The Separation of Small Amounts of Inorganic Cations by Chromatographic Methods. I. Introductory Experiments with Inactive Cations

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Separations of divalent inorganic cations are studied on ion-exchange columns, employing aqueous solutions and partition-elution by means of organic solvents. A mixture of *e. g.* Ba, Ni, Mn, Co, Cu, Zn and Bi is completely separated and collected into small fractions of elutriant.

A new three-phase ion-exchange theory is introduced in order to explain the behaviour during these elutions. It is in agreement with the experimental results and also with earlier published data.

Paper strip separations are studied in *n*-butanol- and different ketone-mixtures with acids. Complete and reproducible separations of a wide combination of ions are obtained with methyl-propyl ketone + HCl in less than 1 hour.

I. INTRODUCTION

In order to find fast methods for a complete separation of chemical elements (or different inorganic ions), produced during bombardments in a cyclotron, chromatographic methods were tested at our laboratory. Compared to old conventional separation methods they have the advantage of being clean, less laborious and most often leading to a complete resolution of a mixture of ions. The disadvantage is primarily that the methods are rather slow, more than 10 hours being needed to effect a separation. If the methods should obtain importance in the study of radioactive elements, this time had to be decreased to at least 3—4 hours. It is otherwise impossible to assay and determine the extremely small fission- and spallation-yields of isotopes with half-lives below or around one hour.

As the purpose was, first to study the spallation products of copper [1], the principal interest was directed to the study of Zn, Cu, Ni, Co, Mn and Fe.

Three different chromatographic methods enable good separations of inorganic ions:

    1. paper chromatography strips,
    2. chromatography on cellulose columns or some other adsorbent as *e.g.* Al,
    3. ion-exchange columns.

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The two latter methods enable the separation of milligram to gram quantities, paper chromatography on the contrary not more than 1 mg of each cation and usually considerably less. Paper chromatography hence necessitates an individual and almost complete separation of the target material before the chromatographic separation starts.

Cellulose columns enable excellent separations of Cu, Co, Ni and Fe[2], provided the flow rate is very small (2—3 drops a minute), and are therefore less convenient for spallation studies.

II. ION-EXCHANGE COLUMNS

A. Experimental variables

Numerous applications of ion-exchange methods to the separation of inorganic ions have been published (see Ref.[3] p. 179 and Ref.[4], p. 221), especially with the rare earth and transuranium elements, and certain rare metals as Zr, Hf, Nb, and Ta. On the contrary very little has been reported about the separation of divalent cations. Co, Ni, Fe, and Ga have been separated on an anion-exchanger with high molarity HCl-solutions [5-6], Mn and Cu partly with 1 N H_2SO_4[7], Cd and Zn with 0.5 N HCl[8] and Na, K, Mg, Ca, Li, Cd, Hg, and Be also partly with 0.7 N HCl.[9] An investigation [10] and an attempt [11] to separate the NH_3-complexes of Ni, Cu, Zn, and Ag has been made, but very poor separations were achieved.

Experimental variables, concerned with the separation of ion mixtures, are well established [3-4], and the most important factors to obtain optimum separations are:

1. low flow rate,
2. high temperature,
3. small particle size of the exchanger,
4. increasing length of the resin column,
5. high capacity exchanger and
6. low adsorbed ion conc.

The attainment of equilibrium is favoured by these six factors. When fast separations are wanted, as in the case of radioactive, shortlived isotopes, high temperature (70—80° C), small particle size, short columns, high capacity exchanger, low adsorbed ion conc. are needed, and the flow rate is then regulated so as to obtain the best separation.

B. Theory

Symbols:	[ ]	activity
	C	concentration in mole/liter
	γ	activity coefficient
	g	gram oven dried (110°) ion exchanger in H^+-form
	$M_{Me^{+2}}$	number of moles of the ion Me^{+2}
	M_1	molecular weight of the resin (Dowex 50) in oven dried H^+-form
	v	volume liquid in the column in ml

A_1 area of cross section of the mobile phase

A_s »   »   »   »   »   »   nonmobile phase (in g/cm)

V eluted volume of solution in ml, when the max.conc. (band) reaches the outlet of the column

p number of theoretical plates of the column.

An ion-exchange reaction of divalent cations with the resin phase in H^+-form can be written:

$$Me^{+2} + 2\ HR \rightleftharpoons MeR + 2\ H^+ \tag{1}$$

$$\frac{(MeR) \cdot (H^+)^2}{(Me^{+2}) \cdot (HR)^2} = K_0 \tag{2}$$

where K_0 is the true exchange constant.

The distribution constant K_d for the reaction, if no complex formation occurs in solution, is defined as

$K_d = $ (conc. Me in resin phase) : (conc. Me^{+2} in liquid phase) in moles $\cdot$ g^{-1} : moles $\cdot$ ml^{-1}

$$\therefore\ K_d = \frac{(M_{Me})_R}{M_{Me^{+2}}} \cdot \frac{v}{g} = \frac{M_{MeR} \cdot 1\ 000}{g \cdot C_{Me^{+2}}} \tag{3}$$

A new equilibrium constant may be defined as

$$K_j = \frac{K_0 \cdot \gamma_{Me^{+2}} \cdot \gamma_{HR}^2}{\gamma_{MeR} \cdot \gamma_{H^+}^2} = \frac{M_{MeR}}{C_{Me^{+2}}} \cdot \frac{C_{H^+}^2 \cdot (M_{MeR} + M_{HR})}{M_{HR}^2} \tag{4}$$

if concentration is expressed in mole fraction in the resin phase and in mole per liter in the liquid.

When Me is present in very low conc. (in the following experiments at most 0.5 % M_{MeR} of the whole resin phase) $M_{HR} \simeq M_{MeR} + M_{HR}$ and

$$K_j = M_1/1\ 000 \cdot K_d \cdot C_{H^+}^2 \tag{5}$$

The plate theory [12–13] is probably the most convenient method of calculating K_d from experimental column separations. Consden [14] has defined

$$R_F = \frac{\text{movement of band}}{\text{movement of advancing front of liquid}} \quad \text{and shown that}$$

$$R_F = \frac{A_1}{A_1 + K_d \cdot A_s} \tag{5}$$

$$\therefore\ K_d = \frac{A_1}{A_s} \cdot \left(\frac{1}{R_F} - 1\right) \tag{6}$$

As $\dfrac{A_1}{A_s} = v/g$ it is simply shown that

$$K_d = \frac{V-v}{g} \tag{7}$$

Further on, it has been shown that

$$p = \frac{2V \cdot (V-v)}{W^2} \tag{8}$$

where W is the half width of the elution curve in ml at an ordinate value of $1/e$ of the maximum.
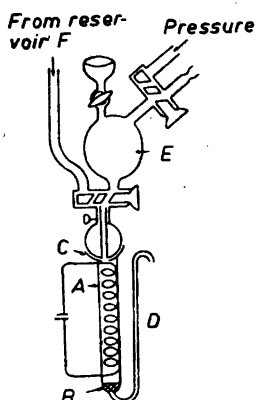
Fig. 1. Experimental column: A resin bed; B glass wool support; C joint, ball-ground; D capillary tube; E 75 ml reservoir.

C. Experimental

Apparatus: The essential apparatus, as shown in Fig. 1, is made of Pyrex glass. A helical resistance thread is wound on the outside of the columns *A* and isolated by asbestos fibre + water-glass. The winding of the thread is adapted to give a constant temperature from 20—90° throughout the whole column-length by varying the applied voltage. The columns have a fixed diameter, 0.8 cm, but different lengths and are easily exchangeable. They are filled with resin (Dowex 50) to the top.

Procedure: The columns are packed with a water-slurry of the resin and then exhaustively washed alternately with 4 *M* HCl and water, and finally with water to remove all the excess of hydrochloric acid. The divalent cation mixture is adsorbed on the top of the column from reservoir *E* (Fig. 1) in a feebly acid solution, the column washed with water to remove the anions and the required temperature obtained by applying a certain calibrated voltage to the resistance thread. The elution is simply performed by passing the desired solvent through the column with a constant flow rate either from the reservoir *E* under air pressure or from *F* under hydrostatic pressure; the effluent collected in small fractions by an automatic sample-changer and analysed for the different cations. All solutions, used in the experiments, are carefully freed from dissolved air bubbles.

Table 1.

Run	Temp. °C	Cu^{+2} added mg	Cu^{+2} found %	Flow-rate ml/min	HCl mola-rity	p	K_d	K_j
1	20	9.24	99.1	0.9 —0.92	0.65	9.8	46.3	3.51
2	20	9.24	100.2	0.7 —0.8	0.70	6.0	34.7	3.07
3	20	8.52		0.65—0.7	0.70		35.9	3.16
4	74	6.16	98.3	0.61—0.66	0.68	18.2	47.9	4.13
5	74	6.20	98.7	0.61—0.71	0.68	17.5	49.0	4.22
6	88	8.52	99.8	0.54—0.62	0.49		91.0	3.94
7	88	9.00	99.2	0.65—0.83	0.58	11.1	65.5	3.88
8	88	8.52		0.64—0.80	0.70		43.1	3.80
9	88	9.09		0.8 —0.9	0.73		41.3	3.96
10	88	9.09		0.51—0.57	0.73		39.2	3.75
11	88	9.21	99.8	0.45—0.63	0.73	21.7	39.7	3.79
12	88	6.24	99.7	0.63—0.80	0.80		28.6	3.30
13	88	9.00	99.7	0.69—0.71	0.86	11.9	21.0	2.79
14	88	8.52		0.54—0.6	0.92		15.8	2.40

D. Experimental results

a) *Studies of the column efficiency with* Cu^{+2}. In order to check the column properties when different experimental variables are changed, elutions were made by HCl, using a column of 12.5 cm length, filled with 3.72 g Dowex 50 (10—20 mesh). Results are collected in Table 1.

From the data in Tables 1 and 2 and the curves in Figs. 2—4 it is apparent that

1) the ion-exchange elution of Cu with HCl at different concentrations is quantitative,
2) it is advantageous to use more elevated temperatures,
3) the influence of small variations of acid conc. on the elution curve is very marked,
4) the equilibrium constant K_j is fairly constant within a large HCl-conc. range (Fig. 4). In eq. (4) it was shown that

$$K_j = K_0 \cdot \frac{\gamma_{Cu^{+2}} \cdot \gamma_{HR}^2}{\gamma_{CuR} \cdot \gamma_{H^+}^2}$$

where K_0 is the true and invariable equilibrium constant. According to Kressman [15] even the ions in the resin phase are almost completely surrounded by an ionic atmosphere, similar to that surrounding the corresponding cations in the aqueous phase, and hence their activity coefficient may be expected to vary in the same manner. The constancy of K_j is in accordance with this view, the steep decrease of K_j for HCl-conc. > 0.75 M being attributed to the onset of Cu-complex formation in the solution phase.

b) *The separation of Cu, Co, and Ni with 0.7 M HCl.* The best separation of these three cations is obtained with 0.7 M HCl. A column, dimensioned 29×0.8 cm, and filled with 8.70 g Dowex 50 (10—20 mesh), was used; and 3 mg each of the cations were adsorbed.
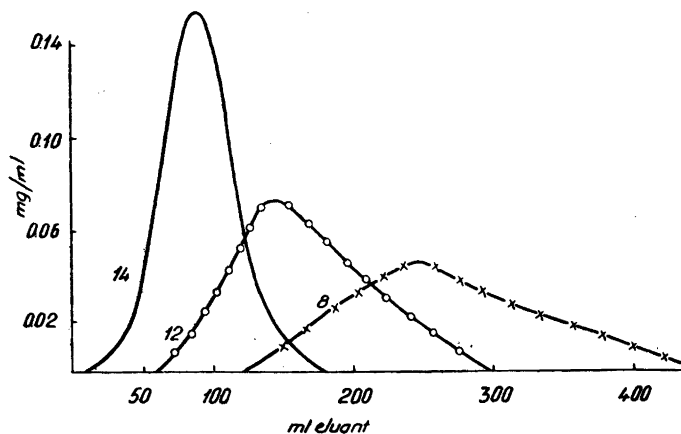

Fig. 2. *Elution curve for* Cu^{+2}; *column dimensions 12.5 $\times$ 0.8 cm; temperature 88°; eluant HCl in different conc. (— sample 14, ○ sample 12, and × sample 8 in Table 1).*
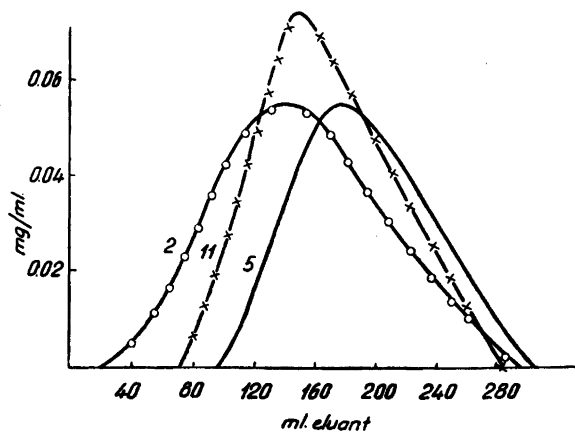
Fig. 3. Elution curves for Cu^{+2} at different temperatures; column dimensions 12.5×0.8 cm; eluant ~ 0.7 M HCl. ($-$ sample 5, $\bigcirc$ sample 2 and $\times$ sample 11 in Table 1.)

The separation factor α_{AB} between two ions A and B is defined as

$$\alpha_{AB} = K_{d_B}/K_{d_A} \qquad\qquad (9)$$

Practical experiences have shown that it is only possible to effect a separation when $\alpha_{AB} > 1.20$. Results are shown in Table 2.

<div align="center">Table 2.</div>

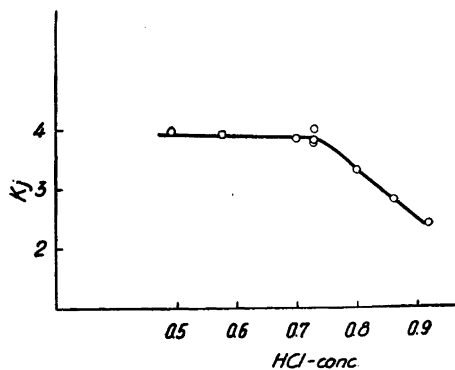| Run	Temp. °C	Flow-rate ml/min	Cu^{+2} fraction ml	K_d	K_j	α_{CuNi}	Ni^{+2} fraction ml	K_d	K_j	Co^{+2} fraction ml	K_d	K_j
1	86	0.40 — 0.42	253 — 560	44.3	3.91	1.47	437 — 645	65.2	5.76	460 — 670	66.1	5.82
2	20	0.37 — 0.42	200 — 410	34.5	3.05	1.10	222 — 465	37.9	3.35	235 —	38.0	3.36
3	86	0.19 — 0.22	275 — 532	42.7	3.76	1.56	436 — 722	66.7	5.88	460 — 740	69.8	6.18
4	86	0.10 — 0.15	340 — 484	43.2	3.82	1.56	486 — 710	67.2	5.92	552 — 740	70.2	6.20

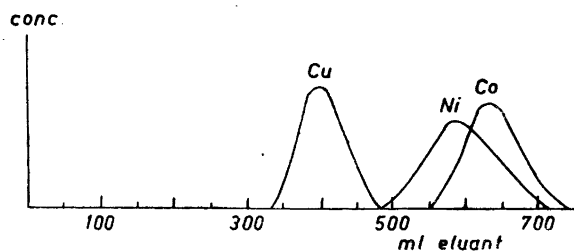Fig. 4. Variation of Kj for Cu^{+2} with HCl-conc.; temp. $88°$.

Fig. 5. *Elution curves in attempt 4, Table 2. Eluant 0.7 M HCl; temp. 86°; flow rate 0.12 ml/min; column dim. 29 × 0.8 cm with Dowex 50 (10−20 mesh).*

Table 2 and Fig. 5 together with a comparison to the data in Table 1 show that
   1) Cu is separated from Ni and Co at 86°, though not the last two, (α_{NiCo} = 1.04 in run 4),
   2) K_d and K_j are independent of column length as well as of flow rate, provided that equilibrium is attained. With longer columns and slower flow rates p increases, attaining a value of 145 for Cu in run 4, and hence facilitates the separations, as p principally determines the spreading of the elution peaks.
   The procedure, tested above, is very slow. In run 4, the elution of Cu alone took more than 60 hours.
   c) *Partition elution with methyl-n-propyl ketone.* To effect faster separations than in the preceding section it is necessary to increase the K_d-differences of the ions, and at the same time to maintain the high solubility in the solution. A mixture of methyl-n-propyl ketone and high molarity HCl was found to have these properties. Single phase mixtures are formed with HCl > 7.5 M, the mixture otherwise rapidly separating into two fairly pure phases. Hence the cations can rapidly be adsorbed on the top of the column from aqueous solution, and the water is directly displaced by the lighter ketone-acid mixture at the same time as the elution starts. The apparatus is constructed (Fig. 1) so as to obtain the smallest possible contact area between the ketone- and aqueous-phase in order to only slightly change the acid conc. in the ketone.
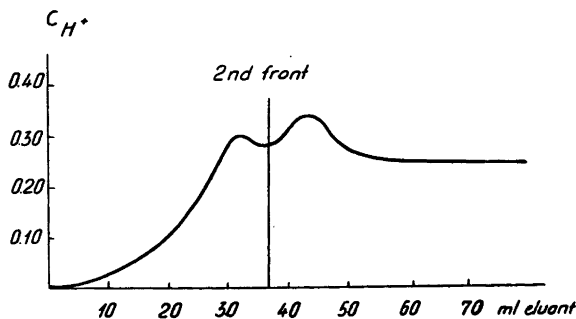

Fig. 6. *C_{H^+} gradient curve; column dimensions 12.6 × 0.9 cm; 3.59 g Dowex 50 100−200 mesh; eluant methyl-iso-propylketone + 2 % conc. HCl; flow rate 0.2−0.25 ml/min.*

A preliminary investigation (Fig. 6; the elution curve starting, when the first drops of ketone are passing out of the column) has revealed that a pH-gradient is developed, the form of which is about the same as in ordinary frontal analysis but with a distinct minimum at the "acid front"; that is to say where a homogeneous effluent is attained and in ordinary paper chromatography a second front developed. The "acid front" is preceded by a ketone-water emulsion with gradually rising H^+-conc. Calculations from experimental data show that a stationary H_2O-phase is held by the resin, and is only very slowly displaced by the solvent. The explanation must be that the ketone molecules, partly polymerised in the acid solution, can only gradually and with greatest difficulty penetrate into the resin phase, and hence a distribution of the HCl-molecules is obtained between a stationary H_2O-phase and a moving ketone phase. The pH in the inner solution of the resin falls, until the same H^+-normality is obtained as in the outer solution. At the same time, in the ketone phase the H^+-conc. is gradually diminishing during the passage through the column, a two-phase emulsion being formed as soon as the HCl-normality < 7.5. Hence during the elution an H^+-band is moving down the column, preceded by a ketone-water emulsion with gradually rising H^+-conc.

The regeneration of the column is easily performed by alternately passing 8 M HCl and H_2O. The elution procedure is the same as that already discussed in Section C. An accurate quantitative analysis was not performed. The solutions were prepared some days before the experiments, gas-bubbles otherwise being evolved in the column.

Experimental conditions: 3.52 g Dowex 50 (100—200 mesh) in H^+-form; column dimensions 12.2 × 0.9 cm; temperature 20°; 0.5 mg each of examined cations; eluant methyl-n-propyl ketone + varying % and molarity HCl.

Table 3 indicates calculated K_d and R_F and Figs. 7 and 8 the elution curves for two experiments.

Table 3.

Run	Flow-rate	Acid conc. M	Cu^{+2}		Co^{+2}		Mn^{+2}		Zn^{+2}		Cd^{+2}		Bi^{+3}	
			K_d	R_F	K_d	R_F	K_d	R_F	K_d	R_F	K_d	R_F	K_d	R_F
1	0.11—0.14	0.16	15.4	0.065	23.5	0.043			12.7	0.078				
2	0.20—0.30	0.16	15.2	0.070	24.0	0.044			12.2	0.088			7.05	0.150
3	0.09—0.12	0.18	13.4	0.080	19.8	0.054					7.70	0.126		
4	0.08—0.10	0.20	11.8				38.7							
5	0.12—0.20	0.20	11.4	0.086	18.8	0.057			8.3	0.114	7.75	0.12	5.75	0.185
6	0.12—0.14	0.24	9.6		15.7				6.2		5.6		4.20	
7	0.11—0.16	0.30	6.9	0.133	10.6	0.092	20.2	0.05	3.76	0.22				

As is shown in Figs. 7 and 8, a large mixture of divalent cations can be separated, if the eluant is successively changed and the flow rate low. In Fig. 7 the separations were complete without any contamination in the different fractions. In Fig. 8 almost complete separations were obtained except with Cd and Zn, which were impossible to separate with the eluant employed, and Cu, with 95 % collected in its own fraction but with traces in the Mn-fraction after changing the HCl-conc.
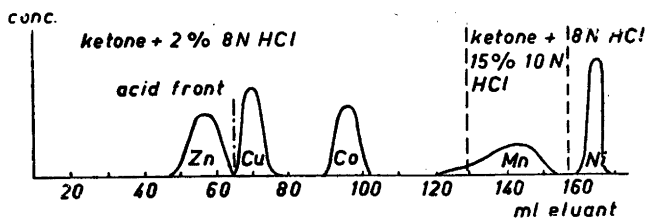
Fig. 7. Elution curves for 0.5 mg Zn, Cu, Co, Mn and Ni (as chlorides); flow rate
~ 0.12 ml/min.

Serious complications appear, when Fe-ions are present. In spite of their large solubility in the ketone they cannot be eluted in a single fraction. Fe is partly eluted earlier than Bi, but much Fe-contamination appears during the whole elution. Further, Fe renders the complete separation of the other cations, investigated, more difficult; Cu-ions especially become considerably retained. The same difficulties were observed, eluting ion-exchange columns with dilute acids as well as paper strips with ketone-acid mixtures; in the latter case, however, only with higher Fe-conc. (in paper strip scale).

Experiments have shown K_d to be independent of Cl^--conc. With the assumption of true ion-exchange in the resin phase and a distribution as Me^{+2} between ketone and aqueous solution with almost all Me^{+2} in the ketone phase, eq. (10) is obtained. K_{part} is defined as in eq. (14).

$$K_0 = M_1/1\,000 \cdot K_d \cdot K_{part} \cdot C_{H^+}^2 \cdot \frac{\gamma_{MeR} \cdot \gamma_{H^+}^2}{\gamma_{HR}^2 \cdot \gamma_{MeKet}} \tag{10}$$

The mechanism, deduced experimentally, seems to be in agreement with this equation, but in spite of this the results in Table 3 do not satisfy the above equation, the hydrochloric acid dependence being less. Calculations, based on assumptions of complex anion formation, distribution as anions etc. give even worse agreements. Either the variations of the total activity coefficient product must be large and partly compensate the $C_{H^+}^2$-variations, or the assumption about ion-exchange in a solid resin phase is in error. As the experimental
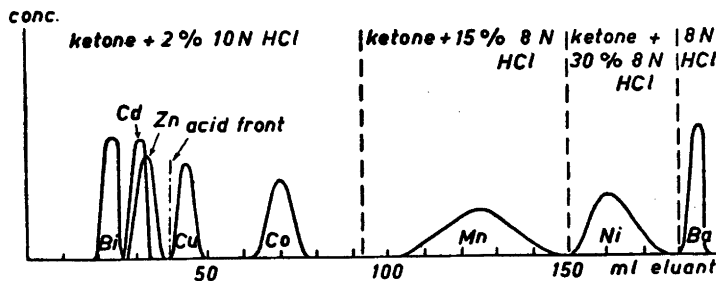

Fig. 8. Elution curves for 0.5 mg Bi, Cd, Zn, Cu, Co, Mn, Ni and Ba (as chlorides); flow rate ~ 0.16 ml/min.

data are in complete agreement with cellulose chromatography with the same solvents, and the rapid elution of Bi^{+3} is in direct contradiction to ordinary ion-exchange results, the latter seems to be the case.

A new theory. In explaining these discrepancies as well as the other observations a new ion-exchange theory has been elaborated, which is in agreement with most of the vast published data, as well as these new partition elution experiments. The whole ion-exchange process is regarded as a three-component mechanism with a solid phase, an inner solution, firmly maintained by and inseparable, even by centrifuge, from the resin, and an outer solution. The exchange with a divalent metal ion becomes, conc. in inner solution indexed i and other symbols as before.

$$Me_i^{+2} + 2HR \rightleftharpoons 2\ H_i^+ + MeR$$

$$Me^{+2} + 2\ H_i^+ \rightleftharpoons Me_i^{+2} + 2\ H^+$$
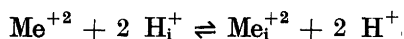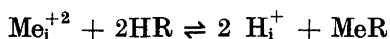
$$\frac{[H^+]_i^2 \cdot [MeR]}{[Me^{+2}]_i \cdot [HR]^2} = K_0' \tag{11}$$

$$\frac{[Me^{+2}]_i \cdot [H^+]^2}{[Me^{+2}] \cdot [H^+]_i^2} = K_0'' \tag{12}$$

K_0' and K_0'' are true equilibrium constants and $K_0' \cdot K_0'' = K_0$, the constant defined in eq. (2). A new definition of the distribution constant K_d is now introduced, as it is convenient to have all conc. per ml and not as before in g in the resin phase. If the resin volume is v_R ml

$$K_d' = \frac{(C_{Me})_R + (C_{Me^{+2}})_i}{C_{Me^{+2}}} = \frac{M_{MeR} \cdot 1\ 000/v_R + (C_{Me^{+2}})_i}{C_{Me^{+2}}} \tag{13}$$

As long as $(C_{Me^{+2}})_i$ is fairly small, compared to the fraction in the resin, which is always so in aqueous solutions, a fast distribution between inner and outer solutions is obtained, and the equations, concerning only two phases, are approximately valid. In highly acid organic solvent mixtures, however, where only the acid molecules + water can rapidly penetrate into the inner solution, the acid conc. of the inner solution will become very high, the equilibrium in eq. (11) displaced so that all Me is in the inner solution, hence eq. (12) will become completely rate determining, and eq. (11) may be neglected. As the reaction is independent of Cl^--conc., the distribution in the outer solution is written

$$(Me^{+2})_{H_2O} \rightleftharpoons (Me)_{Ket} \quad \text{and} \quad \frac{[Me]_{Ket}}{[Me^{+2}]} = K_{part} \tag{14}$$

where K_{part} is not a constant but a function of pH in the outer solution.

$$K_d' = \frac{(C_{Me^{+2}})_i}{C_{Me^{+2}} + (C_{Me})_{Ket}} \tag{15}$$

$$\therefore\ K_d' = \frac{K_0'' \cdot [H^+]_i^2}{[H^+]^2 \cdot (\gamma_{Me^{+2}})_i} \cdot \frac{1}{(K_{part}/\gamma_{MeKet}) + 1/\gamma_{Me^{+2}}} \tag{16}$$

With the new definition of K_d', eq. (7) is transformed to

$$K_d' = \frac{V-v}{v_i} \tag{17}$$

where v_i is the volume of the inner solution, and depends on resin swelling and hence of $[H^+]_i$.

The distribution and the phases in eq. (15) are exactly the same as in paper strip separations, and this explains the great resemblance of the two methods. Using only 2 % HCl in the ketone, $C_{Me^{+2}}$ may be omitted in eq. (15) and

$$\therefore \quad K_d' \simeq \frac{K_0'' \cdot [H^+]_i^2}{[H^+]^2} \cdot \frac{\gamma_{MeKet}}{K_{part} \cdot (\gamma_{Me^{+2}})_i} \tag{18}$$

When elution begins, the H^+-conc. is very low in the inner solution, the distribution of H^+ between inner and outer solution rapid and hence $[H^+]_i^2/[H^+]^2 \simeq 1$ for a given Me during the entire elution. Hence the second factor in eq. (18) determines the variations of K_d' with acide onc. in the elutriant and predominantly that of K_{part}, as most probably the variations of γ are small, when the initial Me-conc. is as small as in the experiments, carried out.

It has not yet been possible to verify the deduced eq. (18), approximated as suggested above, in the experiments of Table 3, as the H^+-dependence of K_{part} is unknown, as well as the exact values of v_i. The latter was, however, found to decrease slightly with increasing C_{H^+} in the eluant, and hence in Table 3 the variations of K_d' are somewhat smaller than those of K_d as

$$K_d' = K_d \cdot g/v_i \tag{19}$$

The data of Table 3 indicate that

$$K_d' \cdot C_{H^+} = \text{constant} \tag{20}$$

which is in accordance with the view in Fig. 7 of a pH-gradient moving through the column and the different cations always travelling with the same pH.

$$\therefore \quad K_{part} \simeq C_{H^+} \times \text{constant}.$$

III. PAPER STRIPS SEPARATIONS

A. Experimental variables

Paper strip separations have proved to be very valuable in inorganic analysis and have been thoroughly studied at different laboratories, above all by a research team at Teddington, Pollard *et al.* in Bristol, Lacourt *et al.* in Bruxelles and Lederer in Australia (see Refs. [16],[17]). Complete separations have been attained in groups of 3—5 cations and anions.

It is almost impossible to verify by mathematical calculations and previous experiments that a certain separation can be effected. Experimental testing is always necessary, since many variables influence the separation mechanism, and very small variations can lead to very great changes in separation efficiency. The most important variables are:

1) form and dimensions of the chromatographic chamber and elution mode,
2) atmosphere in the chamber,
3) elutriant, employed,
4) form, dimensions, sort and pretreatment of paper, employed,
5) concentration and acidity of initial cation mixtures,
6) place of and treatment at the point of application to the paper,
7) equilibrium during, and length of elution, and
8) temperature.

If all the variables above are held constant, reproducible results may be obtained, very careful and slow experiments, however, being necessary. The present investigation was, however, carried out in order to find rapid methods, and hence the chief object was to find optimum conditions of the above factors to enable fast and complete resolution of mixtures of ions.

B.   E x p e r i m e n t a l

Apparatus. All experiments were carried out by the descending technique. The chromatograph chamber is made of glass, as strong acids are used during elution, and is closed by a glass cover, absolutely tight fitting.

Paper strips. Munktell OB filter papers are employed. The strips are cut $45° \times 3.5$ cm.

Technique. A small spot of the investigated cation solutions ($0.005-0.010$ mg each) is applied by a pipetting device to the middle of the paper, 7.5 cm from the upper edge, and dried in an air-stream. Four paper strips are placed in the chamber and partly or entirely·equilibrated with the "atmosphere" from a solvent on the bed of the chamber; the desired eluting mixture is allowed to diffuse down a fixed length of the strips and finally evaporated from the strips in a hood, usually over night. A suitable reagent, sprayed by an atomizer, developes the positions of the cations.

Stock solutions. Chloride or nitrate solutions (anions in K-, Na-, or H-form) were prepared with 5 mg metal per ml and with varying acidity.

Preparation of solvents. Only pure solvents were used, all organic ones dried, redistilled and a fraction near the boiling point used. All two-phase solvent mixtures were thoroughly shaken and the two layers separated. The water layer was used as bottom solvent in the chamber.

Analytical reagents. Most sensitive spot test reagents, especially when spraying HCl-eluted strips, were found to be:

Rubeanic acid (saturated in ethanol) + NH_3: Cu^{+2}, Co^{+2}, and Ni^{+2},
Diphenylcarbazide (1 % in ethanol) + NH_3: Zn^{+2}, Tl^{+3}, Hg^+, Hg^{+2}, Mn^{+2}, Cr^{+3}
Dithizone (15 % in chloroform) + NH_3: Cd^{+2}, Tl^+, As^{+3}
Cadion (0.02 % in ethanol + 1 % $2N$ NaOH): Cd^{+2}
Dimethylaminobenzalrhodanin (0.03 % in ethanol) + NH_3: Ag^+, Hg^+, Hg^{+2}
p,p'-Tetramethyldiaminodiphenylmethane (0.5 % in 5 % citric acid): Au^{+3}
Alizarin (0.1 % in ethanol) + NH_3: Ca^{+2}, Sn^{+2}, Sn^{+4}, Sb^{+5}, Zr^{+4}, Y^{+3}, Pr^{+3}, Th^{+4}, BO_3^{-3}, Ti^{+4}
Aluminon (0.1 % in ethanol) + NH_3: Be^{+2}, Ga^{+3}, Al^{+3}, La^{+3}, Fe^{+2}, Fe^{+3}
Quinalizarin (0.01 % in ethanol) + NH_3: Mg^{+2}
a,a'-Dipyridyliodide: As^{+5}, Pd^{+2}, Sb^{+5}
Cinchoniniodide: Pd^{+2}, Pt^{+4}, Bi^{+3}
Chromotropic acid (5 % in water): Ti^{+3}
Phosphomolybdic acid (5 % in water): Sb^{+3}, Sn^{+2}
Pyrogallol (5 % in ethanol): Ce^{+3}, VO_4^{-3}, VO^{+2}, MoO_4^{-2}, WO_4^{-2}
NH_3 + *o*-Toluidine (2 % in ethanol): Ir^{+4}, CrO_4^{-2}, MnO_4^-, Cr^{+3} (H_2O_2)
Dipicrylamine: Cs^+, Rb^+, K^+
Violuric acid (0.1 M in water) + NH_3: Li^+, Na^+
$K_4Fe(CN)_6$: UO_2^{+2}

Measurements of R_F-values. The mid-point of the spot, where the investigated solution is applied to the paper, and the front border of the solvent front are the reference points of R_F-measurements. Unfortunately most published data only report one value of the R_F. As the spreading of the different spots can vary greatly, this indication gives rather a poor measure of the separation efficiency. Mostly two values are noted here, one for the front and the other for the rear of the spot. Where only one value is reported, the "centre of gravity" of the spot is measured.

In the following tables all R_F-values are means of several experiments.

C. Results

Most of the variables, mentioned earlier, were investigated to determine the optimum conditions of fast separations and their relative influence on R_F.

1) *Dimensions of the chamber etc.* The heights and cylindrical forms of all chambers, employed, were about the same, and the descending technique was always used, being more rapid than the ascending one. This variable is hence almost constant.

2) *"Atmosphere"*. It has been shown [18] that variations of "atmospheric" conditions in the chamber can completely alter separations, previously obtained. In these experiments the "atmosphere" solvent was entirely another than the elutriant.

A comparative study of the influence on R_F as well as of the degree of separation of a cation mixture, eluted by methyl-n-propyl ketone + HCl directly after insertion of the paper strips in the chamber, was conducted by varying the "atmosphere" content in both ketone, HCl and water. Results are shown in Tables 4—5.

Together with Table 6 the above tables indicate the great influence of "atmospheric" conditions on the R_F. In certain cases (Co and Cu) the elution order can become reversed, merely by changing the "atmosphere" a little.

It is impossible to prevent a partial evaporation of the solvent mixture on the chamber-bed. This was clearly demonstrated, as R_F-values, obtained in "old chambers" with HCl-mixtures, diminished greatly. On the contrary it is

Table 4. R_F of different cations; elutriant methyl-n-propyl ketone + conc. HCl; "atmospheric" conditions changed; volumes in ml.

Eluant +	10 % HCl		15 % HCl				20 % HCl		30 % HCl
Atmosphere	H_2O		H_2O				H_2O		H_2O
Ions	0	30	0	3	10	30	0	30	0
Ni	0.02	0.03	0.015	0.025	0.03	0.04	0.06	0.08	0.28
Mn	0.13	0.10	0.23	0.18	0.17	0.15	0.225	0.19	
Bi^{+3}			0.48		0.44				
Co	0.60	0.37	0.67	0.56	0.50	0.44	0.60	0.52	0.86
Cu	0.65	0.74	0.67	0.64	0.62	0.62	0.66	0.63	0.79
Zn	0.75	0.82	0.81	0.78	0.75		0.84	0.81	
Cd	0.80	0.84	0.82	0.82	0.79		0.86	0.83	
Fe^{+2}				0.96	0.94		0.96	0.94	
Acid front	0.74	0.74	0.81	0.78	0.75	0.71	0.83	0.81	

Table 5.

Eluant +	5 % HCl	10 % HCl	15 % HCl				30 % HCl
Atmosphere / Ions	30 ket. + 5 conc. HCl + 8 H₂O	30 ket. + 5 conc. HCl + 8 H₂O	30 ket. + 10 H₂O	30 ket. + 4 H₂O	30 ket. + 10 8N HCl	30 ket. + 10 8N HCl + 5 H₂O	30 ket. + 10 8N HCl + 5 H₂O
Ni	0.01	0.02	0.03		0.04	0.03	0.10
Mn	0.11	0.16	0.08		0.26	0.12	0.29
Bi^{+3}	0.32		0.33	0.32		0.46	0.58
Co	0.41	0.60	0.30		0.69	0.46	0.74
Cu	0.50	0.74	0.47	0.42	0.65	0.58	0.74
Zn		0.82	0.54		0.75	0.68	0.85
Cd			0.59	0.55	0.86	0.76	0.86
Fe^{+2}	0.91	0.90	0.84		0.95	0.90	0.93
Acid front	0.55	0.78	0.51	0.47		0.64	

advantageous to use solvent mixtures, up to one month old, as eluants, provided these are stored in well stoppered bottles. It is true that the solution darkens, due to the formation of small amounts of certain polymerisation products, but, depending on their concentration in the "acid front" during elution, the front turns clearly visible so as to facilitate certain separations.

Both the results in Tables 4 and 5 and the observations from "old chambers" indicate the strong dependence of R_F on the % HCl in the "atmosphere". When it decreases, the R_F-values also diminish, primarily owing to the decrease of the R_F of the "acid front".

To hold the "atmospheric" variable as constant as possible in the following experiments, a freshly prepared "atmospheric" solvent was used each time with the same composition as in the eluant.

3) *Solvents employed.* In order to avoid tailing of the ions, owing to their linkage to active points of the cellulose, it has been found necessary to use strong acid mixtures in inorganic paper strip separations. Two different methods have proved to be the most efficient, either employing a complexing solvent mixture, the acid concentration being rather low so as not to prevent complex formation, or a strongly acid one-phase mixture. Both methods have been tested in this investigation.

a) Separations with one-phase mixtures of ketone + HCl: A careful investigation was carried out to find the separation efficiency, when the acid concentration was varied in different ketones, as well as the equilibrium between paper strips and "atmosphere" at the beginning of elution. Results, illustrated in Table 6, indicate that, among others, the following separations may be obtained: α) Ni, Mn, Bi, Co, Cu, Zn, Cd, and Fe, as well as Fe, Mn, Co, Zn, and Cr-Al, if the acid concentration and "atmospheric" conditions are controlled; Cr and Al can not be separated; β) Ag, Hg, Tl, and Pb, as well as Pb, Bi, Cu, and Cd, with exact control of the separation variables; γ) Au, Pd, Pt, and Ir^{+3}; δ) Ca, Mg, and Ba-Sr, if very long elution is performed; Ba and Sr are impossible to separate; ε) Li, K, Rb, and Cs; K and Rb, however, separate only partly

Table 6. R_F-values.

Ions	II	III *	III	IV *	IV	V	VI	VII
Ag+	0—0.49	0.30—0.40	0.16—0.55	0.53—0.66	0.26—0.57	0.26—0.98	0.33—0.63	0.05—0.34
Hg+	0; 0.71—0.92			0.73—0.88	0.79—0.89	0.84—0.91	0; 0.82—0.97	0; 0.75—0.92 0.58—0.75
Hg+2	0.12—0.86	0.70—0.80	0.73—0.87	0.8		0.78—0.94	0.73—0.95	0.63—0.76
Tl+	tail	0—0.16	0—0.19	0—0.19	0—0.19	0—0.38	0—0.19	0—0.17
Tl+3				0—0.19	0—0.19			0—0.16
Pb+2	0.01—0.15	0.15—0.24	0.13—0.27	0.15—0.23	0.12—0.23	0.10—0.32	0.10—0.25	0.11—0.20
Bi+3	0.31—0.54	0.38—0.87	0.35—0.43	0.40	0.41—0.60	0.47—0.61	0.32—0.51	0.30—0.36
As+3			0.56—0.60	0.62				0.58—0.61
Sb+3	0.83—0.97	0.80—0.92	0.78—0.96	0.90	0.91—0.98	0.86—0.97	0.85—0.94	0.82—0.87
Sn+2	0; 0.79—0.97	0.84—0.93 tail	0.76—0.97	0.93	0.86—0.99	0.81—0.98	0.80—0.92	0.84—0.89
As+5	0.57—0.74	0.44—0.46	0.58—0.60	0.70	0.83—0.88	0.80—0.90	0.72—0.80	0.53—0.60
Sb+5			0; 0.80—0.93		0; 0.88—0.95	0.89—0.94		0; 0.81—0.98
Sn+4	0	0	0	0	0	0; 0.90—0.94	0	0; 0.88—0.94
Cu+2	0.41—0.51	0.30—0.36	0.42—0.51	0.59—0.61	0.65—0.76	0.55—0.67	0.48—0.66	0.41—0.49
Cd+2	0.76—0.89	0.45—0.52	0.65—0.78	0.75	0.82—0.93	0.80—0.95	0.82—0.92	0.69—0.77
Mn+2	0.02—0.06	0.06—0.16	0.06—0.11	0.14	0.15—0.22	0.21—0.34	0.17—0.30	0.10—0.16
Co+2	0.17—0.31	0.22—0.29	0.25—0.34	0.50	0.65—0.82	0.66—0.85	0.48—0.76	0.48—0.56
Ni+2	0	0.04—0.09	0.03—0.08	0.02—0.04	0.01—0.06	0.02—0.07	0.01—0.05	0.02—0.07
Zn+2	0.51—0.75	0.46—0.49	0.57—0.61	0.72	0.80—0.93	0.74—0.92	0.63—0.87	0.57—0.60
Fe+2	0.31—0.97 tail	0.65—0.92	0.62—0.95	0.90 tail	0; 0.88—0.98	0.85—1.0 tail	0; 0.82—0.96	0; 0.72—0.94
Fe+3	0; 0.82—0.91	0.92—0.97	0.71—0.76	0.96 tail	0; 0.89—0.98	0.90—1.0 tail	0; 0.83—0.95	0; 0.90—0.98
Cr+3	0		0—0.06	0.03	0—0.03	0—0.09	0—0.05	0—0.05
Al+3	0		0—0.06	0.03	0—0.03	0.01—0.08	0—0.04	0—0.06
Ga+3	0; 0.88—0.95		0; 0.84—0.91		0; 0.88—0.97	0.91—0.97	0; 0.88—0.93	0; 0.84—0.91
Ca+2	0		0.01—0.04	0.01	0.01—0.04	0.02—0.07	0—0.03	0.02—0.06
Ba+2			0	0	0	0—0.02	0	0
Sr+2			0—0.01	0				0—0.04
Mg+2	0—0.02		0.07—0.11	0.03	0.01—0.05	0.05—0.12	0.01—0.05	0.03—0.09
Li+	0—0.02				0.12—0.15	0.24—0.29	0.10—0.12	0.11—0.15
Na+					0—0.06			0—0.08
K+	0		0.05—0.06		0.03—0.05	0.08—0.12	0.02—0.05	0.05—0.07
Rb+	0		0.05—0.06			0.10—0.12	0.03—0.06	0.09—0.11
Cs+			0.07—0.08		0.05—0.07	0.16—0.20	0.06—0.09	0.06—0.10
Au+3	0.88—0.97	0.83—0.95	0.82—0.89		0.84—0.93	0.90—0.97	0.87—0.94	0.90—0.95
Pd+2	0.16—0.20 tail	0.44—0.46	0.40—0.49	0.50—0.80	0.47—0.90	0.68—0.96	0; 0.33—0.52	0.28—0.36
Pt+4	0.17—0.30 0.40—0.51	0.45—0.50 0.68—0.74	0.59—0.68	0.78	0.45—0.83	0.70—0.83	0.43—0.81	0.49—0.65
Ir+4			0.41—0.49		0.58—0.68	0.13—0.15	0.07—0.13	0.04—0.08 0.39—0.45

Ions	II	III *	III	IV *	IV	V	VI	VII
Be+²	0—0.04		0.09—0.30		0—0.17	0.22—0.34	0—0.22	0.08—0.16
Ti+³	0—0.02		0—0.07		0—0.11	0.08—0.15	0—0.08	0.04—0.09
VO+²	0—0.03		0.04—0.11		0.04—0.10	0.07—0.18	0—0.11	0.05—0.11
VO₄-²			0.04—0.11 tail		0.03—0.10 tail	0.07—0.18		0.05—0.10 tail
MoO₄-²	0.89—0.97		0.78—0.92		0.88—0.94	0.87—0.93	0.88—0.94	0.87—0.94
WO₄-²	0; tail		0	0.03	0; tail	0; tail	0; tail	0
UO₂+²	0.34—0.61	0.54—0.64	0.58—0.64	0.78	0.74—0.89	0.81—0.94	0.81—0.96	0.62—0.74
Th+⁴	0		0	0.03	0	0—0.03	0	0—0.03
Zr+⁴	0—0.02		0—0.03		0; tail	0—0.22	0—0.12	
MnO₄-	0.03—0.08		0.06—0.12		0.14—0.22	0.20—0.32	0.12—0.22	0.08—0.15
CrO₄-²	0—0.03		0—0.05		0—0.06	0—0.13	0—0.06	0—0.12
BO₃-³	0.18—0.25		0.34—0.44		0.32—0.43	0.45—0.67	0.41—0.52	0.28—0.36
Ce+³	0		0.02—0.05	0.01	0—0.03	0—0.04	0—0.02	0—0.03
Y+³	0		0—0.05		0—0.02	0—0.06	0—0.03	0.01—0.04
Pr+³			0—0.04		0—0.03			0—0.03
La+³			0—0.03		0—0.03			0—0.03
Acid-front	0.54	0.45	0.59	0.70	0.85	—	0.67	0.60

Ions	I*	I
Bi+³	0—0.91	0—0.38
Cu+²	0; tail	0.10—0.45
Cd+²	0—0.47	0.36—0.74
Mn+²		0
Co+²		0—0.05
Ni+²		0
Zn+²	0; tail	0; 0.09—0.77
Fe+²		0—0.83

The eluants in the different experiments are indicated:
   I methyl-*n*-propylketone + 2 % 10N HCl
   II   »   »   »   + 5 »   »   »
   III   »   »   »   + 15 »   8N   »
   IV   »   »   »   + 15 »   10N   »
   V   »   »   »   + 25 »   8N   »
   VI methyl-*iso*-propyl-ketone + 15 % 10N HCl
   VII   »   » butyl   »   + 15 »   »   »

   *, non-equilibrium between paper and atmosphere; elution started directly after the insertion of the strips in the chamber.
   Without *, equilibration during 16 hours.

from each other; ζ) Sn+⁴, Bi+³, Sb+³, and As; η) W, Mo, V, and U; ∂) Ti, Th, and U; ϰ) Ga from Al and Tl.

   Metal ions with different valency states are most often rapidly reduced by the cellulose during elution, as is apparent from the agreement of R_F's in

Table 6 of the pairs Hg^+—Hg^{+2}, Fe^{+2}—Fe^{+3}, Tl^+—Tl^{+3}, Mn^{+2}—MnO_4^- and Cr^{+3}—CrO_4^{-2}. Weak tailing and hence slow reduction was observed for VO_4^{-3} and Ti^{+4}. Exceptions are Sn^{+4}—Sn^{+2}, where the higher valence ion is strongly adsorbed by the cellulose and no reduction therefore occurs; As^{+5}—As^{+3}, where an investigation has revealed that only very feeble reduction occurs in spite of the R_F's being about the same; and Ir^{+4}—Ir^{+3}, where, depending on the solvent and H^+-conc., Ir^{+4} may be reduced [18].

b) *n*-Butanol elutions: Only two-phase solvent mixtures were investigated. Pure *n*-butanol as well as mixtures with HCl, HNO_3, citric acid and NH_4OH were used. As previously published data are exhaustive, and R_F-values, obtained with the same eluant, mostly agree with these, no data will be mentioned but only some observations: α) As, Sb, and Sn in one of their two valence-states are almost always separated by HNO_3, citric acid and mixtures of these; β) the difficultly separable Al^{+3} and Cr^{+3} may be separated by *n*-butanol + 5 % citric acid + 2 N HNO_3 (2 : 1 : 1), the bands, however, nearly touch; γ) a partial or complete neutralisation of the acids with NH_4OH and thereby higher pH only diminishes the R_F's, renders the separations more difficult, and increases the spreading of the spots: δ) it was found difficult to reproduce previously published R_F's of ions, where the acid concentration of the stock solutions have to be high to prevent hydrolysis (especially As, Sb, and Sn), if exactly the same initial solutions were not prepared. This is due to the feeble acidity in the organic phase of two-phase mixtures, which is hence considerably changed by the strong acid concentration in the initial spot.

4) *Filter paper.* Munktell OB was employed in all experiments. Small amounts of Cu, located in bands in the paper, necessitate prior separation of Cu. Further, the adsorbing capacity of ions is not as high, and the paper not as homogeneous as Whatman 1, but the advantage of fast diffusion was considered more important.

The form and dimension of all paper strips was the same and the solvent front diffused the same length in each experiment, but in spite of this the variable can not be regarded as held constant, as paper strips are neither absolutely homogeneous nor mutually completely alike. This caused variations in R_F from paper strip to paper strip, as the diffusion rates, especially that of the "acid front", vary considerably (up to 20 %) on account of the varying intersections of the stationary and moving phases.

5) *Initial solutions of ions.* An investigation was made into the effect of changing the H^+-concentration (HNO_3 and HCl) of the initial spots of Cu, Co, Ni, Fe, Mn, Zn, Ag, Hg, and VO^{+2}, thereafter eluted by ketone-HCl mixtures, but only small changes in R_F could be noted, and the tailing of Ag, Hg, Fe, and VO was not diminished. As previously mentioned, the effect of changing the initial acid concentration can be great when two-phase mixtures are employed.

Usually no difference was observed by using chlorides or nitrates in the initial solutions. When chlorides, weakly acidic or neutral, were eluted by butanol-HNO_3 mixtures, the same R_F's were found as those, previously reported by Pollard *et al.* with nitrates. Ketonic solvents were also tested and with one exception, Bi, the same R_F's were obtained.

In a mixture of Ba, Ni, Mn, Co, Cu, Zn, Cd, and Fe, eluted by ketonic solvents, large concentrations of one or two of the ions did not affect the R_F's of the other ions. No displacement effect could be observed, even when serious tailing of the more concentrated ions were obtained into the areas of the other ions. Neither did Na^+ in large concentration disturb the separations; NH_4-salts, however, even in moderate concentration completely altered the separations and produced long tails of all the ions.

The spreading of the spots of some cations after elution was measured, varying amounts initially applied to the strips in about the same area. Results are shown in Table 7.

Table 7. *Eluant: methyl-n-propyl ketone* $+$ *15 % 8 N HCl; equilibration during a night before elution; acid front* $R_F \sim 0.68$.

mg applied	R_F of eluted cations					
	Ni^{+2}	Mn^{+2}	Co^{+2}	Cu^{+2}	Zn^{+2}	Fe^{+2}
0.005	0.03 — 0.06	0.08 — 0.12	0.30 — 0.37	0.43 — 0.54	0.67 — 0.80	0.84 — 0.90
0.010	0.03 — 0.06	0.08 — 0.13	0.30 — 0.38	0.43 — 0.54	0.67 — 0.81	0.83 — 0.80
0.025	0.02 — 0.07	0.07 — 0.13	0.30 — 0.41	0.41 — 0.68	0.68 — 0.77	0.83 — 0.90
0.050	0.01 — 0.07	0.05 — 0.13	0.30 — 0.41	0.40 — 0.87	0.68 — 0.78	0.84 — 0.92; 0
0.200	0.01 — 0.07	0.04 — 0.15 tail	0.26 — 0.41	0.39 — 0.87	0.69 — 0.80	0.70 — 1.00; 0 tail
0.400	0 — 0.07	0.04 — 0.16 tail	0.25 — 0.40		0.69 — 0.82	0.50 — 1.00; 0 tail
1.00	0 — 0.08	0 — 0.16	0.21 — 0.36	0.36 — 0.86	0.69 — 0.85	0 — 1.00
2.00	0 — 0.09	0 — 0.17	0.12 — 0.36		0.69 — 0.88	0 — 1.00

Table 7 indicates that only amounts < 0.025 mg of each cation are well separated. Identical experiments were performed with methyl-*iso*-propyl ketone $+$ 15 % 10 N HCl. The same dependence on applied weight was obtained; the spreading, however, was a little larger.

Table 7 also shows that Ni or Mn, Co or Zn can be separated in amounts of more than 1 mg. A combined elution by ketone $+$ 8 N HCl and ketone $+$ 10 N HCl leads to very good separations, but unfortunately only a max. 0.025 mg Cu and Fe can be present. By applying the stock solutions in different concentration and varying the subsequent degree of drying an attempt was made to diminish the tailing and retention of Cu and Fe in higher concentration, but only small improvements were attained.

6) *Application to the paper strips.* The solutions were always applied to about the same area and at the same distance from the upper ends of the strips. Further, it is advantageous to apply in small spots and not in bands, since the long tails, produced at the outer edges of the strips, render the cutting of the paper more difficult, particularly when invisible radioactive isotopes are separated [1].

Only slight effects could be observed by varying the degree of drying after application. Hence the variable is nearly constant.

7) *Equilibrium.* The very strong influence on R_F-values, caused by different states of equilibrium between paper strips and "atmosphere" at the beginning of elution, is indicated in Table 6, particularly by a comparison between values of solvent mixture I. Apart from some exceptions, *e.g.* Ag$^+$, more distinct spots and better separations are attained after equilibration. Otherwise the elution is performed with different conditions at the start and at the end, since the absorbtion of "atmospheric" vapours by the cellulose is fast at first but decreases exponentially with time.

Even when investigating shortlived radioactive isotopes it is favourable always to equilibrate for at least 15 minutes.

8) *Temperature.* Temperature differences influence vapour pressures, equilibrium constants and diffusion rates and hence also R_F's. However, an investigation revealed that by working at room-temperature, held constant to within $\pm 3°$ C, R_F-differences were small, and the variable can be considered as held constant.

1—8) *Summary.* Among the investigated variables only three have a powerful influence on the R_F's, obtained: eluant + "atmosphere", equilibration and paper. The first two principally determine R_F-values and separation efficiency and may be used and applied in such a way that good separations are obtained. Differences in paper strips cannot be controlled and chiefly determine the observed variance of R_F from experiment to experiment, when the same conditions are otherwise used. Fortunately, only the absolute values of R_F vary, the separation efficiency being feebly affected.

With the technique employed, and with the ketonic solvent as elutriant the entire chromatographic separation takes less than one hour, and is hence applicable to spallation studies.

D. Discussion

The great similarity has previously been mentioned between paper strip separations and partition elutions with ion-exchange columns, eluted by the same one-phase solvent mixture. The experimental results of the two procedures make possible an interpretation of the mechanism in paper chromatography. At the application of the ion-mixture to the paper the ions are adsorbed on active points in the cellulose and in the water phase, always bound in ordinary, not especially dried paper. During the equilibration, for instance with ketone + 8 N HCl as eluant, the water phase increases, but only after several days is complete saturation attained. At the same time HCl, as well as ketone, is dissolved in the water phase. When elution starts, the eluant begins to diffuse down the paper, water is partly adsorbed by the incompletely saturated cellulose and HCl strongly adsorbed in the cellulose water phase, until the H$^+$-concentration becomes the same as in the elutriant (8 N). An "acid front" is developed, moving down the paper with a one-phase ketone mixture behind and a ketone-water emulsion (two-phase mixtures when H$^+$ < 7.5 M) in front of it, the latter with a rapidly increasing pH-gradient and a gradually diminishing water content, the volume of which depends on the equilibration time. When the solvent front, almost pure ketone, reaches the initial spot, a distribution of the applied ions starts to occur between the moving ketone, the station-

ary water phase, feebly acidified by the "atmosphere", and the active points in the cellulose. The significance of the latter at first is predominant, the ions being retained unless their solubilities in the pure ketone are high, but rapidly diminishes, as the acid concentration in the stationary phase increases. Pure partition between stationary acid water and ketone-water emulsion now occurs, different ions moving with a particular pH. Even behind the "acid front" partition occurs between a stationary highly acid water phase and the moving one-phase mixture.

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