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# Cation Exchange in Tartaric Acid-Nitric Acid and in Tartaric Acid-Ammonium Tartrate Solution

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**Cation exchange distribution coefficients are presented for 46 elements in tartaric acid-nitric acid and in tartaric acid-ammonium tartrate mixtures with AG 50W-X8, a sulfonated polystyrene resin. The ion exchange behavior of the elements in tartrate-containing media is discussed. A selectivity series of elements in tartrate media according to their tendency to tartrate complex formation is presented together with three multielement elution curves demonstrating the separation of the element combinations Sn(IV)-In-Zn-Cd, Mo(VI)-U(VI)-Ni(II)-Mn(II), and Ti(IV)-Sc-Al-Ca.**

The first application of tartrate as complexing agent for the separation of elements by ion exchange chromatography is probably found in a paper by Tompkins and Mayer (1) who determined cation exchange separation factors for the lanthanide pair promethium-europium with various complexing agents and showed that the factor in tartrate was larger than that in citrate, the reagent commonly used for lanthanide separations in those days. Relatively few papers, most of them describing the separation of only a few elements by cation exchange in tartrate media have appeared sporadically since then. Copper has been retained as cationic ammine complex from tartrate solutions containing excess ammonia and separated from aluminum (2), lead (3), and tin(IV) and antimony(III) (4). Copper(II), zinc, and nickel(II) (5) and also cadmium (6) have been separated in a similar way from gallium. Antimony(III) has been separated from tin(II) by selective elution with 2% tartaric acid of pH 1 (adjusted with HCl) (7), antimony(V), tin(II), and tin(IV) from iron(III), copper(II), cobalt(II), and cadmium by elution with 20% tartaric acid (8), iron(III) from magnesium by elution with 20% tartaric acid-tartrate of pH 3 (9), and lead from tin(IV), antimony(V), niobium(V), tantalum(V), tungsten(VI), and molybdenum(VI) by eluting these elements with 0.25 M tartaric acid containing 0.01 M nitric acid while lead is retained (10).

The first systematic study of cation exchange distribution coefficients in tartrate media has probably been presented by Qureshi et al. (11). Only the elements Ti(IV), V(V), Fe(III), Nb(V), and U(VI) were included, and there is some uncertainty in the results. Later studies by Dadone et al. (12) and Simek (13) also investigated a limited number of elements (seven and five, respectively). A study of a large number of elements was presented by Rouchaud and Revel (14). Unfortunately the results were presented as curves which allow only an approximate estimation of the actual values of the distribution coefficients. Furthermore, the distribution coefficients were determined as a function of tartaric acid concentration at a single concentration (0.3 M) of nitric acid. Numerous elements, e.g., V, Nb, Th, Sn, Bi, Pb, and Tl were not included in the study. Some of these form stable tartrate complexes and for this reason should be interesting.

The cation exchange distribution coefficients of a large number of elements have been measured in tartaric acid-nitric acid and in tartaric acid-ammonium tartrate mixtures and these data are reported below. A discussion of the separation

possibilities offered by this system is also presented.

## EXPERIMENTAL SECTION

**Reagents and Apparatus.** The AG 50W-X8 sulfonated polystyrene cation exchanger marketed by BIO-RAD laboratories of Richmond, CA, was used for this study. Resin of 100-200 mesh particle size was employed for distribution coefficient determinations and resin of 200-400 mesh for column work. Water was distilled and for further purification was passed through an Elgastat deionizer. Only reagents of A.R. quality were used. Tantalum, niobium, and gallium were obtained as the chlorides (>99.9% pure) in closed ampules from Fluka A.G., Buchs, Switzerland, and scandium as the oxide was from the same source.

Standard solutions were in most cases prepared from the nitrate of the elements or from the oxides dissolved in nitric acid and evaporated to dryness (scandium and lanthanides). In a few cases, when the nitrates were not easily available and tendency to chloride formation was not sufficiently strong to influence distributions at the low chloride concentration involved, the chlorides were used. Solutions of multivalent elements with tendencies to hydrolysis such as Nb(V), Sn(IV), Zr, Ti(IV), Al, In, Ga, Th, Sb(III), and Fe(III) were prepared in 1 M tartaric acid. Titanium(IV) solution was prepared from titanium(III) solution by oxidation with hydrogen peroxide after tartaric acid had been added. Tantalum(V) chloride (0.02 M) was dissolved in 1.25 M tartaric acid and bismuth nitrate was prepared in 0.25 M nitric acid.

Borosilicate glass tubes of 23 mm i.d. and about 400 mm in length were used as columns, fitted with a no. 2 porosity glass sinter and a burette tap at the bottom and a B19 joint at the top. The columns were filled with a slurry of the AG50 resin in the hydrogen form until the settled resin form reached the 60 mL mark. The resin was then converted to the ammonium form by passing through about 200 mL of 1 M ammonium nitrate. The excess of ammonium nitrate was removed with deionized water.

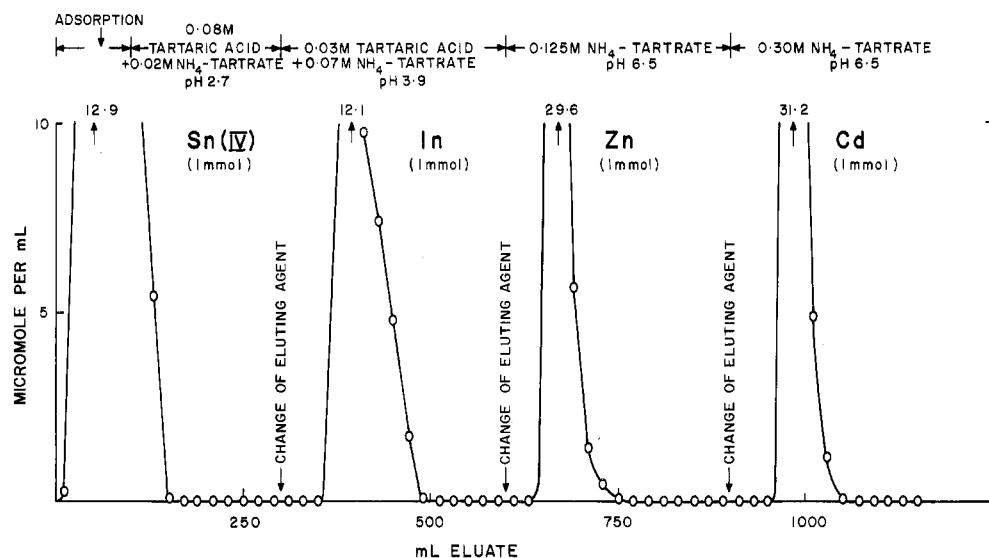
Atomic absorption measurements were carried out with a Varian-Techtron AA-5 instrument. A Zeiss PMQII was used for spectrophotometric measurements.

**Distribution Coefficients.** The resin was dried at 60 °C in a Gallenkamp vacuum pistol with magnesium perchlorate (anhydrous) as drying agent and kept in a desiccator over the same drying agent. Residual water was determined by drying at 120 °C and the weights of resin were corrected accordingly.

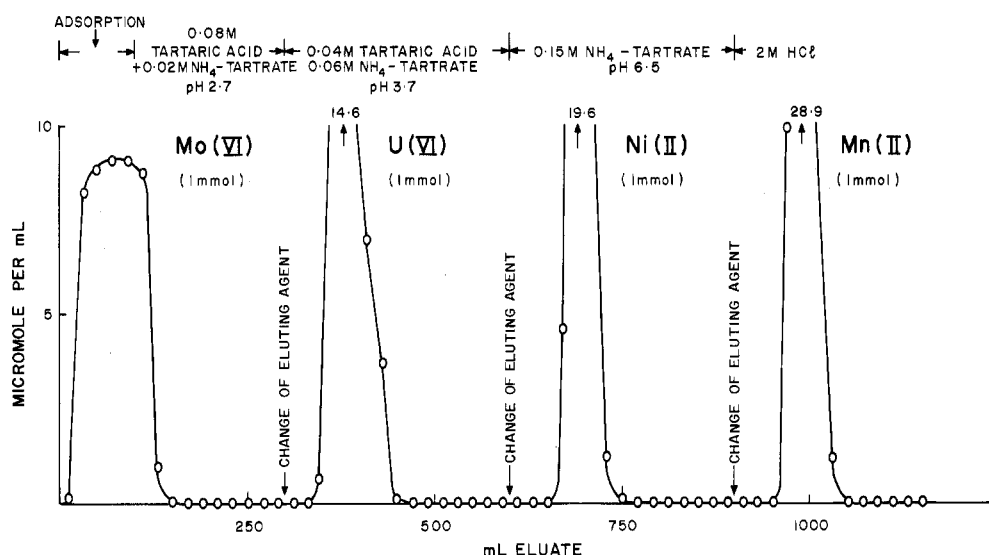
Distribution coefficients were determined by equilibrating 2.500 g of dry resin in the hydrogen form with 250 mL of solution and shaking for 24 h in a mechanical shaker at 20 °C. The solutions contained the concentrations of tartaric acid and nitric acid shown in Tables I and II. Concentrations of tartaric acid and ammonium tartrate with their corresponding pH values which apply to another set of coefficients are listed in Table III.

Where the resin could be ignited without loss of the particular element, it was separated by filtration using a filter paper and ashed at low temperature and the ash dissolved or weighed directly. Otherwise the resin was transferred to a short large-diameter column, to facilitate elution. The amounts of the elements in both the aqueous and the resin phase were then determined by appropriate analytical methods. From the results equilibrium distribution coefficients (15) were calculated and are presented in Tables I-III.

Usually 5 exchange milliequivalents were used for equilibration, but in some cases smaller amounts had to be used either because of limited solubilities or because only limited amounts of an expensive reagent were available (gallium and scandium).



**Figure 1.** Elution curve Sn(IV)–In–Zn–Cd: 60 mL (20 g) AG 50W-X8 resin, 200–400 mesh; column length 145 cm,  $\phi$  23 mm; low rate  $4.0 \pm 0.5$  mL; column in  $\text{NH}_4$  form.



**Figure 2.** Elution curve Mo(VI)–U(VI)–Ni(II)–Mn(II). Conditions are as for Figure 1.

**Elution Curves.** *a. Sn(IV)–In–Zn–Cd.* A resin column containing 60 mL (20 g) of AG 50S-X8 cation exchanger of 200–400 mesh particle size, converted to the  $\text{NH}_4^+$  form as described earlier, was equilibrated by passing through 50 mL of a solution 0.08 M in tartaric acid and 0.02 M in ammonium tartrate. A solution containing about 1 mmol of each Sn(IV), In, Zn, and Cd in 100 mL of 0.08 M tartaric acid and 0.02 M ammonium tartrate was then passed through the column. Tin (IV), which passed partially through the column in the adsorption step, was eluted with a further 200 mL of this solution. Indium was then eluted with 300 mL of 0.03 M tartaric acid–0.07 M ammonium tartrate and zinc with 300 mL of 0.125 M ammonium tartrate (pH 6.5). Cadmium was finally eluted with 250 mL of 0.30 M of ammonium tartrate. The flow rate was  $4.0 \pm 0.5$  mL/min throughout. Fractions of 20 mL volume were taken with an automatic fractionator from the beginning of the adsorption step and the amounts of the elements in the fractions were determined by suitable analytical methods (AA for all four elements in this case). The experimental curve is presented in Figure 1.

*b. Mo(VI)–U(VI)–Ni(II)–Mn(II).* For examination of the elution properties of Mo(VI), U(VI), Ni(II), and Mn(II) a mixture containing 1 mmol of each of these in 100 mL of 0.08 M tartaric acid–0.02 M ammonium tartrate was passed onto a column containing 60 mL of AG 50 cation exchange resin as described above. Elution was carried out with the following sequence of reagents: 200 mL of 0.08 M tartaric acid–0.02 M ammonium tartrate for Mo(VI), 300 mL of 0.04 M tartaric acid–0.06 M

ammonium tartrate for U(VI), 300 mL of 0.15 M ammonium tartrate (pH 6.5) for nickel(II), and 250 mL of 0.30 M ammonium tartrate for manganese(II). The flow rate and fraction size collected were the same as before. Atomic absorption spectrometry after suitable dilution (Mo, Ni, Mn), or spectrophotometry (U) were used for element analysis. The experimental curve is shown in Figure 2.

*c. Ti(IV)–Sc(III)–Al–Ca.* A solution containing 1 mmol each of Ti(IV), Al, and Ca, and 0.5 mmol of Sc in 100 mL of 0.08 M tartaric acid–0.02 M ammonium tartrate was absorbed on a column also prepared as described above. The elution sequence in this case, 250 mL of 0.08 M tartaric acid–0.02 M ammonium tartrate for titanium(IV), 300 mL of 0.05 M tartaric acid–0.05 M ammonium tartrate for scandium, 300 mL of 0.02 M tartaric acid–0.8 M ammonium tartrate for aluminum, and 200 mL of 3 M nitric acid for calcium, yielded the curve shown in Figure 3. Aluminum and calcium were determined by atomic absorption and titanium and scandium by spectrophotometry.

## DISCUSSION

The distribution coefficients for tartaric acid–tartrate mixtures were determined by using resin in the hydrogen form. Because of this some ammonium ions are absorbed on the resin and the pH of the mixture decreases during equilibrium. The pH value before and after equilibration is indicated in Table III. When a column is used in the ammonium form,

Table I. Distribution Coefficients in Tartaric Acid-HNO<sub>3</sub> Mixtures (0.10 M Tartaric Acid-Variations of HNO<sub>3</sub>)  
distribution coefficients, with HNO<sub>3</sub> molarity

element	0	0.01 M	0.10 M	0.20 M	0.50 M	1.0 M
Th	>10 <sup>5</sup>	>10 <sup>5</sup>	>10 <sup>5</sup>	>10 <sup>5</sup>	>10 <sup>4</sup>	1090
La	>10 <sup>4</sup>	>10 <sup>4</sup>	>10 <sup>4</sup>	>10 <sup>4</sup>	1880	264
Ce(III)	>10 <sup>4</sup>	>10 <sup>4</sup>	>10 <sup>4</sup>	>10 <sup>4</sup>	1810	248
Yb	>10 <sup>4</sup>	>10 <sup>4</sup>	>10 <sup>4</sup>	>10 <sup>4</sup>	1130	192
Y	>10 <sup>4</sup>	>10 <sup>4</sup>	>10 <sup>4</sup>	>10 <sup>4</sup>	1020	173
Gd	>10 <sup>4</sup>	>10 <sup>4</sup>	>10 <sup>4</sup>	>10 <sup>4</sup>	995	166
In	>10 <sup>4</sup>	>10 <sup>4</sup>	>10 <sup>4</sup>	>10 <sup>4</sup>	675	119
Sc <sup>a</sup>	>10 <sup>4</sup>	>10 <sup>4</sup>	>10 <sup>4</sup>	3240	485	114
Ga <sup>b</sup>	>10 <sup>4</sup>	>10 <sup>4</sup>	>10 <sup>4</sup>	6400	610	104
Fe(III)	>10 <sup>4</sup>	>10 <sup>4</sup>	5400	2200	396	92
Al	>10 <sup>4</sup>	>10 <sup>4</sup>	>10 <sup>4</sup>	4400	387	84
Ba	>10 <sup>4</sup>	>10 <sup>4</sup>	4300	1440	230	66
Bi(III) <sup>c</sup>	prec	>10 <sup>4</sup>	3600	3100	444	53
Cr(III)	930	894	336	173	83	49.0
Sr	>10 <sup>4</sup>	>10 <sup>4</sup>	2800	795	144	39.0
Ca	>10 <sup>4</sup>	>10 <sup>4</sup>	1480	480	111	35.1
Pb(II)	>10 <sup>4</sup>	>10 <sup>4</sup>	3400	1003	158	32.6
Mn(II)	>10 <sup>4</sup>	>10 <sup>4</sup>	1080	358	89	29.1
Co(II)	>10 <sup>4</sup>	>10 <sup>4</sup>	1060	358	88	29.1
Ni(II)	>10 <sup>4</sup>	8600	1012	357	86	27.8
Cd	>10 <sup>4</sup>	>10 <sup>4</sup>	1084	356	84	27.7
Zn	>10 <sup>4</sup>	9300	924	320	78	27.1
Cu(II)	>10 <sup>4</sup>	7100	901	330	80	26.5
U(VI)	>10 <sup>4</sup>	8900	895	271	72	26.4
Tl(I) <sup>b</sup>	1800	1200	254	130	47.7	23.9
Cr(III) <sup>d</sup>	136	130	93	58	34.5	22.8
Mg	8300	5400	863	264	68	22.7
Hg(II) <sup>b</sup>	hydrol	hydrol (290)	495	187	74	22.5
Ag(I) <sup>b</sup>	1440	940	190	94	38.2	18.5
V(IV)	1620	1520	441	176	43.4	14.8
Be	3680	2560	526	159	49	14.7
Ti(IV) <sup>e</sup>	542	614	529	295	64	14.1
V(V) <sup>f</sup>	18.9	23.8	47.2	38.2	17.2	8.7
Zr	1.6	1.6	1.7	2.7	3.3	4.1
Sn(IV)	1.4	1.8	2.7	3.8	4.0	3.4
Sb(III)	0.4	0.6	0.6	0.7	0.7	0.7
Mo(VI)	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
W(VI)	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
As(III)	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Nb(V) <sup>b</sup>	<0.6	<0.6	1.0	prec	prec	prec
Ta(V) <sup>b</sup>	prec	prec	prec	prec	prec	prec
Li, Na, K, Rb, Cs	coefficients similar to those in pure nitric acid					

<sup>a</sup> 0.5 mmol. <sup>b</sup> 1 mmol. <sup>c</sup> 0.33 mmol. <sup>d</sup> Standard solution boiled for 1 h in about 1.5 M tartaric acid. <sup>e</sup> H<sub>2</sub>O<sub>2</sub> present. <sup>f</sup> 0.03% H<sub>2</sub>O<sub>2</sub> present, 1 h of equilibration.

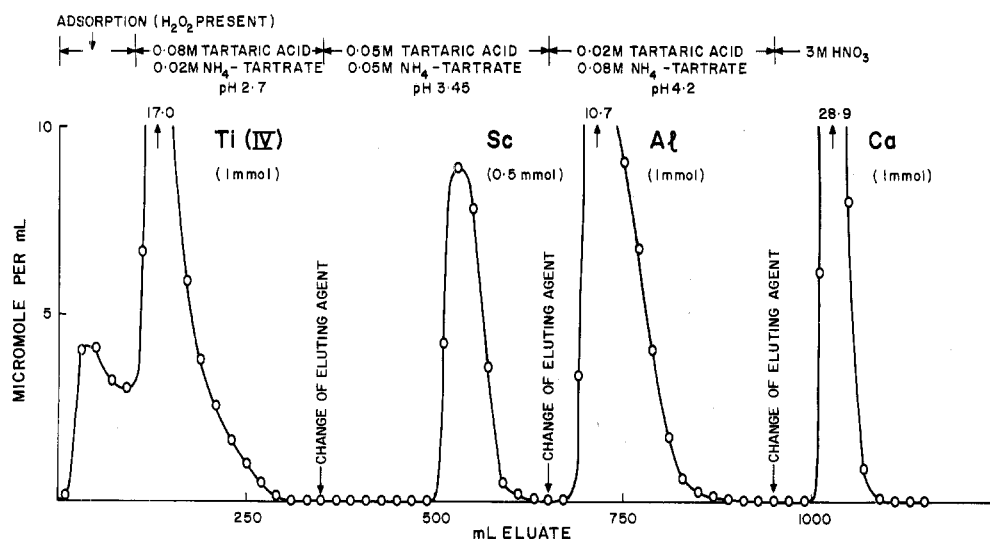


Figure 3. Elution curve Ti(IV)-Sc-Al-Ca. Conditions are as for Figure 1.

the ammonium tartrate concentration should be decreased by about 0.02 M and the tartaric acid increased to make the

coefficients given in Table III applicable to the elution procedure.

Table II. Distribution Coefficients in Tartaric Acid-HNO<sub>3</sub> Mixtures (0.25 M Tartaric Acid-Variou Amounts of HNO<sub>3</sub>)

element	distribution coefficients, with HNO <sub>3</sub> molarity					
	0	0.10 M	0.10 M	0.20 M	0.50 M	1.0 M
Th	>10 <sup>5</sup>	>10 <sup>5</sup>	>10 <sup>5</sup>	~10 <sup>5</sup>	4900	710
La	>10 <sup>4</sup>	>10 <sup>4</sup>	>10 <sup>4</sup>	>10 <sup>4</sup>	1820	259
Ga <sup>b</sup>	>10 <sup>4</sup>	>10 <sup>4</sup>	>10 <sup>4</sup>	6300	605	103
Fe(III)	>10 <sup>4</sup>	8400	5100	2050	370	89
Sc <sup>a</sup>	>10 <sup>4</sup>	>10 <sup>4</sup>	7900	2200	334	83
Al	>10 <sup>4</sup>	>10 <sup>4</sup>	>10 <sup>4</sup>	4300	383	81
Bi(III) <sup>c</sup>	prec	4000	2540	1180	220	37.1
Mn(II)	>10 <sup>4</sup>	>10 <sup>4</sup>	1020	358	88	29.0
Pb(II)	>10 <sup>4</sup>	>10 <sup>4</sup>	2580	813	136	28.3
Ni(II)	>10 <sup>4</sup>	8200	1000	348	83	28.1
Cu(II)	5500	4100	727	298	80	27.8
Cd	>10 <sup>4</sup>	8400	925	339	83	27.7
Zn	9000	6600	793	299	80	27.2
U(VI)	3500	2600	523	227	66	25.6
V(IV)	354	310	209	129	41.1	14.2
Ti(IV) <sup>d</sup>	55	62	113	120	51	13.3
V(V) <sup>e</sup>	29.1	33.9	55	63	27.4	12.1
Zr	0.8	0.9	1.0	1.2	1.4	1.8
Sn(IV)	0.9	0.9	1.4	1.8	1.7	1.7
Sb(III)	0.4	0.5	0.4	0.6	0.5	0.4
Mo(VI)	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
W(VI)	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
As(III)	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Nb(V) <sup>b</sup>	<0.5	<0.5	<0.5	<0.5	prec	prec
Ta(V) <sup>b</sup>	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Li, Na, K, Rb, Cs, and other elements of Table I	coefficients similar to those in pure nitric acid					

<sup>a</sup> 0.5 mmol. <sup>b</sup> 1 mmol. <sup>c</sup> 0.33 mmol. <sup>d</sup> H<sub>2</sub>O<sub>2</sub> present. <sup>e</sup> 0.03% H<sub>2</sub>O present, 1 h of equilibration.

Table III. Distribution Coefficients in Tartaric Acid-Ammonium Tartrate Mixtures

tartaric acid NH <sub>4</sub> tartrate	0.10 M	0.09 M	0.08 M	0.06 M	0.04 M	0.02 M	0.01 M	nil	extra 1 M ammonia		
	nil	0.01 M	0.02 M	0.04 M	0.06 M	0.08 M	0.09 M	0.10 M	10 mL	12.6 mL	20 mL
pH before equ.	2.0	2.35	2.71	3.2	3.65	4.2	4.6	6.5			
pH after equ.	1.8	2.0	2.2	2.7	3.1	3.6	3.8	4.1	5.0	6.4	8.2
Ba	>10 <sup>4</sup>	>10 <sup>4</sup>	>10 <sup>4</sup>	>10 <sup>4</sup>	8600	3100	1980	1310	690	570	570
Sr	>10 <sup>4</sup>	>10 <sup>4</sup>	>10 <sup>4</sup>	>10 <sup>4</sup>	3900	1160	760	470	263	236	229
Mg	8300	4200	2400	810	410	248	209	160	96	87	83
Ca	>10 <sup>4</sup>	>10 <sup>4</sup>	>10 <sup>4</sup>	4400	1180	342	235	151	86	78	76
Mn(II)	>10 <sup>4</sup>	~10 <sup>4</sup>	3700	980	420	190	152	120	78	70	(4.3) oxid
La	>10 <sup>4</sup>	>10 <sup>4</sup>	>10 <sup>4</sup>	>10 <sup>4</sup>	2400	338	156	prec	prec	prec	prec
Cd	>10 <sup>4</sup>	6100	3200	890	310	144	144	80	46	42	133
Co(II)	>10 <sup>4</sup>	8800	3800	1700	314	122	99	59	33.1	18.3	13.8
Co(II) <sup>a</sup>	>10 <sup>4</sup>	>10 <sup>4</sup>	~10 <sup>4</sup>	3200	550	187	146	78	38.2	19.8	14.4
Ce(III)	>10 <sup>4</sup>	>10 <sup>4</sup>	>10 <sup>4</sup>	>10 <sup>4</sup>	1350	167	76	prec	prec	prec	prec
Pb(II) <sup>b</sup>	>10 <sup>4</sup>	>10 <sup>4</sup>	>10 <sup>4</sup>	8200	1160	215	105	58	18.5	13.1	10.9
Ni(II)	>10 <sup>4</sup>	~10 <sup>4</sup>	5800	850	218	74	50	28.8	16.0	10.8	17.1
Zn	>10 <sup>4</sup>	5500	2400	510	143	43.5	28.6	20.5	10.5	8.6	15.4
Y	>10 <sup>4</sup>	>10 <sup>4</sup>	>10 <sup>4</sup>	4600	500	74	31.7	16.1	prec	prec	prec
Al	>10 <sup>4</sup>	>10 <sup>4</sup>	>10 <sup>4</sup>	3400	154	17.0	6.3	1.7	<0.5	<0.5	<0.5
Cu(II)	>10 <sup>4</sup>	4100	2500	231	67	prec	prec	prec	3.4	2.0	16.0
Cu(II) <sup>c</sup>	>10 <sup>4</sup>	9800	6300	1130	94	15.1	7.4	4.6	3.1	2.2	16.1
In	>10 <sup>4</sup>	>10 <sup>4</sup>	>10 <sup>4</sup>	1800	85	6.6	3.9	2.2	1.1	0.8	(29.3) hydrol
Fe(III)	>10 <sup>4</sup>	~10 <sup>4</sup>	1800	44	10.2	6.6	4.4	3.2	hydrol	hydrol	hydrol
Fe(III) <sup>d</sup>	>10 <sup>4</sup>	>10 <sup>4</sup>	8100	62	17.7	16.5	11.5	8.1	2.2	2.1	(6.2) hydrol
U(VI)	>10 <sup>4</sup>	5400	2000	189	21.1	2.1	<0.5	<0.5	<0.5	<0.5	<0.5
Sc	>10 <sup>4</sup>	>10 <sup>4</sup>	>10 <sup>4</sup>	301	12.5	3.6	1.8	1.5	1.1	0.8	prec
Th	>10 <sup>5</sup>	>10 <sup>5</sup>	>10 <sup>4</sup>	55	1.1	0.5	<0.5	<0.5	<0.5	<0.5	<0.5
V(IV)	1600	720	299	36.2	1.5	0.9	<0.5	<0.5	<0.5	<0.5	<0.5
Ti(IV) <sup>e</sup>	640	310	127	10.6	4.8	1.8	1.4	(11.6) hydrol	hydrol	hydrol	hydrol
Sn(IV)	1.4	1.5	1.3	1.1	0.6	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5

<sup>a</sup> 1 mmol. <sup>b</sup> 0.01 mmol. <sup>c</sup> 0.5 mmol. <sup>d</sup> 0.33 mmol. <sup>e</sup> H<sub>2</sub>O<sub>2</sub> present.

Due to the fact that the resin was used in the hydrogen form in our own study, the distribution coefficients listed in Table

III seem to agree reasonably well with those published by Dadone et al. (12), though minor differences exist. For ex-

ample our separation factor for the Cd-Co(II) pair in 0.1 M tartrate at an equilibrium pH of 4.1 is only about 1.4–1.5 when a correction for high loading is applied, while the coefficients in Dadone's table correspond to a factor of about 2.7. Our distribution coefficients and the separation factor derived from an elution curve are in agreement whereas an examination of the elution curve presented by Dadone reveals that the distribution coefficient for cobalt(II) based on dry weight of resin is about 60 and not 32 as given in his table. This would also lead to a separation factor of about 1.4–1.5 for the Cd-Co(II) pair in agreement with our observation.

We do not find that the distribution coefficients of uranium(VI), iron(III), and vanadium(V) are constant over a wide concentration range of tartaric acid as Qureshi et al. (11) have reported. However we found that vanadium(V) is slowly reduced to vanadium(IV) in tartrate solution, even in the presence of hydrogen peroxide. Vanadium(IV) is also adsorbed less strongly than uranium(VI) and its adsorption decreases with increasing tartaric acid concentration (Table I and II). Our results do explain the large discrepancy between the observations of Dadone et al. and Qureshi for the adsorption of iron(III) mentioned by Dadone (12). Dadone et al. used a resin in the ammonium form while Qureshi et al. used a resin in the hydrogen form. Our results in Tables I and II show that iron(III) is adsorbed very strongly from tartaric acid by a resin in the hydrogen form, but Table III also indicates that, when the resin has taken up enough ammonium ions (or is in the ammonium form originally), the distribution coefficient of iron(III) decreases markedly with tartrate concentration confirming both the results of Dadone et al. and those of Qureshi et al. at least qualitatively.

The fact that Zr, Sn(IV), Nb(V), Ta(V), Mo(VI), and W(VI) are very strongly complexed by tartrate, even in nitric acid solution, and are not retained by a cation exchange resin, while Ti(IV), Th, Fe(III), Al and almost all other cationic elements are, is the outstanding feature of this system. The relatively strong retention of titanium and the large separation factor for the Ti-Zr pair ( $Sr_{Zr,Ti} \geq 100$ ) indicate that such a medium should be especially useful for separating small or trace amounts of titanium from large amounts of zirconium. In most other ion exchange procedures proposed for the separation of these two elements, zirconium is retained more strongly. The behavior of the above group of elements has already been applied to their separation from lead (10).

While the ion exchange behavior of zirconium and the other elements named above is almost entirely dominated by the tartrate component in tartaric-nitric acid mixtures, the other elements behave differently. A few, like Ti(IV), V(IV), and U(VI), are still somewhat influenced by the tartaric acid concentration, especially in the range of low nitric acid concentrations, but many others are nearly independent of the tartaric acid concentration and are almost entirely influenced by the concentration of nitric acid.

In tartaric acid-ammonium tartrate mixtures the situation is different. With increasing pH the tartrate concentration rises to such levels that even barium, the cation with the least tendency to form tartrate complexes, except for the alkalis, is affected.

Arranging the elements according to their decreasing tendency to tartrate complex formation and increasing ion exchange adsorption the following adsorption sequence is obtained: Ta(V)  $\approx$  Nb(V)  $\approx$  Mo(VI)  $\approx$  W(VI)  $\approx$  As(III)  $\approx$  Se(IV)  $\approx$  Sn(IV)  $\approx$  Zr  $\approx$  Hf  $\approx$  (Ti(IV) < V(IV) < Th < Sc < U(VI) < Fe(III) < In < Cu(II)  $\approx$  Al < Y < Zn < Ni(II) < Pb(II) < Ce(III) < Co(II) < Cd < La < Mn(II) < Ca < Mg < Sr < Ba

**Summary of Possible Separations.** Sn(IV), Zr, Nb(V), Ta(V), Mo(VI), W(VI), Sb(III), and As(III). These elements

are not adsorbed from tartaric acid solutions containing low concentrations of nitric acid and thus can be separated from all other elements in the tables. Zr, Sn(IV), and Ta(V) require 0.25 M tartaric acid to suppress hydrolysis and to avoid tailing. Fairly large amounts of tantalum precipitate at all nitric acid concentrations when only 0.1 M tartaric acid is present. Niobium does so only when the nitric acid concentration is about 0.2 M or higher. When 0.25 M tartaric acid is present tantalum does not precipitate in nitric acid concentrations up to 1 M, but niobium does at 0.5 M or higher.

**Ti(IV).** This element also forms quite stable tartrate complexes. However while it is retained by the cation exchange resin from tartaric acid solutions containing free nitric acid (and also hydrogen peroxide) its distribution coefficient decreases rapidly with increasing concentration of tartaric acid, especially at the lowest nitric acid concentrations. At higher nitric acid concentrations, the influence of tartrate complexation decreases progressively. Sn(IV), Zr, Nb(V), etc. can be separated from titanium in a solution 0.25 M in tartaric acid and 0.1 M in nitric acid. Titanium(IV) is not adsorbed from 0.08 tartaric acid plus 0.02 M ammonium tartrate (pH 2.7) by a column in the ammonium form. Elements such as Al, Ca, Mg, U(VI), Sc, In, Cu(II), the lanthanides and many others (Table III) are retained. Fe(III), Th, and V(IV) are also retained more strongly than titanium, but conditions for quantitative separation seem to be rather critical.

**V(IV), Th, Sc, and Fe(III).** From 0.05 M tartaric acid plus 0.05 M ammonium tartrate (pH 3.4) all these elements are not adsorbed by a resin column in the ammonium form and can be separated from Al, Y, the lanthanides, Zn, Pb(II), Co(II), Cd, Mn(II) and the alkaline earths which are retained. Once adsorbed thorium and iron(III) exhibit very serious tailing and cannot be eluted quantitatively with tartrate buffer solutions. Scandium also tails.

**In, Cu(II), and Al.** These elements are not adsorbed from 0.02 M tartaric acid plus 0.08 M ammonium tartrate (pH 4.2) using a column in the ammonium form and can be separated from Pb(II), Co(II), Cd, Mn(II), Y, the lanthanides, and the alkaline earths which are retained. Indium is not adsorbed from 0.03 M tartaric acid plus 0.07 M ammonium tartrate (pH 3.9) and can be separated from Zn and Ni(II) in addition to the above elements.

**Zn and Ni(II).** These two elements can be eluted with 0.125 M ammonium tartrate (pH 6.5) while Cd, Mn(II), and the alkaline earth elements are still retained.

**Co(II), Cd, and Mn(II).** The tartrate complexes of these elements are not very stable and the elements are retained up to fairly high pH values. Cobalt(II) can be eluted with 0.15 M ammonium tartrate (pH 6.5) and separated from manganese(II) and the alkaline earth elements (except beryllium) which are retained. For the separation from cadmium 0.125 M ammonium tartrate (pH 6.5) is preferable, although the separation factor is still only about 2.3.

**Pb(II) and Bi(III).** The tartrate of bismuth(III) is practically insoluble in tartrate solutions not containing free nitric acid and that of lead(II) has a low solubility. Both elements can be adsorbed from tartaric acid solution containing about 0.2 M nitric acid to separate them from the multivalent group (Zr, Sn(IV), etc.). Indium, copper(II), and many other elements can be eluted with 0.02 M tartaric acid plus 0.08 M ammonium tartrate (pH 4.2) while lead is still retained. In addition, small amounts of lead can be eluted with 0.125 M ammonium tartrate (pH 6.5) while manganese(II) and the alkaline earth elements (except beryllium) are retained.

**V(IV) and Cr(III).** Vanadium(V) is not stable in tartaric acid or tartrate containing solutions. A slow reduction to vanadium(IV) takes place even in the presence of an initial excess of hydrogen peroxide. The change of the initial or-

ange-yellow color of the solution to a greenish blue one, indicating the partial conversion to the four-valent state, is clearly visible even after only 1 h of equilibrium time. After 24 h equilibration the reduction is almost complete and the distribution coefficients obtained are very similar to those for vanadium(IV).

Coefficients for chromium(III) depend very markedly on the history of the solution. Very indistinct bands representing various chromium ion species appear in column operations at room temperature. This is due to the slow ligand exchange rates of chromium(III).

Although the potential for element separation in the tartrate system is high more attractive alternatives are usually available. A molecule such as tartrate often is troublesome to remove. Only when it is already present in the system or has been added to prevent hydrolysis of elements such as tantalum and niobium should separations in tartrate media be considered as a first choice. The outstanding exception to this philosophy is the group separation of Zr, Sn(IV), etc. from all other elements that was considered earlier in the discussion. The only alternative would mean the use of a

system containing hydrofluoric acid.

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# Indirect Photometric Chromatography

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**Indirect photometric chromatography is a sensitive single-column ion analysis method developed from the concept that photometers may be used to detect transparent ionic species. The use of light-absorbing eluent ions in an ion-exchange mode enables sample ions to appear as "troughs" in the base line absorbance as transparent sample ions substitute for the light-absorbing displacing ions. The elution times of these troughs vary with the ion injected and their depths (or areas) are proportional to the amount of sample injected. Notable advantages of the new technique are its single column simplicity, its applicability to a wide range of ionic species, and an inherently greater sensitivity than single-column conductometric approaches.**

Ion determination by liquid chromatography is often frustrated not by separation problems but by detection problems. An example is the problem of determining the many important inorganic ions that are not light-absorbing. Whereas the separation of such transparent ions may be conveniently effected on ion exchange resin columns, their detection and measurement by conventional photometric means are thwarted since they are optically indistinguishable from the transparent eluents commonly prescribed.

The technique known as ion chromatography (1, 2) was developed to circumvent the detection problem posed by transparent sample ions. In just 6 years it has become a widely practiced and popular method addressing problems in a great variety of areas (2). Ion chromatography (IC) usually comprises a two-column arrangement followed by a conductance detector where the first column serves to separate the ions of interest while the second column, the suppressor, serves to lower the conductance of the eluent while usually increasing

the conductance of the eluted sample ions. The suppressor column in IC becomes exhausted in the course of normal usage and must be periodically regenerated or replaced—usually regenerated. Whereas this regeneration step has been automated in commercial instruments so that it is relatively unobtrusive or is made continuous as in the recently developed hollow fiber suppressor (3), it would nevertheless be desirable and advantageous for the following reasons to develop single column (suppressorless) methods for the many nonchromophoric ions.

(1) Decreased complexity of the instrumentation should yield a concomitant increase in reliability. This is a very important factor in penetrating the process control area with chromatographic methods where the demands for unattended and relatively maintenance-free operation have high priority.

(2) Reduced dead volume as a result of eliminating the suppressor will yield faster analysis and somewhat improved resolution.

Suppressorless single-column conductometric methods of ion analysis have been described in earlier literature (4-7). The limitations of these approaches have been elaborated by Pohl and Johnson (8) who point to the problem inherent in attempting to determine accurately the often times small changes in eluent conductivity that accompany the replacement of eluent ions by sample ions—both of which are conducting. They argue the sensitivity advantage to be gained by adding a suppressor that effectively "removes" the conductance of the eluent.

We would like to report a single column approach that solves the monitoring problem in a different manner while retaining much of the sensitivity of the original ion chromatography method. This new technique is derived from a comprehensive development of the concept that photometers may be used to monitor the many "transparent" ionic species