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FAST SEPARATION OF Ti(IV), As(III), W(VI), Au(III) FROM NUMEROUS METAL IONS AND OF Fe-Al-Ti BY PAPER CHROMATOGRAPHY

MOHSIN QURESHI AND FAHMIDA KHAN

Department of Chemistry, Aligarh Muslim University, Aligarh (India)

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SUMMARY

Ti⁴⁺ has been successfully separated from its binary mixtures with 32 cations using formic acid-hydrochloric acid-acetone (3:5:2). The cations include Cu²⁺, Al³⁺, Fe³⁺, V⁴⁺, Mo⁶⁺, W⁶⁺, Zr⁴⁺, Th⁴⁺, Ni²⁺ and Co²⁺. Ti⁴⁺ stays at the point of application while other ions have R_F values greater than 0.5. The separation is successful in the presence of acetate, tartrate, formate and citrate. Au³⁺ and W⁶⁺ have been separated from numerous metal ions using 70 % nitric acid-*n*-butanol (6:4). W⁶⁺ stays at the point of application while Au³⁺ goes to the solvent front. As³⁺ has been separated from its binary mixtures with 25 cations using pure formic acid as the eluent. The ions studied include Sb³⁺, Cu²⁺, and Sn²⁺. The presence of common anions does not affect this separation. W⁶⁺ has been separated from its binary mixtures with 35 ions. The ions include Mo⁶⁺, Ti⁴⁺, Th⁴⁺, UO₂²⁺, V⁴⁺, Co²⁺, Ni²⁺ and Pd²⁺. Separation of Fe³⁺-Al³⁺-Ti⁴⁺ has been achieved using formic acid-hydrochloric acid-acetone (3:4:3). The separation is successful in the presence of common anions and no special method for the preparation of the sample is necessary.

Paper chromatography offers a simple solution to many analytical problems. The aim is to achieve fast, reliable and selective separations of mixtures which are otherwise difficult to separate. These separations should be possible in the presence of anions and cations which are likely to be encountered in practical work. It should also be possible to separate one ion in trace quantities in the presence of large quantities of other ions. Some separations of this nature have been described earlier. Ti(IV) has been separated from iron, tin, arsenic, beryllium, thorium, cobalt and antimony in 22 h by ELBEH AND ABOU-ELNAGA¹. In this separation tartrate, citrate, oxalate, formate, acetate, and ammonium radicals interfere. MAGEE AND HEADRIDGE² have also separated 100 μ Ti(IV) from zirconium, aluminum, indium, zinc, thallium, gallium in 16 h. Fe-Al-Ti was separated by LACOURT³ in only 240-330 min. In her separation the sample must be prepared in a definite manner and a special shape of paper is necessary, if a small quantity of one cation is to be separated from a large quantity of another cation. Au(III) has been separated from numerous metal ions by

WELLS⁴. In this separation sodium chlorate has to be added to the solvent system to prevent double spot formation. As(III)⁵ has been separated by paper chromatography from numerous metal ions but the separation takes 20 h. As far as we are aware no separation of tungsten from numerous metal ions has been reported until now. A systematic study of different solvent systems was therefore made and the results achieved are summarized in this report.

EXPERIMENTAL

Apparatus

Development was performed in 20 × 5 cm glass jars, using the ascending method on 14.5 × 3 cm Whatman No. 1 paper strips.

Reagents

Only reagent grade chemicals were used.

Cation solutions

All test solutions were 0.1 *M* unless otherwise stated. Zirconium and thorium nitrates and thorium chloride were made in 0.1 *M* nitric acid and 0.1 *M* HCl, respectively. Zirconium oxychloride was dissolved in 3.5 *N* HCl. As(III) was prepared by dissolving arsenious oxide in 0.1 *M* nitric acid. Sn(II), Sn(IV), Sb(III) and Ti(IV) were dissolved as chlorides in 4 *M* hydrochloric acid. The rest of the cations were dissolved as nitrates in 0.1 *M* nitric acid. Molybdenum oxide was dissolved in dilute NaOH and neutralized with dilute HCl. Sodium tungstate was dissolved in distilled water.

Detectors

The following detectors were used for the detection of the cations noted against each:

Yellow ammonium sulphide. Ag(I), Hg(I), Hg(II), Bi(III), Pb(II).

1% aluminon in 1% ammonium acetate: Cr(III), Al(III), Ca(II), Sr(II), Ba(II), Mg(II).

10% aqueous solution of potassium iodide. Tl(I), Tl(III).

0.1% alcoholic solution of alizarin. Rare earths.

2% dithizone in chloroform. As(III), Sb(III), Zn(II), Cd(II).

1-2% aqueous solution of potassium ferrocyanide. Fe(III), Cu(II), UO₂²⁺, V(IV).

Stannous chloride in 4 M HCl. Pt(IV), Pd(II).

Alcoholic solution of 2% dimethyl-glyoxime. Ni(II), Co(II).

5% aqueous chromatropic acid. Ti(IV).

Time of conditioning was always 10 min. All R_F values are the average of two replicates. Sample size was approximately 0.0014 ml. Valence states were those given in Table I. When an ion is chromatographed in two valence states only the lower valence state has been indicated. To indicate the compactness of zones, R_F values of leading and trailing edges are given. Solvent ascent was always 12.5 cm unless otherwise stated. Time of development and temperature are given in Table I when the solvent is mentioned first. In all later separations, the time of development and temperature were the same as earlier mentioned unless otherwise stated.

RESULTS

Separation of Ti(IV) from numerous metal ions

The following systems were found to be suitable for this separation:

(b) Formic acid–hydrochloric acid–acetone (3:3:4)

(c) Formic acid–hydrochloric acid–acetone (3:4:3)

(d) Formic acid–hydrochloric acid–acetone (3:5:2).

The R_F values of numerous metal ions in these systems are given in Table I. The actual separation of titanium from the more important ions was tried in all these systems (Table II). Since system (d) gave the best results for the separation of titanium

TABLE I

R_F VALUES OF CATIONS IN SOME IMPORTANT SOLVENTS

F = Formic acid; H = hydrochloric acid; A = acetone; N = 70% nitric acid; B = *n*-butanol.

Cations	F ^a	F.H.A. ^b (3:3:4)	F.H.A. ^c (3:4:3)	F.H.A. ^d (3:5:2)	N.B. ^e (6:4)
Ag(I)	0.00–0.60	0.00–0.68	0.40–0.77	0.60–0.81	0.00–0.33
Pb(II)	0.00–0.64	0.21–0.62	0.36–0.54	0.63–0.84	0.31–0.51
Hg(I)	0.00–0.16 0.61–0.70	0.00–0.72	0.00–0.80	0.00–0.74	0.00
Hg(II)	0.00–0.68	0.64–0.78	0.61–0.76	0.62–0.75	0.60–0.78
Cu(II)	0.58–0.74	0.56–0.68	0.62–0.75	0.64–0.78	0.42–0.52
Bi(III)	0.14–0.27	0.44–0.62	0.50–0.66	0.54–0.73	0.51–0.66
Cd(II)	0.26–0.71	0.64–0.76	0.74–0.85	0.67–0.78	0.40–0.51
As(III)	0.00–0.13	0.79–0.90	0.78–0.90	0.78–0.90	0.50–0.66
Sb(III)	0.39–0.56	0.00, 0.58–1.0	0.53–0.66	0.61–0.80	0.75–0.91
Sn(II)	0.46–0.55	0.68–0.75	0.55–0.72	0.54–0.68	0.70–1.0
Sn(IV)	0.46–0.59	0.61–0.78	0.55–0.79	0.53–0.70	0.60–0.91
Pd(II)	0.00–0.23	0.43–0.60	0.36–0.54	0.38–0.62	0.34–0.77
Tl(I)	0.53–0.72	0.00–0.59	0.00–0.59	0.28–0.80	0.43–0.59
Rb(I)	0.68–0.94	0.50–0.68	0.62–0.79	0.68–0.81	0.48–0.65
Fe(II)	0.69–0.89	0.75–1.0	0.80–0.92	0.72–0.87	0.29–0.48
Fe(III)	0.73–0.87	0.80–1.0	0.80–0.92	0.72–0.87	0.31–0.53
Cr(III)	0.73–0.92	0.21–0.45	0.44–0.67	0.60–0.75	0.28–0.51
Al(III)	0.68–0.88	0.21–0.45	0.37–0.53	0.57–0.76	0.30–0.52
Ni(II)	0.68–0.84	0.21–0.39	0.33–0.47	0.54–0.72	0.30–0.48
Co(II)	0.75–0.90	0.58–0.76	0.62–0.73	0.68–0.80	0.37–0.53
Mn(II)	0.69–0.89	0.46–0.66	0.54–0.68	0.59–0.74	0.34–0.50
Zn(II)	0.21–0.66	0.64–0.75	0.66–0.79	0.66–0.78	0.31–0.55
Ca(II)	0.71–0.83	0.23–0.38	0.28–0.44	0.41–0.54	0.35–0.54
Ba(II)	0.71–0.81	0.00–0.31	0.00–0.29	0.62–0.75	0.00–0.48
Sr(II)	0.73–0.85	0.23–0.32	0.20–0.31	0.33–0.50	0.27–0.38
Mg(II)	0.73–0.86	0.00–0.21	0.52–0.67	0.68–0.82	0.42–0.56
UO ₂ (II)	0.65–0.78	0.54–0.72	0.56–0.68	0.50–0.62	0.61–1.0
V(IV)	0.55–0.70	0.38–0.55	0.45–0.58	0.58–0.75	0.28–0.51
Zr(IV)	0.00–0.87	0.00–0.68	0.49–0.65	0.43–0.62	0.50–0.68
Th(IV)	0.00–0.80	0.16–0.44	0.31–0.48	0.40–0.65	0.47–0.71
Ce(III)	0.00–0.91	0.13–0.42	0.36–0.54	0.49–0.66	0.40–0.58
Ce(IV)	0.00–0.64	0.19–0.44	0.36–0.51	0.40–0.59	0.37–0.53
Ga(III)	0.39–0.63	0.90–1.0	0.80–1.0	0.76–1.0	0.35–0.67
In(III)	0.33–0.66	0.59–0.75	0.48–0.64	0.50–0.68	0.40–0.60
La(III)	0.00–0.90	0.22–0.43	0.38–0.53	0.48–0.65	0.35–0.57
Y(III)	0.68–0.90	0.21–0.51	0.50–0.63	0.59–0.77	0.33–0.54

(continued on p. 225)

TABLE I (continued)

Cations	F^a	$F.H.A.^b$ (3:3:4)	$F.H.A.^c$ (3:4:3)	$F.H.A.^d$ (3:5:2)	$N.B.^e$ (6:4)
Ti(IV)	0.00-0.28	0.00-0.14	0.03-0.19	0.05-0.16	0.40-0.56
Mo(VI)	0.00-0.17	0.00 0.62-0.80	0.50-0.70	0.54-0.68	0.23-0.43
W(VI)	0.00	0.00 0.64-0.75	0.62-0.75	0.54-0.64	0.00
Pt(IV)	0.00-0.58	0.31-0.55	0.50-0.58	0.50-0.62	0.48-0.71
Se(IV)	0.00-0.26	0.84-0.96	0.00-0.12	0.38-1.0	0.66-0.89
Te(IV)	0.00-0.13	0.53-0.75	0.79-0.93	0.44-0.66	0.36-0.55
K(I)	0.73-0.84	0.48-0.66	0.53-0.74	0.70-0.89	
Cs(I)	0.88-1.0	0.54-0.68	0.58-0.77	0.77-1.0	0.60-0.75
NH ₄ (I)	0.76-0.87	0.62-0.75	0.67-0.81	0.60-0.84	0.46-0.63
Au(III)	0.23-0.57	0.00	0.62-0.73	0.00	0.94-1.0
Nb(V)		0.58-0.77	0.00	0.75-0.89	
		0.00	0.00	0.00	
		0.62-0.75	0.75-0.88	0.75-0.89	

^a Separation of arsenic from numerous metal ions; time of development 1 h; temperature 31°.

^b Separation of Ga-Al-Zn; time of development 1 h 30 min; temperature 29°.

^c Separation of Fe-Al-Ti; time of development 2 h; temperature 30°.

^d Separation of titanium from numerous metal ions; time of development 1 h; temperature 29°.

^e Separation of gold and tungsten from numerous metal ions; time of development 2 h 30 min; temperature 22-23°.

in binary mixtures it was studied for the separation of titanium in the presence of impurities and anions (Tables III and IV). In binary mixtures Fe and Ni were used most owing to their obvious importance. Titanium was also successfully separated from Fe, Ni or Mo in the ratios of (1:100) and (100:1) (Table V).

Separation of mixtures containing titanium

Separation of numerous mixtures containing titanium was practical using hydrochloric acid-formic acid-acetone (5:3:2). The more important results are given below:

R_F values are given in parentheses and the mixtures separated were:

Ti (0.03-0.14), Pt (0.41-0.58), Fe (0.71-0.83)

Ti (0.06-0.25), Zr (0.41-0.63), Fe (0.73-0.89)

Ti (0.00-0.16), Th (0.39-0.66), Fe (0.61-0.83)

Ti (0.02-0.20), Sr (0.26-0.56), Mg (0.78-0.92)

Ti (0.06-0.18), UO₂²⁺ (0.43-0.63), Fe (0.69-0.89).

Specific chromatographic detection of titanium

Titanium is easily detected with chromotropic acid after prior elution with hydrochloric acid-formic acid-acetone (5:3:2). None of the cations and anions which interfere in the chromotropic acid test affect the detection. The results are given in Table VI.

TABLE II
SEPARATION OF BINARY MIXTURES OF TITANIUM

Mixtures	<i>R_F</i> values					
	<i>F.H.A.</i> (3:3:4)		<i>F.H.A.</i> (3:4:3)		<i>F.H.A.</i> (3:5:2)	
	<i>Ti</i>	<i>Other ion</i>	<i>Ti</i>	<i>Other ion</i>	<i>Ti</i>	<i>Other ion</i>
Ti-Cu	0.00-0.12	0.54-0.68	0.00-0.12	0.54-0.68	0.00-0.16	0.62-0.77
Ti-Bi	0.00-0.12	0.38-0.56	0.00-0.11	0.42-0.62	0.04-0.16	0.53-0.73
Ti-Cd	0.00-0.14	0.64-0.76	0.00-0.11	0.73-0.84	0.05-0.16	0.67-0.78
Ti-Hg	0.00-0.11	0.63-0.77	0.03-0.19	0.61-0.76	0.04-0.16	0.62-0.75
Ti-Fe(II)	0.00-0.11	0.74-1.0	0.02-0.20	0.80-0.92	0.04-0.16	0.72-0.37
Ti-Al	0.00-0.12	0.21-0.43	0.03-0.20	0.36-0.53	0.04-0.16	0.57-0.76
Ti-Fe	0.00-0.12	0.74-1.0	0.03-0.19	0.78-0.93	0.04-0.18	0.68-0.85
Ti-Ni	0.00-0.11	0.21-0.39	0.04-0.20	0.32-0.47	0.04-0.18	0.54-0.72
Ti-Co	0.00-0.11	0.56-0.76	0.04-0.19	0.62-0.72	0.04-0.18	0.68-0.80
Ti-Mn	0.00-0.12	0.43-0.65	0.03-0.20	0.53-0.67	0.04-0.16	0.59-0.74
Ti-Cr	0.00-0.18	0.44-0.67	0.03-0.19	0.20-0.45	0.07-0.19	0.56-0.68
Ti-Mg	0.00-0.12	0.64-0.77	0.03-0.20	0.51-0.66	0.04-0.18	0.68-0.82
Ti-UO ₂ ²⁺	0.00-0.12	0.54-0.72	0.02-0.19	0.54-0.68	0.03-0.20	0.50-0.62
Ti-V	0.00-0.12	0.37-0.55	0.02-0.19	0.44-0.57	0.04-0.18	0.58-0.75
Ti-Sn(II)	0.00-0.12	0.67-0.75	0.02-0.18	0.54-0.71	0.04-0.20	0.54-0.68
Ti-La			0.03-0.20	0.36-0.52	0.04-0.18	0.48-0.65
Ti-Th			0.02-0.20	0.30-0.48	0.04-0.18	0.40-0.65
Ti-Y			0.02-0.18	0.50-0.63	0.04-0.20	0.59-0.77
Ti-Ce(III)			0.02-0.20	0.34-0.54	0.04-0.20	0.49-0.66
Ti-Te	0.00-0.11	0.53-0.74	0.02-0.18	0.53-0.74	0.04-0.20	0.44-0.66
Ti-Ce			0.02-0.20	0.34-0.51	0.03-0.20	0.40-0.59
Ti-Pt	0.00-0.11	0.31-0.54	0.02-0.18	0.50-0.58	0.04-0.20	0.50-0.62
Ti-Sn	0.00-0.12	0.60-0.77	0.02-0.20	0.55-0.70	0.04-0.20	0.53-0.70
Ti-Zr			0.03-0.20	0.48-0.64	0.03-0.20	0.42-0.62
Ti-Mo			0.02-0.20	0.48-0.70	0.02-0.18	0.54-0.68
Ti-W			0.02-0.18	0.61-0.74	0.04-0.20	0.54-0.64
Ti-Ga			0.03-0.18	0.80-1.0	0.02-0.20	0.76-1.0
Ti-In			0.02-0.18	0.47-0.63	0.04-0.20	0.50-0.68
Ti-K					0.03-0.20	0.70-0.89
Ti-Cs					0.03-0.18	0.77-1.0
Ti-Rb					0.02-0.18	0.60-0.80
Ti-BO ₃					0.02-0.18	0.77-1.0

Separation of Fe-Cu-Ni-Ti

This separation is very neatly achieved using the system formic acid-HCl-acetone (3:4:3) (see Table VII).

Separation of Fe-Al-Ti

These ions are best separated from one another using the system formic acid-hydrochloric acid-acetone (3:4:3). This separation is also successful in the presence of various anions (Table VIII) and also in varying ratios (Table IX). The effect of sample preparation on the separation of Fe-Al-Ti was also studied. This system also proved very helpful for the separation of traces of Ti(IV) from large quantities of Fe and Al.

TABLE III

SEPARATION OF TITANIUM FROM OTHER CATIONS IN THE PRESENCE OF IMPURITIES

Titanium: cation: impurity (1:1:3)

Mixture separated	Impurity present											
	Ammonium		Oxalate		Tartrate		Formate		Acetate		Citrate	
	Ti	Other ion	Ti	Other ion	Ti	Other ion	Ti	Other ion	Ti	Other ion	Ti	Other ion
Ti-Mo	0.08-0.20	0.58-0.75	0.03-0.17	0.50-0.75	0.05-0.19	0.60-0.75	0.06-0.24	0.50-0.68	0.00-0.19	0.50-0.68	0.00-0.14	0.43-0.66
Ti-Cr	0.05-0.19	0.78-0.88	0.03-0.17	0.77-0.87	0.06-0.19	0.54-0.66	0.06-0.19	0.56-0.68	0.07-0.18	0.52-0.63	0.06-0.15	0.66-0.81
Ti-Fe	0.06-0.17	0.71-0.85	0.08-0.19	0.62-0.78	0.04-0.15	0.73-0.84	0.07-0.18	0.68-0.82	0.04-0.14	0.68-0.81	0.06-0.18	0.69-0.85
Ti-Al	0.07-0.19	0.60-0.75	0.05-0.19	0.52-0.68	0.02-0.13	0.59-0.70	0.06-0.19	0.46-0.58	0.03-0.19	0.58-0.74	0.02-0.14	0.52-0.64
Ti-Ni	0.04-0.19	0.58-0.74	0.11-0.27	0.55-0.71	0.06-0.19	0.55-0.68	0.09-0.28	0.56-0.68	0.08-0.25	0.57-0.68	0.06-0.18	0.53-0.68
Ti-V	0.06-0.17	0.58-0.74	0.00-0.09	0.55-0.71	0.09-0.13	0.56-0.68	0.07-0.19	0.64-0.68	0.06-0.17	0.53-0.68	0.00-0.07	0.53-0.71

TABLE IV

EFFECT OF ANIONS ON THE SEPARATION OF TITANIUM FROM IRON OR NICKEL

Ti:Fe or Ni:anions (1:1:3).

Anion present	R_F in Ti-Fe mixtures		R_F in Ti-Ni mixtures	
	Ti	Fe	Ti	Ni
Chlorate	0.06-0.19	0.74-0.86	0.07-0.19	0.54-0.66
Sulphate	0.06-0.19	0.74-0.84	0.00-0.12	0.54-0.66
Fluoride	0.12-0.25	0.68-0.81	0.04-0.14	0.49-0.62
Nitrate	0.04-0.13	0.70-0.89	0.05-0.16	0.53-0.66
Bromide	0.00-0.12	0.66-0.78	0.00-0.08	0.46-0.56
Sulphide	0.07-0.19	0.71-0.81		
Chloride	0.12-0.25	0.68-0.81	0.06-0.19	0.56-0.66
Iodide	0.06-0.18	0.68-0.81	0.05-0.17	0.50-0.62
Tellurite	0.09-0.19	0.66-0.81	0.04-0.17	0.53-0.65
Arsenite	0.09-0.20	0.68-0.81	0.06-0.22	0.57-0.75
Iodate	0.06-0.19	0.68-0.81	0.04-0.19	0.50-0.63
Chromate	0.06-0.19	0.68-0.81	0.06-0.19	0.53-0.66
Bromate	0.07-0.19	0.68-0.81	0.05-0.22	0.53-0.65
Thiocyanate	0.06-0.17	0.66-0.81	0.06-0.19	0.53-0.65
Dichromate	0.07-0.17	0.68-0.81	0.06-0.22	0.53-0.68
Molybdate	0.07-0.17	0.68-0.81	0.06-0.23	0.56-0.68
Selenite	0.05-0.19	0.68-0.81	0.06-0.24	0.53-0.68
Arsenate	0.06-0.23	0.75-0.85	0.08-0.25	0.54-0.68

Separation of As(III) from numerous metal ions

Pure formic acid proved best for this separation (Table I). Numerous binary mixtures of arsenic could be separated using this solvent system (Table X). Some important binary separations were studied in greater detail (Tables XI and XII).

Separation of tungsten from numerous metal ions

The best system for this separation was found to be 70% nitric acid-*n*-butanol (6:4). The results are given in Table I. Binary mixtures of tungsten were also successfully separated as shown in Table XIV. Successful separation of tungsten and molybdenum was also achieved under varying conditions (Tables XV and XVI). Some other solvents for the separation of tungsten and molybdenum are given in Table XIII.

Separation of gold from numerous metal ions

70% nitric acid-*n*-butanol (6:4) solvent proved very efficient for the separation of gold from numerous metal ions (Table I). Binary mixtures containing gold are easily separated as shown in Table XVII.

Miscellaneous important separations

Other important separations which were achieved practically are given in Table VII.

DISCUSSION

The separation of titanium from numerous metal ions described here is probably the best yet reported. The separation is fast and unaffected by the presence of com-

TABLE V
SEPARATION OF TITANIUM FROM Fe, Ni OR Mo IN DIFFERENT RATIOS

Mixture separated	Ratio of Ti: other ion							
	1:10		1:100		10:1		100:1	
	<i>R_F</i> value Ti	<i>R_F</i> value other ion	<i>R_F</i> value Ti	<i>R_F</i> value other ion	<i>R_F</i> value Ti	<i>R_F</i> value other ion	<i>R_F</i> value Ti	<i>R_F</i> value other ion
Ti-Fe	0.10-0.20	0.66-0.81	0.12-0.24	0.68-0.82	0.12-0.25	0.69-0.82	0.08-0.23	0.69-0.81
Ti-Ni	0.06-0.19	0.54-0.68	0.05-0.18	0.52-0.74	0.08-0.25	0.56-0.67		
Ti-Mo	0.09-0.19	0.55-0.75	0.06-0.19	0.53-0.73	0.06-0.19	0.56-0.68		

plexing anions like tartrate and citrate. This is because of the high hydrochloric acid concentration in the solvent system. The separation does not need any special preparation of the sample and is unaffected by the presence of various ions which are likely to be encountered in practice. The R_F values of Fe-Al-Ti are evenly spaced from 0-1 and therefore it is possible to handle mixtures of varying ratios more easily. Thus it is possible to separate Ti-Al-Fe (1:1:1000) without using any special shape of paper.

TABLE VI
DETECTION OF TITANIUM IN MIXTURES

Mixture	Microgram of Ti	Microgram of other ion	R_F value of Ti	R_F value of other ion
Ti-UO ₂ ²⁺	0.26	94.50	0.02-0.20	0.43-0.72
Ti-Co	0.26	42.0	0.02-0.12	0.52-0.84
Ti-Mn	0.26	39.90	0.02-0.14	0.54-0.86
Ti-Ni	0.26	42.0	0.01-0.14	0.42-0.77
Ti-Cr	0.26	21.0	0.00-0.12	0.41-0.72
Ti-Cu	0.26	43.10	0.06-0.17	0.53-0.77
Ti-Fe	0.26	27.30	0.03-0.17	0.64-0.90
Ti-(Fe + Cu + Mn + Al + Ca + Mg + Zn)	26	26	0.01-0.09	Fe 0.69-0.90 Cu 0.53-0.77 Mn 0.54-0.86 Al 0.52-0.69 Ca 0.41-0.54 Mg 0.78-0.92 Zn 0.66-0.78

TABLE VII
SOME OTHER IMPORTANT SEPARATIONS

Solvent system	R_F values and mixture separated			
Formic acid-hydrochloric acid-acetone (3:3:4)	Zn	(0.63-0.83)	Al	(0.17-0.47)
	UO ₂ ²⁺	(0.56-0.68)	V	(0.41-0.54)
	Th	(0.12-0.31)	V	(0.33-0.57)
	Ni	(0.19-0.39)	Cu	(0.52-0.71)
	Ni	(0.21-0.41)	Co	(0.60-0.75)
	Al	(0.28-0.43)	Zn	(0.60-0.77)
Formic acid-hydrochloric acid-acetone (3:4:3)	Fe	(0.86-0.94)	Al	(0.20-0.40)
	Fe	(0.93-1.0)	Cu	(0.60-0.70)
	Ti	(0.00-0.15)		Ti (0.00-0.12) Ni (0.30-0.41)
Formic acid-hydrochloric acid-acetone (3:5:2)	Ti	(0.03-0.14)	Pt	(0.41-0.58)
	Ti	(0.06-0.25)	Zr	(0.41-0.63)
	Ti	(0.00-0.16)	Th	(0.39-0.66)
	Ti	(0.02-0.20)	Sr	(0.26-0.50)
	Ti	(0.06-0.18)	UO ₂ ²⁺	(0.43-0.63)
<i>n</i> -Butanol-70% nitric acid (6:4)	Te	(0.37-0.55)	Se	(0.67-0.83)
	Au	(0.90-1.00)	Pd	(0.52-0.68)
	Au	(0.90-1.0)	Pt	(0.52-0.65)

TABLE VIII

SEPARATION OF Fe-Al-Ti IN THE PRESENCE OF ANIONS
Fe-Al-Ti:anions (1:1:1:3).

<i>Anion present</i>	<i>R_F values</i>		
	<i>Fe</i>	<i>Al</i>	<i>Ti</i>
Chromate	0.82-0.94	0.41-0.62	0.00-0.19
Iodide	0.87-1.0	0.43-0.60	0.08-0.25
Dichromate	0.83-0.93	0.44-0.62	0.08-0.20
Bromate	0.79-0.93	0.38-0.54	0.08-0.20
Oxalate	0.75-1.0	0.33-0.50	0.03-0.14
Thiocyanate	0.81-0.95	0.37-0.54	0.04-0.19
Nitrate	0.83-0.95	0.37-0.54	0.00-0.15
Arsenite	0.83-0.94	0.40-0.56	0.04-0.18
Acetate	0.85-1.0	0.41-0.57	0.04-0.19
Selenite	0.83-0.93	0.38-0.55	0.03-0.18
Tellurite	0.81-0.96	0.33-0.51	0.00-0.15
Iodate	0.86-0.96	0.41-0.56	0.04-0.18
Arsenate	0.87-0.95	0.41-0.56	0.05-0.19
Sulphate	0.81-0.95	0.37-0.56	0.02-0.19
Citrate	0.85-0.98	0.40-0.60	0.05-0.20
Sulphide	0.81-0.96	0.37-0.52	0.05-0.19
Fluoride	0.85-0.98	0.43-0.59	0.05-0.19
Chlorate	0.85-0.97	0.39-0.54	0.04-0.18
Molybdate	0.87-0.99	0.39-0.55	0.03-0.19
Tartrate	0.82-0.98	0.41-0.56	0.06-0.20
Phosphate	0.89-0.99	0.40-0.54	0.04-0.19
Bromide	0.81-0.93	0.40-0.56	0.03-0.19
Formate	0.79-0.93	0.37-0.56	0.03-0.17

TABLE IX

SEPARATION OF Fe-Al-Ti IN DIFFERENT RATIOS

<i>Ratio of Fe:Al:Ti in the mixture</i>	<i>R_F values</i>		
	<i>Fe</i>	<i>Al</i>	<i>Ti</i>
10:10:1	0.81-0.96	0.37-0.57	0.05-0.17
1:10:1	0.81-0.93	0.37-0.56	0.03-0.19
10:1:1	0.78-0.92	0.43-0.56	0.04-0.17
10:1:10	0.73-0.92	0.36-0.50	0.00-0.14
1:10:10	0.85-0.96	0.37-0.55	0.00-0.19
1:1:10	0.87-1.0	0.40-0.54	0.00-0.21
1000:1:1	0.87-1.0	0.43-0.58	0.08-0.23

TABLE X

SEPARATION OF BINARY MIXTURES OF ARSENIC WITH NUMEROUS METAL IONS

Temperature: 22°; solvent: formic acid.

Mixture	R_F values	
	Arsenic	Other ion
As-Sb	0.00-0.08	0.40-0.52
As-Tl	0.00-0.02	0.61-0.79
As-V	0.00-0.02	0.62-0.80
As-Co	0.00-0.02	0.62-0.85
As-Sn	0.00-0.03	0.28-0.44
As-NH ₄	0.04-0.21	0.66-0.74
As-Mg	0.00-0.03	0.80-1.0
As-Mn	0.00-0.09	0.64-0.88
As-Zn	0.00-0.02	0.21-0.66
As-Ga	0.02-0.14	0.39-0.63
As-In	0.00-0.02	0.03-0.66
As-Be	0.00-0.03	0.82-0.94
As-Sr	0.00-0.02	0.70-0.85
As-Ba	0.00-0.04	0.70-0.81
As-Ca	0.00	0.64-0.80
As-UO ₂ ²⁺	0.00-0.02	0.62-0.73
As-Fe	0.00-0.02	0.58-0.74
As-Cr	0.00-0.04	0.69-0.93
As-K	0.00-0.03	0.73-0.84
As-Rb	0.02-0.12	0.68-0.94
As-Cs	0.02-0.14	0.88-1.0
As-Al	0.04-0.14	0.71-0.89
As-Fe(II)	0.00-0.04	0.36-0.77
As-Cu	0.00-0.09	0.39-0.67
As-Ni	0.00-0.03	0.65-0.87

TABLE XI

SEPARATION OF ARSENIC FROM OTHER CATIONS IN VARYING RATIOS

Temperature: 23-24°.

Mixture	R_F values		
	Ratio	Arsenic	Other ion
As-Sb	10:1	0.00-0.09	0.45-0.54
	100:1	0.00-0.07	0.38-0.51
	1:10	0.01-0.09	0.45-0.54
	1:100	0.02-0.16	0.41-0.60
As-Sn(II)	1:10	0.00-0.11	0.34-0.54
	1:100	0.00-0.04	0.32-0.52
	10:1	0.00-0.09	0.35-0.55
	100:1	0.00-0.10	0.37-0.52
As-Sn	10:1	0.00-0.12	0.35-0.42
	100:1	0.00-0.07	0.26-0.42
	1:10	0.00-0.07	0.19-0.43
	1:100	0.00-1.0	

TABLE XII

EFFECT OF FOREIGN IONS ON THE SEPARATION OF ARSENIC-ANTIMONY

As-Sb-foreign ion (1:1:3).

Temperature: 24-25°; solvent: formic acid.

Foreign ion	R_F values	
	Arsenic	Antimony
Fluoride	0.00-0.12	0.45-0.60
Thiocyanate	0.00-0.12	0.43-0.60
Sulphate	0.00-0.06	0.24-0.38
Oxalate	0.00-0.09	0.26-0.38
Phosphate	0.00-0.08	0.24-0.38
Formate	0.00-0.06	0.22-0.34
Sulphite	0.00-0.14	0.45-0.60
Sulphide	0.00-0.07	0.45-0.55
Citrate	0.00-0.04	0.27-0.39
Tartrate	0.00-0.09	0.23-0.36
Nitrate	0.00-0.05	0.45-0.55
Iodate	0.00-0.05	0.43-0.53
Chloride	0.00-0.05	0.43-0.53
Iodide	0.00-0.10	0.42-0.52
Bromide	0.00-0.07	0.48-0.58

TABLE XIII

SOME USEFUL SYSTEMS FOR THE SEPARATION OF TUNGSTEN AND MOLYBDENUM

Solvent system		R_F values	
		Mo	W
70 % nitric acid-40 % sodium tartrate	(8:2)	0.44-0.72	0.00-0.12
70 % nitric acid- <i>n</i> -butanol	(2:1)	0.24-0.36	0.00
	(6:4)	0.23-0.43	0.00

Various other mixtures containing Ti are also easily separated *e.g.*, Fe, Ti, Ni and Cu. The separation of arsenic developed here is much faster than the separation reported earlier and almost all important ions are easily separated. The separation of gold is attained in 70 % HNO₃-*n*-butanol (6:4). The high concentration of nitric acid prevents reduction of gold and no oxidizing agent has to be incorporated in the sample solution. Gold is easily separated from Pt, Pd, Ir, Ru and other metal ions in one hour. This is therefore probably the best separation of gold from numerous metal ions. Sometimes

TABLE XIV

SEPARATION OF BINARY MIXTURES OF TUNGSTEN

Solvent: 70 % nitric acid-*n*-butanol (6:4); temperature: 22-23°; time of development: 2 h 30 min.

Mixture	R_F values	
	W	Other ion
W-Mo	0.00	0.23-0.43
W-Ti	0.00-0.13	0.31-0.47
W-NH ₄	0.00	0.44-0.61
W-Th	0.00	0.20-0.72
W-Mg	0.00	0.33-0.46
W-UO ₂ ²⁺	0.00	0.33-0.46
W-Sr	0.00	0.27-0.38
W-Ca	0.00	0.36-0.46
W-Fe	0.00	0.47-0.58
W-Mn	0.00	0.34-0.50
W-V	0.00	0.35-0.51
W-Co	0.00	0.38-0.51
W-Ni	0.00	0.31-0.46
W-In	0.00	0.34-0.46
W-Ga	0.00	0.33-0.63
W-Y	0.00	0.32-0.48
W-La	0.00	0.36-0.48
W-Ce(III)	0.00	0.30-0.42
W-K	0.00	0.40-0.50
W-Rb	0.00	0.54-0.65
W-Pb	0.00	0.13-0.43
W-Cs	0.00	0.54-0.64
W-Se	0.00	0.64-0.84
W-Cr	0.00	0.32-0.48
W-Zn	0.00	0.33-0.48
W-Al	0.00	0.38-0.48
W-Pt	0.00	0.48-0.71
W-As	0.00	0.54-0.67
W-Pd	0.00	0.39-0.77
W-Sb	0.00	0.76-0.94
W-Hg	0.00	0.60-0.78
W-Te	0.00	0.39-0.56
W-Bi	0.00	0.47-0.66
W-Tl(I)	0.00	0.50-0.63
W-Be	0.00	0.52-0.63

TABLE XV

SEPARATION OF TUNGSTEN FROM IMPORTANT IONS IN DIFFERENT RATIOS

Mixture	Ratio	R_F values	
		W	Other ion
Mo-W	1:10	0.00	0.21-0.42
	1:100	0.00	0.18-0.32
	10:1	0.00	0.26-0.44
	100:1	0.00	0.23-0.41
W-Co	1:100	0.00	0.34-0.51
W-V	1:100	0.00	0.31-0.43
W-Ni	1:100	0.00	0.31-0.47
W-Ti	1:100	0.00	0.31-0.50
W-Fe	1:100	0.00	0.19-0.50

TABLE XVI

SEPARATION OF MOLYBDENUM AND TUNGSTEN IN THE PRESENCE OF FOREIGN ION

W: Mo:foreign ion (1:1:3).

Temperature: 29-30°.

Foreign ion	R_F values	
	W	Mo
Chromium	0.00	0.27-0.40
Iron	0.00	0.27-0.37
Cobalt	0.00	0.27-0.39
Vanadium	0.00	0.36-0.48
Nickel	0.00	0.27-0.37
Phosphate	0.00	0.30-0.45
Borate	0.00	0.29-0.44
Citrate	0.00	0.27-0.40
Tartrate	0.00	0.25-0.38

TABLE XVII

SEPARATION OF GOLD FROM OTHER IONS IN DIFFERENT RATIOS

Solvent: 70% nitric acid-*n*-butanol (6:4); time of development: 2 h 30 min; temperature: 26-27°.

Mixture	Ratio	Au	Other ion
Au-Ga	1:10	0.86-1.0	0.29-0.50
Au-Se	1:10	0.90-1.0	0.67-0.81
Au-Hg	1:10	0.90-1.0	0.67-0.75
Au-V	1:10	0.89-1.0	0.39-0.54
Au-Te	1:10	0.90-1.0	0.35-0.54
Au-Cr	1:10	0.91-1.0	0.25-0.37
Au-Pd	1:10	0.90-1.0	0.53-0.67
Au-As	1:10	0.90-1.0	0.50-0.62
Au-Fe	1:10	0.90-1.0	0.36-0.51
Au-Ni	1:10	0.89-1.0	0.31-0.45
Au-Cu	1:10	0.90-1.0	0.42-0.53
Au-Ir	1:10	0.92-1.0	0.00-0.12
Au-Fe	1:1000	0.90-1.0	0.27-0.62
Au-Ni	1:1000	0.86-1.0	0.31-0.58

when binary mixtures of tungstate were chromatographed a precipitate appeared owing to the formation of an insoluble tungstate. The precipitate was dissolved by adding the least quantity of tartaric acid. This however did not interfere in the separations. Tungsten is probably precipitated as oxide and remains at the point of application while most metal ions migrate in the highly acidic medium.

The separation of arsenic from numerous metal ions utilizes pure formic acid as an eluent. In order to understand the chemistry of the test formic acid was added to the cation solutions. The following gave precipitates; Ag(I), Hg(I), Hg(II), Pd(II), W(VI) and Ru(III). All these show tailing when chromatographed with formic acid except W(VI) which is probably precipitated very rapidly and remains on the point of application. Arsenic did not give a precipitate with formic acid. Therefore, it is not

a case of precipitation even though As remains on the point of application but probably because the paper is more polar than formic acid and arsenic does not form a complex with this acid. Cations which form complexes with formic acid show greater migration, *i.e.*, Ni(II), Co(II), Mn(II) etc.

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REFERENCES

- 1 I. I. M. ELBEIH AND M. A. ABOU-ELNAGA, *Anal. Chim. Acta.*, 17 (1957) 397.
 - 2 R. J. MAGEE AND J. B. HEADRIDGE, *Analyst*, 82 (1957) 95.
 - 3 A. LACOURT, G. H. SOMMEREYNS AND G. WANTIER, *Proc. Intern. Congr. Anal. Chem., Oxford, England, 1952*, p. 387.
 - 4 N. F. KEMBER AND R. A. WELLS, *Analyst*, 76 (1951) 579.
 - 5 I. I. M. ELBEIH, J. F. W. MCOMIE AND F. H. POLLARD, *Discussions Faraday Soc.*, 7 (1949) 183.
- J. Chromatog.*, 34 (1968) 222-236