Separation Science and Technology

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

Separation of Metal Ions on Titanium(IV) Molybdate Papers

Jagdish P. Rawat[a]; S. Qasim Mujtaba[a]
[a] DEPARTMENT OF CHEMISTRY, ALIGARH MUSLIM UNIVERSITY, ALIGARH, U.P., INDIA

To cite this Article Rawat, Jagdish P. and Mujtaba, S. Qasim(1975) 'Separation of Metal Ions on Titanium(IV) Molybdate Papers', Separation Science and Technology, 10: 2, 151 — 160

To link to this Article: DOI: 10.1080/00372367508058997

URL: http://dx.doi.org/10.1080/00372367508058997

SEPARATION SCIENCE, 10(2), pp. 151–160, 1975

Separation of Metal Ions on Titanium(IV) Molybdate Papers

JAGDISH P. RAWAT and S. QASIM MUJTABA

DEPARTMENT OF CHEMISTRY
ALIGARH MUSLIM UNIVERSITY
ALIGARH (U.P), INDIA

Abstract

Papers impregnated with titanic molybdate have been used to chromatograph various cations in sodium nitrate solutions of 0.1 to 4 *M* concentrations. Various important separations are listed. The movement of the cations is proportional to the activity of the developing medium. Various plots are made to discuss the theoretical behavior of movement of cations on these papers.

INTRODUCTION

Paper chromatography has long been used for the separation of metal ions. The importance of this technique has further increased by the use of papers impregnated with ion exchangers. Lederer and Kertes (*1*) proposed an equation to determine the valency of cation by measuring the slope of a straight line obtained on plotting pH vs R_m for papers impregnated with Dowex-50. Alberti (*2*, *3*) separated alkali metals and alkaline earths using zirconium phosphate impregnated papers and studied the validity of Lederer's equation. They took the papers in Na^+ or K^+ form and then elution was made with increasing concentrations of Na^+ or K^+. A similar equation to Lederer's was applicable with the only difference that $-\log Na^+$ was taken in place of pH Qureshi, Rawat, and Sharma (*4*) studied the chromatographic behavior of 47 metal ions on titanium arsenate papers. It was shown that Lederer's equation was obeyed by the titanium arsenate papers in the sodium form if the activity of the ions was considered in place of concentration. In this paper we have summarized our studies on titanium molybdate papers in Na^+ form for various concentrations of sodium nitrate.

EXPERIMENTAL

Apparatus

Chromatography was performed on 14 × 3.5 cm Whatman No. 1 paper strips in 20 × 5 cm glass jars.

Reagents

Chemicals and solvents were of analytical grade.

Preparation of Ion-Exchange Papers

Paper strips were first impregnated in 0.25 *M* titanic chloride solution for 3 to 5 sec, and the excess of reagent was removed by placing the strips on filter sheets. The strips were allowed to dry for 15 min. at room temperature. The strips were then dipped in 0.25 *M* sodium molybdate solution for 15 sec, and the excess solution was drained off and the strips were placed over a filter sheet. The strips were converted into Na^+ form by dipping in 0.5 *M* sodium nitrate solution and then washed with demineralized water in order to remove the excess of reagents. Finally the strips were dried at room temperature before being used for chromatography.

Test Solutions

Solutions of chlorides, nitrates, or sulfates (0.1 *M*) of most of the cations were prepared in 0.1 *M* solutions of the corresponding acids. Ceric sulfate was prepared in 3 *N* H_2SO_4. Mercuric nitrate solution was prepared in 0.5 *N* HNO_3. Potassium chloride, cesium chloride, and rubidium chloride solutions, all 0.1 *M*, were prepared in water.

Detectors

Dilute yellow ammonium sulfide solution was used to detect Ag^+, Pb^{2+}, Hg^{2+}, Cd^{2+}, and Cu^{2+}. Fe^{3+}, V^{4+}, and $UO_2{}^{2+}$ were detected with aqueous potassium ferrocyanide, fresh solution of sodium cobalt nitrate was used to detect K^+, Rb^+, and Cs^+. A 0.1 % alcoholic solution of Alizarine Red S was used to detect La^{3+}, Ce^{3+}, Ce^{4+}, Zr^{4+}, Th^{4+}, Nd^{3+}, Gd^{3+}, Tm^{3+}, Eu^{3+}, Dy^{3+}, and Tb^{3+}. To detect Al^{3+}, the paper strip was dipped in aqueous Aluminon solution and then washed with ammonium acetate solution. A fresh aqueous sodium rhodizonate solution in neutral medium was used to detect Ba^{2+} and Sr^{2+}. Co^{2+} and Ni^{2+} were detected with 1 % ammonical dimethyl glyoxime solution.

TABLE 1

R_F Values of Metal Ions on Titanium Molybdate Papers with Varying Concentrations of Sodium Nitrate as Eluent

	Concentrations (*M*)						
Cations	0.1	0.5	1.0	1.5	2.0	3.0	4.0
Ag^+	—	0.06	0.11	0.15	0.19	0.27	—
K^+	0.17	0.41	0.62	0.68	0.72	0.83	0.83
Rb^+	—	0.30	0.45	0.50	0.59	0.69	—
CS^+	—	0.13	0.25	0.30	0.38	0.46	—
Hg_2^{2+}	0.13	0.19	0.21	0.29	0.30	0.46	0.47
Pb^{2+}	0.02	0.04	0.08	0.10	0.15	0.25	0.32
Cd^{2+}	—	0.76	0.80	0.90	0.95	—	—
Cu^{2+}	0.29	0.59	0.75	0.80	0.97	0.97	—
Co^{2+}	0.59	0.68	0.76	0.84	0.90	0.90	—
Ni^{2+}	0.10	0.44	0.76	0.86	0.92	—	—
Fe^{2+}	0.62	0.72	0.80	0.84	0.90	—	—
Fe^{3+}	0.04	0.06	0.10	0.11	0.17	0.24	0.25
Ce^{3+}	0.12	0.19	0.32	0.40	0.50	—	—
Al^{3+}	0.58	0.64	0.69	0.80	0.90	0.95	0.95
Ba^{2+}	0.14	0.21	0.40	0.50	0.65	0.80	—
Sr^{2+}	0.22	0.51	0.68	0.83	0.95	0.97	—
Nd^{3+}	0.04	0.09	0.18	0.22	0.25	—	—
La^{3+}	0.09	0.12	0.60	0.80	0.86	—	—
Dy^{3+}	0.08	0.15	0.18	0.24	0.24	—	—
Tm^{3+}	0.20	0.26	0.31	0.35	0.36	—	—
Gd^{3+}	0.07	0.20	0.32	0.41	0.42	—	—
Tb^{3+}	—	0.09	0.38	0.75	0.84	0.90	—
UO_2^{2+}	0.08	0.14	0.18	0.20	0.24	—	—
VO^{2+}	—	0.06	0.11	0.21	0.29	0.40	—
Ce^{4+}	—	0.02	0.06	0.13	0.30	0.75	1.0
Th^{4+}	0.10	0.13	0.16	0.16	0.17	—	—
Zr^{4+}	0.00	0.00	0.00	0.00	0.00	—	—
Hf^{4+}	0.00	0.00	0.00	0.00	—	—	—

PROCEDURE

The chromatograms were developed as reported earlier (*5*). As eluent we used sodium nitrate solutions at concentrations ranging from 0.1 to 4 *M*.

RESULTS

Table 1 describes the R_F values of the metal ions studied. Various important separations were achieved in different systems. These are sum-

TABLE 2

Separations Achieved Experimently on Titanium Molybdate Papers (25 min)

	Separation achieved	Solvent, $NaNO_3$ (*M*)
1.	Cs^+(0.06)—K^+(0.35–0.55)	0.1
2.	Fe^{3+}(0.2)—Co^{2+}(0.84)	0.1
3.	Fe^{3+}(0.2)—Al^{3+}(0.54)	0.1
4.	Fe^{3+}(0.21)—Fe^{2+}(0.4–0.55)	0.1
5.	Pb^{2+}(0.0–0.05)—Ba^{2+}(0.17–0.38) —Sr^{2+}(0.65–0.75)	0.5
6.	Fe^{3+}(0.0–0.15)—Ni^{2+}(0.74–0.85)	0.5
7.	Hg_2^{2+}(0.0–0.05)—Fe^{2+}(0.72–0.84)	0.5
8.	Ag^+(0.0–0.20)—Cd^{2+}(0.88–0.98)	0.5
9.	Hg_2^{2+}(0.0–0.06)—Cd^{2+}(0.80–0.94)	0.5
10.	Pb^{2+}(0–0.05)—Cd^{2+}(0.80–0.93)	0.5
11.	Fe^{3+}(0–0.18)—Co^{2+}(0.65–0.80)	0.5
12.	Cu^{2+}(0.25–0.50)—Fe^{2+}(0.72–0.85)	0.5
13.	Pb^{2+}(0–0.12)—Ni^{2+}(0.75–0.95)	0.5
14.	Fe^{3+}(0–0.15)—Sr^{2+}(0.66–0.72)	0.5
15.	Fe^{3+}(0–0.18)—Cd^{2+}(0.70–0.94)	0.5
16.	Hg_2^{2+}(0–0.08)—Ni^{2+}(0.78–0.90)	0.5
17.	Ag^+(0.0–0.18)—Ni^{2+}(0.78–0.86)	0.5
18.	Pb^{2+}(0.0–0.08)—Co^{2+}(0.75–0.88)	0.5
19.	Pb^{2+}(0.0–0.08)—Fe^{2+}(0.65–0.82)	0.5
20.	Pb^{2+}(0.0–0.08)—Al^{3+}(0.76–0.90)	0.5
21.	Ba^{2+}(0.35–0.45)—Sr^{2+}(0.85–0.90)	1.0
22.	Hg_2^{2+}(0.0–0.08)—Cu^{2+}(0.76–0.88)	1.0
23.	Hg_2^{2+}(0.0–0.08)—Co^{2+}(0.82–0.96)	1.0
24.	Ag^+(0.0–0.02)—Cu^{2+}(0.68–0.82)	1.0
25.	Fe^{3+}(0.0–0.20)—Cu^{2+}(0.60–0.75)	1.0
26.	Pb^{2+}(0.0–0.18)—Cu^{2+}(0.75–0.80)	1.0
27.	VO^{2+}(0.21)—Fe^{2+}(0.82–1.0)	1.5
28.	Zr^{4+}(0.00) from numerous metal ions	2.0
29.	Hf^{4+}(0.00) from numerous metal ions	2.0

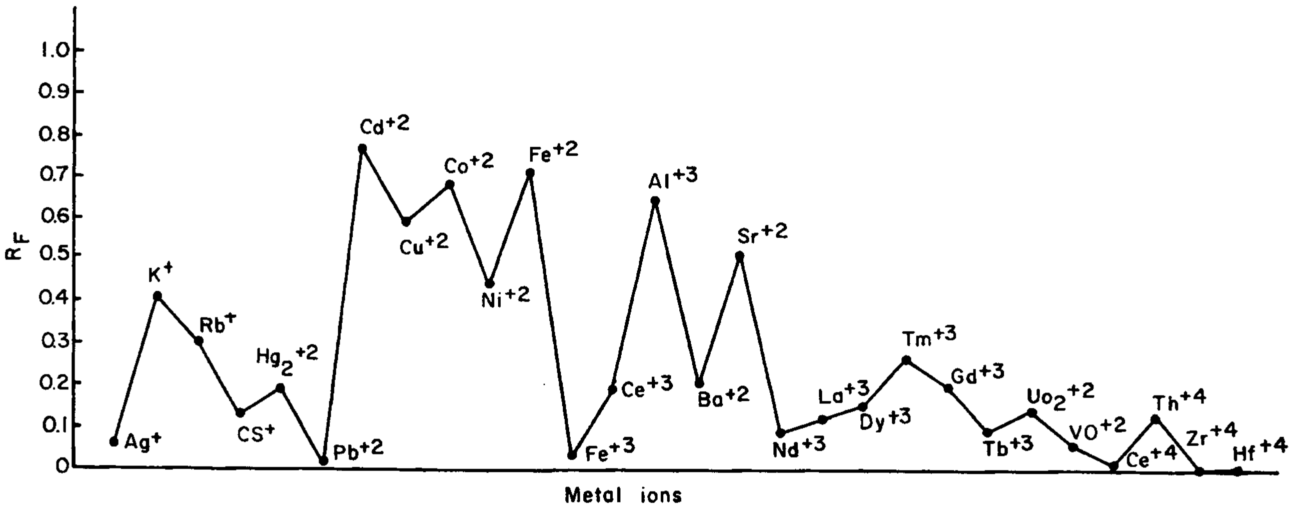

FIG. 1. R_F values of metal ions in 0.5 *M* $NaNO_3$.

TABLE 3

R_m Values of Some Cations as Function of a_{Na^+}

	R_m Values					
$-\log a_{Na^+}$	K^+	Rb^+	Cs^+	Ag^+	Ni^{2+}	La^{3+}
1.1681	0.6887	1.0048	—	1.6908	0.9542	1.0048
0.4868	0.1581	0.3680	0.8256	1.1949	0.1047	0.8653
0.2168	0.2126	0.1047	0.4772	0.9080	−0.5006	−0.1761
0.0516	−0.3274	0.00	0.3680	0.7533	−0.8201	−0.6021
−0.0630	−0.4101	−0.1581	0.2126	0.6297	−1.0607	−0.8201
−0.2340	−0.6021	−0.3294	—	—	—	—

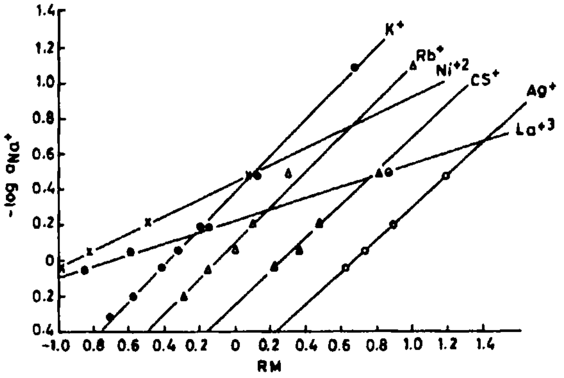

FIG. 2. Plot of $-\log a_{Na^+}$ vs R_m.

marized in Table 2. A large number of separations were obtained in 0.5 *M* $NaNO_3$. R_F values of metal ions in this system are plotted in Fig. 1. Cations having tailing are shown by dotted lines. In order to study the effect of the counterions concentration on R_m valves, and to check the validity of Lederer's equation for titanium molybdate papers, R_m values were plotted as a function of $-\log a_{Na^+}$. For this study we have chosen only those cations which gave compact spots. The results are given in Table 3 and Fig. 2.

DISCUSSION

Results from Table 1 show that titanium molybdate is a selective ion exchanger, and papers impregnated with titanium molybdate give selective

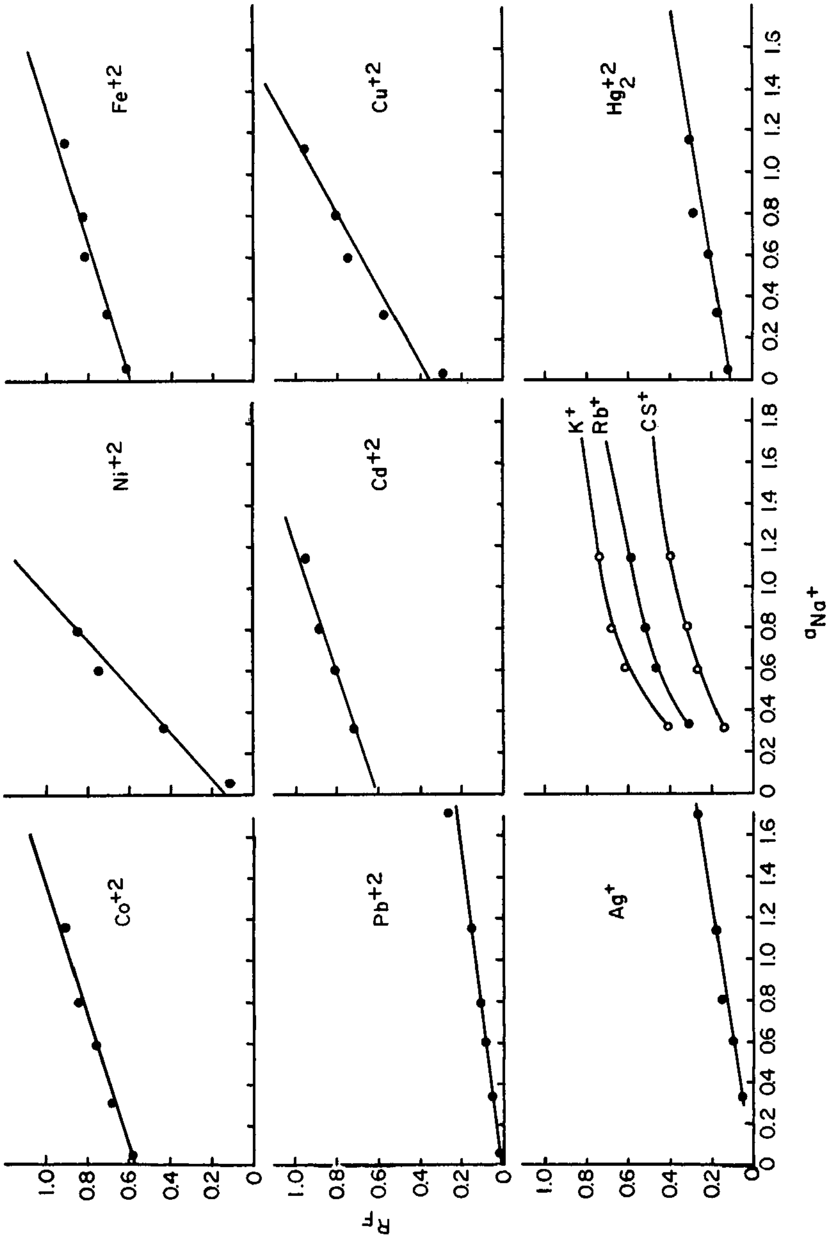

FIG. 3. Plots of R_F vs a_{Na^+}.

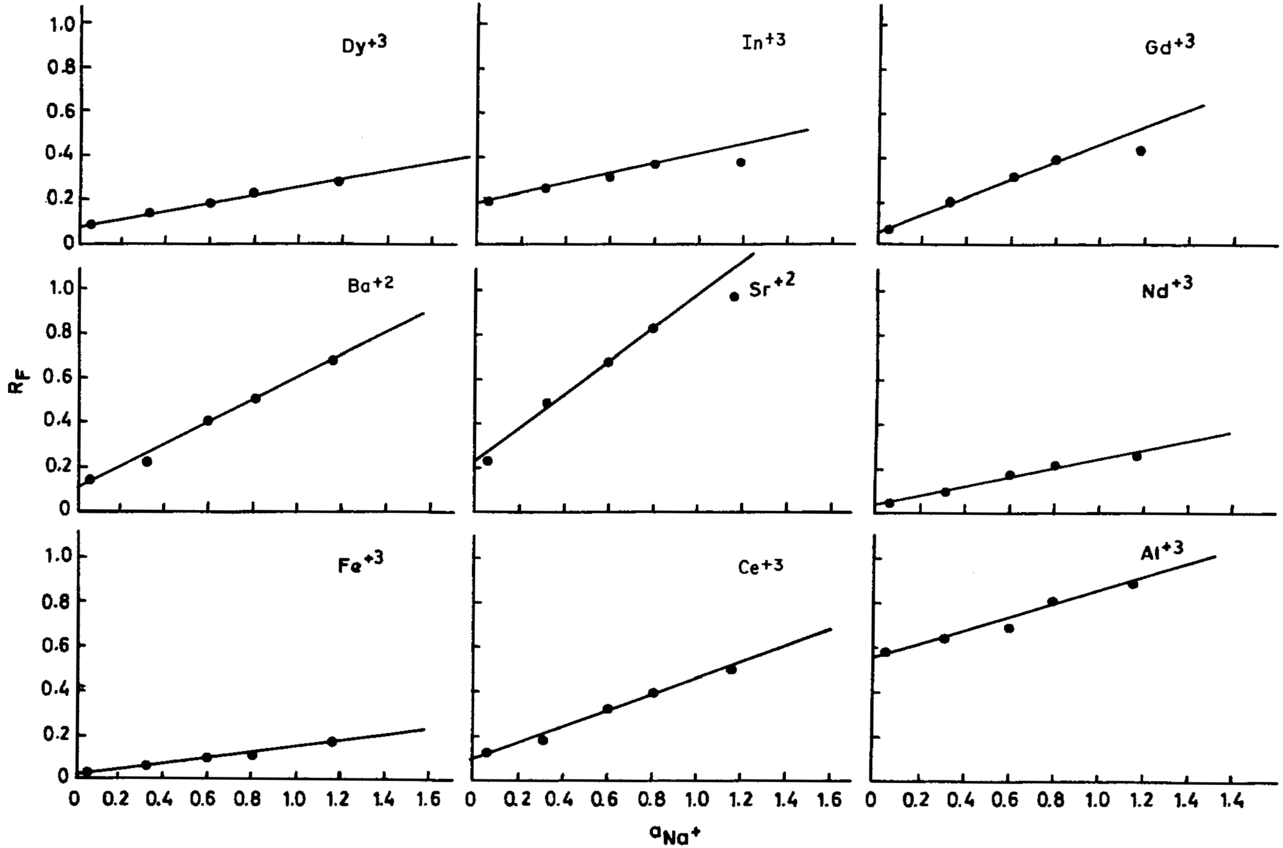

FIG. 4. Plots of R_F vs a_{Na^+}.

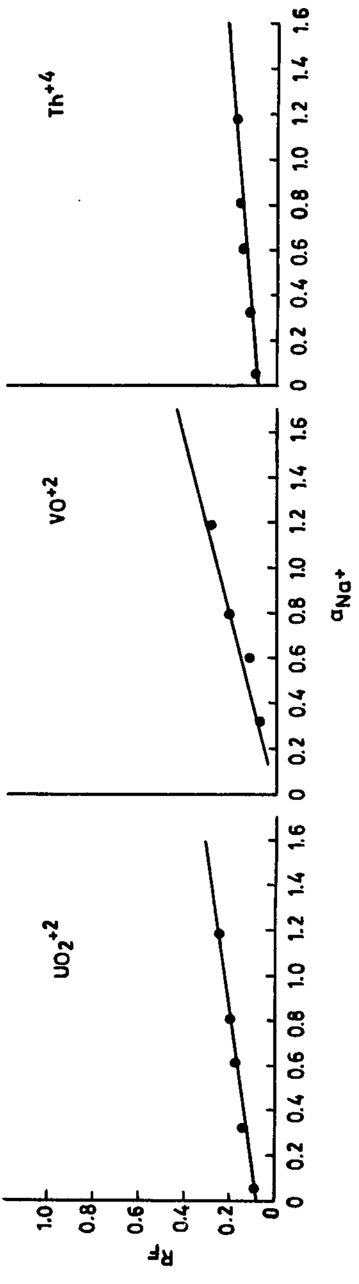

FIG. 5. Plots of R_F vs a_{Na^+}.

separations in simple aqueous $NaNO_3$ solutions. The ion exchange process plays the primary role in the chromatography of metal ions using these papers. R_F value increases as the activity of the developing solution increases. If we plot R_F of various metal ions against the activity of the developing solution, straight lines are obtained in most of the cases (Figs. 3–5). This supports the theory that the exchange of metal ions by Na^+ ions increases as the activity (or concentration) of Na^+ ions increases.

In order to see the validity of Lederer's equation, $n\text{pH} = R_m + \text{constant}$, we have plotted $-\log a_{Na^+}$ against R_m for certain metal ions which gave compact spots. The slope of these lines is equal to the valency of these cations, and the equation is $-n \log a_{Na^+} = R_m + \text{cost.}$ R_F values of metal ions are also related to their distribution coefficients on titanium molybdate exchange (*6*). For higher distribution coefficients, we observe lower R_F values. This behavior is expected because when the distribution coefficient is higher, then the ion is strongly held by the ion exchanger and is less easily allowed to move further, giving a lower value of R_F. This trend is confirmed by noting the R_F values of some common metal ions in 0.5 *M* sodium nitrate and their distribution coefficient in water. The following trends were obtained:

R_F value: $Pb^{2+} > Ba^{2+} > K^+ > Sr^{2+} > Cu^{2+} > Al^{3+} > Co^{2+} > Cd^{2+}$
K_d values: $Pb^{2+} < Ba^{2+} < K^+ < Sr^{2+} < Al^{3+} < Cu^{2+} < Co^{2+} < Cd^{2+}$

Acknowledgment

The authors are grateful to Prof. W. Rahman for research facilities.

REFERENCES

1. M. Lederer and S. Kertes, *Anal. Chim. Acta*, *15*, 226 (1956).
2. G. Alberti, F. Dobici, and G. Grassini, *J. Chromatogr.*, *8*, 103 (1962).
3. G. Alberti and G. Grassini, *Ibid.*, *4*, 83 (1960).
4. M. Qureshi, J. P. Rawat, and V. Sharma, *Talanta*, *20*, 266 (1973).
5. M. Qureshi and J. P. Rawat, *Separ. Sci.*, *7*, 297 (1972).
6. M. Qureshi and H. S. Rathore, *J. Chem. Soc.*, *A*, 2516 (1969).

Received by editor June 24, 1974