This article was downloaded by:
On: *25 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Separation Science and Technology

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Paper Chromatographic Separation of Arsenic Valences

M. Subbaiyan[a]; P. B. Janardhan[a]
[a] ANALYTICAL AND INORGANIC CHEMISTRY DEPARTMENT, UNIVERSITY OF MADRAS A. C. COLLEGE CAMPUS, MADRAS, SOUTH INDIA

To cite this Article Subbaiyan, M. and Janardhan, P. B.(1972) 'Paper Chromatographic Separation of Arsenic Valences', Separation Science and Technology, 7: 4, 425 — 431

To link to this Article: DOI: 10.1080/00372367208055585

URL: http://dx.doi.org/10.1080/00372367208055585

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

SEPARATION SCIENCE, 7(4), pp. 425–431, 1972

NOTE

Paper Chromatographic Separation of Arsenic Valences

M. SUBBAIYAN and P. B. JANARDHAN

ANALYTICAL AND INORGANIC CHEMISTRY DEPARTMENT
UNIVERSITY OF MADRAS
A. C. COLLEGE CAMPUS
MADRAS-25, SOUTH INDIA

Abstract

Separation of As(III) from As(V) by paper chromatography is described. The choice of suitable eluent is indicated. An explanation is offered for the observed separation on the basis of complexation and solvation of the arsenic ions.

There are but a few publications (*1–5*) related to the chromatographic separation of valency states of arsenic. Earlier works make use of treated papers and confine themselves to observations without offering explanations. The present work gives a method for separating and estimating AsO_3^{3-} and AsO_4^{3-} on untreated paper, besides giving appropriate explanations for the observations.

The method finds use in the field of insecticides, vegetation sprays, and antifouling paints wherein the quantity of the highly toxic AsO_3^{3-} (*6*) has to be controlled with respect to AsO_4^{3-}.

EXPERIMENTAL

Preparation of Solutions

Arsenic(III) solution was prepared by dissolving a weighed amount of AR As_2O_3 in a minimum amount of $N/5$ NaOH solution. A part of the above solution was oxidized with concentrated HNO_3 to give As(V) solution. The pH's of the made-up solutions were adjusted to 6 and 9 by neutralization. Mixtures for separation were prepared as and when required by mixing suitable aliquotes of the above solutions.

Spraying Reagent

A 1% ammoniacal silver nitrate solution, when sprayed on the chromatogram, gives a yellow color with arsenite and a chocolate brown color with arsenate. Its sensitivity is 1 γ of arsenic. The colors produced are not stable for long.

Twelve centimeter circles of Whatman paper No. 1 were used. A desiccator of 12-in. diameter was used as the chromatographic chamber. A solution of arsenic was spotted at the center of the filter paper circle using an Agla micrometer syringe and the spot was dried under a hot-air blower. The chromatogram was prepared by Rutter's technique (*7*). The choice of eluents was guided by their polarity, viscosity, and solubilization (*8*). The following solvents and their mixtures were used with and without the presence of acid or alkali: methanol, ethanol, *n*-propanol, *n*-butanol, and ethyl acetate. The distance from the center of the spot to the outer boundary of the chromatographic band was measured and related to the solvent front to calculate the R_f values.

OBSERVATION

The results obtained with different eluents and the spotting solution at pH 6 and 9 are presented in Table 1. Separation becomes difficult with acidulated eluents, because both the ions migrate together to the solvent boundary due to rapid desorption. Water, with its high dielectric constant of 78.54, pushes both the ions chromatographically to the solvent boundary without effecting separation, whereas with methanol (dielectric constant 32.63) the migration of AsO_4^{3-} is considerably retarded (R_f 0.37 compared with 0.89 of AsO_3^{3-}). With solvents of lesser polarity, such as ethanol, AsO_4^{3-} migrates very little whereas AsO_3^{3-} continues to migrate appreciably. This is also the case when the pH of the spotting solution is 9. In the case of propanol and butanol the migration of AsO_3^{3-} is not satisfactory because of diffusion. In ethyl acetate (dielectric constant 6.02) both the ions refuse to move.

It is interesting to note that AsO_4^{3-} gives two bands in Nos. 2, 7a, 7b, and 10c of Table 1, indicating the presence of two migrating species. The outer bands are less intense than the inner ones.

TABLE 1

		pH 6		pH 9	
		R_f values of[a]		R_f values of[a]	
No.	Eluent	AsO_3^{3-}	AsO_4^{3-}	AsO_3^{3-}	AsO_4^{3-}
1	Water	1.00	1.00	0.97	1.00
2	Methanol	0.89	0.37 (IB) 0.69 (OB)	0.89	0.38
3	Ethanol	0.85	0.19	0.77	0.00
4	*n*-Propanol	Diffused	0.00	0.00	0.00
5	*n*-Butanol	Diffused	0.00	0.00	0.00
6	Ethyl acetate	0.00	0.00	0.00	0.00
7	MeOH:water				
	a) 90:10	—	—	0.91	0.42 (IB) 0.67 (OB)
	b) 80:20	0.89	0.57 (IB) 0.74 (OB)	0.92	0.51 (IB) 0.74 (OB)
	c) 50:50	0.90	0.88	—	—
	d) 20:80	0.92	1.00	—	—
8	MeOH:ethyl acetate				
	a) 80:20	0.88	0.00	—	—
	b) 50:50	0.87	0.00	—	—
	c) 20:80	0.62	0.00	—	—
9	MeOH:ethyl acetate:water				
	a) 30:60:10	0.71	0.00	—	—
	b) 40:50:10	0.72	0.16	—	—
	c) 50:40:10	0.87	0.20	—	—
	d) 70:20:10	0.90	0.23	—	—
10	EtOH:water				
	a) 95:5	—	—	0.83	0.00
	b) 90:10	—	—	0.85	0.00
	c) 80:20	—	—	0.86	0.29 (IB) 0.54 (OB)

[a] Average of four readings. (IB) = Inner band. (OB) = Outer band.

DISCUSSION

Spotting Solution at pH 6

Separation of AsO_3^{3-} and AsO_4^{3-} is not possible when water and methanol are used either individually or as a mixture (see Nos. 1, 2, and 7). This is an expected observation because at pH 6 the species are

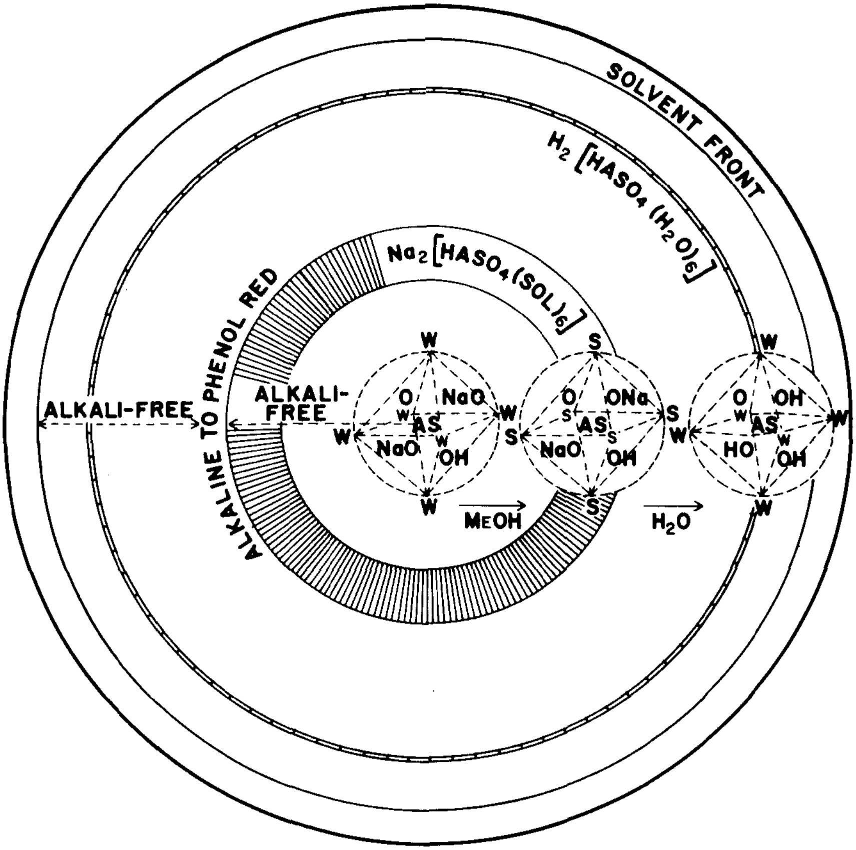


FIG. 1. Explanation for the double bands of AsO_4^{3-} in water–alcohol mixtures. W = water. S = solvent.

strongly hydrated as $H_3[AsO_3(H_2O)_3]$ and $Na[H_2AsO_4(H_2O)_6]$ (*10*). They move equally fast under the rapid desorption effect of hydrogen ions (*9*) and strong solubilization by the solvent. In Nos. 8 and 9 of Table 1 the R_f values of AsO_3^{3-} and AsO_4^{3-} differ widely, indicating the possibility of separation. The greater δR_f in No. 8 than in No. 9 may indicate better separation in the former. But practically speaking, it is the other way around; the separation in No. 9 is better than in No. 8 due to the sharpness of the boundaries in the former. The presence of water in No. 9 is responsible for this marked difference. In the eluent No. 8, control of polarity alone is brought about, while in No. 9, in addition to the control of polarity, there is also better solubilization due to the presence of water.

Spotting Solution at pH 9

The slightly greater R_f value of AsO_4^{3-} (see No. 1, pH 9 of Table 1) can be explained on the basis of the coordination chemistry of arsenite and arsenate. AsO_4^{3-} gives a more ionic coordination shell than the distorted tetrahedron of AsO_3^{3-}. Following the principle of "like solubilizes the like," the more ionic AsO_4^{3-} is more solubilized by the highly polar water and hence it has a slightly greater R_f.

Chromatographic migration under the influence of highly polar water leads to partial or total hydrolysis:

$$Na[H_2As(OH)_6] + H_2O \rightarrow H_3[As(OH)_6] + NaOH$$

In the case of AsO_3^{3-} the hydrolysis is total, yielding the homogeneous species $H_3[AsO_3(H_2O)_3]$. In the less polar solvents it moves as $H_3[AsO_3(H_2O)_x(Sol)_y]$ and hence has the lower R_f. However, in all instances AsO_3^{3-} moves only as a single species, as indicated by the single band.

AsO_4^{3-} exhibits two bands in some cases (Nos. 2, 7a, 7b, and 10c). AsO_4^{3-} can exist as $Na[H_2AsO_4(H_2O)_6]$ at pH 6 and as $Na_2[HAsO_4(H_2O)_6]$ at pH 9. In water, both these species move as such to the boundary, and therefore AsO_4^{3-} shows only a single band in water. With other eluents such as methanol there is a tendency for the water of solubilization to be replaced to a greater or lesser extent by solvent molecules (Fig. 1).

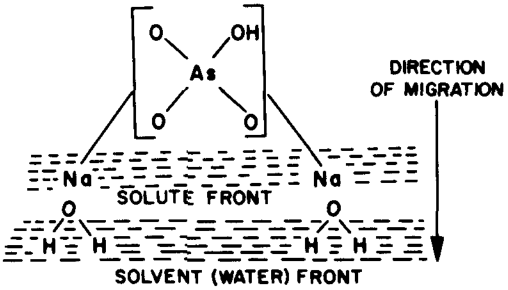
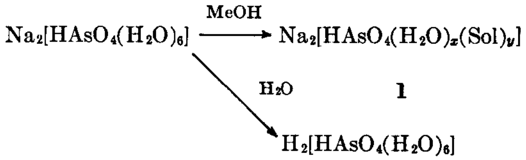


FIG. 2. Diagrammatic representation of orientation of sodium arsenate during chromatographic migration.

This results in partial solvolysis and hydrolysis:



$$\begin{tikzcd}
Na_2[HAsO_4(H_2O)_6] \arrow[r, "MeOH"] \arrow[dr, "H_2O"] & Na_2[HAsO_4(H_2O)_x(Sol)_y] \\
 & H_2[HAsO_4(H_2O)_6]
\end{tikzcd}$$

1

2

Complex x, being more acidic, moves faster than Complex 1. This explains the two bands observed for AsO_4^{3-} in some cases. That the outer band consists of the hydrolyzed species 2, deprived of alkalinity, is shown by the fact that it gives a negative test for alkali with phenol red indicator, while the inner band is distinctly alkaline.

A peripheral alkalinity was also observed in the case of chromatographic bands produced with water as eluent. It is therefore presumed that the sodium arsenate species becomes oriented during migration, the sodium ions facing the polar solvent front and the arsenic moiety trailing behind (*9*) (Fig. 2).

As the percentage of water increases in relation to methanol in the eluent, the tendency for replacement of water of solubilization by

TABLE 2

Estimation of AsO_3^{3-} and AsO_4^{3-} after Chromatographic Separation

	AsO_3^{3-} (μg)			AsO_4^{3-} (μg)		
Eluent	Spotted	Estimated[a]	Error	Spotted	Estimated[a]	Error
	Spotting solution pH 6					
MeOH:ethyl acetate:water						
a) 30:60:10	75.35	73.7	−1.65	83.58	80.4	−3.18
b) 40:50:10	75.35	72.0	−3.35	83.58	79.8	−3.78
c) 50:40:10	75.35	71.4	−3.95	83.58	81.3	−2.28
d) 70:20:10	75.35	72.6	−2.75	83.58	80.9	−2.68
	Spotting solution at pH 9					
Ethanol:water						
a) 95:5	75.35	72.1	−3.25	83.58	80.6	−2.98
b) 90:10	75.35	72.4	−2.95	83.58	81.5	−2.08

[a] Average of at least four estimations.

methanol becomes less or nil. Therefore, AsO_4^{3-} yields only a single band in Nos. 7c and 7d.

From the data given in Table 1, it was found that the solvent systems Nos. 9a, 9b, 9c, 9d, 10a, and 10b are suitable for good separation of AsO_3^{3-} and AsO_4^{3-}. These solvent systems were adopted for subsequent separations.

ESTIMATION

The AsO_3^{3-} and AsO_4^{3-} in the mixed solutions were separated by the paper chromatographic technique described above. The respective bands were carefully cut out and shredded. The arsenic content in them was estimated by the Gutzeit technique (*11*) (see Table 2).

REFERENCES

1. F. H. Pollard, J. F. W. McOmie and A. J. Banister, *Chem. Ind.* (London), *49*, 1598 (1955).

2. S. Nakano, *J. Chem. Soc., Japan, Pure Chem. Sect.*, *77*(5), 673 (1956).

3. A. Murata, *Ibid.*, *78*(4), 520 (1957).

4. L. Ossicini, *J. Chromatogr.*, *9*, 114 (1962).

5. M. N. Sastri and A. P. Rao, *Ibid.*, *9*, 250 (1962).

6. R. H. Vallance, *A Textbook of Inorganic Chemistry*, Vol. 6, Part 4, Griffin, London, 1938, p. 301.

7. L. Rutter, *Nature*, *161*, 435 (1948); *Analyst*, *75*, 37 (1950).

8. A. Paul and P. B. Janardhan, *Bull. Chem. Soc. Japan*, *40*(5), 1131 (1967).

9. P. B. Janardhan and A. Paul, *Indian J. Chem.*, *5*(7), 297 (1967).

10. H. Remy, *Treatise on Inorganic Chemistry*, Vol. 1, Elsevier, London, 1956, pp. 651–658.

11. R. C. Griffin, *Technical Methods of Analysis*, 2nd ed., McGraw-Hill, New York, 1955, pp. 339–340.

Received by editor August 8, 1971