THE SEPARATION OF SCANDIUM BY CATION EXCHANGE IN ACID AMMONIUM SULFATE MEDIA

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The considerable data regarding the ion exchange behavior of Sc(III) in different media already available and recent results have been reviewed in several papers[1-4], so that they will not be discussed here. A systematic survey of the cation exchange behavior of Sc(III) and many other metal ions in acid $(NH_4)_2SO_4$ media indicates that the distribution coefficient of Sc(III) differed sufficiently from that of many other metal ions to ensure good separation. Sc(III) exhibits weak adsorption, while many other ions adsorb strongly from the sulfate media on a strong acid cation exchanger, such as Dowex 50W-X8.

Cation exchange distribution coefficients with BIO-RAD AG50W-X8 have currently been presented for 45 cations in H_2SO_4 media by STRELOW, RETHEMEYER AND BOTHMA[5]. However, no information is available on the behavior of Sc(III) in sulfate media. STRELOW AND BOTHMA[3] have also effected the cation exchange separation of Sc(III) from Y(III) and the rare earths by elution with $2 N H_2SO_4$ using a column of AG Dowex 50W-X8 resin. The Sc(III), which is eluted first, shows a marked tailing effect. Flow rates are also critical because of the slow exchange rate of Sc(III) in H_2SO_4 media. These difficulties have been overcome completely in this work. It will be demonstrated that the Sc(III) can quickly be separated as a narrow band from Y(III) and the rare earths, as well as many other cations, by elution with $0.3 M (NH_4)_2SO_4$–$0.025 M H_2SO_4$ solution, which is a considerably lower sulfate concentration than that employed by STRELOW AND BOTHMA.

EXPERIMENTAL

Apparatus and reagents

Ion-exchange resin. A strong acid type cation exchanger, Dowex 50W-X8, hydrogen form, 100–200 mesh was used. The resin was pretreated in a large column by washing with $2 M NH_4 SCN$–$0.5 M HCl$ solution, followed by $3 M HCl$ solution, and finally with deionized water. The resin was removed from the column and stored in a desiccator over a saturated KBr solution.

Ion-exchange column. Five grams of dried resin were slurried with water and poured into a conventional ion exchange column, 0.9 cm I.D., pulled to a tip, and plugged with glass wool at the outlet of the column. The resin bed was approximately 10 cm long. Unless otherwise mentioned, this size of column was employed throughout the work. For difficult separations a somewhat longer column, 1.0 cm I.D. and 14 cm

long (bed height), was used. The eluent was fed from a 200 ml separatory funnel whose stem was attached to the top of the column with rubber tubing.

Stock solutions. Stock solutions of metal ions were mostly prepared by dissolving their oxide, chloride or sulfate in HCl to give 10 to 20 mg of each metal ion per ml of 0.5 M HCl solution. Exceptions are the stock solutions of Mo(VI), Ti(IV) and Bi(III). Appropriate amounts of $(NH_4)_6Mo_7O_{24} \cdot 4 H_2O$ were dissolved in 0.025 M H_2SO_4 to give about 25 mg Mo(VI) per ml. The solution of Ti(IV) was prepared by dissolving titanium metal in HF–HNO$_3$ mixture, fuming with H_2SO_4 to expel HF and finally dissolving the residue in 1 M H_2SO_4 to give 0.6 mg Ti(IV) per ml. A solution approximately 20 mg of Bi(III) per ml of 1 M HNO$_3$ was prepared. The strength of each stock solution was determined by conventional analytical methods (see Table I).

TABLE I

ANALYTICAL METHODS USED

Ions	*Method*
Sc(III), Y(III), La(III), Sm(III), Lu(III), Bi(III)	Titration with EDTA using xylenol orange as indicator
Mg(II), Mn(II), Zn(II), Cd(II)	Titration with EDTA using eriochrome black T as indicator
Fe(III)	Titration with EDTA using variamine blue B as indicator
Al(III), V(IV), Co(II), Ni(II), Ga(III), In(III)	Titration with EDTA using a mixture of 1-(2-pyridylazo)-2-naphthol and Cu EDTA as indicator
Ca(II)	Titration with EDTA using 2-hydroxy-1-(2-hydroxy-4-sulfo-1-naphthylazo)-3-naphthioic acid as indicator
Cu(II)	Titration with EDTA using 1-(2-pyridylazo)-2-naphthol as indicator
Cr(III)	Back-titration with Mn(II) ion in excess of EDTA using eriochrome black T as indicator
Hg(II)	Substitution-titration with EDTA in presence of MgEDTA using eriochrome black T as indicator
Ti(IV)	Colorimetrically with H_2O_2 as reagent
Zr(IV)	Gravimetrically with NH$_4$OH as precipitant
Mo(VI)	Gravimetrically with α-benzoinoxime as precipitant

Distribution coefficient measurement

The distribution coefficient of Sc(III) and the rare earths was determined by a column elution method and a batch method, respectively. About 1 mg of Sc(III) was loaded on to the top of the column and eluted with $(NH_4)_2SO_4$ solutions of various concentrations, keeping the concentration of free sulfuric acid constant at 0.025 M. From the elution profile curve thus obtained the distribution coefficient, K_d, was calculated as described previously[6]. The distribution coefficients for the rare earths were obtained in a similar way by the batch method[6].

Procedure

The sample mixture is loaded on to the column in dilute mineral acid solution so that a sharp adsorption band develops near the top of the column. Excess free acid in the sample solution should be avoided to ensure good separation. Heavy loading should also be avoided, the loading usually being kept less than about 10 % of the total exchange capacity of the column. If necessary, the column is washed down with small quantities of water. Sc(III) is first removed from the column by elution

with 0.3 M $(NH_4)_2SO_4$–0.025 M H_2SO_4, and is quantitatively recovered in the fraction of effluent ranging between 20 and 35 ml. The flow rate is not critical and is usually adjusted to 0.5 to 1.5 ml per min. The other metal ions listed in Table II remain adsorbed on the column. These ions can easily be stripped from the column with 3 to 6 M HCl. Useful eluents for In(III), Cr(III), and Fe(III) are given in the footnote to Table II.

TABLE II

SEPARATION OF Sc(III) FROM FOREIGN METALS IN $(NH_4)_2SO_4$ MEDIA

Sc (mg)		Foreign ions (mg)		
Added	Found		Added	Found
0.863	0.863	Al(III)	11.9	12.1
0.863	0.869	Ca(II)	37.6	38.4
0.863	0.865	Cd(II)	17.2	17.1
0.863	0.863	Co(II)	11.8	11.7
0.863	0.881	Cr(III)**	10.2	10.2
0.863	0.859	Cu(II)	25.9	26.1
0.863	0.869	Fe(III)***	7.1	7.2
0.863	0.885	Ga(III)	18.6	18.9
0.863	0.885	In(III)*,***	11.4	11.7
0.863	0.858	La(III)	98.4	101.4
		La(III)	52.8	Total of
0.863	0.857	Sm(III)	30.0	100.2 %
		Y(III)	22.6	recovered
0.863	0.865	Lu(III)	1.27	1.29
0.863	0.865	Mg(II)*	7.15	7.29
0.863	0.859	Mn(II)	32.4	32.3
0.863	0.861	Ni(II)*	30.5	30.9
0.863	0.864	Sm(III)	97.7	97.6
0.863	0.861	Sm(III)	135.2	138.3
0.863	0.863	Y(III)	45.2	45.3
0.883	0.863	Zn(II)	14.8	14.9

* Longer column used.
** Eluted by 10 ml of 10% H_2SO_4 after removal of Sc(III).
*** Eluted by 40 ml of 1 M $(NH_4)_2SO_4$–0.025 M H_2SO_4 after removal of Sc(III).

When Sc(III) is accompanied by Fe(III), Sc(III) is preferentially eluted with about 110 ml of 0.15 M $(NH_4)_2SO_4$–0.025 M H_2SO_4 solution. Sc(III) is recovered first in the effluent fraction, 70 to 110 ml, and can thus be separated from Fe(III). To ensure the effective separation of Sc(III) from Hg(II), V(IV), Mo(VI), Ti(IV) and Bi(III), the sample solution is treated with a suitable complexing agent for the interfering ions so that they show only slight or no adsorption on the resin. Sc(III), which remains on the column, is then stripped with 0.3 M $(NH_4)_2SO_4$–0.025 M H_2SO_4 as before. The necessary information is outlined in Table III. The methods used for analysis of the effluents are listed in Table I.

RESULTS AND DISCUSSION

Fig. 1 gives the values for the distribution coefficients of Sc(III) as a function of $(NH_4)_2SO_4$ concentration. For comparison the values obtained by STRELOW et al.[5] for Sc(III) in H_2SO_4 media are also shown. It can be seen that the values for

TABLE III

QUANTITATIVE SEPARATION OF Sc(III) FROM FOREIGN METAL IONS IN DIFFERENT MEDIA

Sc (mg)		Foreign ions (mg)			Eluent used for metal ions
Added	Found		Added	Found	
0.863	0.877	Bi(III)	37.6	37.7	Bi eluted in the effluent from 2 M HNO_3 sample solution
0.863	0.854	Hg(II)	180.0	193.4	Hg eluted in the effluent from 0.5 M HCl sample solution
0.863	0.861	Mo(VI)	25.8	25.4	Mo eluted in the effluent from 0.3 M $(NH_4)_2SO_4$–
0.863	0.864	Ti(IV)	5.8	5.8	0.025 M H_2SO_4 solution
0.863	0.881	V(IV)	18.3	18.3	Ti eluted with 40 ml of 2% H_2O_2–1 M H_2SO_4 V eluted with 15 ml of 1% H_2O_2
0.863	0.871	Zr(IV)*	2.30	2.36	Zr eluted with 8 ml of 1 M $(NH_4)_2SO_4$–0.025 M H_2SO_4

* Longer column used.

the distribution coefficient of Sc(III) are significantly lower in sulfate media than in H_2SO_4 media. Therefore, the sulfate media would provide more efficient removal of Sc(III) from the column, ensuring good separation. Difference in slope of the distribution curves suggests that the dominant complex species formed should differ between sulfate and H_2SO_4 media.

In Fig. 2 single elution curves for Sc(III) are shown; these were obtained by elution with both $(NH_4)_2SO_4$ and H_2SO_4 solutions. Contrasted to the curves obtained with H_2SO_4, those with $(NH_4)_2SO_4$ show a fairly sharp elution band. In order to elute Sc(III) within a 20 ml fraction of effluent, the concentration of H_2SO_4 would have to be raised to more than 3 N, which would cause serious difficulties in the subsequent effluent analysis of Sc(III). Flow rate is not critical in the $(NH_4)_2SO_4$ elution, the shape of the elution band being unaffected by increasing the rate up to at least 1.5 ml per min.

The values for the distribution coefficients of "average" rare earths are also shown in Fig. 1. The values for the rare earths ranging from La(III), through Sm(III), to Lu(III) do not differ markedly from each other, so that they may be approximated as single values for the "average" rare earths. The distribution coefficient of average rare earths diminishes more rapidly with increasing concentration of $(NH_4)_2SO_4$ than that of Sc(III). The separation factor, $Kd_{av.R.E.}/Kd_{Sc}$, works out to be 2.2 and 15 at 1 M $(NH_4)_2SO_4$–0.025 M H_2SO_4 and 0.3 M $(NH_4)_2SO_4$–0.025 M H_2SO_4 respectively. The separation factor appears to favor the separation of Sc(III) and the rare earths over the $(NH_4)_2SO_4$ concentration range tested with a shorter column. The results for a separation of Sc(III), with 0.3 M $(NH_4)_2SO_4$–0.025 M H_2SO_4 elution, from Y(III) and the rare earths are quoted in Table II. Small quantities of Sc(III) can quantitatively be recovered in as little as a 15 ml fraction of effluent, while 100 times more Y(III) and rare earths as Sc(III) remain adsorbed on the column. They can be removed from the column by elution with 6 M HCl. Many other cations including Al(III), Ca(II), Cd(II), Co(II), Cr(III), Cu(II), Ga(III), In(III), Mg(II), Mn(II), Ni(II) and Zn(II) are easily separated in this way. The results of these separations are also listed in Table II. Th(IV) and Be(II) behave like Sc(III) so that their separation is difficult in this cation exchange–sulfate system.
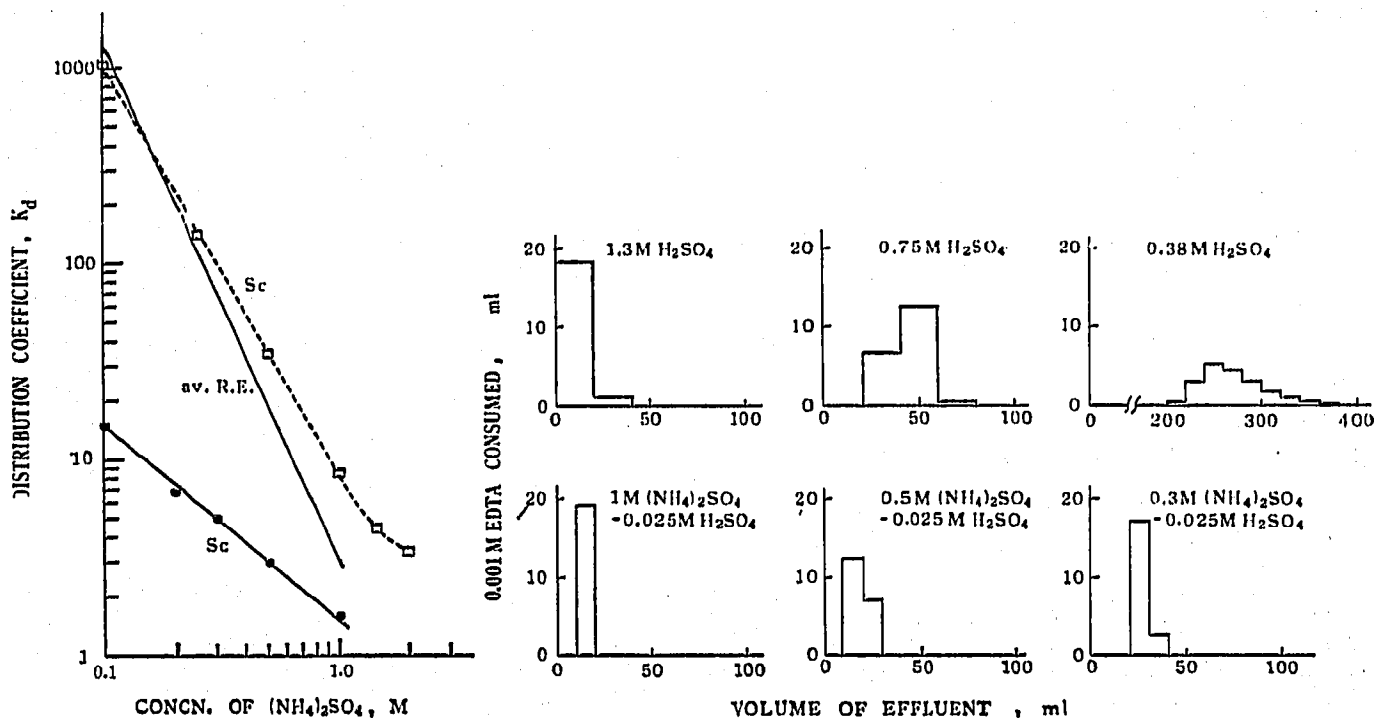
Fig. 1. Distribution coefficients of Sc(III) and "average" rare earths as a function of $(NH_4)_2SO_4$ concentration. Free acid concentration is kept constant at 0.025 M H_2SO_4. Resin, Dowex 50W-X8 (●————●) = Sc(III); (————) = "Average" rare earths; (□————□) = Values for Sc(III) in H_2SO_4 media as given by STRELOW, RETHEMEYER AND BOTHMA[5]. Numerical values of abscissa stand for H_2SO_4 concentration.

Fig. 2. Single elution curves for Sc(III). Upper: Eluted with H_2SO_4 of various concentrations. Lower: Eluted with $(NH_4)_2SO_4$ of various concentrations. Free acid concentration is kept constant at 0.025 M H_2SO_4.

Anion exchange chromatography in $(NH_4)_2SO_4$ media[4] permits the separation of Sc(III) from them, although it takes a considerable time to achieve the chromatographic run.

Mo(VI) does not adsorb from 0.3 M $(NH_4)_2SO_4$-0.025 M H_2SO_4 solution to any great extent on the cation exchange resin. By feeding the sample, adjusted to 0.3 M sulfate in 0.025 M H_2SO_4, on to the column and subsequent washing with the same solution, Mo(VI) can be eluted from the sample solution prior to the breakthrough of Sc(III). Zr(IV) exhibits a slight adsorption from the acid sulfate media. It can be separated from Sc(III) by elution with 1 M $(NH_4)_2SO_4$-0.025 M H_2SO_4, thus being eluted as a very sharp band, immediately followed by Sc(III). V(IV) and Ti(IV) are eluted rapidly prior to Sc(III) with 1 % H_2O_2 and 2 % H_2O_2-1 M H_2SO_4, respectively. Sc(III) is then removed by passing 20 ml of 0.3 M $(NH_4)_2SO_4$-0.025 M H_2SO_4 down the column. The separation of Hg(II) and Bi(III) from Sc(III) is simply conducted by feeding the sample solution, adjusted to 0.5 M in HCl for Hg(II) and to 2 M in HNO_3 for Bi(III), respectively, on to the column and then washing with the same solution. Both elements are eluted in the effluent from the sample solution, while Sc(III) remains on the top of the column. The results of the separations are given in Table III. The present ion exchange method for Sc(III) offers advantages in speed, selectivity and ease of effluent analysis for Sc(III).

SUMMARY

A study of the adsorption of metal ions, in acid sulfate media, on a strong-acid type cation exchange resin, Dowex 50W-X8, indicates that the difference between the distribution coefficients of Sc(III) and many other ions is sufficiently large for good separation. This fact makes it possible to develop a cation exchange chromatographic procedure for the separation of Sc(III) from other ions. Sc(III) can be eluted with 0.3 M $(NH_4)_2SO_4$–0.025 M H_2SO_4, while Al(III), Ca(II), Cd(II), Co(II), Cr(III), Cu(II), Ga(III), In(III), Mg(II), Mn(II), Ni(II), Y(III) and the rare earths, and Zn(II) remain adsorbed on the column. Ions forming stable sulfatocomplexes or other types of complex are eluted earlier in the effluent from the sample solution. Suitable elution systems for these ions are given. Separation of Sc(III) from 23 metal ions is reported.

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