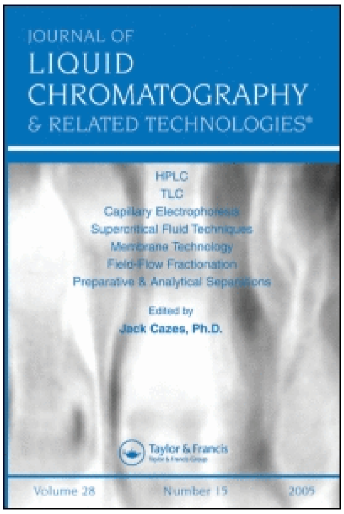

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

Chromatography on Papers Impregnated with Zinc Silicate: A New Adsorbent for Qualitative and Quantitative Separation of Amines

J. P. Rawat[a]; M. Iqbal[a]; Masood Akhtar Khan[a]
[a] Department of Chemistry, Aligarh Muslim University, ALIGARII, INDIA

To cite this Article Rawat, J. P. , Iqbal, M. and Khan, Masood Akhtar(1983) 'Chromatography on Papers Impregnated with Zinc Silicate: A New Adsorbent for Qualitative and Quantitative Separation of Amines', Journal of Liquid Chromatography & Related Technologies, 6: 5, 959 — 972

To link to this Article: DOI: 10.1080/01483918308067018

URL: http://dx.doi.org/10.1080/01483918308067018

JOURNAL OF LIQUID CHROMATOGRAPHY, 6(5), 959-972 (1983)

CHROMATOGRAPHY ON PAPERS IMPREGNATED WITH ZINC SILICATE: A NEW ADSORBENT FOR QUALITATIVE AND QUANTITATIVE SEPARATION OF AMINES

J.P.Rawat, M.Iqbal and Masood Akhtar Khan,

Department of Chemistry,
Aligarh Muslim University,
ALIGARH-202001 (INDIA).

ABSTRACT

Papers impregnated with zinc silicate have been used for the chromatographic studies of amines taken in the form of their hydrochlorides. R_f values of various amines have been determined and compared with its behaviour on plain papers. Quantitative separations of dimethylamine from methylamine, α-naphthylamine, o-toluidine and o-nitroaniline; o-phenylenediamine from m-phenylenediamine; diphenylamine from piperidine have also been achieved on columns loaded with zinc silicate exchanger.

INTRODUCTION

Both papers and column chromatographic studies of amines have been reported by various workers (1-4).

0148-3919/83/0605-0959$3.50/0

It was noted in these methods that undissociated amines had little interaction with the adsorbents used. Hence some preferred to use ligand exchange chromatography for the separation of such amines by virtue of their ability to form complexes of different stability with the loaded metal (5-7). However, if the salts of amines were prepared, the ion exchange would have played the primary role for such separations. Stannic molybdate has only been used to date for the paper and column chromatographic separations of amines with this method (8). In our present studies we have separated amine ions taken in the form of their hydrochlorides on papers impregnated with zinc silicate, an inorganic ion exchanger. On the basis of difference in R_f values, some of the amines have also been separated on columns of zinc silicate exchanger.

MATERIALS AND METHODS

Apparatus: Glass jars 20 x 5 cms and Whatmann No. 3 paper strips of 14 x 3 cms were used for ascending chromatographic studies.

Reagents: Zinc nitrate (BDH), sodium silicate (Riedel, Germany) were used for the preparation of ion exchange strips and zinc silicate. All other chemicals used were of analytical grade.

Preparation of ion exchange papers: Impregnated papers were prepared by dipping the strips (Whatmann No. 3, 14 x 3 cms) first in a 0.1M solution of zinc nitrate and were allowed to dry at room temperature for 20 minutes. They were then dipped in a 0.1M solution of sodium silicate for about 5 seconds. The strips were placed over a filter sheet for the excess of the reagent solution to drain off. These strips were completely dried at room temperature and then washed twice with distilled water to remove the excess of the reagent. Finally they were dried at room temperature and used for chromatographic studies.

Preparation of aminehydrochlorides: The dry HCl gas was first obtained by dropwise addition of concentrated hydrochloric acid into concentrated sulfuric acid. The evolved HCl gas was allowed to pass through the amine solution in ether. Aminehydrochlorides so obtained were either in solid or liquid form and were immiscible with ether. One percent solution of aminehydrochlorides were then prepared in water.

Detectors: p-Dimethylaminobenzaldehyde (p-DAB) and ninhydrin were used for the detection of various aminehydrochlorides. The ninhydrin detector was prepared by dissolving 0.2 gm of ninhydrin in 100 ml of n-butanol saturated with water. p-Dimethylaminobenzaldehyde detector was prepared in ethanol + hydrochloric acid mixture taken in the ratio 19:1. Ninhydrin was used to detect methylamine, dimethylamine, tripentylamine and piperidine and p-DAB for α- and B-naphthylamine, ortho- and para-toluidine; ortho-, para- and metanitroaniline; ortho- and meta-phenylenediamine; diphenylamine; pyridine, benzylamine and p-anisidine.

Procedure: The sample solutions were spotted with the help of fine capillaries on the ion exchange papers. The strips were conditioned in the chromatographic jars containing the solvent for about 10 minutes. The strips were then dipped in the solvent to allow the solvent to ascend to a distance of 11 cms in each case.

Synthesis of zinc silicate: Zinc silicate (9) was prepared by mixing 0.1M solutions of zinc nitrate and sodium silicate in the volume ratio 1:1. The white gelatinous precipitate so formed was kept standing at room temperature for 24 hours. This was then filtered, washed and dried in an oven at 40°C. The dried product so obtained was washed again with demineralized water and retained for use in column operations.

Separations: For separation studies a glass column having a height of 30 cm and diameter 0.69 cm was used in which 2 gm of zinc silicate was taken on its glass wool support. The flow rate of the effluent was adjusted at 5-6 drops/min. The eluate containing amine was analysed spectrophotometrically (10).

RESULTS AND DISCUSSION

The adsorption of undissociated amines on ion exchanger is not possible owing to their molecular structures. Two alternative ways have been suggested for their selective retention and their subsequent resolution in a mixture:

(i) The cation exchanger is taken in a metal form to enable it to form complexes of different stabilities with the amines.

(ii) The amines are taken in ionic form by their conversion to hydrochlorides.

While the former method suffers from the disadvantage of lack of materials which firmly hold the metal ion, the latter is simple and easy to accomplish. In our present method we have chromatographed 17 amine-hydrochlorides on papers impregnated with zinc silicate, a fairly good adsorbent.

The behaviour of different aminehydrochlorides on papers impregnated with zinc silicate has been studied in aqueous and non-aqueous media. The developers used were DMW and solutions of different concentrations of hydrochloric acid (0.005M, 0.01M and 0.1M HCl). For studies in nonaqueous medium, 100% acetone and acetone + hydrochloric acid mixture in the ratio 1:1 were used. The R_f values obtained are shown in Table 1. For the sake of comparison, R_f values of the aminehydrochlorides were also determined on untreated papers in the same developers. The results are presented in Table 2.

The results of Tables 1 and 2 show that on zinc silicate papers aminehydrochlorides are selectively absorbed while an unretarted movement of most of the amines is observed on the plain papers. This implies that zinc silicate, being a good adsorbent, selectively retains certain amines (amines with very low R_f values). Zinc silicate is an extremely weak cation exchanger and preferably takes up H^+ from the solution. Hence the use of hydrochloric acid solution resulted in the movement of aminehydrochlorides when different concentrations of HCl were used as developers. R_f values increased with increase in concentration of HCl. Higher concentrations of HCl furnished greater number of H^+ ions which in turn displaced the amines in the zinc silicate layers. Zinc silicate being less stable in higher concentrations of mineral acids, use of hydrochloric acid concentration higher than 0.1M was avoided.

TABLE - 1

R_f values of aminehydrochlorides on papers impregnated with zinc silicate

Sl. No.	Aminehydrochloride	R_f values					
		DMW	0.005M HCl	0.01M HCl	0.1M HCl	Acetone 100%	Acetone + 0.1M HCl (1:1)
1.	α-naphthylamine	0.40	0.46	0.48	0.50	0.95	0.91
2.	B-naphthylamine	0.37	0.40	0.46	0.54	0.92	0.89
3.	Piperidine	0.80	0.83	0.88	0.90	0.81	0.95
4.	o-nitroaniline	0.60	0.50	0.56	0.59	0.90	0.96
5.	m-nitroaniline	0.61	0.68	0.72	0.75	0.87	0.90
6.	p-nitroaniline	0.51	0.54	0.55	0.61	T	0.92
7.	o-toluidine	0.38	0.46	0.54	0.60	T	0.90
8.	p-toluidine	0.69	0.70	0.73	0.77	0.90	0.91
9.	Pyridine	0.75	0.79	0.82	0.86	T	0.94
10.	Methylamine	0.90	0.92	0.93	0.96	T	0.80
11.	Dimethylamine	0.00	0.02	0.04	0.37	0.01	0.78
12.	Diphenylamine	0.00	0.09	0.20	0.40	T	0.69
13.	Tripentylamine	0.63	0.69	0.80	0.92	T	0.78
14.	o-phenylenediamine	0.00	0.00	0.00	0.18	0.0	0.63
15.	m-phenylenediamine	0.52	0.61	0.64	0.70	T	0.86
16.	Benzylamine	0.24	0.26	0.30	0.47	T	0.85
17.	p-anisidine	0.77	0.79	0.81	0.86	T	0.81

DMW = Demineralized water; T = Trailing from point of application to solvent front.

TABLE - 2

R_f values of aminehydrochlorides on plain papers

Sl. No.	Aminehydrochloride	R_f values			
		DMW	0.005M HCl	0.01M HCl	0.10M HCl
1.	α-naphthylamine	0.55	0.68	0.74	0.78
2.	B-naphthylamine	0.54	0.58	0.70	0.82
3.	Piperidine	0.86	0.89	0.93	0.96
4.	o-nitroaniline	0.68	0.74	0.79	0.88
5.	m-nitroaniline	0.73	0.76	0.80	0.95
6.	p-nitroaniline	0.60	0.72	0.79	0.88
7.	o-toluidine	0.58	0.68	0.74	0.83
8.	p-toluidine	0.78	0.80	0.88	0.91
9.	Pyridine	0.82	0.84	0.86	0.88
10.	Methylamine	0.78	0.88	0.92	0.98
11.	Dimethylamine	0.64	0.69	0.73	0.76
12.	Diphenylamine	0.82	0.84	0.88	0.92
13.	Tripentylamine	0.70	0.73	0.77	0.82
14.	o-phenylenediamino	0.60	0.63	0.65	0.66
15.	m-phenylenediamine	0.50	0.54	0.59	0.64
16.	Benzylamine	0.25	0.30	0.46	0.60
17.	p-anisidine	0.90	0.92	0.93	0.94

DMW = Demineralized water.

TABLE - 3

Separations achieved on zinc silicate papers

Binary separations

Solvent system - 0.005M HCl:

(i) Dimethylamine (0.02) from methylamine (0.92), α-naphthylamine (0.46), B-naphthylamine (0.40), benzylamine (0.26), piperidine (0.83), tripentylamine (0.69), p-anisidine (0.79).

(ii) Diphenylamine (0.09) from α-naphthylamine (0.46), B-naphthylamine (0.40), o-toluidine (0.46), p-toluidine (0.70), o-nitroaniline (0.50), p-nitroaniline (0.54), m-nitroaniline (0.68), pyridine (0.79), piperidine (0.83) and p-anisidine (0.79).

(iii) o-phenylenediamine (0.00) from m-phenylenediamine (0.61).

(iv) o-toluidine (0.46) from p-toluidine (0.70).

(v) Benzylamine (0.26) from piperidine (0.50), pyridine (0.79) and methylamine (0.92).

Ternary separations

Solvent system - H_2O:

(i) Dimethylamine (0.00) - o-toluidine (0.38) - piperidine (0.80).

(ii) Dimethylamine (0.00) - α-naphthylamine (0.40) - methylamine (0.90).

(iii) o-phenylenediamine (0.0) - benzylamine (0.24) - methylamine (0.90).

TABLE - 4

Some separations on zinc silicate columns

Sl. No.	Separations	Eluents	Volume of effluent (ml)	Amount of amine-hydrochloride		% Error
				Loaded (µg)	Found (µg)	
1.	Methylamine	DMW	40	3600	3630	0.83
	Dimethylamine	Acetone+0.10M HCl (1:1)	50	2600	2590	0.38
2.	α-naphthylamine	DMW	50	5000	4980	0.40
	Dimethylamine	Acetone+0.10M HCl (1:1)	50	2600	2605	0.19
3.	o-toluidine	DMW	40	4100	4140	0.97
	Dimethylamine	Acetone+0.10M HCl (1:1)	50	2600	2600	0.00
4.	o-nitroaniline	DMW	40	4500	4475	0.55
	Dimethylamine	Acetone+0.10M HCl (1:1)	50	2600	2590	0.38
5.	m-phenylenediamine	DMW	40	4550	4500	1.11
	o-phenylenediamine	Acetone+0.10M HCl (1:1)	50	4750	4730	0.42
6.	Piperidine	DMW	30	2000	2000	0.00
	Diphenylamine	Acetone+0.10M HCl (1:1)	40	4000	3960	1.00

DMW - Demineralized water.

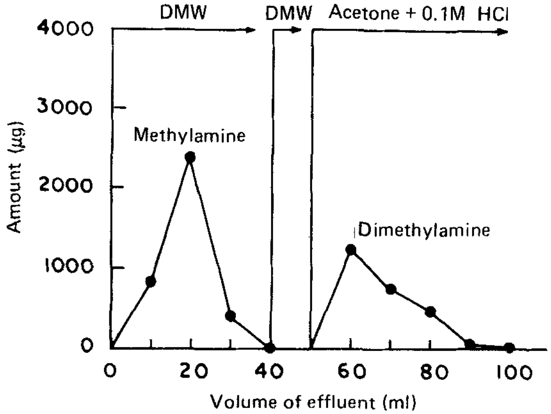

FIG. 1A Separation of Methylamine from Dimethylamine.

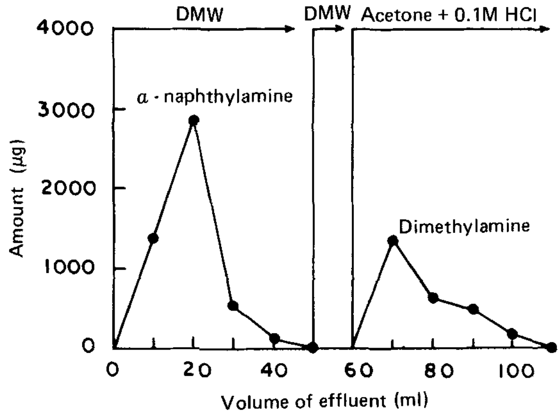

FIG. 1B Separation of α-Naphthylamine from Dimethylamine.

Separations of aninehydrochlorides were tried on zinc silicate papers on the basis of their behaviour in different developers used. In some cases the differences in R_f values were so large that many ternary separations too were possible. The binary and

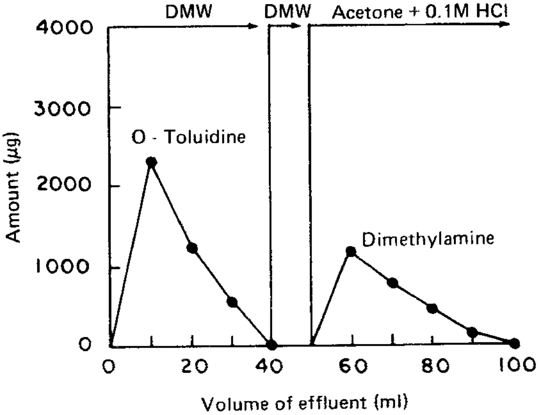

FIG. 1C Separation of O-Toluidine from Dimethylamine.

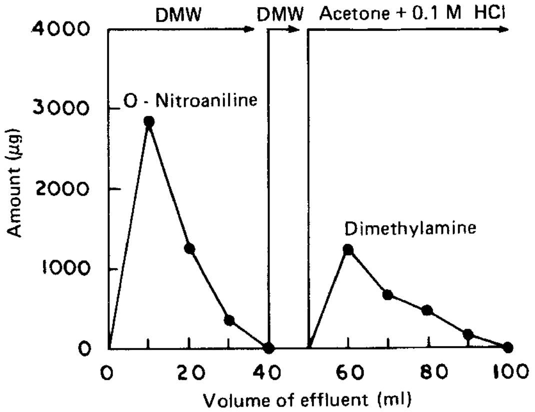

FIG. 1D Separation of O-Nitroaniline from Dimethylamine.

ternary separations practically achieved are reported in Table 3.

The separations found to be possible on paper chromatograms were also tried on columns loaded with zinc silicate exchanger. The behaviour of amine ions

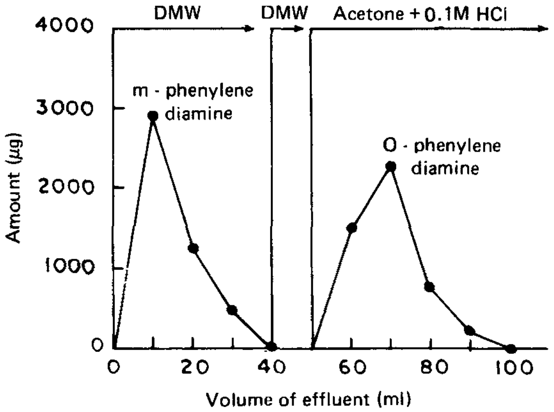

FIG. 1E Separation of m-Phenylenediamine from O-Phenylenediamine.

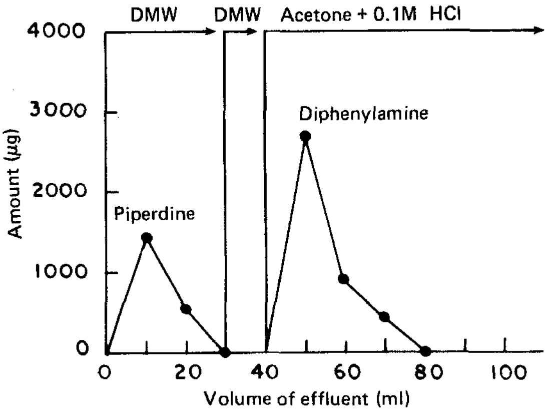

FIG. 1F Separation of Piperidine from Diphenylamine.

on the impregnated papers reflects the exact pattern of elution. O-phenylenediamine being extremely adsorptive was retained on the column while its m-isomer came out unadsorbed. The adsorbed amine ion was then eluted with acetone + 0.10M HCl mixture. The amine in the eluate was determined spectrophotometrically. The quantitative separations practically achieved are summarized in Table 4 and the order of elution and the eluents used are shown in Figure 1.

ACKNOWLEDGEMENT

Authors are thankful to Prof. W.Rahman, Chairman, Department of Chemistry, for providing research facilities. Two of us (M.I.) and (M.A.K.) are thankful to C.S.I.R., New Delhi for financial assistance.

REFERENCES

1. Gasparic,J. and Skutil,J. Micro chim Acta, 4, 395, 1975.
2. Shimizu,I. J.Chromatogr. 118(1), 96, 1976.
3. Wall,R.A. J.Chromatogr. 60, 195, 1971.
4. Yoshino,Y. Kinoshita,H. and Sugiyana, Nippon Kagaku Zasshi, 86, 405, 1965.
5. Walton,H.F. in Marinsky,J.A. and Marcus,Y. (Editor), Ion exchange and solvent extraction, Marcel Dekker, New York, 4, 121, 1973.
6. Walton,H.F. and Navratil,J.D. Anal.Chem., 47, 1975.
7. Funasaka,W. Fujimura,K. and Kuriyama,S. Bunseki Kagaku (Jap.Anal.) 19, 104, 1970.
8. Rawat,J.P. and Singh,J.P. Sep.Sci., 12(3), 281, 1977.
9. Rawat,J.P. and Iqbal,M. J.Liq.Chromatogr., 3, 591 (1980).
10. Rawat,J.P. and Singh,J.P. Anal.Chem., 47, 738, 1975.