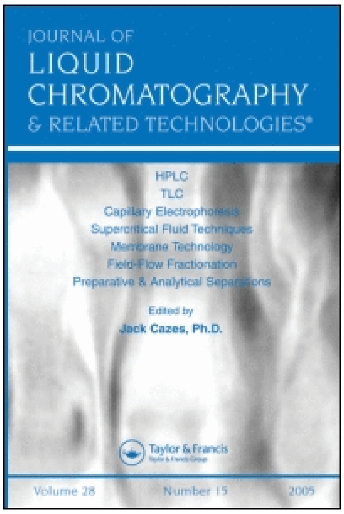

**Journal of Liquid Chromatography & Related Technologies**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

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**To cite this Article** Varshney, K. G. , Khan, Asif A. and Anwar, S.(1985) 'Chromatography of Alkaline Earths and Transition Metals on TIN(IV) Arsenosilicate and Arsenophosphate thin Layers in Buffered EDTA Solutions', Journal of Liquid Chromatography & Related Technologies, 8: 7, 1347 — 1353
**To link to this Article: DOI:** 10.1080/01483918508067148
**URL:** http://dx.doi.org/10.1080/01483918508067148

JOURNAL OF LIQUID CHROMATOGRAPHY, 8(7), 1347-1353 (1985)

# CHROMATOGRAPHY OF ALKALINE EARTHS AND TRANSITION METALS ON TIN(IV) ARSENOSILICATE AND ARSENOPHOSPHATE THIN LAYERS IN BUFFERED EDTA SOLUTIONS

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## ABSTRACT

The complex forming ability of ethylene diamine tetraacetic acid at various pH values and the ion exchange behavior of tin(IV) arsenosilicate and arsenophosphate cation exchangers have been combined in a chromatographic study of some metal ions. As a result some interesting observations have been made, which have led to certain analytically difficult separations such as $Ca^{2+}$-$Sr^{2+}$, $Ca^{2+}$-$Ba^{2+}$ and $Hg^{2+}$ from $Cu^{2+}$, $Ni^{2+}$, $Zn^{2+}$, $Co^{2+}$ and $Mn^{2+}$.

0148-3919/85/0807-1347$3.50/0

## INTRODUCTION

Zabin and Rollins (1) were probably the first to use inorganic ion exchangers such as zirconium phosphate and zirconium oxide for the separation of $Ni^{2+}$, $Co^{2+}$, $Pb^{2+}$, $Fe^{3+}$, $Ag^{+}$, $Hg^{2+}$, $Cd^{2+}$ and $Cu^{2+}$. Other workers (2-5) have also used such materials, but generally with a binder, which makes the interpretation somewhat difficult. Qureshi and coworkers (6-8) utilized some binder free thin layers of inorganic ion exchangers and achieved a few analytically important metal separations. Ethylene diamine tetra-acetic acid (EDTA) is an excellent complex forming agent, its complex forming ability being dependant on pH. However this property of EDTA has not been explored well in thin layer chromatography of metal ions. In the present study we have used EDTA as a developer at various pH values to achieve differential movements of certain metal ions on tin(IV) arsenosilicate and arsenophosphate thin layers.

## EXPERIMENTAL

### Apparatus

TLC applicator of M/S Toshniwal (India) was used to prepare thin layers of 0.1 mm thickness. The plates were developed in glass jars (20 x 5 cms).

### Reagents and Chemicals

All reagents and chemicals used were of Analar grade.

## Preparation of the ion exchange materials and thin layers

### Stannic arsenosilicate (SAS)

Decimolar solutions of stannic chloride hydrated ($SnCl_4.5H_2O$), disodium hydrogen arsenate ($Na_2HAsO_4.7H_2O$) and sodium metasilicate ($Na_2SiO_3.5H_2O$) were mixed in a volume ratio (1:1:1) with stirring and the pH was adjusted to $\sim 1$ by adding nitric acid. The slurry was allowed to stand overnight, filtered and washed to remove the excess of materials. It was dried at 40°C and converted into the $H^+$ form by keeping in 1M $HNO_3$ for 24 hours. Finally, it was washed several times with demineralized water till the effluent became neutral.

### Stannic arsenophosphate (SAP)

It was prepared as above by taking disodium hydrogen orthophosphate ($Na_2HPO_4$) instead of the meta silicate.

The inorganic ion exchanger was powdered and slurried with a little demineralized water. The slurry was then spread over the glass plates using an applicator to prepare thin layers of 0.1 mm thickness and the plates were dried at room temperature before use. The test solutions were placed with the help of capillaries on the starting line and dried. Development was then made in ordinary glass jars using the ascending technique.

### Test solutions and detection reagents

Decimolar solutions were prepared of the following metal ions by dissolving their nitrates or chlorides in water with corresponding mineral acid to prevent hydrolysis: $Cr^{3+}$, $Mn^{2+}$, $Fe^{3+}$, $Co^{2+}$, $Ni^{2+}$, $Cu^{2+}$, $Zn^{2+}$, $Cd^{2+}$, $Pb^{2+}$, $Hg^{2+}$, $Ca^{2+}$, $Sr^{2+}$, $Ba^{2+}$. Detection was made by the following reagents.

| | |
|---|---|
| Alizarin red S : | $Ca^{2+}$ |
| Dimethyl glyoxime : | $Ni^{2+}$, $Co^{2+}$ |
| Diphenyl carbazide : | $Cr^{3+}$, $Mn^{2+}$, $Zn^{2+}$ |
| Yellow ammonium sulphide: | $Cd^{2+}$, $Pb^{2+}$, $Hg^{2+}$ |
| Sodium rhodizonate : | $Sr^{2+}$, $Ba^{2+}$ |
| Potassium ferrocyanide : | $Cu^{2+}$, $Fe^{3+}$ |

### Solvent systems

Buffered EDTA solutions were prepared by mixing 10 ml of 0.1M EDTA with 5 ml each of the various buffers. To obtain the buffer solutions (9) of required pH values following amounts of 0.2N NaOH were poured into 100 ml mixture of the phosphoric, acetic and boric acids (0.04M respectively).

| NaOH, 0.2N (ml) | 0.0 | 25.0 | 42.5 | 60.0 | 77.0 | 100.0 |
|---|---|---|---|---|---|---|
| pH | 1.81 | 4.10 | 6.09 | 7.96 | 9.91 | 11.98 |

## RESULTS AND DISCUSSION

At different pH values EDTA forms (10) different ionic species ($H_3Y^-$, $H_2Y^{2-}$, $HY^{3-}$ and $Y^{4-}$) and the metal-EDTA complexes formed have varying apparent stability constants ($K_H$). Movement of metal ions should, therefore, be governed, to a large extent, by the pH of the EDTA solution when used as a developer. Figure-1 shows a variation of $R_f$ value with pH on SAP and SAS layers. It is observed that $R_f$ generally decreases with an increase in pH upto 6.0, beyond which it increases in some cases. It

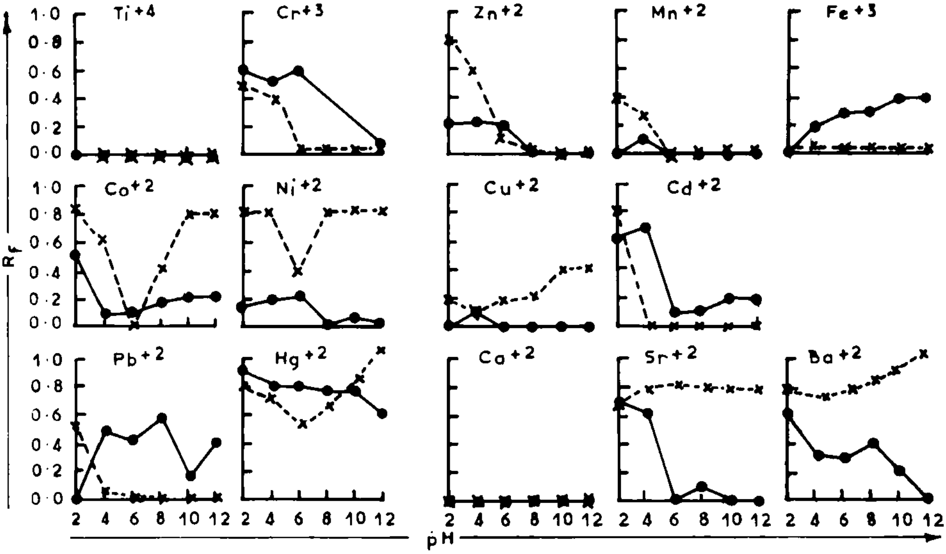

FIG. 1 Plot of $R_f$ versus pH for Different Metal Ions on Stannic Arsenophosphate and Stannic Arsenosilicate Thin Layers Using EDTA Solutions as Solvents.

●——●——● SAP
×---×---× SAS

may be due to the fact that at lower pH, due to the predominance of the $H_3Y^-$ form of EDTA the complexes are generally +vely charged. They may, thus, get exchanged with $H^+$ on the SAP and SAS cation exchange layers. At higher pH values EDTA may remain in the $H_2Y^{2-}$, $HY^{3-}$ and $Y^{4-}$ forms and the metal complexes now formed may be either neutral or -vely charged. Thus, they can move easily on a cation exchanger layer. A comparison of $R_f$ values on these two thin layers shows that while $Fe^{3+}$ is completely adsorbed on SAS at all pH values, its movement increases with a pH rise on SAP. $Cr^{3+}$, on the other hand, moves appreciably ($R_f \sim 0.4$) upto pH 4 on SAS. It may be due to a difference in the ion exchange behaviour of SAS and SAP for these metal ions. $Ti^{4+}$ does not move ($R_f = 0$) on either of the two layers at all pH values. It may be accounted to the excessive hydrolysis as well as a strong adsorption of this ion on these layers. Alkaline earths (Ca,Ba,Sr) behave differently. $Ca^{2+}$ appears to be so strongly held up by these materials that its $R_f$ value remains zero at all pH values. $Sr^{2+}$ and $Ba^{2+}$, however, move appreciably on SAS layers. Their movement decreases with pH on SAP layers.

On the basis of the differential movement of the metal ions on SAS and SAP thin layers in EDTA solutions of different pH, certain important analytical separations have been made possible. For example $Ca^{2+}$-$Ba^{2+}$, $Ca^{2+}$-$Sr^{2+}$, $Zn^{2+}$-$Cd^{2+}$, $Pb^{2+}$-$Hg^{2+}$, $Ni^{2+}$-$Mn^{2+}$, $Co^{2+}$-$Mn^{2+}$, $Ni^{2+}$-$Cr^{3+}$, $Co^{2+}$-$Cr^{3+}$ and $Fe^{3+}$-$Cr^{3+}$ separations can be achieved on a suitable ion exchange layer if the pH of the EDTA solution is properly adjusted.

## ACKNOWLEDGEMENTS

Authors are thankful to Dr. K.T.Naseem for research facilities and to the U.G.C. and C.S.I.R. (India) for the financial assistance.

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