CHROM. 24 230

Effect of solvent composition and pH on R_F values of metal ions on titanium tungstate-impregnated papers in aqueous nitric acid, acetone–nitric acid and butanol–nitric acid systems

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ABSTRACT

The chromatographic behaviour of 50 cations on titanium (IV) tungstate-impregnated papers in 10^{-5}–5 M HNO$_3$, butanol–8 M HNO$_3$ and HNO$_3$–acetone–water systems was studied, together with the effect of pH on R_F values. For most cations, $R_F = a + bC^2$, where C is the nitric acid concentration. The effect of mole fractions of HNO$_3$, acetone and water on R_F values is explained. A large number of analytically important binary and ternary separations are reported. Quantitative separation of Pb^{2+} and Hg^{2+} from binary mixtures containing larger amounts of other metal ions was achieved.

INTRODUCTION

Titanium(IV)-based exchangers have been found to possess promising chemical and thermal stability and have been extensively used in column chromatography [1], thin-layer chromatography [2,3] and paper chromatography [4,5] of metal ions. Of these, titanium(IV) tungstate has proved to be the most stable in acids [1,6] and exhibits good ion-exchange capacity. Qureshi and Husain [7] studied the chromatography of metal ions on titanium(IV) tungstate-impregnated papers. Recently, electrochromatography of a number of metal ions in complex-forming acids and their sodium salts has also been carried out [8]. These papers are very selective and a number of metal ion separations were achieved.

However, in the above studies, no effort was made to study the effect of solvent composition on the

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retention factor, the effect of pH on the R_F values of metal ions has not been studied and not many ions were studied in a number of aqueous and mixed solvent systems.

In this work, nitric acid was chosen because it is a non-complexing acid and the understanding of the equilibria is simplified. Acetone does not solvate ions significantly and hence it is easy to study the mechanism of migration. Butanol was chosen because of our earlier experience [9,10] that it gives clear and useful separations.

EXPERIMENTAL

Apparatus

Chromatography was performed on 15 × 3.0 cm Whatman No. 1 paper strips in glass jars of 21 × 5 cm I.D. A Bausch and Lomb Spectronic-20 spectrophotometer was used for measurements.

Reagents

Analytical-reagent grade chemicals and reagents

Fig. 1. Plots of R_F vs. pH of HNO$_3$ systems; Pd^{2+}, Fe^{3+}, VO$_2^+$, UO$_2^{2+}$, Cu^{2+}, Ni^{2+}, Co^{2+}, Al^{3+}, Zn^{2+}, Mn^{2+}, Ir^{4+}, Mg^{2+}, K$^+$, Rb$^+$, Cs$^+$, Sr^{2+}, Tl^{3+}, Cd^{2+}, La^{3+}, Ru^{3+}, Ca^{2+}, Y^{3+}, Ce^{3+}, Ce^{4+}, Nb^{5+} and Pt^{3+} have $R_F > 0.75$ at all pH values.

were used. In butanol–HNO₃ systems 8 M HNO₃ was used and in pH studies 10^{-5}–1 M HNO₃.

Test solutions and detection

Test solutions containing 0.1 M chlorides, nitrates or sulphates of cations were prepared in a small amount of the corresponding acids. Conventional spot test reagents were used for detection purposes.

Preparation of ion-exchange papers

A 0.25 M solution of titanium(IV) chloride and a 0.25 M solution of sodium tungstate were prepared in distilled water. Paper strips were first passed through titanium(IV) chloride solution for 3–5 s and the excess of the chloride was removed by placing the strips on a filter-paper sheet. The strips were then dipped in sodium tungstate solution for 5 s and the excess was drained off. The strips were dried at room temperature overnight, washed three times with distilled water in order to remove excess reagents and finally allowed to dry at room temperature for 12 h and used as such. These papers were found to possess considerable ion-exchange capacity. For K⁺ ion (K⁺–H⁺ exchange), the exchange capacity is 0.35 mequiv. per gram of treated paper as determined by column experiments (saturation method) [11].

Procedure

For qualitative work. The sample solution was applied (one or two spots) on paper strips. The chromatograms were conditioned for 5–10 min, then the solvent was allowed to ascend 11 cm from the starting line on the paper in all instances.

For quantitative work. Stock solutions of lead nitrate and mercury(II) nitrate were prepared in demineralized water. Pb²⁺ and Hg²⁺ were loaded with the help of a lambda pipette in the form of a streak. The cations to be separated were also applied in the amounts shown in Table II. Development was performed in the chosen solvent systems. In all instances, ascent 11 cm from the starting line on titanium(IV) tungstate-impregnated papers was allowed. A pilot paper was run simultaneously in order to locate the exact position of the spot with the help of the chromogenic agent. The area of the working paper corresponding to the detected spot on the pilot paper was cut out and Pb²⁺ and Hg²⁺ were eluted with 1 M HNO₃ and 1 M H₂SO₄,

respectively. The volume of the solution in each instance was then reduced to about 10 ml by heating on a hot-plate. Pb²⁺ and Hg²⁺ were detected spectrophotometrically [12] using dithizone in carbon tetrachloride at 520 and 485 nm, respectively.

Solvent systems

Fifty cations were chromatographed in the following 31 solvent systems: (a) nine HNO₃ systems with concentrations of 1, 2, 3, 5, 0.1, 0.01, 0.001, 0.0001 and 0.00001 M; (b) six butanol–8 M HNO₃ systems in the proportions (1) 10:0, (2) 9:1, (3) 8:2, (4) 7:3, (5) 6:4 and (6) 5:5; and (c) sixteen solvent systems containing HNO₃–acetone–water in the proportions (1) 1:1:1, (2) 1:1:2, (3) 1:1:3, (4) 1:1:4, (5) 1:1:5, (6) 1:1:6, (7) 1:2:1, (8) 1:3:1, (9) 1:4:1, (10) 1:5:1, (11) 1:6:1, (12) 2:1:1, (13) 3:1:1, (14) 4:1:1, (15) 5:1:1 and (16) 6:1:1.

RESULTS AND DISCUSSION

In order to check the reproducibility of R_F values, five sets of some ions were chromatographed in 1.0, 0.1 and 0.01 M HNO₃. It was observed that the variation does not exceed 10% of the average R_F values. The complete R_F data have not been given for the sake of brevity. The effect of pH and solvent composition was studied only for those cations where $R_F < 0.75$. A large number of binary and ternary separations on impregnated papers were achieved as a direct result of the selectivity shown by the ion exchanger and the solvent studied. The few important ones achieved in aqueous HNO₃ systems are Ag⁺–Bi³⁺–Cu²⁺, Sb³⁺–Sn²⁺–Sn⁴⁺, Ag⁺–Pb²⁺–Cd²⁺ and Tl⁺–Ga³⁺–Zn²⁺. Butanol–8 M HNO₃ systems were found to be useful in effecting the separations, *viz.*, Al³⁺–Zn²⁺–Tl³⁺, Bi³⁺–Hg²⁺–Tl³⁺, Zr⁴⁺–Th⁴⁺–Sb³⁺, Fe³⁺ or Cr³⁺–Mn²⁺–Pt⁴⁺, Mo⁶⁺–VO²⁺–UO₂²⁺, Mn²⁺–Zn²⁺–Hg²⁺ and Se⁴⁺–La³⁺ or Y³⁺–Au³⁺. Quaternary separation of Ag⁺–Pb²⁺–Bi³⁺–Pt⁴⁺ was also achieved with butanol–8 M HNO₃ (1:1). Some useful ternary separations in HNO₃–acetone–water systems are Ba²⁺–Sr²⁺–Ca²⁺, Tl⁺–Bi³⁺–Hg²⁺, Ag⁺–Tl⁺–Tl³⁺ and Mo⁶⁺–Mn²⁺–Cr³⁺.

Aqueous nitric acid systems

In aqueous nitric acid systems (10^{-5}–1 M), the plots of R_F *versus* pH (Fig. 1) reveal certain interest-

ing points. For some cations such as Tl^{3+}, Fe^{3+}, Ni^{2+}, Co^{2+}, Ba^{2+}, Sr^{2+}, Mn^{2+}, Pr^{3+}, Cd^{2+}, Zn^{2+}, Al^{3+}, Cr^{3+}, K^+, Rb^+, Cs^+, Y^{3+}, Zr^{4+}, Ce^{3+} and Nd^{3+}, the R_F value first increases from pH 0 to 1 and then becomes almost constant. Above pH 1, there is not much increase in the R_F value for most of the cations, possibly because the pH of the solution does not affect the ion-exchange capacity of titanium(IV) tungstate significantly. Qureshi et al. [1] have shown that the ion-exchange capacity of Ti(IV)-based exchangers does not change if the pH of the solution is below 10. However, a sharp increase in ion-exchange capacity is observed as the pH is raised above 10. This is probably due to the hydrolysis of the exchange material at higher pH. According to them,

Ti(IV)-based ion exchangers behave like weakly acidic cation exchangers, which differs from the findings of Szirtes et al. [13]. Only titanium phosphate shows a moderately strong acid behaviour. For Pb^{2+}, Hg_2^{2+}, Sb^{3+}, Hg^{2+}, Ga^{3+}, Bi^{3+}, Sn^{2+}, Th^{4+} and Mg^{2+} the R_F is maximum at pH 2. With Bi^{3+}, Sb^{3+} and Pb^{2+} there is a sharp decrease in the R_F value beyond pH 2. The same trend is also observed with Sn^{2+}, for which the R_F decreases from 0.9 to 0.1 as the pH increases from 3 to 4. In all these instances, the sharp decrease in R_F value may be due to the excessive hydrolysis of these cations in the acidic solutions.

Ag^+ shows exceptional behaviour, having almost zero R_F value owing to its interaction with the
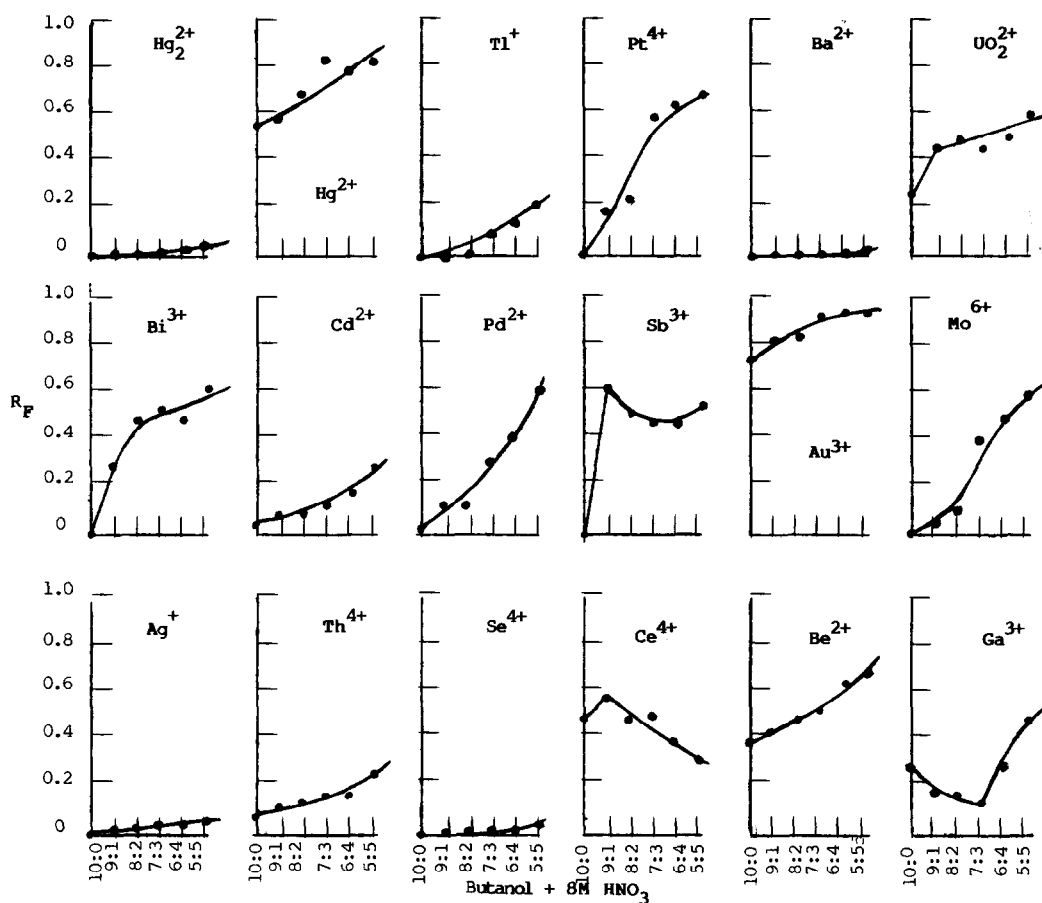

Fig. 2. Plots of R_F vs. butanol–8 M HNO_3 proportions. Tl^{3+} has $R_F > 0.75$. Pb^{2+}, Fe^{2+}, Sn^{2+}, Sr^{2+}, Cr^{3+}, K^+, Rb^+, Cs^+, Y^{3+}, Zr^{4+}, Ru^{3+}, La^{3+}, In^{3+} and Pr^{3+} have the same trend as Tl^+. Fe^{3+}, Mg^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Al^{3+}, Ca^{2+}, Th^{4+}, Ce^{3+} and Nd^{3+} have the same trend as Cd^{2+}.

exchanger. It has been shown by Murray and Fuerstenau [14], that cations are preferably exchanged when the gel has a negative surface charge. They explained this on the assumption that the adsorption of Ag^+ is due to Ag^+–matrix interaction. At pH 1, Hg^{2+} has a low R_F value whereas the lanthanides have R_F values of almost 1. This can be explained on the basis that on titanium(IV) tungstate columns Hg^{2+} is significantly adsorbed in HNO_3 media having a higher K_d value whereas the lanthanides have the lowest K_d values, thereby showing higher R_F values on titanium(IV) tungstate papers.

Butanol–nitric acid systems

Butanol–8 M HNO_3 in various ratios is an excellent solvent system with numerous possibilities for analytically difficult separations. Some of these have actually been achieved. The great advantage of the ion-exchange papers is that the spots are more compact than on the plain papers and therefore there is very little tailing on these papers. It is obvious from Fig. 2 that for most of the monovalent and bivalent ions, as the HNO_3 concentration increases the R_F value also increases. Titanium(IV) tungstate in these systems appears to behave only as a sorbent and not as an exchanger. This may be partly due to the low ion-exchange capacity of titanium(IV) tungstate in butanol–HNO_3 media and partly to the small degree of ionization of metal salts in butanol media.

In order to understand the mechanism of sorption and the effect of nitric acid on this mechanism, it was decided to correlate the R_F values of the metal ions with C, the nitric acid concentration. A plot of R_F versus C^2 gave straight lines passing through the origin for K^+, Rb^+ and Cs^+. The same trend was observed for the majority of cations and only in a few instances were significant intercepts obtained, e.g., with Be^{2+}, Hg^{2+} and Au^{3+}. The R_F value can therefore be represented by a simple equation, $R_F = a + bC^2$, where a is the intercept and b is the slope; a is probably dependent on the solubility in butanol of the salt concerned, e.g., KCl if K^+ is chromatographed. Thus, $a = 0$ for K^+, Rb^+ and Cs^+ as their chlorides have very low solubilities (the solubilities of KCl and CsCl are 0.624 and 0.621 wt.%, respectively) in butanol. Hg^{2+} has a large intercept owing to the higher solubility of mercury(II) chloride in butanol (the solubility of $HgCl_2$ is 15.5 wt.%). The data for Be and Au chlorides are not available but they must have significant solubilities in butanol.

It is apparent from Table I that with K^+, Rb^+ and Cs^+ the slope decreases from Cs^+ to K^+ owing to the decrease in the size of the ion. Similarly, the slope decreases as one goes from Rb^+ to Zr^{4+} and from Cs^+ to La^{3+} (right across the Periodic Table). This is due to an increase in charge and a decrease in size. Other cations follow the same trend and the only apparent exception is Fe (0.49) and Co (0.56). In this instance the Pauling radius of Co^{2+} is higher than that of Fe^{3+} and hence the R_F value of Co^{2+} should be greater than that of Fe^{3+}. The charge also favours the smaller R_F for Fe^{3+}.

HNO_3–acetone–water system

A plot of R_F versus mole fraction (X) (Fig. 3) gives some interesting results. In order to have a clear idea

TABLE I

VALUES OF b FOR DIFFERENT METAL IONS IN THE EQUATION $R_F = a + bC^2$

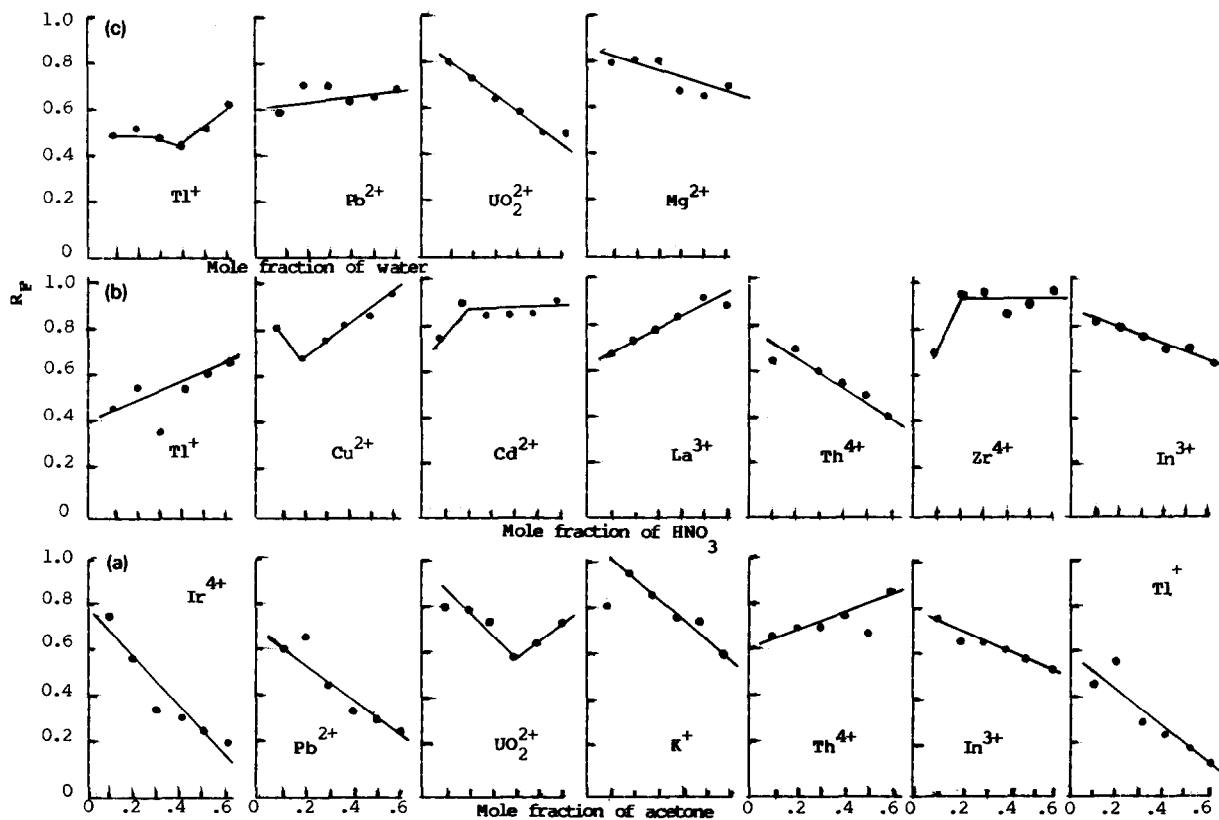| Metal ion	b	Metal ion	b	Metal ion	b	Metal ion	b
K^+	0.81	Ca^{2+}	0.56	Fe^{3+}	0.49	In^{3+}	0.75
Rb^+	1.00	Hg^{2+}	0.71	Al^{3+}	0.78	Pr^{3+}	0.75
Cs^+	1.16	Cd^{2+}	0.63	Au^{3+}	0.66	Nd^{3+}	0.25
Tl^+	0.37	Pb^{2+}	0.63	Y^{3+}	0.57	Zr^{4+}	0.48
Co^{2+}	0.56	Mg^{2+}	0.44	Ce^{3+}	0.43	Th^{4+}	0.56
Be^{2+}	0.86	Cu^{2+}	0.54	Ru^{3+}	0.63		
Sr^{2+}	0.82	Ni^{2+}	0.66	La^{3+}	0.72		

Fig. 3. Plots of R_F vs. mole fractions of acetone, HNO_3 and water. (a) Sm^{3+}, Be^{2+}, Mg^{2+}, Pd^{2+}, Al^{3+}, Ba^{2+}, Fe^{3+}, Cu^{2+}, Cd^{2+}, VO^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Mn^{2+} and Zr^{4+} have the same trend as In^{3+}. Tl^{3+} and Ce^{4+} have $R_F > 0.75$ at all pH. (b) Co^{2+}, Zn^{2+}, Ni^{2+}, Mn^{2+}, Y^{3+}, Be^{2+}, VO^{2+}, Sm^{3+}, Mg^{2+}, Pd^{2+}, Al^{3+}, Bi^{3+}, Hg^{2+} and Ce^{4+} have $R_F > 0.75$. Tl^{3+}, Pb^{2+} and Ba^{2+} have the same trend as La^{3+}. (c) Zr^{4+}, Cd^{2+}, Co^{2+}, Ni^{2+}, La^{3+}, Zn^{2+}, VO^{2+}, Sm^{3+}, Pr^{3+}, Cu^{2+}, Y^{3+}, Al^{3+}, Mn^{2+}, Hg^{2+}, Bi^{3+}, Ce^{4+}, In^{3+} and Be^{2+} have $R_F > 0.75$. Th^{4+} has the same trend as Mg^{2+}.

of the effect of solvent composition on R_F values, we shall consider these plots as R_F versus the mole fraction of acetone, nitric acid and water.

Effect of mole fraction of acetone on R_F values. Fig. 3a was plotted for the systems in which the mole ratio of water and nitric acid remains constant and only the proportion of acetone is continuously increased, i.e., for HNO_3–acetone–water systems in the volume ratios 1:1:1, 1:2:1, 1:3:1, 1:4:1, 1:5:1 and 1:6:1. With these systems, straight lines are obtained which in most instances are parallel to one another. Surprisingly, there is no effect of charge, size or nature of the cation on the slopes of the lines. Thus, for Co^{2+}, Cd^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, Mn^{2+}, In^{3+}, Sm^{3+}, Mg^{2+}, Pd^{2+}, Al^{3+}, Ba^{2+}, Fe^{3+}, K^+, VO^{2+}

and Zr^{4+} the decrease in R_F with increase in mole fraction of acetone is due to the decrease in the number of hydrogen ions competing for the exchange sites. Hence it follows that when the aqueous and non-aqueous solvents are both non-complexing and the $HNO_3:H_2O$ ratio remains constant, the R_F value is almost always dependent on the number of H^+ ions competing for the exchange sites. However, the behaviour of Th^{4+} is different as it gives higher R_F values, perhaps because thorium nitrate is very soluble in acetone [15] and water, in addition to its highly complexing nature in nitrate systems. If the factors of adsorption and ion exchange are neglected, the movement of a substance on a paper chromatogram is a function of its solubility in the

developing solvent. The R_F values of Tl^+ and Pb^{2+} at higher acetone concentrations are low because these ions interact strongly either with the cation or anion of the exchanger.

Effect of mole fraction of HNO_3 on R_F values. Fig. 3b shows the plots for the systems where the water: acetone mole ratio remains constant while the nitric acid mole fraction is constantly increased, *i.e.*, for HNO_3–acetone–water systems in the volume ratios 1:1:1, 2:1:1, 3:1:1, 4:1:1, 5:1:1 and 6:1:1. These curves are also very revealing. The R_F values generally increase linearly with increasing mole fraction of HNO_3 except for Th^{4+}, Ce^{4+} and In^{3+}. The increased R_F is now easily explained in terms of the increase in the number of H^+ ions competing with the cations for the exchange sites. The R_F of Th^{4+} decreases with increase in the mole fraction of HNO_3 because it means a decrease in the acetone concentration and, as explained earlier, Th^{4+} is

highly soluble in acetone. In^{3+} is an exception, the R_F value decreasing with increase in the mole fraction of HNO_3. There is no significant change in the R_F value of Ce^{4+}, which remains almost constant with change in HNO_3 concentration.

Effect of mole fraction of water on R_F values. In Fig. 3c we have plotted R_F values for HNO_3–acetone–water systems in the volume ratios 1:1:1, 1:1:2, 1:1:3, 1:1:4, 1:1:5 and 1:1:6, the mole ratio of acetone to nitric acid remaining constant while the mole fraction of water is increased. An increase in the mole fraction of water means an increase in the ionization of HNO_3 and, therefore, the R_F values increase linearly with increasing mole fraction of water. The exceptions are UO_2^{2+}, Pb^{2+}, Th^{4+} and Mg^{2+}. With UO_2^{2+}, with an increase in the mole fraction of water there is a greater formation of the insoluble uranyl tungstate, resulting in a decrease in the R_F value. A similar explanation applies to Pb^{2+} and Th^{4+}.

TABLE II

QUANTITATIVE SEPARATION OF Hg^{2+} AND Pb^{2+} FROM BINARY AND SYNTHETIC MIXTURES IN BUTANOL AND IN 0.001 M HNO_3

Amount of Hg^{2+} applied (μg)	Amount of other metal ion applied (μg)	Amount of Hg^{2+} found (μg)	Amount of Pb^{2+} applied (μg)	Amount of other metal ion applied (μg)	Amount of Pb^{2+} found (μg)
100	Hg_2^{2+} 200	95	100	Ag^+ 107	100
100	Tl^+ 204	98	100	Hg^{2+} 200	101
100	Bi^{3+} 208	100	100	Tl^{3+} 204	105
100	Cd^{2+} 112	95	100	Cd^{2+} 112	100
100	Pd^{2+} 106	100	100	Pd^{2+} 106	102
100	Sb^{3+} 121	99	100	Fe^{3+} 55)	100
100	Ag^+ 107	100	100	Cu^{2+} 63	95
100	Pb^{2+} 207	100	100	Ni^{2+} 58	98
100	Fe^{3+} 55	100	100	Co^{2+} 58	100
100	Cu^{2+} 63	95	100	Al^{3+} 26	102
100	Ni^{2+} 58	102	100	Be^{2+} 9	100
100	Co^{2+} 58	105	100	Zn^{2+} 65	100
100	Ba^{2+} 137	100	100	Mn^{2+} 54	101
100	Sr^{2+} 87	104	100	Ba^{2+} 137	104
100	Ca^{2+} 40	100	100	Sr^{2+} 87	100
10	Mixture	10	100	Mg^{2+} 24	102
50	Mixture	49.5	100	Ca^{2+} 40	103
100	Mixture	100	10	Mixture	10
200	Mixture	198	50	Mixture	50
400	Mixture	404	100	Mixture	98
			200	Mixture	197
			400	Mixture	402

Application

The advantage of this work is that Pb^{2+} and Hg^{2+} have been quantitatively separated from binary mixtures containing larger amounts of other metal ions such as Ag^+, Tl^+, Cd^{2+}, Pd^{2+}, Sb^{3+}, Cu^{2+}, Ni^{2+}, Ba^{2+}, Sr^{2+} and Ca^{2+} (Table II). It has been observed that the method works well within an error range of 5%. The method works satisfactorily even for the separation of Pb^{2+} from alloys containing these metals. Synthetic alloy samples of Pb^{2+} with other metal ions were prepared by mixing various metallic solutions in certain ratios so that they correspond to the actual metallic proportions in standard alloys, and then these samples were tried on titanium(IV) tungstate papers and the metal ion separations were achieved.

CONCLUSION

For most cations, there is a significant adsorption in the pH range 0–1. The sharp decrease in the R_F values of few ions above pH 2 is due to excessive hydrolysis in the acidic media. pH 2 is the most favourable acidity for ion exchange for Pb^{2+}, Hg^{2+}, Hg_2^{2+}, Sb^{3+}, Ga^{3+}, Bi^{3+}, Sn^{2+}, Th^{4+} and Mg^{2+}. Ag^+ is selectively adsorbed on these papers due to Ag^+–matrix interaction. The pH does not affect the ion-exchange capacity of titanium(IV) tungstate significantly in the pH range 0–5, which is in agreement with the observations made by Qureshi *et al.* [1].

In butanol–HNO_3 systems, titanium(IV) tungstate behaves only as a sorbent and not as an exchanger. The R_F values depend on the square of the nitric acid concentration.

In nitric acid–acetone–water systems, at higher acetone concentration the exchange phenomenon is not significant owing to a smaller number of H^+ ions competing for exchange sites. For most of the ions, the R_F value is linearly dependent on the mole fractions of HNO_3 and H_2O.

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