

A SPECIFIC METHOD FOR THE SEPARATION OF RHENIUM BY ANION EXCHANGE CHROMATOGRAPHY

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Systematic investigations on the ion exchange behavior of metals in thiocyanate media are rather scarce¹⁻⁶. We have shown that the distribution coefficient of Re(VII) on Dowex 1 in thiocyanate-chloride media exhibited a rather unique feature: the K_d value has a minimum at 0.5 M NH_4SCN and increases at both higher and lower concentrations of NH_4SCN with a fixed concentration of HCl (0.5 M HCl)⁷. This behavior of Re(VII) provided a basis for quantitative anion exchange separation of Re(VII) from Mo(VI) and Tc(VII), which are strongly adsorbed on the column under the same conditions. Although there are several available methods for the separation of Re(VII)^{8,9}, a specific method is still lacking. This work has been extended in a more comprehensive manner and detailed results are presented below on the separation of Re(VII) from a considerable number of metal ions as well as Mo(VI) and Tc(VII) using a NH_4SCN -HCl eluent with an anion exchange column.

EXPERIMENTAL

Apparatus, reagents and solutions

All chemicals used were of analytical reagent grade, unless otherwise stated. A strong base type anion exchanger, Dowex 1, X-8, 100-200 mesh particle size, in the thiocyanate form, was used. The pretreatment of the resin and the column preparation are the same as those described in the previous paper⁷. The resulting resin bed was 1.0 cm in diameter and 6.5 cm long. Stock solutions of metal ions were prepared by dissolving appropriate amounts of the chloride, oxide or carbonate of the metals in HCl and diluting to a definite volume to give 10 mg metal ions per ml of 0.5 M HCl. Two exceptions are W(VI) and V(V) solutions, which are prepared from $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ and NH_4VO_3 , respectively. Further dilution of the stock solution was made whenever necessary with 0.5 M HCl. Triplicate determinations were performed using an appropriate analytical method to standardize each stock solution. The Sn(IV), Sb(III) and Bi(III) solutions were unstable at the concentration of free acid employed (0.5 M HCl). They were stabilized by adding more acid to give a free acid concentration of 3 M HCl.

Procedure

Before use the resin bed should be washed thoroughly with several column

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volumes of 0.5 M NH₄SCN–0.5 M HCl solution. The sample solution is adjusted to approximately 10 ml, which is 0.5 M in NH₄SCN and 0.5 M in HCl. The samples is then placed on the column dropwise. When the sample solution almost reaches the top of the column bed, it is eluted with 0.5 M NH₄SCN–0.5 M HCl solution at a flow rate of 1 ml/min, and the effluent is collected. The removal of non-adsorbable elements listed in Table II is complete in the first 25 ml of effluent. Elution is continued with the same eluent to remove Re(VII). Re(VII) is completely recovered in the next 40 to 150 ml of effluent. The remaining elements are stripped from the column with the appropriate amount of eluent listed in Table IV. The methods employed for the analysis of the effluent are summarized in Table I.

TABLE I
ANALYTICAL METHODS USED

<i>Cation</i>	<i>Method</i>
Re(VII)	Colorimetrically with KSCN–SnCl ₂
Li(I), Na(I), K(I)	Flame-photometrically
Be(II)	Colorimetrically as complex with 8-hydroxyquinoline
Zn(II), Cd(II), Mg(II), Mn(II)	Titration with EDTA using Eriochrome Black T as indicator
Hg(II)	Colorimetrically with Dithizone
Cu(II), Ca(II), Ni(II), Co(II)	Titration with EDTA using Murexide as indicator
Ba(II)	Titration with EDTA using Pyrocatechol Violet as indicator
Y(III), Ce(III), Eu(III), Dy(III), Er(III), Th(IV), Bi(III)	Titration with EDTA using Xylenol Orange as indicator
Al(III), In(III), Ga(III)	Titration with EDTA using Cu-Pan* as indicator
Zr(IV)	Colorimetrically with Alizarin S
Ge(IV)	Colorimetrically with Phenylfluorone
Sn(IV), W(VI)	Colorimetrically with Dithiol
V(V)	Colorimetrically with sodium tungstate
As(III)	Colorimetrically with ammonium molybdate
Sb(III)	Colorimetrically with potassium iodide
Cr(III)	Colorimetrically using its characteristic absorption band at 610 mμ
Se(IV), Te(IV)	Colorimetrically as metallic colloid after reduction with stannous chloride
Fe(III)	Titration with EDTA using Variamine Blue B as indicator
Ru(III)	Colorimetrically with thiourea
U(VI)	Colorimetrically with hydrogen peroxide

* Cu-Pan is a mixture of 1-(2-pyridylazo)-2-naphthol and Cu-EDTA.

RESULTS AND DISCUSSION

The study of the elution behavior of individual metal ions indicates that Li(I), Na(I), K(I), Be(II), Mg(II), Ca(II), Ba(II), Ge(IV), As(III), Cr(III), Al(III), Y(III), Ce(III), Eu(III), Dy(III), and Er(III) do not show any marked adsorption from the 0.5 M NH₄SCN–0.5 M HCl solution, so that they are completely recovered from the

column in the first 25 ml fraction of the effluent. Quantitative data for actual separations using the 0.5 *M* NH₄SCN–0.5 *M* HCl eluent are given in Table II.

With the elution conditions above, the greater part of the Te(IV), amounting to 75 %, comes through from the sample solution, the remainder being retained on the resin. Thus Re(VII) can be quantitatively separated from Te(IV). However, the

TABLE II

QUANTITATIVE SEPARATION OF Re(VII) FROM FOREIGN METAL IONS ON ANION EXCHANGE COLUMNS

Foreign ions	Taken (mg)		Recovered (mg)	
	Re	Foreign ions	Re	Foreign ions
Li(I)	2.00	1.51	1.93	1.51
Na(I)	2.00	10.0	1.97	10.0
K(I)	2.00	10.0	2.05	10.0
Be(II)	2.00	4.00	1.93	4.11
Mg(II)	1.00	20.0	1.07	19.5
Ca(II)	1.00	20.0	1.08	19.2
Ba(II)	1.00	20.0	1.04	20.3
Al(III)	2.00	8.50	2.04	8.43
Y(III)	1.00	2.40	1.03	2.33
Ce(III)	2.00	7.70	1.99	7.67
Eu(III)	2.00	9.82	2.02	9.50
Dy(III)	2.00	9.10	2.01	8.97
Er(III)	2.00	9.85	2.09	9.65
Cr(III)	2.00	10.0	1.90	10.0
As(III)	2.00	4.00	2.05	3.94
Ge(IV)	2.00	1.00	2.14	0.99
Te(IV) (tellurite)	2.00	4.00	2.01	3.95
Se(IV) (selenite)	2.00	20.0	2.02	19.9

partial retention of Te(IV) on the column can be avoided by decreasing the concentration of NH₄SCN down to 0.05 *M*, at a fixed concentration of HCl (0.5 *M*). Contrary to Te(IV), Se(IV) is strongly adsorbed by the resin from the 0.5 *M* NH₄SCN–0.5 *M* HCl solution. Where Se(IV) is adsorbed there is actually no adequate eluting agent to remove it effectively from the column. Fortunately the adsorbability of Se(IV) on the resin decreases rapidly with decreasing concentration of NH₄SCN, approaching zero at 0.025 *M* NH₄SCN at the fixed concentration of HCl (0.5 *M*). Therefore Se(IV) can be quantitatively collected in the first 25 ml fraction of the effluent, while Re(VII) is retained on the top of the column under the same conditions. Afterwards Re(VII) is successfully eluted with 0.5 *M* NH₄SCN–0.5 *M* HCl.

Mn(II), Ni(II), Th(IV) and Zr(IV) do not separate from Re(VII) clearly with the elution conditions given in the above procedure. Certain amounts of these elements come through in the same fraction as Re(VII). This difficulty can be overcome by decreasing the concentration of NH₄SCN to 0.025 *M*, keeping the HCl concentration constant at 0.5 *M* so that these metal ions show practically no adsorption on the resin.

For each pair of elements, a profile elution curve was obtained by collecting fractions and determining the metal content of each. The profile curves thus obtained

are illustrated in Fig. 1 for the pairs Re(VII)-Mn(II) and Re(VII)-Th(IV). Results of the quantitative separations of Re(VII) from Th(IV), Zr(IV), Ni(II), and Mn(II) are given in Table III.

The curves in Fig. 1 show that there is essentially no tailing of bands.

TABLE III

QUANTITATIVE SEPARATION OF Re(VII) FROM Th(IV), Zr(IV), Ni(II), AND Mn(II) ON ANION EXCHANGE COLUMNS

Foreign ions	Taken (mg)		Recovered (mg)	
	Re	Foreign ions	Re	Foreign ions
Mn(II)	2.00	5.34	1.94	5.25
Th(IV)	2.00	7.25	2.07	7.25
Ni(II)	1.00	5.02	1.03	5.20
Zr(IV)	2.00	9.95	2.04	9.65

Almost all the ions which form thiocyanate complexes are strongly retained on the top of the resin bed. Thus the separation of Re(VII) from most of the metals belonging to the thiocyanate group will be sharp. Data on the separation of synthetic mixtures of Re(VII) and other individual metal ions are quoted in Table IV under the condition stated in the procedure. Because of the strong adsorbabilities of the elements listed in Table IV from the thiocyanate-chloride medium there are some difficulties in the choice of a suitable eluent for the successful elution of individual metal ions.

Eluents finally found suitable for the successful elution of different cations are given in Table IV along with the data on the separation. Re(VII) can be separated with good results from any of the separated ions which are present in high proportions relative to Re(VII). Sn(II) caused difficulty at first in the elution of Re(VII) so that

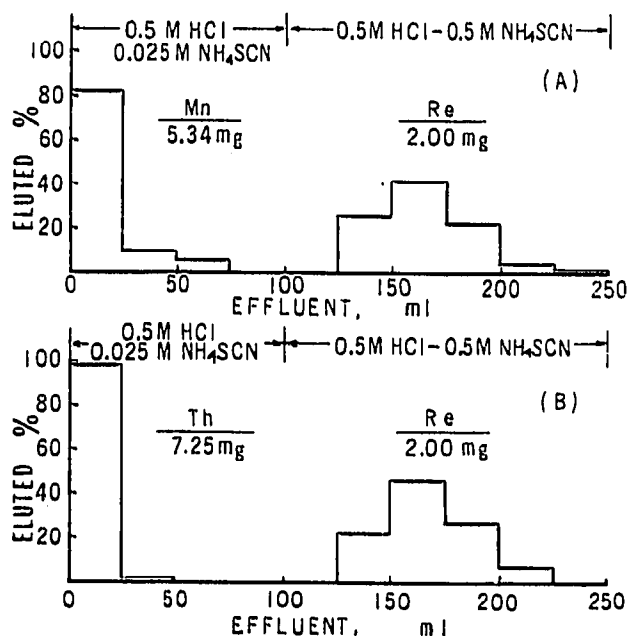


Fig. 1. Profile curves of separations of Re(VII)-Mn(II) and Re(VII)-Th(IV).

TABLE IV
SEPARATION OF RHENIUM FROM FOREIGN METAL IONS

<i>Re (mg)</i>		<i>Foreign ions (mg)</i>		<i>Eluent used for metal ions</i>	
<i>Taken</i>	<i>Found</i>	<i>Taken</i>	<i>Found</i>		
2.00	1.92	Ga(III)	9.68	9.78	Ga quantitatively eluted with 150 ml of 0.5 M H ₂ SO ₄
2.00	1.88	In(III)	8.64	8.64	In quantitatively eluted with 275 ml of 0.5 M HNO ₃
2.00	1.98	Sb(III)	2.32	2.35	Sb quantitatively eluted with 100 ml of 0.5 M H ₂ SO ₄
2.00	2.04	W(VI)	4.00	4.00	W quantitatively eluted with 25 ml 0.5 M NaOH-0.5 M NaCl
2.00	1.98	Bi(III)	4.45	4.50	Bi quantitatively eluted with 125 ml of 0.5 M H ₂ SO ₄
2.00	1.95	Fe(III)	4.94	5.60	Fe quantitatively eluted with 300 ml of 0.5 M HNO ₃
1.00	0.94	U(VI)	5.10	4.74	93% uranyl recovered by elution with 250 ml of 1 M HCl
2.00	2.00	Sn(IV)	2.95	2.93	Sn quantitatively eluted with 25 ml of 0.5 M NaOH-0.5 M NaCl
2.00	1.98	V(V)	4.74	4.73	V quantitatively eluted with 150 ml of 2 M NaOH
2.00	2.02	Cu(II)	4.94	4.90	Cu quantitatively eluted with 125 ml of 0.5 M NH ₄ OH-0.5 M NH ₄ Cl
1.00	1.04	Zn(II)	11.0	10.0	Zn quantitatively eluted with 100 ml of 1 M HClO ₄
1.00	1.07	Cd(II)	10.5	10.6	Cd quantitatively eluted with 100 ml of 1 M HClO ₄
1.00	0.96	Co(II)	5.10	5.20	Co quantitatively eluted with 100 ml of 1 M HClO ₄

both Re(VII) and Sn(II) came through partially from the sample solution on elution with 0.5 M NH₄SCN-0.5 M HCl. Re(VII) failed to break through further in the subsequent fraction of the same effluent. This difficulty can be simply avoided by oxidizing Sn(II) to the tetravalent state with H₂O₂ prior to column separation. Sn(IV) shows strong adsorption on the column, but can be easily stripped by elution with 0.5 M NaCl-0.5 M NaOH solution, as indicated in Table IV.

The separation of Re(VII) from Hg(II) and Ru(III) is complete with the procedure employed. However, considerable difficulty was encountered in stripping Hg(II) and Ru(III), which remain in a band near the top of the column. We have not yet found any suitable eluting system to remove them from the column.

The flow rate of the eluent has a considerable effect on the shape of the elution band of Re(VII). At a flow rate of 0.5 ml/min the total volume of eluent (0.5 M NH₄SCN-0.5 M HCl) required to strip Re(VII) from the column was 60 to 70 ml, about half of that obtained at a flow rate of 1 ml/min.

To study the effect of the cross-linking of the resin on the elution behavior of Re(VII), Dowex 1, X-4, X-8, and X-10 were selected to obtain elution profile curves. With higher cross-linking, Re(VII) tends to break through in the later fraction of effluent. However, there is actually no difference in the complete elution amongst the resin types employed.

In Fig. 2 the effect of cross-linking on the shape of the elution band is illus-

trated. It can also be seen that the elution band using the resin of lower cross-linking tends to show negative skewness, while that using a resin of higher cross-linking shows positive skewness. It is worth noting here that it was possible in the previous work⁷ to strip Re(VII) from the Dowex 1, X-8 column of the same size as employed here by eluting at the flow rate of 1 ml/min with approximately 40 ml of 0.5 M NH_4SCN -0.5 M HCl, which is almost less than half that required in this work.

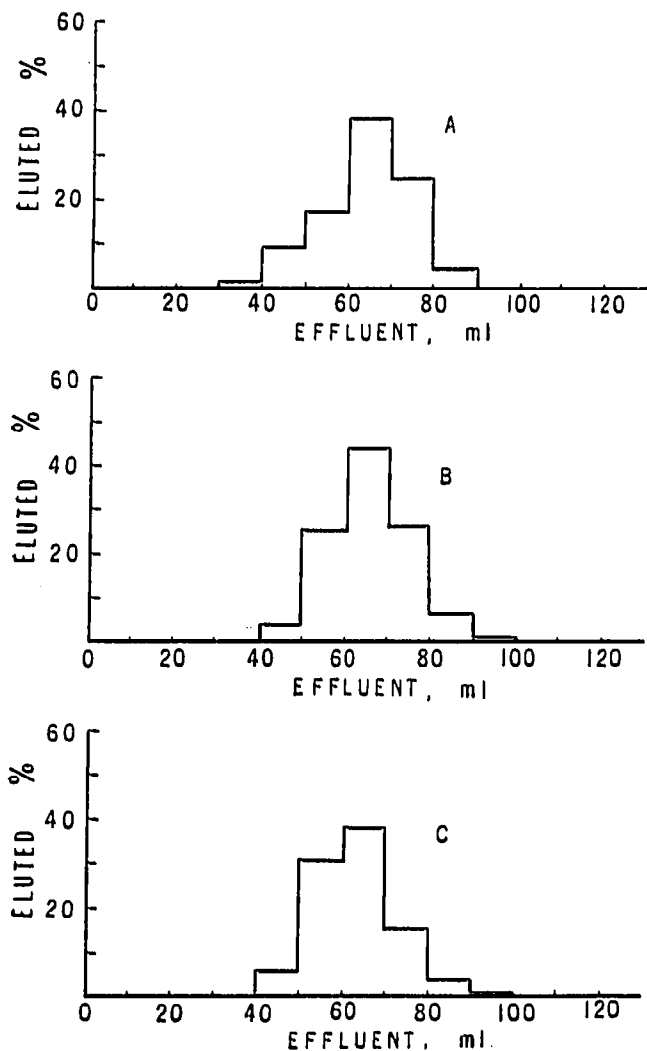


Fig. 2. Effect of cross-linking on the elution behavior of Re(VII). (A) Dowex 1, X-4, 200-400 mesh, flow rate 0.5 ml/min; (B) Dowex 1, X-8, 200-400 mesh, flow rate 0.5 ml/min; (C) Dowex 1, X-10, 200-400 mesh, flow rate 0.5 ml/min.

Although an explanation of this point cannot be given at present, it seems likely that a change in resin lot would have a considerable effect on the elution band width of Re(VII).

SUMMARY

A systematic survey of the adsorbabilities of cations with a strong base type resin, Dowex 1, X-8, in a thiocyanate-hydrochloric acid system indicates that the

difference between the distribution coefficient of Re(VII) and those of a considerable number of other ions is large enough for good separation. This fact provides the means of developing an anion exchange chromatographic procedure for the separation of Re(VII) from other ions. Re(VII) is eluted with 0.5 M NH_4SCN -0.5 M HCl, while alkali metals, alkaline earth metals, rare earths, Y(III), Cr(III), Al(III), As(III) and Ge(IV) are eluted earlier in the effluent from the sample solution. Ions forming thiocyanate complexes such as Zn(II), Cd(II), Hg(II), Cu(II), In(III), Ga(III), Sn(IV), V(V), Sb(III), Sb(V), Bi(III), W(VI), Fe(III), Co(II), Ru(III) and U(VI), are retained on the column. An effective eluting system for these ions is also given. Separations of Re(VII) from 38 metal ions are reported.

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