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

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To cite this Article Mehta, V. P. and Khopkar, S. M.(1982) 'Cation Exchange Chromatographic Elution and Separation of Rubidium', Separation Science and Technology, 17: 3, 495 — 505

To link to this Article: DOI: 10.1080/01496398208068554

URL: http://dx.doi.org/10.1080/01496398208068554

SEPARATION SCIENCE AND TECHNOLOGY, 17(3), pp. 495–505, 1982

NOTE

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Abstract

The systematic cation exchange chromatographic separation of rubidium on Dowex 50W-X8 was carried out with mineral acids and their salts as eluants. A selectivity scale for various eluants in terms of the elution constant was devised. Rubidium was separated from a large number of elements in binary mixtures by the process of gradient or selective elutions or selective sorption. The noteworthy feature of the method is the sequential separation of rubidium from alkali as well as alkaline earth elements.

INTRODUCTION

Systematic cation exchange chromatographic studies of rubidium on Dowex 50W-X8 are lacking. Although some work was carried out on the separation of rubidium from other alkali metals (*1*), inorganic ion exchangers were extensively used in most of such separations. Since such studies were carried out with radioactive elements or studies were effected at higher temperature, synthetic organic resins could not be used for such a purpose.

Work on Bio Rad AG 50W-X8 has shown that rubidium has a very high distribution coefficient in dilute mineral acids (*2, 3*) which in turn facilitated the separation of rubidum from sodium and cesium (*4*). In the case of its separation from potassium on Wofatit KPS 16X, it was necessary to use large volumes of eluants (*5*) as it was strongly bound to the resin. Its separation from cesium was possible in smaller ratios on Cationite KU-1 (*6*). For the first time, mixed solvent systems involving phenol, methanol, and hydrochloric acid were employed for the separation of rubidium from potassium and cesium (*7*). Some attempts to explore sodium hydroxide (*8*) and EDTA as the eluant (*9*) were made in the past. The interferences of other alkali metals during ion-exchange separations (*10*) were detected in flame emission methods. However, some methods permitted the separation of rubidium from other alkali metals (*11, 12*).

This paper presents systematic investigations on the cation-exchange chromatographic separation of rubidium on Dowex 50W-X8. Various mineral acids and their salts were used as eluants. It was possible to separate rubidium from a large number of elements.

EXPERIMENTAL

Apparatus and Reagents

The ion-exchange column (1.4 × 20 cm) was similar to the one described earlier (*13*). An automatic fraction collector (Emnvee Eng., India) fitted with a 25-mL siphon and a digital flame photometer (Associated Instrument Manufacturers India Ltd., India) was used. A stock solution of rubidium was prepared by dissolving 1.767 g of rubidium chloride (Riedel Hahn, Germany) in 250 mL of distilled water and was standardized (*14*). It contained 5.0 mg/mL of rubidium. Dowex 50W-X8 (Dow Chemical Co., Midland, Michigan), 20–50 mesh, H^+ form, was used.

Procedure

An aliquot of the solution, containing 5.0 mg of rubidium, was sorbed on the column. After flushing the column with 25 mL of distilled water, elutions were carried out with various eluants (Table 1, Figs. 1 and 2). The effluent lot was collected in 25 mL fractions. Rubidium from each fraction was determined by flame emission techniques. With mineral acid as an eluant, the fractions were evaporated to dryness before the determination of rubidium.

RESULTS AND DISCUSSION

The peak elution volume was ascertained from elution analysis (Table 1). From peak elution volume, the elution constant (E) and weight and volume distribution coefficient (D_w and D_v) were calculated using the relationship (*13, 15*)

$$E = dA/(V_{\max} - \gamma) \quad (1)$$

$$D_v = 1/E \quad (2)$$

$$= \rho D_w \quad (3)$$

TABLE 1

Cation Exchange Behavior of Rubidium on Dowex 50W-X8 (H^+ form)

Eluant	M	Peak elution volume, V_{max} (mL)	Total volume of eluant V_t (mL)	Elution constant (E)	Volume distribution coefficient D_v
HCl	0.5	375	450	0.086	11.62
	1	175	225	0.195	5.13
	2	100	150	0.374	2.67
	3	75	125	0.537	1.86
H_2SO_4	0.5	225	275[a]	0.149	6.73
	1	100	200	0.374	2.67
	1.5	75	125	0.537	1.86
HNO_3	0.5	300	400	0.109	9.17
	1	150	200	0.232	4.30
	2	75	150	0.537	1.86
	3	50	150	0.951	1.05
NaCl	1	125	175	0.287	3.49
	2	75	200	0.537	1.86
	3	50	175	0.951	1.05
$NaNO_3$	2	75	150	0.537	1.86
	3	50	150	0.951	1.05
Na_2SO_4	0.5	100	175	0.374	2.67
	1	75	150	0.537	1.86
	2	50	125	0.951	1.05
NH_4Cl	1	100	150	0.374	2.67
	2	75	150	0.537	1.86
	3	50	125	0.951	1.05
NH_4NO_3	1	75	150	0.537	1.86
$(NH_4)_2SO_4$	0.5	100	150	0.374	2.67
	1	75	150	0.537	1.86
	2	50	125	0.951	1.05
CH_3COONH_4	1	100	200	0.374	2.67
	2	75	125	0.537	1.86
	3	75	150	0.537	1.86

[a] Recoveries were 100% in all cases except that involving 0.5 M sulfuric acid where the recovery was 94.5%.

where d = column height, A = area of cross section, V_{max} = peak elution volume in mL, γ = free column volume in mL, E = elution constant, D_v = volume or bed distribution coefficient, D_w = weight distribution coefficient, and ρ = density of resin in g/mL.

It is seen that the smaller the peak elution volume (V_{max}), the larger will be

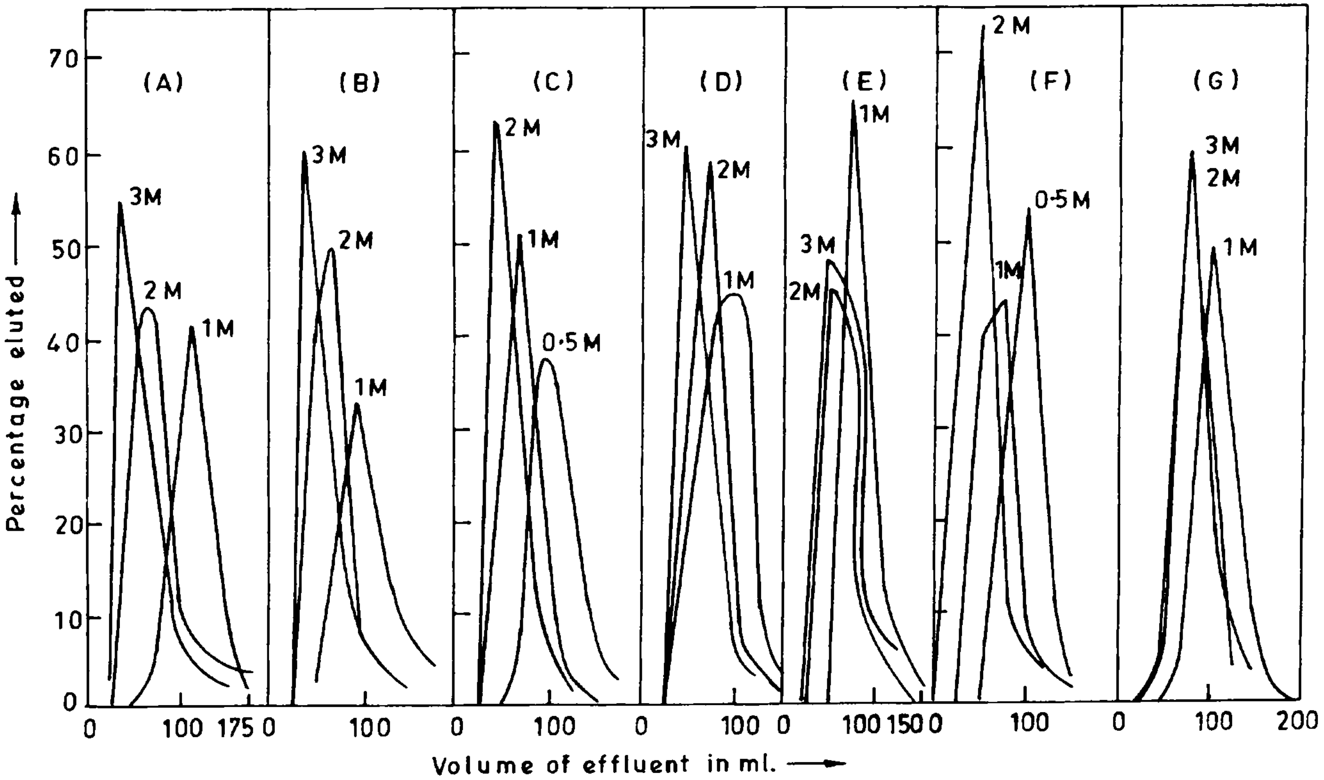

FIG. 1. Cation exchange behavior of rubidium with salts as eluants. (A) Sodium chloride, (B) sodium nitrate, (C) sodium sulfate, (D) ammonium chloride, (E) ammonium nitrate, (F) ammonium sulfate, and (G) ammonium acetate. Flow rate = 1 mL/min. Mesh size = 20–50.

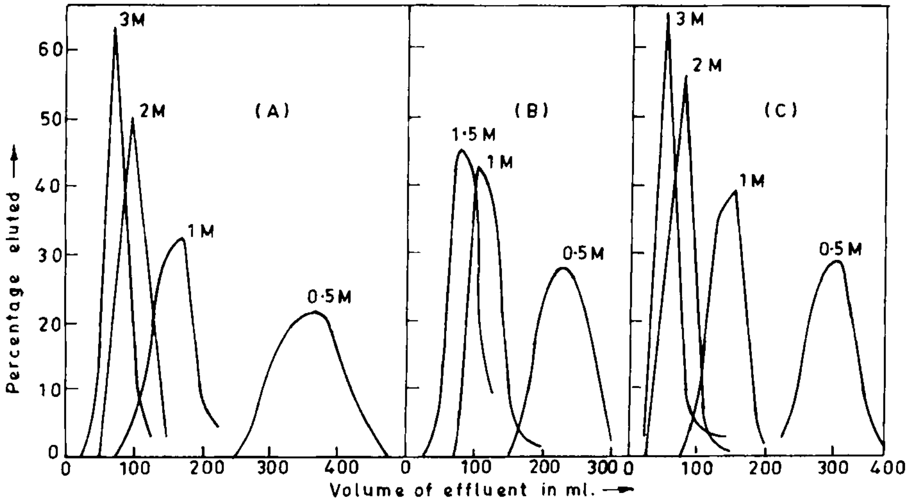

FIG. 2. Cation exchange behavior of rubidium with mineral acids as eluants. (A) Hydrochloric acid, (B) sulfuric acid, and (C) nitric acid. Flow rate = 1 mL/min. Mesh size = 20–50.

the magnitude of elution constant (*E*). In other words, eluants with a larger value of the elution constant or a smaller value of the volume distribution coefficient are considered to be better.

Hence, on the basis of the magnitude of the elution constant, the eluants can be arranged in the decreasing order of their efficiency, selectivity scale as $Na_2SO_4 \geq (NH_4)_2SO_4 \geq NH_4NO_3 > NaNO_3 \geq NH_4Cl \geq CH_3COONH_4 > NaCl > HNO_3 > HCl > H_2SO_4$. This indicates that mineral acids are less efficient than their corresponding salts as the eluants for rubidium on Dowex 50W-X8.

The study of other eluants (such organic acids as malonic, citric, or tartaric acid and mixtures such as methanol, ethanol, dioxane, acetone, or tetrahydrofuran with 1 *M* hydrochloric acid) has shown that they were poor eluants for rubidium. Therefore, throughout the work, especially in separations, 1 *M* sodium chloride or 1 *M* hydrochloric was used as eluants as they had a large elution constant. Since for them the peak elution volume was as small as 125–175 mL, the time required for the complete elution was small.

ION-EXCHANGE SEPARATIONS

Selective Elution of Rubidium Later with Specific Eluants

From the selectivity scale given above it can be seen that certain eluants are poor eluants for rubidium; however, some of them are efficient for ions

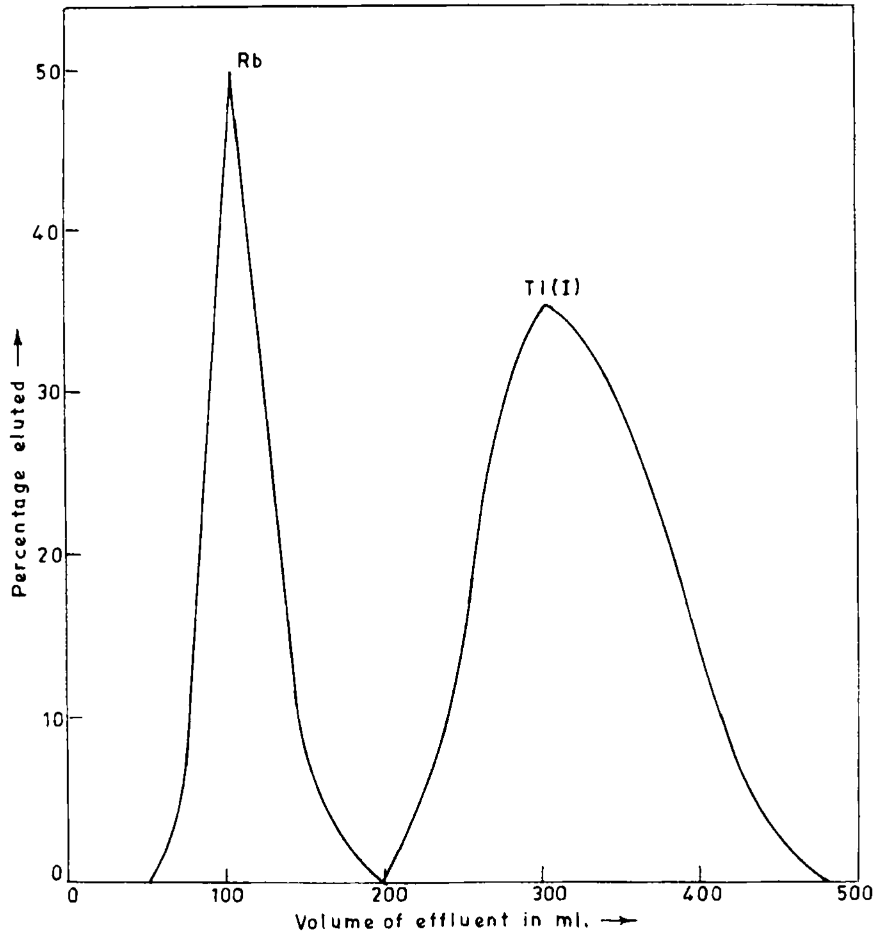

FIG. 3. Sequential separation of Rb from Tl(I) on Dowex 50W-X8 with 1 *M* ammonium acetate. Column = 1.4 × 20 cm. Flow rate = 1 mL/min. Mesh size = 20–50.

such as cadmium, mercury(II), bismuth(III), uranium(VI), and vanadium(IV). The process of gradient elution involves the utilization of the same eluant in varying concentrations. Thus, after passing the mixture of the aforesaid ions with rubidium on the column, it was possible to selectively elute these foreign ions with 0.5 *M* hydrochloric acid followed by elution of rubidium with 1 *M* hydrochloric acid. Similarly, those elutions which involve the use of more than one eluant were termed "selective elutions." For instance, silver and yttrium were separated from rubidium by the process of selective elution. Thus, silver was eluted with 0.5 *M* sulfuric acid and yttrium was eluted with 0.5 *M* ammonium acetate, whereas rubidium was subsequently eluted with 1 *M* hydrochloric acid. The separation of copper(II) or cerium(III) from rubidium was also possible by selective elution of copper(II) with 5% malonic acid at pH 4.8 or elution of cerium(III) with 5% citric acid at pH 2.7 followed by the elution of rubidium with 1 *M* hydrochloric acid (Table 2).

Selective Elution of Rubidium First with Specific Eluants

When the mixture of rubidium with foreign ions such as scandium and lanthanon was passed on the column, all were sorbed by the resin. Hydrochloric acid (1 *M*) was an efficient eluant for rubidium but not for these ions, hence rubidium was eluted first with 1 *M* hydrochloric acid followed by the elution of other ions with 4 *M* hydrochloric acid. It was separated from cobalt by its elution with 1 *M* nitric acid and cobalt was eluted with 4 *M* nitric acid.

TABLE 2

Ion Exchange Separations (Rb added = 5 mg; flow rate = 1 mL/min)

Foreign ion	Amount added (mg)
Cd	6.3
Hg(II)	5.5
Bi	5.0
U(VI)	5.1
V(IV)	5.0
Ag	5.2[a]
Y	5.0
Cu(II)	10.0
Ce(VI)	8.0
Sc	5.2
Ln	4 to 6
Co	4.8
Tl(I)	7.0
Ti(IV)	4.9
Zr(IV)	4.7
Hf(IV)	4.0
Sb(III)	5.0
$Cr_2O_7^{2-}$	10.0
MoO_4^{2-}	6.3
TeO_3^{2-}	20.0
AsO_3^{3-}	13.6
VO_3^-	10.1

[a] Recoveries were 100% in all cases except for silver, where the recovery was 91%.

The composite elution curve for the separation of rubidium and thallium(I) with 1 *M* ammonium acetate as an eluant is shown in Fig. 3. In the first 200 mL, the rubidium was collected; thallium was recovered from the next 250 mL of the eluant.

Separation of Rubidium by Selective Sorption

The process of selective sorption involves the sorption of definite ions under a set of experimental conditions. For instance, if a mixture of cation along with negatively charged species is passed through the cation-exchange column, only the former is selectively retained by the resin. In such a process the anionic species is not retained by the resin. This facilitated separation.

Titanium(IV), zirconium(IV), hafnium(IV), and antimony(III) form anionic citrate complexes with 5% citric acid at pH 2.7. On passing them on the column with rubidium, only rubidium was sorbed on the column. After washing the column with water, rubidium was eluted with 1 *M* hydrochloric acid. Similarly, anions such as dichromate, molybdate, tellurite, arsenite, and vanadate were separated by the process of selective sorption.

Separation of Rubidium from Alkaline Earths

The order of sorption for alkaline earths on Dowex 50W-X8 was $Be^{2+} > Mg^{2+} > Rb^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$.

This was exploited for sequential separation. Thus beryllium and magnesium, which were weakly bound to the resin, were eluted with 0.5 *M* hydrochloric acid; rubidium was then eluted with 1 *M* sodium chloride and finally calcium or strontium or barium was eluted with 4 *M* hydrochloric acid (Fig. 4).

Separation of Rubidium from Other Alkali Elements

The affinity series for alkali metals on Dowex 50W-X8 (*16*) is $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$.

Hence, with 0.5 *M* hydrochloric acid, lithium and sodium were eluted, then potassium was eluted with a mixture of ethanol and 1 *M* hydrochloric acid in a 1:1 ratio. Finally, rubidium was eluted with 1 *M* hydrochloric acid or 1 *M* sodium chloride (Fig. 5). An attempt to separate rubidium from cesium was not successful.

In all these separations involving gradient or selective elution or selective sorption, the flow rate was maintained as 1 mL/min. The control of flow rate

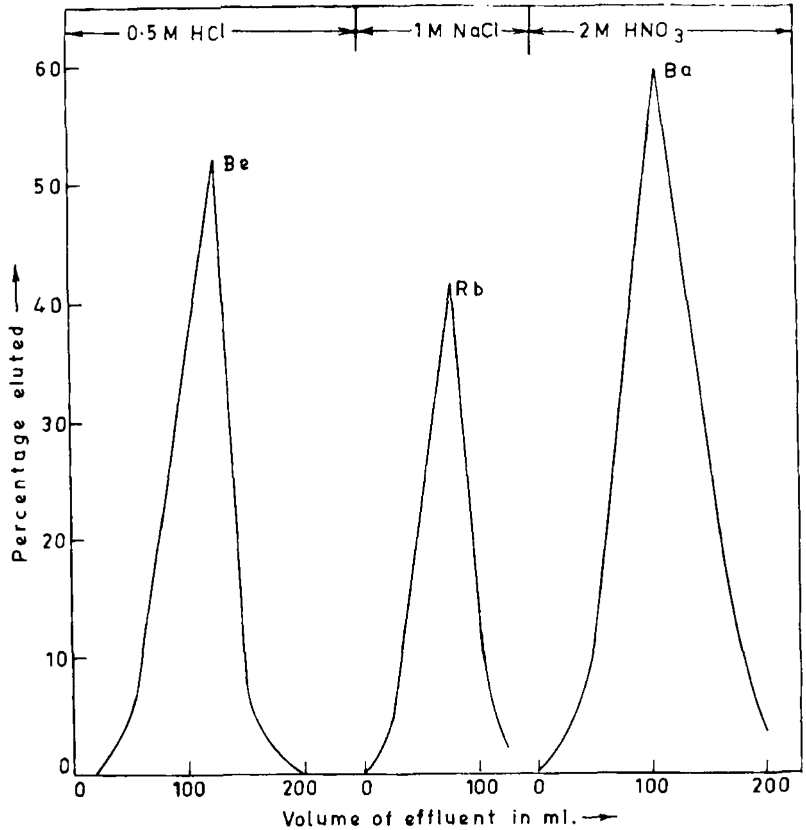

FIG. 4. Sequential separation of Be, Rb, and Ba on Dowex 50W-X8. Column = 1.4 × 20 cm. Flow rate = 1 mL/min. Mesh size = 20–50.

was not critical. However, in order to maintain better equilibrium, it is necessary to employ a uniform flow rate during separations. The alkali and alkaline earth elements were determined by flame photometer. The operation of separation and determination needed just 4 h. The results are reproducible to ±1.5%.

The separation of rubidium from alkali and alkaline earth elements is important because they are associated with each other. The separation of rubidium from mercury(II), uranium(VI), and bismuth(III), which are associated in fission products, is also useful.

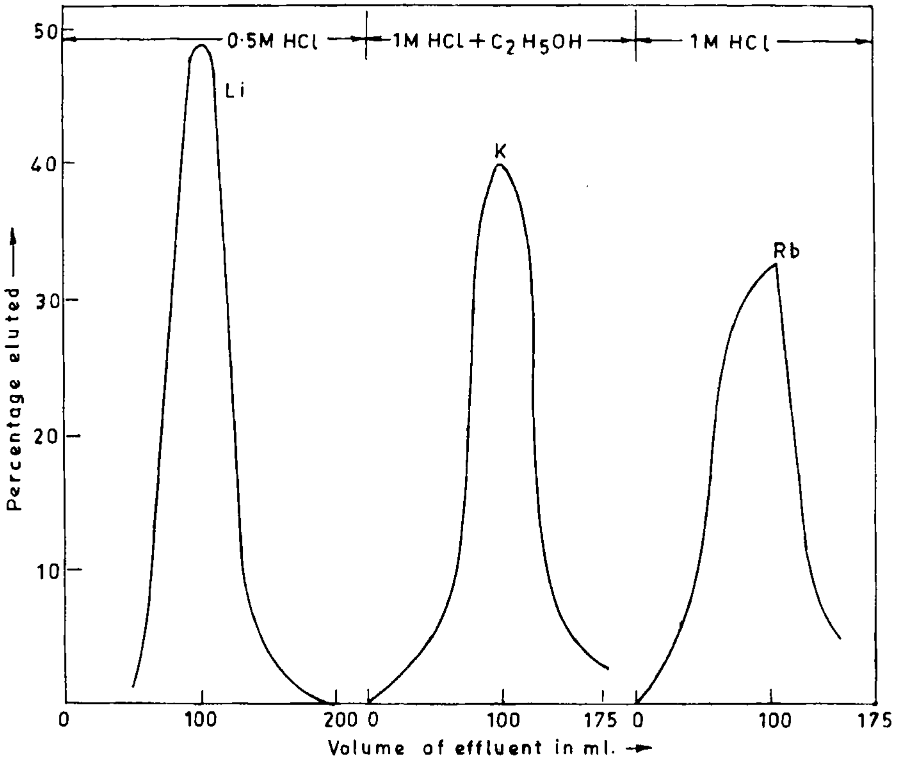

FIG. 5. Sequential separation of Li, K, and Rb on Dowex 50W-X8. Column = 1.4 × 20 cm. Flow rate = 1 mL/min. Mesh size = 20–50.

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Received by editor February 18, 1981