

CHROM. 7716A

## THE USE OF THE AMPHOTERIC ION-EXCHANGE RESIN RETARDION 11A8 FOR INORGANIC SEPARATIONS

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### SUMMARY

The use of the "snake in a cage" amphoteric ion-exchange resin Retardion 11A8 for various separations of inorganic ions was investigated.

Clean separations of Ga(III)–In(III)–Tl(III), Pt(II)–Pd(II), and Na(I)–Ni(II)–Cu(II)–Zn(II) mixtures have been achieved. In acidic media, in which the resin acts mainly as an anion exchanger, some residual activity of the acrylate poly-anion seems to exist, resulting in significant changes in distribution coefficients in comparison with standard anion-exchange resins. In the case of elements that can exist as both cations and anions in solution (*e.g.*, Ni, Co, Cu and Zn), the amphoteric properties of Retardion 11A8 permit more specific isolation of certain elements from complex mixtures than would be possible with the use of monofunctional ion exchangers.

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### INTRODUCTION

Retardion 11A8, which is a "snake in a cage" type of amphoteric ion-exchange resin containing carboxylic and quaternary ammonium exchange groups, was first described in 1957 and has been used since then for the separation of electrolytes from non-electrolytes, desalting of amino acids, etc., by ion retardation<sup>1–3</sup>. Fractionation of some inorganic salt mixtures using water as the eluent has also been reported<sup>1</sup>. The resin has not been used so far for typical radiochemical or analytical separations of inorganic ions, and the investigation of its utility for this purpose was the aim of the present work.

### EXPERIMENTAL

#### *Ion-exchange resin*

The properties of Retardion 11A8 resin used in this study are summarized in Table I. Methods of grinding, fractionating and microscopic determination of particle size have been described earlier<sup>4</sup>. The resin was conditioned by passing successively 2 *N* sodium hydroxide, water and 2 *N* hydrochloric acid through it and finally washing it with a large excess of water until it was free from chlorides. The total anion-

TABLE I  
 PROPERTIES OF RETARDION 11A8 RESIN USED IN THIS STUDY

Exchange capacity (mequiv./g dry resin, self-absorbed)		Bed density (g of dry resin, self-absorbed, per ml of bed), $d_2$	Particle size of fraction used for for column studies
Total	Excess of anion-exchange groups		
	From HCl	From NaCl	
2.95	0.14	0.09	0.420
			20 $\mu\text{m}$ $\leq \varnothing \leq$ 45 $\mu\text{m}$ 40 $\mu\text{m}$ $\leq \varnothing \leq$ 60 $\mu\text{m}$

exchange capacity (milliequivalents per gram of dry resin, self-absorbed) was determined by placing resin with a pre-determined water content in a special centrifuge tube<sup>5</sup>, washing it with 1 *N* hydrochloric acid and then with 0.1 *N* hydrochloric acid, centrifuging at 3000 rpm (*ca.* 900 g) for 15 min, displacing chlorides with 1 *N* sodium hydroxide and titrating them by Volhard's method. The results were corrected for the residual amount of hydrochloric acid retained at the interface of the beads<sup>5</sup>. The exchange capacity due to anion-exchange groups being in excess with respect to carboxylic groups was determined by treating the resin (self-absorbed) with 1 *N* hydrochloric acid or sodium chloride solution, washing with water until free from chlorides, displacing chloride ions with 1 *N* sodium hydroxide and determining them as described above.

The bed density ( $d_2$ ) refers to the self-absorbed form of the resin in pure water.

#### Radioactive tracers and reagents

The following radioactive tracers were used: <sup>134</sup>Cs ( $T_{1/2} = 2.07$  years), <sup>72</sup>Ga ( $T_{1/2} = 14.3$  h), <sup>114m</sup>In ( $T_{1/2} = 50$  days), <sup>204</sup>Tl ( $T_{1/2} = 3.56$  years), <sup>109</sup>Pd ( $T_{1/2} = 13.5$  h), <sup>197</sup>Pt ( $T_{1/2} = 20$  h), <sup>65</sup>Ni ( $T_{1/2} = 2.56$  h), <sup>60</sup>Co ( $T_{1/2} = 5.26$  years), <sup>64</sup>Cu ( $T_{1/2} = 12.8$  h), <sup>65</sup>Zn ( $T_{1/2} = 245$  days) and <sup>24</sup>Na ( $T_{1/2} = 15.0$  h). Most of the isotopes were prepared by neutron irradiation of spectrally pure metals, oxides or nitrates, in the Polish reactor EWA. <sup>109</sup>Pd and <sup>197</sup>Pt tracers were purified from <sup>111</sup>Ag and <sup>199</sup>Au isotopes, respectively (formed from target material by (n,  $\gamma$ ),  $\beta^-$  reactions) by methods described earlier<sup>6,7</sup>. <sup>134</sup>Cs and <sup>24</sup>Na were prepared by irradiation of the respective chlorides and purified from <sup>32</sup>P when necessary<sup>8</sup>.

In order to obtain trivalent thallium tracer, irradiated TlNO<sub>3</sub> was acidified with hydrochloric acid and chlorine gas was bubbled through the resulting suspension of TlCl until it was completely dissolved.

All reagents were of the highest grade available commercially.

#### Apparatus and procedure

Distribution coefficients were determined by batch equilibration and column experiments using the techniques described earlier<sup>4,5,9</sup>. Jacketed glass columns of *ca.* 2 mm I.D. were used and the apparatus for the drop-elution technique was the same as described earlier<sup>4,5,9</sup>. When necessary, the identity of the elution peaks or of the activity remaining on the resin was checked by  $\gamma$ -ray spectrometry.

## RESULTS AND DISCUSSION

*Separation of Ga-In-Tl mixtures*

Weight-distribution coefficients,  $\lambda$  (amount per gram of dry resin, self-absorbed/amount per millilitre of solution) of Ga, In and Tl on Retardion 11A8 in hydrochloric acid medium are shown in Fig. 1. The differences in the values of the distribution coefficients are sufficiently high to permit the clean separation of Ga-In-Tl mixtures by stepwise elution (Fig. 2). Thallium, which shows high distribution

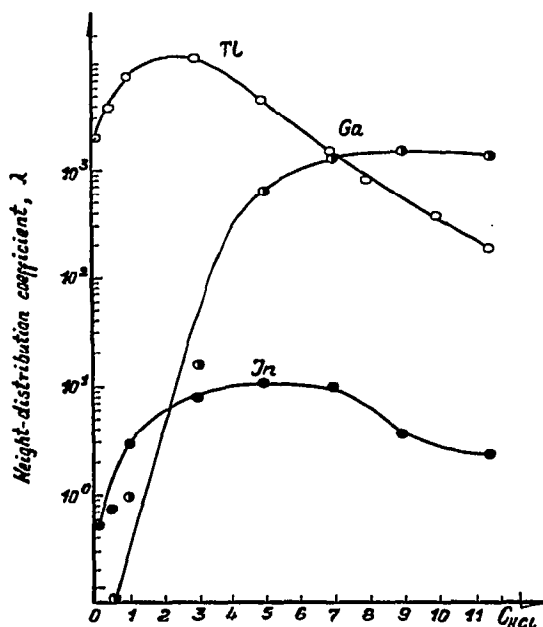


Fig. 1. Weight-distribution coefficients of Ga(III), In(III) and Tl(III) in the system Retardion 11A8-HCl (aq.).

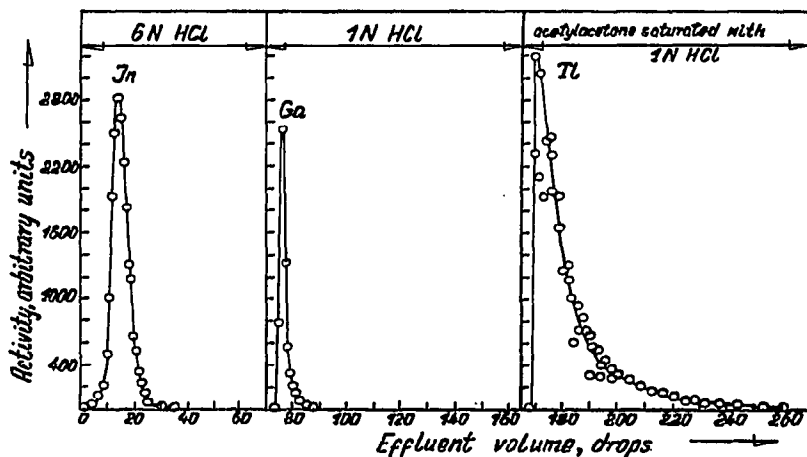


Fig. 2. Separation of In, Ga and Tl. Column:  $2.50 \text{ cm} \times 0.0350 \text{ cm}^2$ , Retardion 11A8 (20-45  $\mu\text{m}$ ). Temperature:  $25^\circ$ . Flow-rate: 2 cm/min.

coefficients over the whole range of hydrochloric acid concentrations, could be quantitatively eluted with acetylacetone saturated with 1 *N* hydrochloric acid. Surprisingly, some other organic solvents which are even more effective in the liquid-liquid extraction of Tl(III), *e.g.*, diethyl ether, failed to elute Tl from the resin.

Comparing the above ion-exchange behaviour with that reported by Kraus *et al.*<sup>10</sup> for group IIIB elements on Dowex 1-X10 resin in hydrochloric acid medium, both similarities and differences in the general character of the  $\log \lambda - C_{\text{HCl}}$  curves were observed. The curve for Tl on Retardion 11A8 has a distinct maximum at  $C_{\text{HCl}} \approx 2.5$  (*cf.*, Fig. 1), which is absent when Dowex 1-X10 resin is used and the maximum values of  $\lambda_{\text{Ga}}$  are lower than those for Dowex 1-X10 by more than two orders of magnitude<sup>10</sup>. The inversion in selectivity between Tl and Ga occurs at  $C_{\text{HCl}} \approx 4.5$  for Dowex 1-X10 and at  $C_{\text{HCl}} \approx 8$  for Retardion 11A8. It is difficult to state unambiguously at present whether the presence of acrylate polyanions or merely the lower nominal degree of cross-linking (Retardion 11A8 is made from Dowex 1-X8 resin<sup>11</sup>) are the reasons for these differences. There is no doubt, however, that much better separations of Ga-In-Tl mixtures can be obtained with this resin (*cf.*, Fig. 2) than those reported<sup>10</sup> for Dowex 1-X10.

#### Separation of the pair Pt-Pd

Weight-distribution coefficients of these elements are shown in Fig. 3. It seemed feasible to elute Pd first with hydrochloric acid and then Pt with another suitable

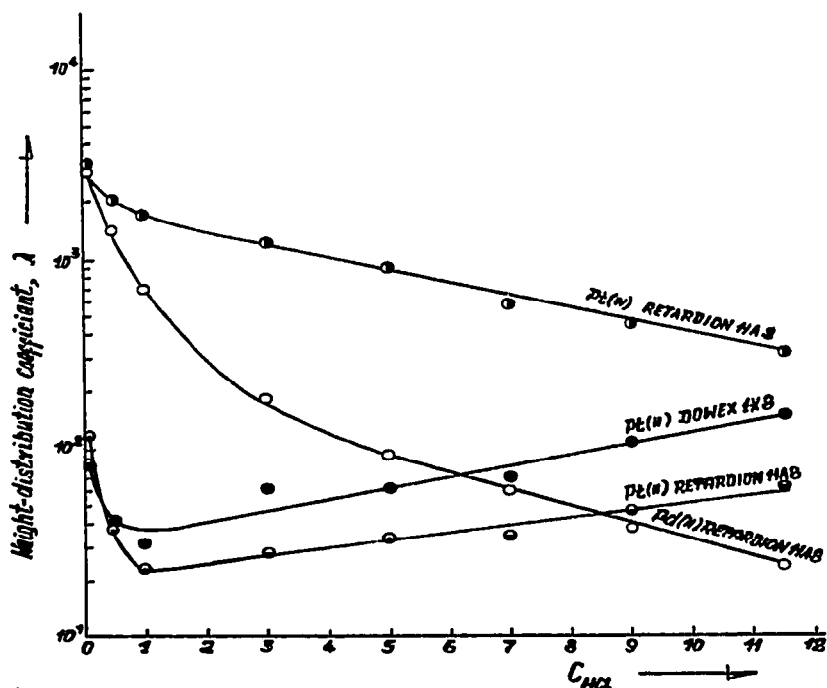


Fig. 3. Weight-distribution coefficients of Pt(IV) (after oxidation with aqua regia), Pt(II) (after reduction with  $\text{N}_2\text{H}_4 \cdot \text{HCl}$ ) and Pd(II) in the systems Retardion 11A8-HCl and Dowex 1-X8-HCl(aq.).

eluent. Unexpectedly, however, it was found that some of the platinum was eluted in a reproducible manner with a distribution coefficient exceeding only slightly that of Pd, while the remainder (*ca.* 50%) remained firmly on the column. Moreover, elution of Pd with hydrochloric acid is a lengthy procedure owing to its relatively high distribution coefficient.

Addition of hydrazinium hydrochloride reduced Pt to the divalent state, which resulted in a considerable decrease in its distribution coefficient. Platinum was then eluted first and could be separated from Pd on a very short column (*cf.*, Fig. 4).

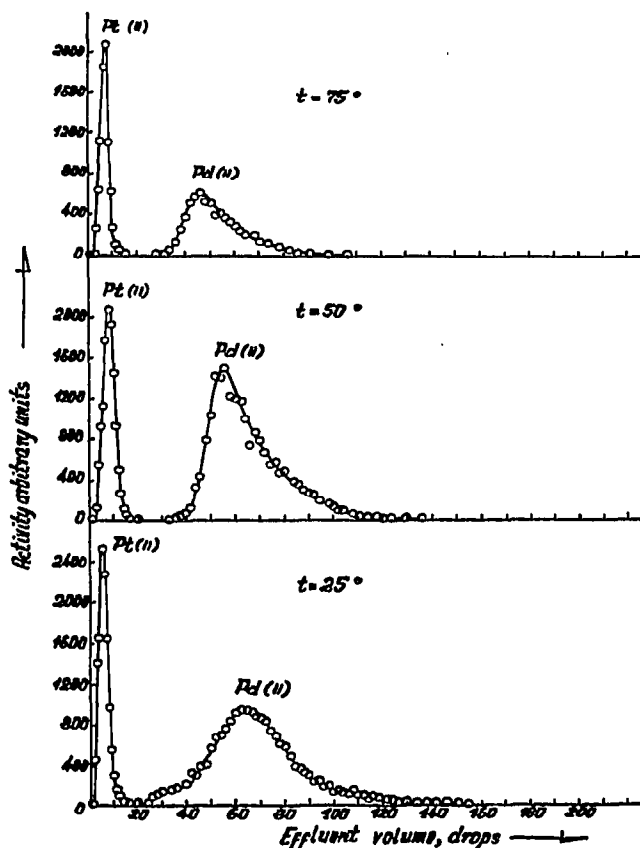


Fig. 4. Effect of temperature on the separation of Pt(II) and Pd(II). Column: 1.0 cm  $\times$  0.0305 cm<sup>2</sup>, Retardion 11A8 (20–45  $\mu$ m). Eluent: 3.4 N HCl. Flow-rate: 2 cm/min.

The effect of temperature on this separation was investigated by repeating the runs at 25, 50 and 75°. Separation factors,  $\alpha_{Pt}^{Pd}$ , were calculated from the elution curves by the equation

$$\alpha_{Pt}^{Pd} = \frac{U_{\max. (Pd)} - (U_0 + V)}{U_{\max. (Pt)} - (U_0 + V)} \quad (1)$$

where  $U_{\max. (Pd)}$  and  $U_{\max. (Pt)}$  are the retention volumes (ml) of the two elements in question,  $U_0$  is the dead volume of the column and  $V$  is the free volume of the resin

bed.  $U_0$  and  $V = i \cdot V_b$  (where  $i$  is the fractional free volume of the bed and  $V_b$  is the bed volume) were determined from separate experiments in which a non-adsorbable tracer ( $^{134}\text{Cs}$ ) was eluted from the same column having two different resin bed lengths, and calculated as described earlier<sup>4,12</sup>. Mathematical analysis of the results confirmed the assumption that in the system Retardion 11A8–hydrochloric acid  $\lambda_{\text{Cs}}$  is approximately zero. Plate heights,  $H$ , were calculated from the relationship<sup>13</sup>

$$H = \frac{L \cdot W^2}{8 (U_{\text{max.}} - U_0)^2} = \frac{L \cdot \sigma^2}{(U_{\text{max.}} - U_0)^2} \quad (2)$$

where

$L$  = length of the resin bed;

$W$  = width of the peak for the  $M = M_{\text{max.}}/e = 0.368 M_{\text{max.}}$  ordinate;

$\sigma = W/2\sqrt{2}$  = standard deviation of the chromatographic peak.

The resolution<sub>3</sub> of the Pt–Pd pair,  $R_3^{\text{Pt-Pd}}$ , was calculated from the equation<sup>13</sup>

$$R_3^{\text{Pt-Pd}} = \frac{U_{\text{max. (Pd)}} - U_{\text{max. (Pt)}}}{3 (\sigma_{\text{Pt}} + \sigma_{\text{Pd}})} \quad (3)$$

The results are summarized in Table II.

TABLE II

EFFECT OF TEMPERATURE ON THE SEPARATION OF Pt–Pd IN THE SYSTEM: RETARDION 11A8–HCl +  $\text{N}_2\text{H}_4 \cdot \text{HCl}$

Temperature (°C)	$H_{\text{Pt}}$ (cm)	$H_{\text{Pd}}$ (cm)	$\alpha_{\text{Pt}}^{\text{Pd}}$	$R_3^{\text{Pt-Pd}}$
25	3.05	0.06	63.2	1.15
50	0.47	0.04	15.1	1.26
75	0.49	0.05	17.4	1.15

Although very short columns had to be used in order to complete the elution of the Pd band in a reasonable time and therefore the results calculated from the Pt peak may be inaccurate, some conclusions are straightforward. An increase in temperature up to 50° has a favourable effect on the separation owing to a decrease in plate height, despite a simultaneous decrease in the separation factor. A further increase in temperature is undesirable. For practical purposes, however, it was preferred to use longer columns at room temperature and to elute the Pd with a 1% thiourea solution as a sharp band (*cf.*, Fig. 5). In another experiment, 5 mg of Pt were similarly separated from trace amounts of Pd.

It is interesting to note (see Fig. 3) that the  $\log \lambda - C_{\text{HCl}}$  curve for Pt(II) on Retardion 11A8 is distinctly lower than the corresponding curve determined for Dowex 1-X8.

The apparent decrease in distribution coefficients, especially at higher hydrochloric acid concentrations, is larger than expected on the basis of differences in exchange capacity alone, if direct proportionality between distribution coefficients and exchange capacity is assumed. It would seem, therefore, that the presence of polyacrylate in the resin phase decreases the bond strength between the metal chloro-complex and the quaternary ammonium functional group.

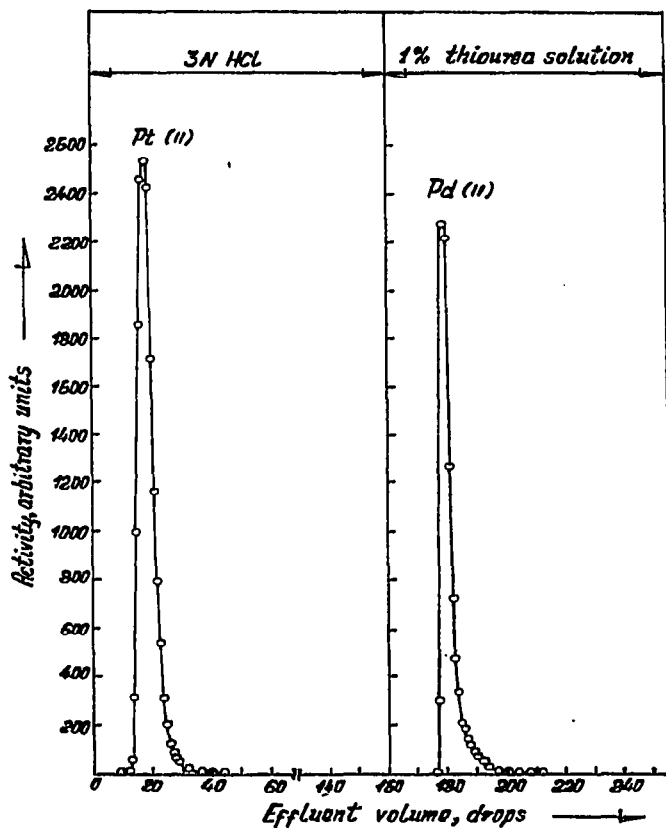


Fig. 5. Separation of Pt(II) (0.52 mg) and Pd(II) (0.0015 mg) by stepwise elution. Column: 4.30 cm  $\times$  0.0305 cm<sup>2</sup>, Retardion 11A8 (20–45  $\mu$ m). Temperature: 25°. Flow-rate: 2 cm/min.

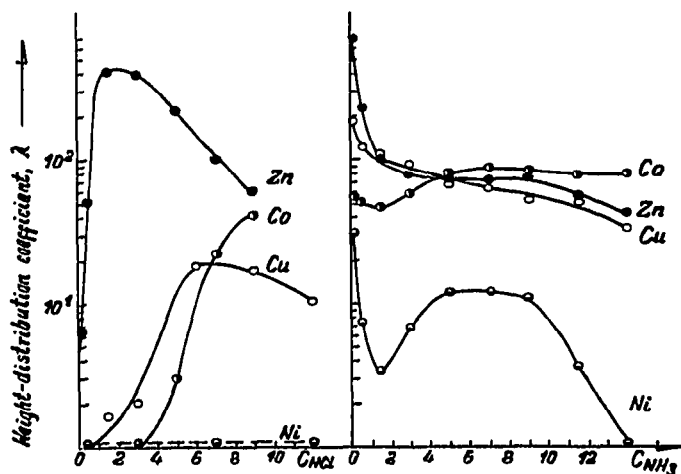


Fig. 6. Weight-distribution coefficients of Ni(II), Cu(II), Co(II) and Zn(II) in the systems Retardion 11A8–HCl(aq.) and Retardion 11A8–NH<sub>3</sub>(aq.).

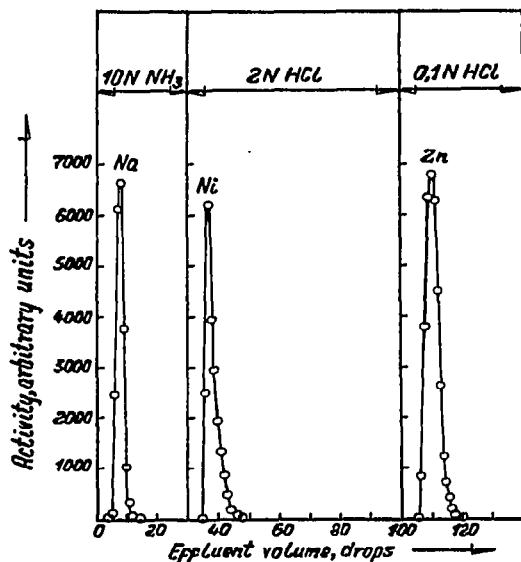


Fig. 7. Separation of Na, Ni and Zn. Column: 5.0 cm  $\times$  0.0306 cm<sup>2</sup>, Retardion 11A8 (40–60  $\mu$ m). Temperature: 25°. Flow-rate: 0.80 cm/min.

#### Separation of Na, Ni, Cu and Zn

In the separations discussed above, Retardion 11A8 acted mainly as an anion exchanger, although some influence of the acrylate polyanion on the distribution coefficients of metal chloride complexes and probably also on the elution behaviour seems to exist. In the case of metals that can form both cationic ammine complexes and anionic chloride complexes<sup>14</sup>, the amphoteric properties of the resin can be fully demonstrated.

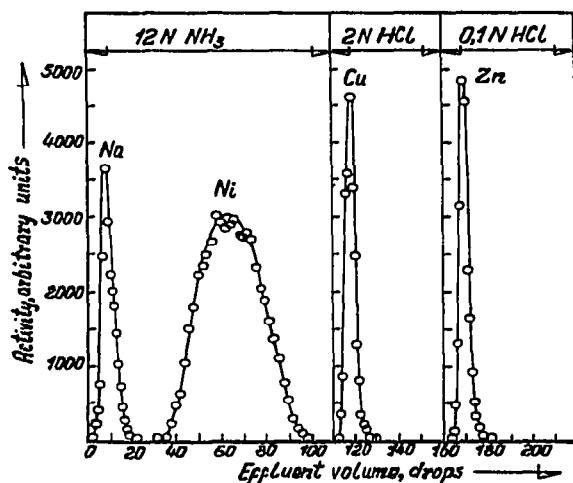


Fig. 8. Separation of Na, Ni, Cu and Zn. Column: 5.0cm  $\times$  0.0324 cm<sup>2</sup>, Retardion 11A8 (40–60  $\mu$ m). Temperature: 25°. Flow-rate: 0.90 cm/min.



Weight-distribution coefficients of Ni, Zn, Cu and Co on Retardion 11A8 in both hydrochloric acid and ammonia solution are shown in Fig. 6. Two separations demonstrating the flexibility of the system are presented in Figs. 7 and 8.

Nickel, which cannot be separated from alkali metals on anion-exchange resins in hydrochloric acid medium, can be taken up here as a cation while sodium passes through, and is subsequently eluted with either hydrochloric acid or ammonia solution. It is interesting to note that elements such as Zn, which have a high affinity to the resin in both the cationic and anionic forms over almost the whole concentration range, can withstand the change in eluent from basic to acidic without any detectable leakage. Such behaviour may be the basis for selective isolation of certain elements from mixtures in a much more specific way than when making use of standard resins with only one type of functional group (cationic or anionic).

## CONCLUSIONS

The results clearly show that Retardion 11A8 can be very useful in radio-chemical and analytical separations. In acidic media, in which the resin acts mainly as an anion exchanger, some residual effect of the polyacrylate in the resin phase seems to exist, resulting in changes in both the distribution coefficients and in the shape of the  $\log \lambda_{\text{HCl}} - C_{\text{HCl}}$  plot in comparison with standard anion-exchange resins.

The amphoteric properties of the resin can be effectively exploited towards elements that can exist both as cations and as anions in solution, depending on the ligands present, pH, etc. It is hoped that in some instances more specific isolation of certain inorganic ions (e.g., those which show amphoteric properties) from complex mixtures can be achieved than that attainable with monofunctional ion exchangers. Further work is needed in order to demonstrate all the possibilities that may be offered by this resin in various inorganic separations.

## ACKNOWLEDGEMENT

The authors thank Mrs A. Kołyga for skilful technical assistance.

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