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Note

Separation of halide anions by gel chromatography

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In recent years, gel chromatography has been applied to the investigation of small inorganic compounds¹. The gel chromatographic behaviour of the halide anions has been investigated. Saunders and Pecsok² determined the K_d values of F^- , Br^- , Cl^- and I^- on a Bio-Gel P-2 column. Egan³ reported the separations of F^- and Cl^- on Bio-Gel P-2, Bio-Gel P-100 and Sephadex G-10 gel columns. Brown and Chitumbo⁴ also reported the selectivity of cellulose gels for F^- , Cl^- , Br^- and I^- , using pure water as the eluent. According to Neddermeyer and Rogers⁵, the volume of an inorganic electrolyte eluted, such as sodium chloride, increased with increase in sample concentration, and all the elution curves were unsymmetrical with a leading edge when pure water was used as the eluent. Moreover, the elution volume of the halide anions varied with different counter cations². When water is used as the eluent, it does not seem to effect the complete separation of mixed halide anions.

This paper describes the separation of fluoride, chloride, bromide and iodide anions on a Sephadex G-15 column and the effect of the counter cations on the elution curves. Solutions of sodium chloride and sodium nitrate were used as background electrolytes.

EXPERIMENTAL

Sample solution

All reagents used were of guaranteed grade from Wako, Osaka, Japan, unless otherwise stated. Sample solutions of fluoride, chloride, bromide and iodide ions were prepared by dissolving their metal salts in the same solution as the eluent. Solutions of Blue Dextran 2000 (Pharmacia, Uppsala, Sweden, 0.2%) used as a standard of K_{av} were prepared in a similar manner to that described above.

Eluents

The eluents used were 0.1 *M* sodium chloride and 0.1 *M* sodium nitrate solutions.

Column

Sephadex G-15 (Pharmacia, dry particle size 40–120 μm), which is a cross-linked dextran gel, was used as the bed material. The dry powder was suspended in an eluent and allowed to swell for 2 days. A slurry of the prepared gel was poured into

a 1.5×45 cm glass tube, with a porous polystyrene disc at the bottom. A small disc of filter-paper served to reduce disturbances at the top of the gel bed. After packing, 500 ml of the eluent were passed through the column in order to settle the gel bed.

Procedure for elution

A 1-ml volume of the sample solution was placed on the top of the bed just as the last few drops of the eluent soaked into the bed. The sample solution was allowed to soak into the gel and then washed in further with two small portions (*ca.* 0.5 ml) of the eluent, and the eluent vessel was attached to the top of the bed and the elution proceeded in the usual manner. The effluent was collected in fractions of *ca.* 1 ml with a drop-count fraction collector. Some fractions were chosen arbitrarily and their volumes were measured so that the fraction volume could be determined.

Concentrations of chloride, bromide and iodide anions were determined by argentimetric titration. Fluoride anion⁶ was determined colorimetrically at 620 nm with the use of Dotite Alfusone (La-alizarin complexone chelate + buffer; Dojine Co., Kumamoto, Japan), each fraction having previously been diluted with a suitable amount of water. The concentration of Blue Dextran was determined colorimetrically at 620 nm.

Calculation of the K_{uv} value

The K_{uv} value is defined by the equation⁷

$$K_{uv} = (V_e - V_0)/(V_t - V_0)$$

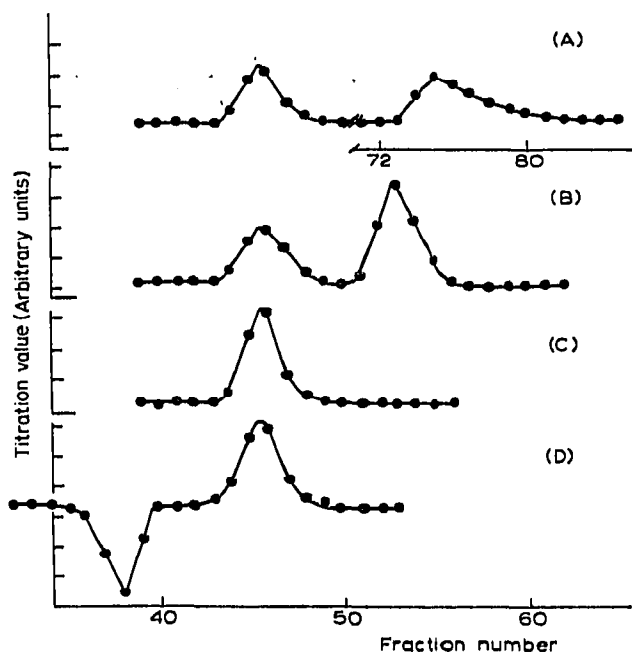


Fig. 1. Elution curves of halide anions chromatographed individually. Column: 1.5×40.6 cm. Eluent: 0.1 M NaCl solution. Sample: 1 ml of 0.05 M each of F^- , Cl^- , Br^- and I^- (sodium salts) in 0.1 M NaCl solution: (A) NaI; (B) NaBr; (C) NaCl; (D) NaF. One fraction = 1.13 ml. $V_0 = 26.30$ ml.

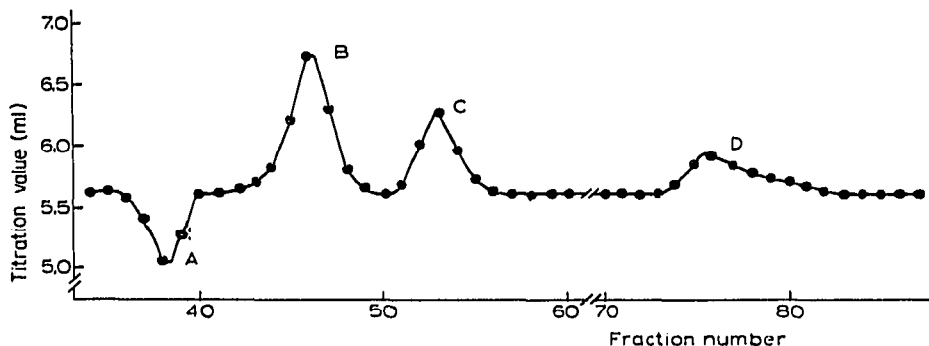


Fig. 2. Elution curve of a mixture of F^- , Br^- and I^- . Column: 1.5×40.6 cm. Eluent: $0.1 M$ NaCl solution. Sample: 1 ml of a mixture containing $0.05 M$ each of I^- , Br^- and F^- (sodium salts) in $0.1 M$ NaCl solution. Peaks: A = F^- ; C = Br^- ; D = I^- . One fraction = 1.31 ml. The second peak (B) is the Cl^- peak caused by the exclusion of the eluting agent from I^- , Br^- and F^- species zones.

where V_t is the total bed volume, V_0 is the void volume outside the gel particles and V_e is the elution volume.

RESULTS AND DISCUSSION

0.1 M Sodium chloride solution as the eluent

Elution profiles of the halide anions, which were chromatographed individually on Sephadex G-15 columns, are shown in Fig. 1. The K_{av} values of the first peaks for sodium iodide (A) and sodium bromide (B) and of the positive peak for sodium fluoride (D) were found to be 0.56, which is virtually identical with that of chloride ion (C).

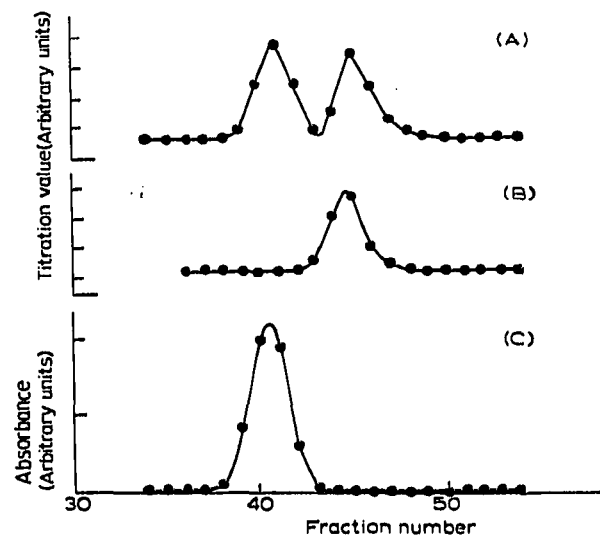


Fig. 3. Effect of Mg^{2+} and Na^+ counter cations. Column: 1.5×40.6 cm. Eluent: $0.1 M$ NaCl solution. Sample: (A) and (C) 1 ml of a mixture of $0.1 M$ NaCl and $0.025 M$ $MgCl_2$; (B) 1 ml of $0.15 M$ NaCl solution. Measurement: (A) and (B) argentimetry; (C) atomic absorption spectrophotometry (at 285.2 nm). One fraction = 1.15 ml.

TABLE I

 K_{av} VALUES OF THE HALIDE ANIONS CHROMATOGRAPHED INDIVIDUALLY

Column: 1.5×40.4 cm. Eluent: $0.1 M$ NaNO_3 solution. Sample: 1 ml of each halide anion in $0.1 M$ NaNO_3 solution.

Anion

F^-	Cl^-	Br^-	I^-
0.35	0.50	0.66	1.09

The second peaks for sodium iodide (A) and sodium bromide (B) show the corresponding halide anions in the sample solutions. The negative peak for sodium fluoride (D) corresponds to the fluoride anion.

Fig. 2 shows an elution curve of a mixture of fluoride, bromide and iodide anions. The four peaks A, B, C and D in Fig. 2 correspond to fluoride, chloride, bromide and iodide anions, respectively. The chloride anion peak is a pseudo-peak caused by the exclusion of the eluting agent from the sample zones⁸. The separation of fluoride, bromide and iodide anions is satisfactory. However, quantitative recoveries for bromide and iodide anions were not obtained because of coprecipitation with silver chloride. The determination of fluoride anion could not be achieved quantitatively by the colorimetric method, probably because of interference with the chloride anion in the eluent.

Fig. 3 shows the effect of a counter cation on the elution curve. The first peak in Fig. 3A corresponds to magnesium chloride and the second peak to sodium chloride, which is excluded from the magnesium chloride zone. Therefore, in order to achieve the quantitative determination of these halides, the eluent should not contain halide anions.

0.1 M Sodium nitrate solution as the eluent

Table I shows the K_{av} values of each halide anion. Fig. 4 shows the elution curve of a mixture of the halides; the halides were separated completely.

Fig. 5 shows the elution curves for sodium chloride–magnesium chloride and sodium chloride–calcium chloride mixtures. A single chloride anion peak was obtained and counter cations showed no interferences. The peaks for fluoride, bromide and iodide anions also showed no interference due to counter cations such as sodium, magnesium and calcium ions. As shown in Figs. 5A and 5B, chloride was separated

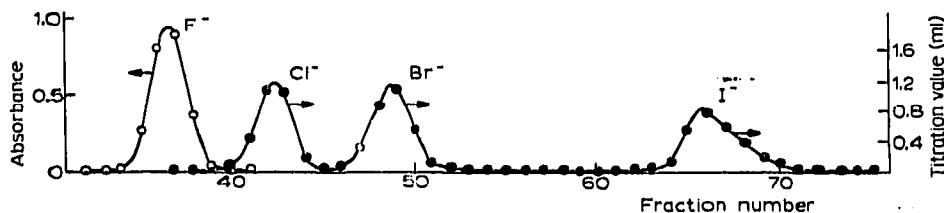


Fig. 4. Separation of F^- , Cl^- , Br^- and I^- . Column: 1.5×40.4 cm. Eluent: $0.1 M$ NaNO_3 solution. Sample: 1 ml of a mixture containing $0.05 M$ each of F^- , Cl^- , Br^- and I^- (sodium salts) in $0.1 M$ NaNO_3 solution. One fraction = 1.15 ml. $V_0 = 26.23$ ml. Flow-rate = 31.36 ml/h.

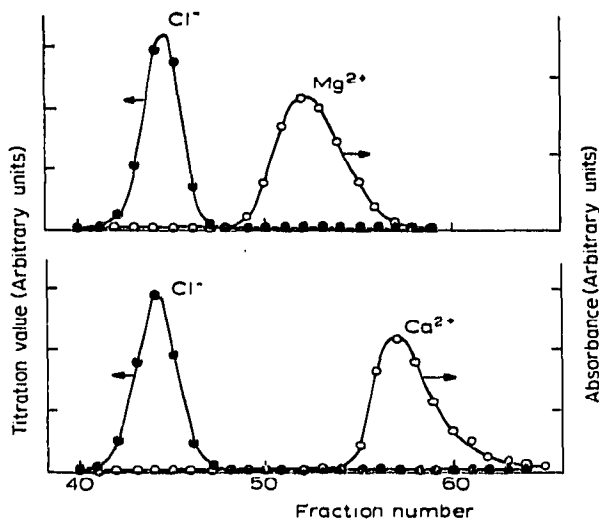


Fig. 5. Effect of Na^+ , Mg^{2+} and Ca^{2+} counter cations. Column: $1.5 \times 40.4\text{cm}$. Eluent: 0.1 M NaNO_3 solution. Sample: (A) 1 ml of a mixture of 0.0125 M NaCl and 0.0125 M MgCl_2 dissolved in the eluent; (B) 1 ml of a mixture of 0.0125 M NaCl and 0.0125 M CaCl_2 dissolved in the eluent. One fraction = 1.10 ml . Measurement: Cl^- (\bullet), argentimetry; Mg^{2+} and Ca^{2+} (\circ), atomic absorption spectrophotometry at 285.2 and 422.7 nm , respectively.

quantitatively from magnesium or calcium cations in the sample solutions. Therefore, it seems that, if the electrical neutrality is taken into account, magnesium and calcium cations on the gel column must be accompanied by the nitrate anion in the eluent, and the chloride anion by the sodium cation.

In Table II are listed the percentage recoveries in the separation of each halide anion. It is concluded that quantitative separations could be carried out satisfactorily by this gel chromatographic method.

The order of elution in Figs. 2 and 4 was $\text{F}^- < \text{Cl}^- < \text{Br}^- < \text{I}^-$. On the

TABLE II
RECOVERY IN THE SEPARATION OF EACH ANION

Anion	Taken (mequiv.)	Found (mequiv.)	Recovery (%)
F^-	0.0531	0.0528	99.4
	0.0249	0.0247	99.2
	0.0011	0.0010	90.9
Cl^-	0.1000	0.0994	99.4
	0.0500	0.0505	101.0
	0.0250	0.0249	99.6
Br^-	0.1000	0.0984	98.4
	0.0489	0.0491	100.4
	0.0250	0.0246	98.4
I^-	0.1000	0.1002	100.2
	0.0500	0.0505	101.0
	0.0252	0.0256	101.6

other hand, the order of the radii of the hydrated ions is $F^- < Cl^- < I^- < Br^-$ (ref. 9). Therefore, the migration of F^- , Cl^- and Br^- , but not I^- , may be caused mainly by the sieving effect. The behaviour of the iodide anion was different from the others: the K_{av} value was greater than unity and the elution curve showed tailing. When sodium nitrate was used as the eluent, the K_{av} value of I^- decreased from 1.41 to 1.05 with an increase in sample concentration from $6 \cdot 10^{-3}$ to $1 \cdot 10^{-1}$ M. Moreover, the same tendency was also observed when sodium chloride solution was used as the eluent. As Brown and Chitumbo⁴ have already demonstrated the specific adsorption of iodide anion on a cellulose gel, the present results for I^- may also be due to the adsorption on the gel matrix.

It was concluded that if fluoride, chloride, bromide and iodide anions are eluted on the Sephadex G-15 column by using 0.1 M sodium nitrate solution as the eluent, these anions could be completely separated, and the counter cations such as Na^+ , Mg^{2+} and Ca^{2+} in the sample solution showed no effect. The gel column used in this study gives reproducible results over a period of three months.

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