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**UNUSUAL SELECTIVITIES OF TITANIUM
ARSENATE LAYERS IN COMPLEX FORMING
ACID SYSTEMS: PREDICTION OF K_{sp} FROM
 R_f VALUES**

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A B S T R A C T

The analytical potential of Ti(IV) arsenate as an ion exchanger has been explored by the thin layer chromatographic technique. Binder-free thin layers of titanium arsenate have been prepared, and several important binary and ternary separations of chemically similar elements have been achieved using 0.1 M citric acid, 0.1 M Tartaric acid and 0.1 M Oxalic acid as the solvents. On the basis of R_f values, the K_{sp} of some metal arsenates have been predicted.

INTRODUCTION

In an ion exchange process, the selectivity depends upon the ion exchange material being used in the process as well as the medium of exchange. Thin layer chromatography offers an interesting method for the separation of metal ions in microgramme quantities. The separation potential of this technique is greatly enhanced if complexation is used. The use of binder free inorganic ion exchangers in thin layer chromatography has received some attention in recent years. (1-6).

Titanium arsenate is known to possess some unusual and promising ion exchange properties (7). Its analytical utility has been demonstrated in paper chromatography of inorganic ions (8, 9). As far as we are aware, no attempt has been made to combine complexation and ion exchange with thin layer chromatography. In this article we wish to show that the combination of these three processes leads to unusual selectivities.

Titanium arsenate show high selectivity at low pH and decompose at high pH, hence weak acids were chosen to prevent the hydrolysis of the exchange material. The complexing acids chosen were oxalic, tartaric and citric. As a result some very important and difficult separations were achieved. An effort has been made to predict on the basis of R_f values, the K_{sp} of some metal arsenates.

MATERIALS AND METHODS

Apparatus

Thin layer chromatography applicator of Toshniwal (India) was used to prepare the layers on (20 x 3 cm) glass plates. The plates were developed in glass jars (20x6 cm).

Reagents

Titanium tetra chloride and sodium arsenate hepta hydrate (Reidel, Germany) were used. All other chemical were of AnalaR grade.

Test Solutions and Detectors

Test solutions were generally prepared in 0.1 M metal nitrates, chlorides or sulphates. A little amount of the corresponding acid is added to prevent hydrolysis. Conventional spot test reagents were used for detection purposes.

Preparation of Thin Layer Plates

Titanium arsenate was prepared by mixing 0.1 M solutions of Titanium chloride and sodium arsenate in the volume ratio of 1:1 at pH 2 and digesting the resulting precipitate at room temperature for 24 hr. After filtering and drying the precipitate was cracked in demineralized water and then placed in 1M HNO_3 to convert it to the H^+ form. The material was finally washed with demineralized water and dried at 40°C . Ten grams of titanium arsenate granules thus obtained were

mixed in about 5 ml of distilled water and the slurry was made by grinding the mixture vigorously in a glass mortar for a long time. This step proved to be very important for complete adhesion. The grinding of the granules must be complete and the slurry should be in the form of a fine paste without any solid particles being left. The slurry was then spread over the clean glass plates with the help of an applicator to give 0.10 mm. thick layers. The plates were ready for use after drying at room temperature.

Procedure

Cation solutions (1-2 drops) were spotted on the plates which were developed in the chosen solvent system by the ascending technique. The ascent of the solvent was fixed at 11 cm. in all cases. After development the plates were dried and the cation spots were detected using appropriate spraying reagent.

RESULTS

The chromatographic behaviour of 50 metal cations on Titanium arsenate layers has been studied using eight solvent systems. The binary and ternary separations achieved experimentally are given in tables 1 and 2. The R_f values reported are only for those metal ions which give compact spots. A plot of R_f versus Atomic numbers for 0.1 M citric acid and 0.1 M nitric acid as solvent is given in Figure 1. In order to check the

TABLE 1

BINARY SEPARATIONS ACHIEVED EXPERIMENTALLY ON TITANIUM ARSENATE LAYERS

Solvent	Separations Achieved ($R_T - R_L$)
0.1 M Oxalic acid	Pb ²⁺ (0.00-0.12) - Mn ²⁺ (0.9-1.0) or Cr ³⁺ (0.85-1.0) Pt ⁴⁺ (0.00-0.00) - Au ³⁺ (0.62-0.72) or Pd ²⁺ (0.85-0.95) or Ru ³⁺ (0.72-0.95) or Ir ³⁺ (0.92-1.0) Se ⁴⁺ (0.00-0.00) - Au ³⁺ (0.62-0.72) Tl ⁺ (0.00-0.10) - Cd ²⁺ or Cu ²⁺ or Hg ²⁺ (0.72-1.0)
0.1 M Citric acid	Pb ²⁺ (0.00-0.00) - Th ⁴⁺ or VO ₂ ⁺ or Cu ²⁺ or Ni ²⁺ or Zn ²⁺ or Mn ²⁺ or Cd ²⁺ or Pd ²⁺ or VO ₂ ⁺ (0.80 - 1.00) W ⁶⁺ (0.60-0.70) - Cr ³⁺ (0.90-1.00) or Th ⁴⁺ (0.90-1.0) Y ³⁺ (0.30-0.45) - La ³⁺ (0.85-1.00) Pb ²⁺ (0.00-0.10) - Cr ³⁺ or Mo ⁶⁺ or W ⁶⁺ (0.60-0.90) Pr ³⁺ (0.40-0.60) - Nd ³⁺ (0.93-1.0)
0.1 M Tartaric acid	Nb ⁵⁺ (0.30-0.55) - Ta ⁵⁺ (0.80-0.95)
0.1 M Oxalic acid + 0.1 M Sodium Oxalate (1:1)	Zr ⁴⁺ (0.05-0.15) - Nd ³⁺ or Ce ³⁺ or Th ⁴⁺ or Ru ³⁺ or La ³⁺ (0.85-1.00). Ni ²⁺ (0.20-0.35) - Co ²⁺ or Fe ³⁺ or Cu ²⁺ or Hg ²⁺ , Al ³⁺ or Cr ³⁺ or Zn ²⁺ or Mn ²⁺ or Au ³⁺ or Ba ²⁺ or Sr ²⁺ or Ga ³⁺ (0.60 - 1.0)
0.1 M Citric acid + 0.1 M Sodium Citrate (1:1)	Ag ⁺ (0.00-0.00) - Cu ²⁺ or Cd ²⁺ or Hg ²⁺ or Pd ²⁺ or Au ³⁺ (0.85-1.00) Pb ²⁺ (0.00-0.10) - UO ₂ ²⁺ (0.75-0.89). Ga ³⁺ (0.60-0.80) - In ³⁺ (0.00-0.20) Ce ³⁺ (0.90-1.00) - Ce ⁴⁺ (0.40-0.60) Th ⁴⁺ (0.90-1.00) - Ce ⁴⁺ (0.40-0.60)
0.1 M Tartaric acid + 0.1 M Sodium tartarate (1:1)	Fe ²⁺ (0.75-0.85) - Fe ³⁺ (0.00-0.16) UO ₂ ²⁺ (0.00-0.15) - VO ₂ ⁺ (0.65-0.75) K ⁺ or Rb ⁺ or Cs ⁺ (0.00-0.10) - Be ²⁺ or Ba ²⁺ or Sr ²⁺ (0.75-0.96) Bi ³⁺ (0.00-0.35) - Cu ²⁺ or Cd ²⁺ or Hg ²⁺ or Zn ²⁺ or Mn ²⁺ (0.70-1.00) Hg ₂ ²⁺ (0.00-0.00) - Hg ²⁺ (0.85-0.95)
1.0 M HCl	Pd ²⁺ (0.00-0.10) - UO ₂ ²⁺ (0.80-0.90) or Th ⁴⁺ (0.85-1.0) K ⁺ (0.50-0.60) - Cs ⁺ (0.10-0.20) or Rb ⁺ (0.20-0.35) Bi ³⁺ (0.80-0.90) - Pb ²⁺ (0.00-0.10) Hg ²⁺ (0.58-0.75) - Pb ²⁺ (0.00 - 0.08).

TABLE 2

TERNARY SEPARATIONS ACHIEVED ON TITANIUM ARSENATE LAYERS

Solvent	Separations Achieved ($R_T - R_L$)
0.1 M Citric acid	Fe^{3+} (0.10-0.22)- W^{6+} (0.60-0.70)- Mn^{2+} (0.85-1.00) or Cr^{3+} (0.90-1.00)
0.1 M Tartaric acid	Cr^{3+} or Th^{4+} (0.90-1.00)- Mo^{6+} (0.45-0.55)- Pb^{2+} (0.00-0.10)
0.1 M Oxalic acid	Zr^{4+} (0.00-0.15)- W^{6+} (0.60-0.70)- Th^{4+} (0.88-0.95)
+ 0.1 M Sodium Oxalate (1:1)	Ag^+ or Pb^{2+} or Zr^{4+} (0.00-0.15)- Mo^{6+} (0.50-0.60)- Cr^{3+} (0.75-0.96). Zr^{4+} (0.00-0.15) - In^{3+} (0.40-0.60)- La^{3+} (0.80-0.95) or UO_2^{2+} or Th^{4+} or Nd^{3+} or Ru^{3+} or Ce^{3+} (0.85-1.0).
1 M HNO_3	Mo^{6+} (0.00-0.25)- W^{6+} (0.58-0.68)- Cr^{3+} (0.90-1.0) Pb^{2+} or Mo^{6+} (0.00-0.20)- UO_2^{2+} (0.48-0.58)- Th^{4+} (0.85-0.95) Fe^{3+} (0.00-0.20)- Ni^{2+} or Co^{2+} (0.50-0.65) - Cr^{3+} or Mn^{2+} (0.85-1.0) K^+ (0.50-0.60)- Rb^+ (0.10-0.30)- Cs^+ (0.00-0.00).

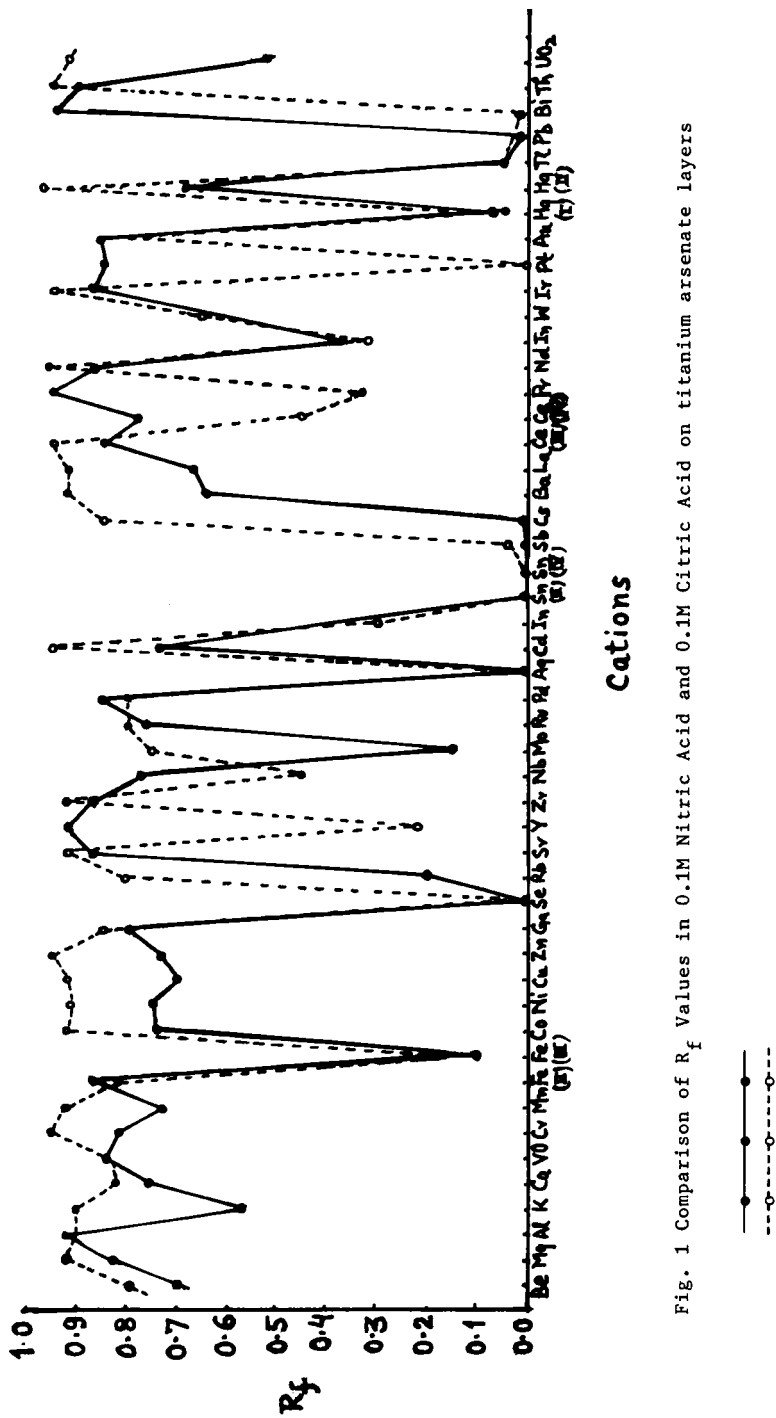


Fig. 1 Comparison of R_f Values in 0.1M Nitric Acid and 0.1M Citric Acid on titanium arsenate layers

reproducibility of the R_f values, some ions were chromatographed in 0.1 M citric acid, 0.1 M oxalic acid and 0.1 M tartaric acid. It was found that the variations does not exceed 10% of the average R_f value. The thin layers of titanium arsenate are quite stable and firm, capable of withstanding the solvent systems and chemical operations.

DISCUSSION

The most interesting feature of this study is a significant difference in R_f values of chemically similar elements leading to fantastic separation possibilities (Table 1 and 2). Thus Ag^+ can be separated from Hg^{2+} , Cu^{2+} , Cd^{2+} and Au^{3+} ; Ga^{3+} from In^{3+} , W^{6+} from Cr^{3+} ; Y^{3+} from La^{3+} ; Zr^{4+} from Th^{4+} ; Ni^{2+} from Co^{2+} ; and K^+ from Cs^+ . Some other important separations achieved are $Fe^{2+} - Fe^{3+}$, $Pr^{3+} - Nd^{3+}$, $Nb^{5+} - Ta^{5+}$, $Ce^{3+} - Ce^{4+}$, $Hg_2^{2+} - Hg^{2+}$, $UO_2^{2+} - VO^{2+}$, $Pb^{2+} - Mn^{2+}$ and $UO_2^{2+} - Th^{4+}$. These interesting separation possibilities arise from two effects (a) The acids chosen form complexes with most of the cations (b) Titanium arsenate layers selectively adsorb certain cations.

A comparison of R_f values in 1.0 M HNO_3 on titanium arsenate layers and titanium arsenate impregnated papers (8) prepared under similar conditions suggests that there is a decrease in the R_f value on layers for almost all cations probably due to the higher adsorption. Greater total ion exchange capacity of the thin layer

plates than that of the papers may be responsible for this decrease. The decrease is more pronounced in case of Ag^+ , Pb^{2+} , Ni^{2+} , Co^{2+} , Fe^{3+} , K^+ , Rb^+ and Cs^+ . This may be due to the fact that titanium arsenate is more selective for these cations and thus there is a greater exchange resulting in much lower R_f values. The only exceptions are Au^{3+} and Nb^{5+} , which exist as anionic species and thus show higher R_f values on the cation exchanger than impregnated papers.

To study the effect of complexation, R_f values were also determined in 0.1 M HNO_3 . A plot of R_f versus cations for 0.1 M citric acid and 0.1 M Nitric acid as solvent (Fig. 1) indicates the increase in the R_f values of certain cations such as Cu^{2+} , UO_2^{2+} , Hg^{2+} , Cd^{2+} , Ni^{2+} , Mn^{2+} , Co^{2+} , La^{3+} , K^+ , Rb^+ , Cs^+ and Mo^{6+} due to the formation of anionic citrate complexes. However for Bi^{3+} , Nb^{5+} and Ce^{4+} , the R_f values are much less in citric acid media probably due to their hydrolysis. Y^{3+} show a lower R_f value due to much less solubility of Yttrium arsenate in citric acid media. The Zero R_f value for Pt^{4+} in citric acid is probably due to the formation of insoluble citrate complex. Similar explanation may also be given for the increase in R_f values of certain cations in 0.1 M tartaric acid and 0.1 M oxalic acid as the two acids form anionic complexes with them.

Ions which have zero R_f values may do so owing to (i) precipitation, (ii) ion exchange, and (iii) strong adsorption due to high charge. In order to simulate

conditions on thin layers, sodium arsenate was added to the cation solution followed by the solvent. A number of ions precipitate under these conditions (Table 3). In these cases the precipitation mechanism holds good. For other ion, Sb^{3+} and Bi^{3+} hydrolyses and Pt^{4+} and Zr^{4+} are strongly adsorbed owing to their high charge. Se^{4+} probably forms insoluble titanium selenite resulting in the Zero R_f value. A very low R_f value for Tl^+ is probably due to the formation of thallos arsenate which is less soluble than thallos nitrate. Sn^{2+} has a very low R_f value in all complexing acid systems due to being more extensively hydrolysed.

It is known that R_f value, amongst other factors, depends upon the solubility product of the metal salts. On correlating the R_f values of the metal ions with the K_{sp} of their arsenates, the following linear relationship is obtained;

$$R_f = 0.50 + 0.0067 \frac{10^3}{-\log K_{sp}}$$

Fig. 2 shows this linear relationship. With the help of this equation it is possible to predict the K_{sp} values of different metal arsenates. (Table 4). The K_{sp} values of the various arsenates which have been used in plotting Fig. 2 are given in table 5. Earlier, we have predicted the K_{sp} of metal arsenates from the R_f values of metal ions on stannic arsenate papers (10). The two linear relationships, obtained for impregnated

TABLE 3
PRECIPITATION OF CATIONS IN THE SOLVENT SYSTEMS

Solvent	Cation + Sodium arsenate + Solvent	
	Cations which precipitate	Cations which do not precipitate
0.1 M Oxalic acid	Ag ⁺ , Pb ²⁺ , Bi ³⁺ , Hg ₂ ²⁺ , Sn ²⁺ , Sn ⁴⁺	Sb ³⁺ , Pt ⁴⁺ , Se ⁴⁺
0.1 M Citric acid	Ag ⁺ , Pb ²⁺ , Bi ³⁺ , Hg ₂ ²⁺ , Sn ²⁺ , Sn ⁴⁺	Sb ³⁺ , Pt ⁴⁺ , Se ⁴⁺
0.1 M Tartaric acid	Ag ⁺ , Pb ²⁺ , Bi ³⁺ , Hg ₂ ²⁺ , Sn ²⁺ , Sn ⁴⁺	Sb ³⁺ , Pt ⁴⁺ , Se ⁴⁺ .
0.1 M Oxalic acid + 0.1 M Sodium Oxalate (1:1)	Ag ⁺ , Pb ²⁺ , Bi ³⁺ , Hg ₂ ²⁺ , Sn ²⁺ , Sn ⁴⁺	Sb ³⁺ , Pt ⁴⁺ , Se ⁴⁺ , Zr ⁴⁺
0.1 M Citric acid + 0.1 M Sodium citrate (1:1)	Ag ⁺ , Pb ²⁺ , Bi ³⁺ , Hg ₂ ²⁺ , Sn ⁴⁺ , Sn ²⁺	Sb ³⁺ , Pt ⁴⁺ , Se ⁴⁺ , Zr ⁴⁺
0.1 M Tartaric acid + 0.1 M Sodium tartarate (1:1)	Ag ⁺ , Pb ²⁺ , Bi ³⁺ , Hg ₂ ²⁺ , Sn ²⁺ , Sn ⁴⁺	Sb ³⁺ , Pt ⁴⁺ , Se ⁴⁺
1 M HNO ₃	Ag ⁺ , Pb ²⁺ , Hg ₂ ²⁺ , Sn ²⁺ Sn ⁴⁺	Sb ³⁺ , Se ⁴⁺
1 M HCl	Ag ⁺ , Pb ²⁺ , Hg ₂ ²⁺	Sb ³⁺ , Se ⁴⁺ , Zr ⁴⁺ .

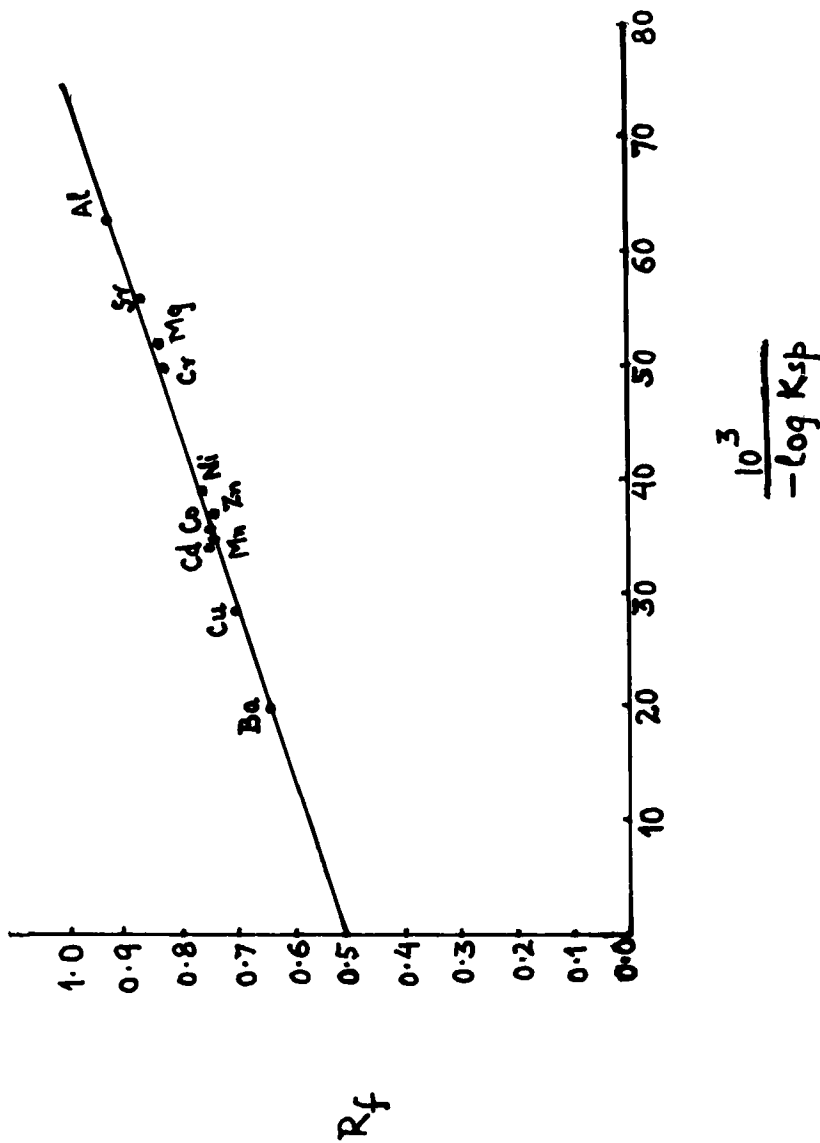


FIG. 2 Plot of R_f vs. $\frac{10^3}{-\log K_{sp}}$ for metal ions in 1.0M HNO_3

TABLE 4

PREDICTED VALUES OF K_{sp} FOR DIFFERENT METAL ARSENATES

Metal arsenate	K_{sp}
Hg ²⁺	5.5×10^{-36}
Nd ³⁺	7.4×10^{-19}
Ce ³⁺	7.3×10^{-20}
Th ⁴⁺	1.8×10^{-17}
VO ²⁺	2.0×10^{-20}
Pd ²⁺	7.3×10^{-26}
Ru ³⁺	1.7×10^{-26}
La ³⁺	6.0×10^{-38}
Be ²⁺	3.2×10^{-34}
Ga ³⁺	4.7×10^{-23}
K ⁺	1.8×10^{-84}
Fe ²⁺	7.4×10^{-19}
Nb ⁵⁺	1.2×10^{-24}
Ce ⁴⁺	1.1×10^{-24}
Pr ³⁺	1.3×10^{-15}
Ir ³⁺	8.0×10^{-19}
Y ³⁺	2.7×10^{-16}

TABLE 5

EXPERIMENTAL VALUES OF K_{sp} FOR SOME METAL ARSENATES

Metal arsenates	K_{sp}
Pb ²⁺	4.1×10^{-36}
Cu ²⁺	7.6×10^{-36}
Cd ²⁺	2.2×10^{-33}
Mn ²⁺	$(1.9) \times 10^{-29}$
Cr ³⁺	$(7.8) \times 10^{-21}$
Zn ²⁺	1.3×10^{-28}
Co ²⁺	7.6×10^{-29}
Sr ²⁺	8.1×10^{-19}
Ca ²⁺	6.8×10^{-19}
Ni ²⁺	$(3.1) \times 10^{-26}$
Al ³⁺	1.6×10^{-16}
Mg ²⁺	2.1×10^{-20}

papers and thin layer plates differ in the sense that in the later case the ionic charge and the bare ion radii has little effect on the R_f value and only the K_{sp} of metal arsenate is the deciding factor.

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