric acid.

The results are summarized in Table IV.

TABLE IV
SEPARATION OF Al, Cu AND Ni FROM Zr, AND Zr FROM Al

Element	Amount (mg)		No. of determinations	Amount in effluent (mg)		Eluent
	Zr	Element		Zr	Element	
Cu	0.2	0.2	4	0.2	0.202	HCl (pH 5)
Ni	0.2	0.8	4	0.2	0.198	
Al	0.2	0.8	5	0.198	0.21	5 · 10 ⁻³ N HCl
Al	4.0	0.1	5	0.104		
Al*	10.0	0.1	6			

* Height of column 30 cm (7 layers of alizarined S; each layer contain red 5 · 10⁻⁴ mole of alizarin red S.

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