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**ION-EXCHANGE BEHAVIOR OF ALKALI METALS
ON TREATED CARBONS**

G. Mohiuddin
W. Y. Hata
J. S. Tolan

Consultants

J. S. Johnson, Jr. and S. Y. Shiao

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Oak Ridge Station
School of Chemical Engineering Practice
Massachusetts Institute of Technology
W. W. Doerr, Director

Oak Ridge National Laboratory
Oak Ridge Tennessee 37830
Operated by
Union Carbide Corporation
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ABSTRACT

The ion-exchange behavior of trace quantities of the alkali-metal ions sodium and cesium, on activated carbon impregnated with zirconium phosphate (referred to here as ZrP), was studied. Impregnated carbon had twice as much ion-exchange activity as unimpregnated, oxidized carbon, and 10 times as much as commercial activated carbons. The distribution coefficient of sodium increased with increasing pH; the distribution coefficient of cesium decreased with increasing pH.

Sodium and cesium were separated with an electrolytic solution of 0.1 M HCl. Preliminary studies indicated that 0.2 M potassium and cesium can also be separated. Distribution coefficients of the supported ZrP were determined by the elution technique and agreed within 20% of the values for pure ZrP calculated from the literature.

1. SUMMARY

The ion-exchange behavior of trace quantities of the alkali-metal ions sodium and cesium, on zirconium phosphate (referred to here as ZrP), was studied. Zirconium phosphate is a useful inorganic ion exchanger; it shows resistance to high temperatures, intense radioactivity, severe acidic conditions, and also exhibits high selectivity (1). Zirconium phosphate was impregnated on carbon supports because pure ZrP forms a gel when exposed to electrolytic solutions (1).

The distribution coefficient, a measure of ionic exchange performance, was experimentally determined by the elution technique for activated carbon as commercially available and oxidized with nitric acid, and oxidized carbon impregnated with ZrP. The ion-exchange behavior was studied for three electrolytic concentrations (0.1, 0.3, and 1.0 M) and three pH levels (1.0, 5.5, and 9.5). At a pH of 9.5 the distribution coefficient for sodium was larger than that for cesium; at a pH of 1.0 the distribution coefficient for cesium was larger. The impregnated carbon showed ten times as much ion exchange activity as unoxidized carbon, and twice as much as oxidized carbon.

The distribution coefficient for pure ZrP was determined by comparing the ion exchange behavior of impregnated carbon and unimpregnated carbon; it was within 20% of the values for pure ZrP calculated from the literature.

Trace quantities of sodium and cesium ions were separated by the impregnated-carbon ion exchanger and 0.1 M HCl. Preliminary studies indicated that these conditions can be used to separate trace amounts of cesium from brine (0.1 M HCl, 0.3 M K^+ , 0.4 M Mg^{++} , and 0.3 M Na^+).

2. INTRODUCTION

2.1 Ion Exchange

The separation of a mixture into pure components is often the most difficult aspect of chemical processing. Chromatographic techniques such as ion exchange are increasingly being used to separate charged species of similar chemical activity because of the low cost, simplicity of equipment, and high selectivity (1). The separation of alkali metals is an important process in the nuclear processing industry (2). Organic ion exchange resins are rugged and durable under normal chemical processing conditions but physically degrade and lose selectivity when exposed to the radioactivity and high temperatures associated with nuclear process waste treatment (2). Inorganic ion exchangers may have the performance characteristics of the organic resins while also showing greatly improved resistance to intense radioactivity, high temperatures, and severe chemical conditions (2).

Many metals, such as zirconium, iron, tin, and titanium, form complexes which exhibit some ion-exchange behavior; titanium oxides are well suited for the separation of uranium from seawater (3). Zirconium phosphate is one of the most effective inorganic ion exchangers for alkali-metal cations (4). Zirconium does not participate in the ionic exchange but does significantly improve the ion-exchange capabilities of the phosphate group (5). The advantages of zirconium phosphate over other metal complexes in ion exchange processes are: it has a stable valence state and will not dissociate from the phosphate if the reaction conditions change (3); it is non-toxic; and it is relatively inexpensive (4).

Anionic organic ion exchangers are used to separate two or more negatively charged species; cationic exchangers separate positively charged species (1). Inorganic ion exchangers can function as either cationic or anionic exchangers, depending on the exchange reaction conditions. This added versatility makes inorganic ion exchangers particularly attractive (4).

The active (charged) sites on zirconium phosphate ion exchangers are the phosphoric acid groups in various oxidation states. The behavior of these groups, and hence, the ion exchange characteristics of zirconium phosphate, may be altered by changing the ionic-exchange reaction conditions (4).

Zirconium phosphate (ZrP) shows excellent ion exchange characteristics, but is difficult to use in practice. Organic resin exchangers are usually prepared as highly porous, spherical beads. The beads are typically placed in a plug-flow reactor through which an electrolytic solution containing the species to be separated is passed (1). The retention time of one ionic species may be greater than that of the other, depending on the exchange behavior of the ion and the exchanger. Zirconium phosphate is difficult to use, because it sometimes forms a colloidal gel when exposed to electrolytic solutions (6). The problem is further compounded by the complex nature of ZrP in that there are at least ten crystalline phases of the compound (1); the ion exchange behavior of all ten have not been fully determined.

Loading ZrP on a porous support, as is done with some noble metals, solves both the colloidal gel problem and increases the fraction of the ZrP exposed to the solution (4). Activated carbon is well-suited as an ionic exchanger support because it has an extremely high surface area (approximately 1000 m²/g), is very inexpensive, and exhibits some ion-exchange behavior itself (1).

Commercial activated carbon is not a good ion-exchanger; however, if the carbon is oxidized with nitric acid, the exchange capabilities dramatically increase (4). Studies show that the increase in activity is because of a change in the surface characteristics of the carbon, not because of an increase in surface area (7).

Shiao (8) developed a method for impregnating either activated or oxidized carbon with ZrP. The carbon is first loaded with ZrP and then is contacted with phosphoric acid. The actual formula of the ZrP complex is unknown.

Ideally a ZrP ion exchanger possesses a phosphorous-to-zirconium ratio of approximately two (1). As already noted, the exact structure of the zirconium complex is not well known. Two possible forms of ZrP are:

and

2.2 Measurement Techniques

There are several ways to determine the characteristics of an ion exchanger. The simplest is the batch (shaking) method (9), in which a known quantity of ion exchanger is equilibrated with a solution containing a radioactively tagged or otherwise recognizable ionic species. The capacity (the amount of ionic species adsorbed) is determined by measuring the adsorbance (uptake) of the charged species by the solid exchanger. Two other characterization techniques utilize changes in influent concentration through a plug-flow reactor. In the breakthrough technique (10) the reactor is first equilibrated with an electrolytic solution. At time zero a step input of tracer is introduced into the influent stream. The tagged ions may have a retention time larger than that of the bulk fluid retention time. The distribution coefficient is a measure of ion exchange and is a function of the difference in retention time. A third method, the elution technique, is similar to the breakthrough technique except that a pulse of traced ionic species is injected into the influent stream. The effluent concentrations obtained from the elution technique are the time derivatives of the concentrations from the breakthrough technique, just as a pulse input is the time derivative of a step change in input concentration. Both exchange tests produce the same distribution coefficient (6).

2.3 Objective and Method of Approach

The overall objective was to compare the alkali-metal ion exchange behavior of carbons impregnated with ZrP with unimpregnated carbons. This objective was met by:

1. Summarizing the thermodynamic ion-exchange behavior of pure ZrP, and comparing the behavior with that obtained experimentally for the impregnated carbon.
2. Experimentally determining the distribution coefficients of cesium ions and sodium ions exchanging with hydrogen ions. The performance of impregnated carbons was compared with that of unimpregnated carbons oxidized with nitric acid (oxidized carbons) and unaltered, commercial, activated carbons (unoxidized carbons). The effect of pH and ionic strength on the distribution coefficient was measured.
3. Separating a mixture of trace quantities of cesium and sodium, and using the results to predict and measure the behavior of a multi-component system.

3. APPARATUS AND PROCEDURE

The apparatus for the determination of distribution coefficients by the elution technique consisted of a 5-ml graduated pipette with feed reservoir, automatic tube changer, and gamma radiation counter. A schematic diagram of the apparatus is shown in Fig. 1.

The 5-ml pipette contained the ion exchange column, packed with impregnated or unimpregnated carbon, as shown in Fig. 2. The column packing procedure is described in Appendix 10.1.

In the elution technique an electrolyte of known pH and concentration was stored in the electrolyte reservoir and fed by gravity into the top of the ion-exchange column. The electrolyte was typically NH_4Cl , NH_4OH , or HCl of concentration 0.1 to 1.0 M. Sodium ion was added to the electrolyte in 10^{-5} M concentration to equilibrate with the glass walls and glass wool. The carbon ion exchange column (bed) was conditioned for the exchange of electrolyte and hydrogen by passing a volume of electrolyte through the column equal to twenty times the volume of the bed (10). The flow from the reservoir was stopped after the bed was equilibrated. The connecting tube was removed, and the liquid in the column was allowed to run down to the top of the bed. A gamma-emitting radioactive tracer, ^{22}Na or ^{137}Cs , was immediately added with a 0.2-ml suction pipette in a 0.075-ml volume of concentration 10^{-9} M. The electrolyte flow was started again when the tracer flowed down to the top of the bed.

Samples with a specified number of drops were collected in plastic tubes under the column. An automatic tube changer moved the tubes directly below the column, then moved them away when the specified number of drops had been collected. The number of drops chosen was small enough to generate a smooth curve for a plot of gamma counts as a function of electrolyte volume, yet large enough to minimize the number of tubes used and counted. The typical sample size was 5 to 10 drops, or about 0.25 to 0.5 ml.

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EXPERIMENTAL APPARATUS

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FIG.
2

The gamma radiation counts were taken by a 64-W gamma counter within half an hour of the collection of the sample. Background radiation was always measured before the first sample was counted to correct the number of counts and to check for proper functioning of the counter. Counting time was 1 min.

The average flow rates ranged from 0.13 ml/min for the column packed with impregnated carbon to 0.8 ml/min for unoxidized carbon. The flow stopped occasionally (once every two or three runs) when air bubbles appeared in the connecting tube or when salts deposited on the bottom of the column.

Experiments were terminated when the counts for a sample fell to background level after reaching the peak. The procedure for performing a ^{137}Cs and ^{22}Na separation was similar to that for a single species except that 0.075 ml of each isotope was injected into the column, and the gamma counts were taken on a Canberra Automatic Counter capable of distinguishing cesium radiation from sodium.

The column was not conditioned with cesium before introduction of the cesium tracer; preconditioning was unnecessary, as discussed in Appendix 10.8. The glass wool also had no effect on the ion-exchange behavior of the system. The test for glass-wool adsorptive capability is discussed in Appendix 10.9.

4. THEORY

4.1 Thermodynamics of Ion Exchange

The distribution coefficients of alkali metals were experimentally determined by the elution technique (10). Examination of the thermodynamics of the ion exchange yields a theoretical distribution coefficient. The anionic species in zirconium phosphate (here called ZrP) is phosphoric acid; the cations are the alkali metals. Ion exchange occurs between the radioactively traced cations and the adsorbed electrolytic ions, because during equilibration the ions in the electrolyte solution, for example, NH_4^+ and H^+ , replace hydrogen ions in phosphoric acid. For ammonium chloride electrolyte the equilibrium ion exchange reaction between NH_4^+ and metal ions, M^+ , is given by:

where

M^+ $\equiv$ metal ions in solution (g/ml)

$\overline{\text{M}^+}$ $\equiv$ adsorbed metal ions (g/g bed)

NH_4^+ = ammonium ions in solution (g/ml)

$\overline{\text{NH}_4}$ = adsorbed ammonium ions (g/g bed)

The equilibrium constant is the ratio of the activities of the products over the reactants as shown by:

$$K_{eq} = \frac{a_{\text{NH}_4^+} a_{\text{M}^+}}{a_{\overline{\text{NH}_4}} a_{\text{M}^+}} \quad (2)$$

where

a_i = activity of species i

K_{eq} = equilibrium constant

Activity is the product of the concentration and the activity coefficient γ_i of a species. For an ideal solution the ratio of activity coefficients is unity (7). The selectivity coefficient $K_{\text{NH}_4}^{\text{M}}$ of a metal ion in an ammonium chloride solution is defined as the equilibrium constant of an ideal solution:

$$K_{eq} K_{\text{NH}_4}^{\text{M}} = \frac{[\text{M}^+][\text{NH}_4^+]}{[\text{M}^+][\overline{\text{NH}_4}]} \quad (3)$$

$[i]$ = concentration of species i

Analogously, K_{H}^{M} is defined by:

$$K_{\text{H}}^{\text{M}} = \frac{[\text{M}^+][\text{H}^+]}{[\text{M}^+][\overline{\text{H}^+}]} \quad (4)$$

where

K_{H}^{M} = selectivity coefficient of hydrogen

The distribution coefficient D_i and the selectivity coefficient $K_{\text{NH}_4}^{\text{M}}$ can be related to each other if the saturation capacity of the exchanger Q_0 (the total number of milliequivalents of exchangeable cations per gram

of bed) and the ionic strength of the initial solution C_0 are known. Ionic strength is calculated (11) as:

$$I = \sum m_i Z_i^2 \quad (5)$$

where

I = total ionic strength (moles/liter)

m_i = concentration (molarity) of species i

Z_i = ionic charge on species i

Equation (5) is applied only to the dissociated species in the electrolytic solution. Ammonium hydroxide does not dissociate appreciably above a pH of 4.7 (12). It therefore contributes zero to total ionic strength at pH greater than 4.7. For sodium in trace quantities exchanging with ammonium at typical electrolytic levels, the ionic strength of the electrolyte is equated to the sum of the sodium and ammonium concentrations as:

$$C_0 = [NH_4^+] + [Na^+] \quad (6)$$

The column capacity is expressed in an analogous way for the adsorbed phases:

$$q_0 = [NH_4^+] + [Na^+] \quad (7)$$

The sodium distribution coefficient is defined as:

$$D_{Na} = \frac{[Na^+]}{[Na^+]} \quad (8)$$

Substituting Eqs. (6) through (8) into Eq. (3) yields:

$$K_{NH_4}^M = D_{Na} \frac{(C_0 - [Na^+])}{(q_0 - [Na^+])} \quad (9)$$

where

$K_{\text{NH}_4}^{\text{M}}$ = selectivity coefficient

The concentration of sodium ions in the solution and adsorbed on the column is 10^{-5} M. The concentrations of ammonium ions in the solution and adsorbed on the column were 0.1 to 1.0 M. Equation (6) implies that $[\text{Na}^+]$ is negligible compared with C_0 , and Eq. (7) implies that $[\text{Na}^+]$ is negligible compared with q_0 . With these two assumptions, Eq. (9) reduces to:

$$K_{\text{NH}_4}^{\text{M}} = \frac{D_{\text{Na}} C_0}{q_0} \quad (10)$$

Equation (10) is solved for D_{Na} , and the base-10 logarithms are taken of all terms to obtain:

$$\text{Log } D_{\text{Na}} = \text{Log} \left(K_{\text{NH}_4}^{\text{M}} q_0 \right) - \text{Log } C_0 \quad (11)$$

A plot of $\text{Log } D_{\text{Na}}$ vs $\text{Log } C_0$ is a straight line of slope -1, if the loading q_0 does not approach the capacity of the column and if the solutions are ideal. If the solutions are non-ideal, Eq. (2) is still valid, but Eq. (11) is not. The non-ideal liquid-phase activity coefficients can be estimated with the Scatchard equation (13).

4.2 Mass-Transfer Limitations

Mass-transfer limitations within the column were examined to determine whether the measured retention times of traced metal ions were a function of diffusion limitations.

The elution of metal cations from a packed column of ion exchange medium was mathematically analyzed by assuming that the system was always at chemical-reaction equilibrium (14): the column operated under film (bulk) diffusion control or pore (particle) diffusion control. Rosen's model assesses the effects of film and pore diffusion of a uniform-velocity liquid flowing through a fixed bed of homogeneous, spherical particles (15). The column length-to-diameter ratio must be greater than 4 for Rosen's model to be applicable.

Film-diffusion limitations were investigated by calculating Rosen's film-diffusion parameter v/X , a ratio of reactor size to mass-transfer rate. This parameter is defined by:

$$v/X = \frac{mVR_f}{Z} \quad (12)$$

where

$$m = \frac{\epsilon}{1-\epsilon}$$

ϵ = bed void fraction

V = interstitial flow velocity, cm/s

R_f = film resistance, s

Z = bed length, cm

When v/X is less than 0.01, film diffusion is not rate-limiting.

Pore-diffusion limitations were investigated by calculating an effective pore diffusivity (D_p) with Rosen's model. Pore diffusivity was calculated from the time of the peak outlet concentration of tracer after injection of the tagged species, particle radius, flow velocity, bed length, distribution coefficient, and Table 1 from Rosen's work (15). The time necessary for diffusion of the electrolyte into a spherical particle was calculated by:

$$t_{\text{diff}} = \frac{0.8 b^2}{D_p} \quad (13)$$

where

b = particle radius

for transient concentration in a uniform sphere with uniform surface concentration (16). The diffusion time was compared with the time required for the tracer-concentration peak to pass by a given particle, determined from flow velocity and peak width. If the time for diffusion into the particle exceeds the time that the tracer was in contact with the particle then the elution was limited by pore diffusion.

The results of the mass-transfer analyses are discussed in Sect. 5.3. Details of the calculations are given in Appendix 10.5.

4.3 Distribution Coefficients from Experimental Data

The distribution coefficient D_i is defined as the ratio of the mass of i adsorbed on the column per unit mass of column to the concentration of i (moles/liter) in the aqueous phase. This ratio, derived in Appendix 10.2.1, is expressed in terms of measurable quantities

$$D_i = \frac{N_{cv}|_{\max}}{\rho_B} \quad (14)$$

where

$N_{cv}|_{\max}$ = the number of column-volumes (volume/volume of bed) of electrolyte between the inlet pulse and the maximum effluent concentration of the tracer

ρ_B = bed density (g/cm³).

The conditions for the experiments to determine D_i are listed in Sect. 5.1. A sample calculation of D_i and a table listing the D_i 's for all the experiments are reported in Appendix 10.2.

The experimentally measured distribution coefficients for impregnated carbon are a weighted average of the distribution coefficients of pure ZrP and oxidized carbon (derived in Appendix 10.2.2) as:

$$D_e = f_c D_c + f_{zp} D_{zp} \quad (15)$$

where

f_c = weight fraction carbon

f_{zp} = weight fraction ZrP

D_c = distribution coefficient, oxidized carbon

D_{zp} = distribution coefficient, pure zirconium phosphate

D_e = distribution coefficient, experimentally measured.

Rearranging Eq. (15) to solve for D_{zp} gives:

$$D_{zp} = \frac{D_e - f_c D_c}{f_{zp}} \quad (16)$$

This form of the distribution coefficient for ZrP is compared directly with literature data, as applied to:

$$\log_{10} D_{ZP} = \log_{10} \left(K_{NH_4}^M q_0 \right) - \log C_0 \quad (11)$$

$K_{NH_4}^M$ and q_0 are tabulated for pure ZrP in the literature (7). Equations (11) and (16) allow direct comparison of literature and experimental data to estimate the effect of impregnation on ion-exchange behavior.

4.4 Composition of Impregnated Carbon

Zirconium phosphate has excellent ion-exchange properties (5), but the behavior on carbon supports has not been fully characterized. Shiao et al. successfully impregnated zirconium oxide on activated carbon and activated carbon oxidized with nitric acid (8) by successive treatments with zirconyl chloride alternated with NH_3 . The supported zirconium oxide was treated with phosphoric acid to form zirconium phosphate (ZrP). Zirconium phosphate is a stable compound and should not wash off the carbon support when electrolyte is passed through it (8).

The crystalline structure of ZrP was determined by X-ray diffraction. Results showed there were no ZrP crystals, which indicates that either the impregnation was unsuccessful or that the ZrP is present in an amorphous form.

The atomic composition of impregnated carbon was determined by X-ray fluorescence. Ion-exchange media are bombarded with X-rays; the emission from excited atoms is monitored to determine the mass percentage of heavy elements (10). X-ray fluorescence does not identify compounds, only the elements within the compound.

The emission spectra from unimpregnated, treated carbon, ZrP (BIORAD), pure zirconium, and pure phosphorous were compared. These spectra indicated that the impregnation was successful and that ZrP must be present in an amorphous form. Both zirconium and phosphorous were found on the carbon support. By assuming a ZrP complex equal to $Zr(OH)_2(HPO_4)_2$ (10) and an activated carbon support of pure carbon, the ZrP complex comprised 30 wt % of the impregnated carbon. This is equivalent to a pure zirconium composition of 8.5 wt %, which agrees with the experimental work by Kullberg and Clearfield (17). The phosphorous-to-zirconium ratio in impregnated carbon was 2.3 to 1.0, which compares very favorably with the theoretical ratio of 2.0 to 1.0 and with the ratio in BIORAD ZrP: 2.1 to 1.0. The results of the X-ray fluorescence analysis are summarized in Table 1. Details of the calculations are shown in Appendix 10.3.

Table 1. X-ray fluorescence analysis

	Commercial ZrP (BIORAD)	ZrP on treated carbon ^a (8)
ZrP complex (wt %)	100	30
Carbon (wt %)	0	70
Zr (wt %)	29	8.5
P/Zr (mole fraction)	2.1	2.3

^aAssumed zirconium phosphate complex = $\text{Zr}(\text{OH}_2)(\text{H}_2\text{PO}_4)_2$.

5. RESULTS

5.1 Distribution Coefficients

Distribution coefficients were measured experimentally on impregnated, oxidized, and unoxidized carbon while varying pH and ionic strength, with ^{137}Cs and ^{22}Na radioactive tracers. The runs are listed in Table 2. The distribution coefficients for all the runs are listed in Table 3. A sample calculation of a distribution coefficient from experimental data is shown in Appendix 10.2. The 95%-confidence limits on the distribution coefficients are $\pm 8\%$ for values of D_i less than 10, and $\pm 4\%$ for values of D_i greater than 10. A summary of the statistical calculations is found in Appendix 10.7.

Impregnated-carbon distribution coefficients were generally higher than those for oxidized carbon, and unoxidized carbon showed the least ion-exchange activity. Sodium distribution coefficients were higher than cesium at high pH (9.5) and lower at low pH (1.0). Distribution coefficients decreased with increasing molarity of the electrolyte. The greatest difference in ionexchange behavior occurred with 0.1 M HCl electrolyte on the impregnated carbon column. The cesium distribution coefficient of 250 was the highest measured in any run, whereas that for sodium was 2.9.

An estimate of the time elapsed during the elution is 4 min multiplied by the distribution coefficient. The longest experiment for $D_e = 250$ lasted 16 h.

Table 2. Experiments

Carbon	Electrolyte	Ionic strength (M)	Tracer
Unoxidized	NH ₄ OH/NH ₄ Cl	1.0, 0.3, 0.1	¹³⁷ Cs, ²² Na
	NH ₄ Cl	1.0, 0.3, 0.1	¹³⁷ Cs, ²² Na
Oxidized	NH ₄ OH/NH ₄ Cl	1.0, 0.3, 0.1	¹³⁷ Cs, ²² Na
	NH ₄ Cl	1.0, 0.3, 0.1	¹³⁷ Cs, ²² Na
	HCl	1.0, 0.3, 0.1	¹³⁷ Cs
Impregnated	NH ₄ OH/NH ₄ Cl	1.0, 0.3, 0.1	¹³⁷ Cs, ²² Na
	NH ₄ Cl	1.0, 0.3, 0.1	¹³⁷ Cs, ²² Na
	HCl	1.0, 0.3, 0.1	¹³⁷ Cs, ²² Na

Table 3. Distribution coefficients

Electrolyte	pH	Sodium tracer ionic strength (<u>M</u>)			Cesium tracer ionic strength (<u>M</u>)		
		0.1	0.3	1.0	0.1	0.3	1.0
<u>Unoxidized carbon</u>							
NH ₄ OH/NH ₄ Cl	9.5	4.4	2.3	1.5	4.6	2.2	1.6
NH ₄ Cl	5.5	1.4	0.85	0.7	2.2	1.4	0.9
HCl	1.0	X ^a	X	X	X	X	X
<u>Oxidized carbon</u>							
NH ₄ OH/NH ₄ Cl	9.5	25.7	16.7	9.6	18.5	5.5	1.74
NH ₄ Cl	5.5	27.2	8.2	3.2	16.5	5.2	1.5
HCl	1.0	X	X	X	28.7	12.6	4.7
<u>Impregnated carbon</u>							
NH ₄ OH/NH ₄ Cl	9.5	45.2	23.8	11.7	26.2	11.3	3.6
NH ₄ Cl	5.5	27.5	12.7	4.6	26.2	10.5	4.6
HCl	1.0	2.9	1.6	1.4	250	77.3	30.5

^aX = not measured.

5.2 Separations

A separation of trace quantities of cesium from sodium using ZrP-impregnated carbon, was performed with 0.1 M HCl as the electrolyte. The results of the separation are shown in Fig. 3. The sodium eluted immediately. After the peak was passed and the radiation returned to background level, 1.0 N NH_4OH and 1.0 M NH_4Cl were introduced into the column to immediately flush out the cesium. The degree of separation was more than 99.99%.

Another separation of trace quantities of cesium and sodium was attempted with the objective of eluting the cesium through the column first, with 1.0 M NH_4OH and 1.0 M NH_4Cl as the electrolyte on impregnated carbon. The results are shown in Fig. 4. The peaks of concentration overlap, indicating that the separation was unsuccessful.

A separation of cesium and potassium was performed for a solution of 0.27 M K^+ , 0.34 M Na^+ , 0.40 M Mg^{++} , and trace quantities of cesium to study the effects of a relatively large ionic load on the ZrP-impregnated-carbon column. The radioactive isotope used to trace the elution of potassium through the column was ^{42}K ; the cesium tracer was ^{137}Cs ; and the electrolyte solution was 0.1 M HCl. The result, shown in Fig. 5, was that the potassium eluted immediately (distribution coefficient of order unity) and the cesium started to approach an exit concentration peak. After 35 cm^3 of electrolyte had flowed through the column (distribution coefficient of order 100), the experiment was terminated because the automatic tube-changer jammed. The experiment ran long enough to show that the K^+ and Cs^+ separation was better than 99% in the first (potassium) peak. This separation is discussed further in Sect. 6.3.

5.3 Mass Transfer in Column

5.3.1 Film Diffusion

The elution of sodium or cesium from a packed column of ion exchange medium was analyzed with the assumption that the system was always at chemical-reaction equilibrium (14), so the column operated under film (bulk) diffusion control or pore (particle) diffusion control. Detailed calculations of the diffusion rates are presented in Appendix 10.5.

The experimental length-to-diameter ratio of the column was at least 5.3, so plug flow was assumed. The particles were 200-mesh and spherical (10). Rosen's (15) film-diffusion parameter was:

$$v/X = \frac{mVR_f}{Z} \quad (12)$$

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SEPARATION OF Na AND Cs IONS

DATE 03/15/82	DRAWN BY GM	FILE NO. X-351	FIG. 3
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Solute: 1 M $\text{NH}_4\text{OH}/\text{NH}_4\text{Cl}$
Ion-exchanger: ZrP-impregnated carbon

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UNSUCCESSFUL SEPARATION OF SODIUM
AND CESIUM IONS

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FIG.
4

BRINE COMPOSITION

0.27 M POTASSIUM
 0.34 M SODIUM
 0.40 M MAGNESIUM
 0.10 M HYDROCHLORIC ACID
 TRACE CESIUM
 pH = 1.0

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SEPARATION OF CESIUM AND POTASSIUM
 IONS FROM BRINE SOLUTION

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FIG.
 5

The analysis was for oxidized-carbon experiments, for which the flow rates are 4 times greater than for impregnated carbon. In this case, $\epsilon = 0.6$ (18), $V = 0.049$ cm/s (obtained from flow rate and pipe diameter), $R_f = 1.67 \times 10^{-2}$ by Satterfield's analysis (19), and $Z = 4.06$ cm. This yields:

$$v/X = 3 \times 10^{-4} \quad (17)$$

For v/X less than 0.01 there is no film-diffusion limitation (15). Therefore, there was no film-diffusion limitation in our experiments.

5.3.2 Pore Diffusion

The effective pore diffusivity D_p was calculated with Rosen's model (15). The experimental data required was for the peak outlet concentration of the tracer, or in Rosen's notation, $C/C_0 = 1/2$. The film-diffusion parameter $v/X = 3.0 \times 10^{-4}$ with Rosen's Table 1 (15). The diffusivity parameter X was obtained because the diffusivity parameter for his model is completely specified as $C/C_0 = 1/2$ and $v/X = 3 \times 10^{-4}$. This leads to:

$$X = \frac{3D_i D_1 Z}{mVb^2} = 4.0 \quad (18)$$

where

D_i = distribution coefficient = 10 (derived in Appendix 10.2)

b = particle radius = 3.7×10^{-3} cm (200 mesh)

X = diffusivity/bed size.

Equation (18) is solved for D_p with the values assigned to D_i , Z , m , V , and b . The result is:

$$D_p = 3.3 \times 10^{-8} \text{ cm}^2/\text{s} \quad (19)$$

The time necessary for diffusion of the electrolyte into the spherical particle is given by (16):

$$t_{\text{diff}} = 0.8 b^2 / D_p \quad (20)$$

or

$$t_{\text{diff}} = 330 \text{ s} \quad (21)$$

The time available to the electrolyte for diffusion into the particle is calculated on the basis of a three-column-volume peak width moving down the column, which was typical for $D_i = 10$. The peak would then be in contact with the particles, at a flow rate of $0.5 \text{ cm}^3/\text{min}$, for $t_{\text{contact}} = 415 \text{ s}$.

Since $t_{\text{contact}} > t_{\text{diff}}$, there was no pore-diffusion limitation in the experiments. For carbon impregnated with ZrP, the flow rate was $0.13 \text{ cm}^3/\text{min}$, or one-fourth as fast as in the oxidized carbon column; and the contact time was 4 times as great.

The elution is always at equilibrium, because neither pore diffusion nor film diffusion were rate-limiting.

6. DISCUSSION

6.1 Distribution Coefficients

Carbon impregnated with ZrP consistently showed greater ion exchange capacity than oxidized carbon, which showed greater activity than unoxidized carbon. This is shown in Figs. 6 through 9.

Sodium and cesium exhibit opposite behavior with respect to the pH of the electrolyte on impregnated carbon. Sodium ion-exchange activity increases with increasing pH, while cesium activity is much greater at low pH as shown in Fig. 10 for a constant ionic strength of 0.1 M . The effect is not as pronounced on unimpregnated carbon, as shown in Fig. 11. These trends are consistent with those reported in the literature for unsupported ZrP (3) and oxidized carbon (8).

In all cases the distribution coefficient decreases with increasing ionic strength of the electrolyte. From Eq. (11), the expected slope of the lines drawn on a log-log plot of distribution coefficient as a function of electrolyte ionic strength is -1 . The slope is close to negative one on oxidized carbon for ion exchanges with distribution coefficients greater than about 10, as shown in Figs. 12 and 13 for sodium and cesium, respectively. The slope is not as steep for the exchanges with lower distribution coefficients. This was an experimental error because of the tracer eluting out of the column so quickly that it was difficult to accurately measure the volume of electrolyte needed to elute the column.

OXIDIZED CARBON SUPPORT
IONIC STRENGTH = 0.1 M

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DISTRIBUTION COEFFICIENTS OF CESIUM
AND SODIUM AS A FUNCTION OF pH

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FIG.
11

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DISTRIBUTION COEFFICIENTS OF SODIUM
ON OXIDIZED CARBON WITH
DIFFERENT ELECTROLYTES

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FIG.
12

Distribution coefficients for carbon impregnated with zirconium phosphate (ZrP) were compared with the theoretical values obtained from thermodynamics. Thermodynamic data are available (7) for pure ZrP, exchanging with cesium, and the theoretical distribution coefficients are calculated by rearranging Eq. (10) and generalizing to ZrP:

$$D_{ZP} = \frac{K_i^M C_o}{q_o} \quad (22)$$

The experimentally determined distribution coefficients are converted to values for pure ZrP by:

$$D_{ZP} = \frac{D_e - f_c D_c}{f_{ZP}} \quad (16)$$

The theoretical and experimental values of D_{ZP} are shown in Fig. 14 for HCl as the electrolyte and in Fig. 15 for NH_4Cl as the electrolyte. The agreement for each datum point is to within 20%. The error may be because of the different values of $K_{NH_4}^M$ at different pH, while we assumed a constant value at all pH's (7). There also may have been partial dissociation of NH_4OH .

6.2 Cesium-Sodium Separation

A separation of cesium from sodium was performed with 0.1 M HCl as the electrolyte on carbon impregnated with ZrP. The results of the elution for cesium and sodium separately were:

$$D_{Cs} = 250$$

$$D_{Na} = 2.9$$

$$S = \text{selectivity ratio} = \frac{D_{Cs}}{D_{Na}} = 86.2$$

$$N = \text{number of theoretical plates for separation (11)} = 248$$

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DISTRIBUTION COEFFICIENTS OF CESIUM
 FOR ZIRCONIUM PHOSPHATE

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FIG.
 14

--- AMPHLETT (7), 1964

— VISUALLY FITTED DATA

I 95% CONFIDENCE LIMITS

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DISTRIBUTION COEFFICIENT OF SODIUM
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FIG.
15

For a system with 248 theoretical plates, the minimum S for a 99.99% separation is 1.04. The described separation is therefore highly favorable, with $S = 86.2$. The number of theoretical plates for separation is a function of the distribution coefficients and the width of the elution peak; the detailed calculation is shown in Appendix 10.4.

The results of the separation are shown in Fig. 3. The sodium eluted immediately because its distribution coefficient is relatively low. Once the number of counts recorded by the gamma counter reached background level after the peak outlet concentration of sodium, 1.0 M NH_4OH and NH_4Cl was introduced to immediately flush out the cesium because the distribution coefficient of cesium in this electrolyte is only 3.6. The separation exceeded 99.99%, as predicted by the plate theory.

Another separation of cesium and sodium was attempted with the objective of eluting the cesium through the column first. Examination of superimposed peaks from the runs with only sodium or cesium ions reveals that the separation was not possible because the peaks overlap. The theoretical number of plates also predicts that the separation will fail, with $S = 3.25$ and $N = 19.2$; the minimum S for this separation is 5.0 (11). The separation was unsuccessful, as shown in Fig. 4. The difference between the superimposed cesium and sodium elution curves and the separation curve could be because of interactions between cesium and sodium which force sodium to elute faster and cesium slower. Calculations of the number of theoretical plates are shown in Appendix 10.4.

6.3 Brine Separation

Promising, though limited, results were obtained for the separation of high concentrations of potassium and trace concentrations of cesium in brine (0.3 M K^+ , 0.4 M Mg^{2+} , 0.3 M Na^+) with 0.1 M HCl electrolyte solution. The potassium eluted almost immediately in a similar manner to the sodium elution during the separation of trace quantities of cesium and sodium. Distribution coefficients in acidic media increase with atomic number (7). Cesium (atomic number 55) was held in the column longer than potassium (atomic number 19).

The cesium exit concentration was increasing after 29 column-volumes of electrolyte eluted through the column. When cesium was the only alkali metal ion exchanging on ZrP-impregnated carbon, in 0.1 M HCl , the cesium exit concentration remained at zero until the 59th sample (54 column-volumes). The cesium distribution coefficient was reduced by nearly 50% when mixed with the brine solution, an effect of the loading approaching the ion exchange capacity of the column. The presence of divalent ions (Mg^{2+}) might also decrease the cesium distribution coefficient because divalent cations displace monovalent cations during ion exchange (7).

7. CONCLUSIONS

1. Experimental data of distribution coefficients of zirconium phosphate (ZrP) agree with literature data to within 10% at low pH. At high pH, there is a 20% difference between the two, probably because of the higher concentration of the solute.

2. ZrP-impregnated carbon shows ion exchange capacity twice as great as oxidized carbon and 10 times as great as unoxidized carbon.

3. Separation of alkali metal ions is possible to 99.99% purity if the selectivity ratio is equal or greater than that required, if the number of theoretical plates of the column is given. Separations of three or more alkali metals are possible.

4. The ion exchange column operates at equilibrium with respect to mass transfer.

8. RECOMMENDATIONS

1. Examine the ion-exchange distribution coefficients of Cs^+ , Na^+ , K^+ , and other alkali ions for the purposes of commercially feasible separations at alkali ionic strengths of the order of 1.0 M.

2. Use the batch equilibration technique to measure distribution coefficients when the elution run-time exceeds about 15 h. This roughly corresponds to distribution coefficients above 250.

9. ACKNOWLEDGEMENT

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10. APPENDIX

10.1 Ion-Exchange-Column Preparation

The ion-exchange column for the determination of distribution coefficients by the elution technique consisted of a 5-ml graduated pipette packed with carbon [impregnated or unimpregnated with zirconium phosphate (ZrP)], and glass wool, as shown in Fig. 2.

The glass wool was tightly packed on the bottom of the column. The volume occupied by the glass wool was measured from the pipette. The void volume of the wool was measured by weighing the pipette and wool; then saturating the glass wool with water and weighing again. The void volume of the glass wool V_w is:

$$V_w = \frac{\Delta M}{\rho_{H_2O}} \quad (23)$$

where

ΔM = difference of mass before and after saturation with water (g)

ρ_{H_2O} = density of water (gm/cm³).

The void volume of the wool was typically 0.4 cm³.

A known mass of 200-mesh carbon, usually 0.5 g, with or without ZrP, was mixed with approximately 100 cm³ of double-distilled, deionized water. The mixture forms a slurry, which was carefully transferred into the reactor by a 0.2-cm³ suction pipette. When the carbon was completely transferred into the column, the bed volume was noted from the pipette.

A slice of glass wool 3-mm thick was placed above the bed to prevent the incoming drops of the tracer and electrolyte from disturbing the uppermost carbon particles. The column was then loaded into the automatic tube-changer, and the tube plus tip volume V_{TT} was determined by measuring the amount of water necessary to fill both. The size of each region of the column for the three columns is summarized in Table 4.

Table 4. Column sizes

Ion. exchanger	Unoxidized carbon	Oxidized carbon	ZrP on oxidized carbon
Bed volume (cm ³)	1.25	1.15	0.9
Bed mass (g)	0.5	0.5	0.4
Glass-wool void volume (cm ³)	0.2	0.4	0.4
Pipette inner diameter (cm)	0.6	0.6	0.6
Bed height (cm)	4.42	4.07	3.18
Volume of tube and tip (cm ³)	0.2	0.2	0.2

10.2 Data Reduction

10.2.1 Calculation of Distribution Coefficient

The distribution coefficient D for a component is defined as the ratio of the mass of the component adsorbed on the ion-exchange bed per unit mass of the bed to the mass of the component in the electrolyte solution per unit volume of the solution (10). Hence:

$$D_i = \frac{M_{i|s}/M_b}{M_{i|aq}/V_s} \quad (24)$$

where

- D_i = the distribution coefficient of component i
- $M_{i|s}$ = mass of component i adsorbed on bed (g)
- $M_{i|aq}$ = mass of component i in solution (g)
- M_b = mass of the bed (g)
- V_s = volume of electrolyte (ml).

Multiplying and dividing the numerator of Eq. (24) by the bed volume yields:

$$D_i = \frac{\left[\frac{M_{i|s}}{V_b} \right] \left[\frac{V_b}{M_b} \right]}{M_{i|aq}/V_s} \quad (25)$$

where

V_b = bed volume.

Rearranging Eq. (25), one obtains:

$$D_i = \frac{V_s}{V_b} \frac{Mi|_s}{Mi|_{aq}} \frac{V_b}{M_b} \quad (26)$$

$Mi|_s/Mi|_{aq} = 1$ (18) when equal moles of the metal ions are on the bed and in solution for a pulse input. This condition is achieved when the electrolyte has the maximum exit concentration of metal ions. The number of column volumes (N_{cv}) of the electrolyte needed to reach this maximum exit concentration is defined as:

$$N_{cv}|_{max} = \frac{V_s}{V_b} \quad (27)$$

The density of the bed is defined as:

$$\rho_b = \frac{M_b}{V_b} \quad (28)$$

Substituting Eqs. (27) and (28) into Eq. (26) yields:

$$D_i = \frac{N_{cv}|_{max}}{\rho_b} \quad (29)$$

A sample calculation of D from the data in Table 5 for ZrP-impregnated oxidized carbon with ^{137}Cs tracer and 0.3 M NH_4Cl electrolyte, follows. Sample numbers are converted to N_{cv} after taking into account the liquid heldup in the void of the bed, the wool, the tip, and the outlet tube before the tracer has entered the column. The equation is:

$$N_{cv} = (N - 0.5) \frac{V_{sa}}{V_b} - \frac{(V_w + V_v + V_{TT})}{V_b} \quad (30)$$

Table 5. Experimental data from
elution technique

Zirconium phosphate on oxidized carbon
Electrolyte = 0.3 M NH_4Cl
Tracer = ^{137}Cs

Sample number	Counts (gamma 64-W counter)
Background	1097
2	1122
5	1067
6	1119
7	1745
8	8372
9	19547
10	21027
11	16642
12	13032
13	9279
14	5806
15	4159
16	2983

where

N = sample number

V_{sa} = sample volume (cm^3)

V_w = glass-wool void-volume (cm^3)

V_v = bed void-volume (cm^3)

V_{TT} = tip plus tube volume (cm^3)

The correction ($N - 0.5$) accounts for the drops in the N^{th} sample, which range from the first drop after the $(N - 1)^{\text{th}}$ sample to the last drop in the N^{th} sample. The average sample number is:

$$\frac{(N - 1) + N}{2} = N - 0.5 \quad (31)$$

The sample volume is measured from the sample tube with a calibrated 1- cm^3 suction pipette. The bed void-volume is approximated as 0.6 times the bed volume (10). The wool void-volume, bed volume, tube-plus-tip volume, and bed mass were measured as described in Appendix 10.1.

For the data in Table 5:

$$V_{sa} = 0.54 \text{ cm}^3$$

$$V_w = 0.4 \text{ cm}^3$$

$$V_b = 0.9 \text{ cm}^3$$

$$V_v = 0.6 \times 0.9 = 0.54 \text{ cm}^3$$

$$V_{TT} = 0.2 \text{ cm}^3$$

$$M_b = 0.4 \text{ g}$$

Substituting into Eq. (30) yields:

$$N_{cv} = (N - 0.5) \frac{0.54 \text{ cm}^3}{0.9 \text{ cm}^3} - \frac{0.4 \text{ cm}^3 + 0.54 \text{ cm}^3 + 0.2 \text{ cm}^3}{0.9 \text{ cm}^3}$$

or

$$N_{cv} = (N - 0.5)(0.6) - 1.27 \quad (32)$$

Use of Eq. (30) and the corrected number of counts after subtracting background transforms the data of Table 5 to that shown in Fig. 16, where number of counts is plotted as a function of N_{cv} .

The maximum number of counts is at $N_{cv}|_{\max} = 4.3$. The distribution coefficient of cesium on oxidized carbon impregnated with ZrP is directly calculated with Eq. (29) as:

$$D = (4.3) \frac{0.9 \text{ cm}^3 \text{ bed}}{0.4 \text{ g bed}} = 9.7$$

10.2.2 Experimental Determination of Distribution Coefficient of Pure Zirconium Phosphate D_{zp}

The distribution coefficient D_i is defined for a component of a homogeneous bed by:

$$D_i = \frac{M_i|_s / M_b}{M_i|_{aq} / V_s} \quad (24)$$

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DETERMINATION OF NUMBER OF
COLUMN VOLUMES

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FIG.
16

The distribution coefficient for a component on a bed consisting of two or more substances is defined analogously as:

$$D_e = \frac{Mi|_s/M_b}{Mi|_{aq}/V_s} \quad (33)$$

where

D_e = the experimentally measured distribution coefficient of the mixed bed.

If it is assumed that the adsorption characteristics of both substances are independent of each other, Eq. (33) for an oxidized carbon and ZrP-impregnated-carbon system is expanded to yield:

$$D_e = \frac{(Mi|_{zp} + Mi|_c) 1/M_b}{Mi|_{aq}/V_s} \quad (34)$$

where

$Mi|_{zp}$ = mass of i adsorbed on impregnated carbon, g

$Mi|_c$ = mass of i adsorbed on oxidized carbon, g.

Equation (34) rearranges to:

$$D_e = \frac{\left[\frac{Mi|_{zp}}{M_{zp}} \right] \times \left[\frac{M_{zp}}{M_b} \right] + \left(\frac{Mi|_c}{M_c} \frac{M_c}{M_b} \right)}{Mi|_{aq}/V_s} \quad (35)$$

where

M_{zp} = mass of zirconium phosphate on bed, g

M_c = mass of oxidized carbon on bed.

If we let $f_c = M_c/M_b$ = weight fraction oxidized carbon in bed, and $f_{zp} = M_{zp}/M_b$ = weight fraction ZrP, the result is:

$$D_e = f_{zp} \frac{M_i|_{zp}/M_{zp}}{M_i|_{aq}/V_s} + f_c \frac{M_i|_c/M_c}{M_i|_{aq}/V_s} \quad (36)$$

If the definition of distribution coefficient from Eq. (24) for pure ZrP or oxidized carbon is applied, then:

$$D_{zp} = \frac{M_i|_{zp}/M_{zp}}{M_i|_{aq}/V_s}$$

$$D_c = \frac{M_i|_c/M_c}{M_i|_{aq}/V_s} \quad (37)$$

where

D_{zp} = distribution coefficient of pure zirconium phosphate

D_c = distribution coefficient of oxidized carbon.

Substituting Eq. (37) into Eq. (35) results in:

$$D_e = f_{zp} D_{zp} + f_c D_c \quad (38)$$

D_e and D_c are measured experimentally, and f_{zp} and f_c are known (Appendix 10.3). Equation (36) has only D_{zp} as an unknown, so it can be readily calculated.

A sample calculation of D_{zp} follows. For 0.1 M HCl electrolyte with ^{137}Cs tracer, the experimentally measured $D_e = 250$. The distribution coefficient for oxidized carbon under the same conditions was 28.7. From Appendix 10.3, $f_{zp} = 0.3$, and $f_c = 0.7$. Substituting into Eq. (38) gives:

$$250 = 0.3 D_{zp} + (28.7)(0.7)$$

which yields

$$D_{zp} = 766$$

10.2.3 Calculation of Distribution Coefficient of Pure Zirconium Phosphate from Literature Data

The distribution coefficient for pure zirconium phosphate D_{zp} is related to quantities tabulated in the literature as:

$$D_{zp} = \frac{K_i^M q_0}{C_0} \quad (22)$$

For ^{137}Cs tracer in 0.1 M HCl electrolyte the ion exchange capacity $q_0 = 0.5 \text{ meq/g bed}$, (7) $K_{\text{NH}_4}^{\text{Cs}} = 127$ (7), and $C_0 = 0.1 \text{ molar}$. Substituting into Eq. (22) yields:

$$D_{zp} = \frac{(127)(0.5) \text{ meq/g}}{0.1 \text{ meq/cm}^3} = 635$$

Other values for the literature calculations of D_{zp} were (7):

$$q_0 = 2.4 \text{ meq/g at pH} = 1$$

$$K_{\text{NH}_4}^{\text{Cs}} = 3.7$$

10.3 Determination of Zirconium Phosphate Weight Fraction

The weight fraction of zirconium phosphate (ZrP) on impregnated carbon was determined by X-ray fluorescence. The emission spectra from commercial ZrP (BIORAD) and from ZrP-impregnated carbon were determined by comparison with emission spectra from pure zirconium and pure phosphorous. The relative energy of each characteristic wavelength determines the weight fraction of each element (10). The results from X-ray fluorescence are given in Table 6.

The ratio of the mole fraction of phosphorous to zirconium is the ratio of the X-ray fluorescence areas divided by the molecular weight.

The chemical composition of zirconium phosphate is assumed to be $\text{Zr}(\text{OH}_2)(\text{H}_2\text{PO}_4)_2$ (10). The molecular weight of the complex equals 319 amu, and that of zirconium is 91. The resulting zirconium mass fraction in the BIORAD sample is:

Table 6. Relative energies

Sample	Relative area (energy)	
	Zirconium	Phosphorous
Pure zirconium phosphate (BIORAD)	99,266	68,592
Impregnated carbon [Shiao (8)]	27,266	20,989

$$\text{Mass fraction Zr (BIORAD)} = \frac{91}{319} = 0.285$$

The mass fraction of zirconium in the ZrP-impregnated sample is calculated as:

$$\begin{aligned} \text{Mass fraction Zr (impregnated)} &= (0.285) \frac{22,266}{94,266} \\ &= 0.083 = 8.3\% \end{aligned}$$

The mass fraction of the ZrP complex in the impregnated carbon sample is then:

$$\text{Mass fraction ZrP (impregnated)} = (0.083) \frac{319}{91} = 0.3 = 30\%$$

The mass fraction of carbon in the impregnated sample is:

$$\text{Mass fraction C} = 1 - 0.3 = 0.7 = 70\%$$

The relative mole fraction P/Zr in the two samples was:

$$\text{Molar ratio P/Zr (BIORAD)} = \left(\frac{68,592}{94,266} \right) \left(\frac{91}{31} \right) = 2.1$$

$$\text{Molar ratio P/Zr (Shiao)} = \left(\frac{20,989}{27,266} \right) \left(\frac{91}{31} \right) = 2.3$$

10.4 Theoretical-Plate Calculations

The number of theoretical plates for separation of a component exchanging in the column is (11):

$$N_i = 8 \left(\frac{V_{\max}}{\beta} \right)^2 \quad (39)$$

where

N_i = number of theoretical plates for species i

$V_{\max}$ = volume of electrolyte needed to reach maximum tracer outlet concentration

β = band width (volume) at $\frac{1}{e}$ x peak counts.

For a cesium and sodium separation:

$$N_T = \left(N_{Cs} N_{Na} \right)^{1/2} \quad (40)$$

where

N_T = total number of plates

N_{Cs} = number of cesium plates

N_{Na} = number of sodium plates.

The first attempted separation used 0.1 M HCl electrolyte. For cesium:

$$V_{\max} = \left(M_{cvl_{\max}} \right) \left(V_{\text{bed}} \right) = (110.9 \text{ beds}) (0.9 \text{ cm}^3/\text{bed})$$

$$V_{\max} = 99.8 \text{ cm}^3$$

and

$$\frac{1}{e} \times \text{peak count} = \left[\frac{1}{2.718} (\text{counts} - \text{background}) \right] + \text{background}$$

Background = 1092 counts/min, and peak = 12,342 counts/min, which results in:

$$\frac{1}{e} \times \text{peak} = \frac{12,342 - 1092}{2718} + 1092 = 5231 \text{ counts/min}$$

Therefore:

$$\beta = \text{peak width} = 4.3 N_{cv}$$

$$= (4.3) \left(0.9 \frac{\text{cm}^3}{\text{col}} \right) = 3.9 \text{ cm}^3$$

Substituting into Eq. (39) yields:

$$N_{Cs} = 8 \left(\frac{99.8 \text{ cm}}{3.9 \text{ cm}} \right)^2 = 5240 \text{ plates}$$

For sodium:

$$V_{\max} = (N_{cv}|_{\max}) V_{\text{bed}} = (1.28)(0.9) = 1.15 \text{ cm}^3$$

$$\begin{aligned} \frac{1}{e} (C_{\max} - \text{background}) + \text{background} &= \frac{32,333 - 1086}{2718} + 1086 \\ &= 12,582 \text{ counts/min} \end{aligned}$$

The peak width is $1.05 N_{cv}$, or

$$\beta = (1.05 \text{ bed}) \left(\frac{0.9 \text{ cm}}{\text{bed}} \right)^2 = 0.95 \text{ cm}^3$$

Substitution into Eq. (39) yields:

$$N_{\text{Na}} = 8 \left(\frac{1.15}{0.95} \right)^2 = 11.7$$

Substitution into Eq. (40) yields:

$$N_{\text{T}} = \left(N_{\text{Cs}} N_{\text{Na}} \right)^{1/2} = \left[(5240)(11.7) \right]^{1/2} = 248$$

The selectivity ratio is:

$$S = \frac{D_{\text{Cs}}}{D_{\text{Na}}} = \frac{250}{2.9} = 86.2$$

The minimum S for 99.99% separation is 1.7 based on an analytical solution with no ion-ion interactions (11). Therefore, this separation is theoretically possible.

The second attempted cesium and sodium separation used 1.0 M NH_4OH and 1.0 M NH_4Cl as the electrolyte.

For cesium:

$$V_{\text{max}} = \left(N_{\text{cv}} |_{\text{max}} \right) V_{\text{bed}} = (1.61)(0.9 \text{ cm}^3/\text{bed}) = 1.45 \text{ cm}^3$$

$$\beta = (1.2 \text{ bed})(0.9 \text{ cm}^3/\text{bed}) = 1.08 \text{ cm}^3$$

yielding

$$N_{\text{Cs}} = 8 \left(\frac{1.45}{1.08} \right)^2 = 14.4$$

For sodium:

$$V_{\max} = (N_{cv}|_{\max} V_{\text{bed}}) = (10.73 \text{ bed})(0.9 \text{ cm}^3/\text{bed}) = 9.67 \text{ cm}^3$$

$$\beta = (6 \text{ beds})(0.9 \text{ cm}^3/\text{bed}) = 5.4 \text{ cm}^3$$

Substitution into Eq. (39) yields:

$$N_{\text{Na}} = 8 \left(\frac{9.67}{5.4} \right)^2 = 25.7 \text{ plates}$$

Substitution into Eq. (40) yields:

$$N_T = \left[(25.7)(14.4) \right]^{1/2} = 19.2 \text{ plates}$$

The selectivity ratio is:

$$S = \frac{D_{\text{Na}}}{D_{\text{Cs}}} = \frac{11.7}{3.6} = 3.25$$

The minimum separation ratio for 19.2 plates is 5 (11). Therefore, the separation fails.

10.5 Mass-Transfer Analysis in Column

If reaction equilibrium at all times is assumed, then film and pore diffusion are of interest. For perfectly spherical, homogeneous particles in a fixed bed, Rosen's model applies (15). The analysis that follows is for a column packed with oxidized carbon, which allowed a faster flow rate than ZrP-impregnated carbon columns.

The parameter that determines whether there is a film-diffusion limitation is:

$$v/X = \frac{mVR_f}{L} \quad (41)$$

where

v/X = film-diffusion parameter

$$m = \frac{\epsilon}{1 - \epsilon}$$

ϵ = void fraction in bed

V = interstitial flow velocity (cm/s)

R_f = film resistance (s)

Z = bed length (cm).

The velocity profile is assumed flat because length/diameter $> 3.2 \text{ cm}/0.6 \text{ cm} = 5.3$.

For our experiments, $\epsilon = 0.6$ (18), $Z = 4.06 \text{ cm}$, and:

$$V = \frac{\dot{Q}}{\epsilon \pi R^2} \quad (42)$$

where

$\dot{Q}$ = volumetric flow rate (cm^3/min)

πR^2 = cross-sectional area of column

R = radius of column.

For our case, $R = 0.3 \text{ cm}$ and $\dot{Q} = 0.5 \text{ cm}^3/\text{min}$, which leads to:

$$V = \frac{(0.5 \text{ cm}^3/\text{min})(\text{min}/60 \text{ s})}{(0.6)(3.14)(0.3 \text{ cm})^2} = 0.049 \text{ cm/s}$$

Film resistance R_f is determined by Satterfield's method (19):

$$R_f = \frac{D_L}{3K_f} \quad (43)$$

where

D_L = film diffusivity (cm^2/s)

K_f = mass-transfer coefficient (cm/s)

$D_L = 1.3 \times 10^{-5} \text{ cm}^2/\text{s}$ (14) for a primarily aqueous phase. The mass-transfer coefficient is calculated as (19):

$$K_f = \frac{1.09 \epsilon V}{(ScRe)^{2/3}} \quad (44)$$

where

$Sc = \text{Schmidt number} = \mu_L / \rho_L D_L$

$\mu_L = \text{liquid viscosity (g/cm s)}$

$\rho_L = \text{liquid density (g/cm}^3\text{)}$

$Re = \text{Reynolds number} = 2R\rho_L \epsilon V / \mu_L$

In this case, $\mu_L / \rho_L = 10^{-2} \text{ cm}^2/\text{s}$ (water) (14) which leads to:

$$Sc = \frac{10^{-2} (\text{cm}^2/\text{s})}{1.3 \times 10^{-5} (\text{cm}^2/\text{s})} = 770$$

$$Re = \frac{(2)(0.6 \text{ cm})(0.6)(0.049 \text{ cm/s})}{10^{-2} \text{ cm}^2/\text{s}} = 1.76$$

Substitution into Eq. (44) yields:

$$K_f = \frac{(1.09)(0.6)(0.049 \text{ cm/s})}{[(770)(1.76)]^{2/3}} = 2.6 \times 10^{-4} \text{ cm/s}$$

Substitution into Eq. (43) yields:

$$R_f = \frac{(1.3 \times 10^{-5} \text{ cm}^2/\text{s})}{(3)(2.6 \times 10^{-4} \text{ cm/s})} = 1.67 \times 10^{-2} \text{ s}$$

Substitution into Eq. (41) yields:

$$v/X = \frac{(0.6/1 - 0.6)(0.049 \text{ cm/s})(1.67 \times 10^{-2} \text{ s})}{4.06 \text{ cm}} = 3.00 \times 10^{-4}$$

The critical value for v/X is 0.01. Therefore, there are no film limitations.

The pore-difusivity parameter for Rosen's model is:

$$X = \frac{3D_p D_i Z}{mVb^2} \quad (45)$$

where

X = pore-difusivity parameter

b = particle radius (cm).

Four our case $D_i = 10$ (typical distribution coefficient; $b = 3.7 \times 10^{-3}$ cm (200 mesh); yielding;

$$X = \frac{(3)(10)(4.06 \text{ cm})}{(0.6/1 - 0.6)(0.049 \text{ cm/s})(3.7 \times 10^{-3} \text{ cm})^2} = 1.2 \times 10^8 D_p$$

Calculation of Rosen's dimensionless time parameter Y/X fixed a value of X , for which D_p is calculated (15).

$$Y/X = \frac{2m}{3D_i} \left(\frac{Vt_e}{Z} - 1 \right) \quad (46)$$

where

t_e = time required to reach the outlet peak in trace concentration.

The elution time t_e is calculated with:

$$t_e = \frac{(N_{cv} |_{\max}) V_{\text{bed}}}{\dot{Q}} = \frac{\rho_B D_i V_{\text{bed}}}{\dot{Q}} \quad (47)$$

The bed volume is 1.15 cm^3 , and the bed density is 0.44 g/cm^3 . The elution time is then:

$$t_e = \frac{(0.44 \text{ g/cm}^3)(10)(1.15 \text{ cm}^3)}{0.5(\text{cm}^3/\text{min})(\text{min}/60 \text{ s})} = 613 \text{ s}$$

Substituting into Eq. (49) yields:

$$Y/X = \frac{2(0.6/1 - 0.6)}{(3)(10)} \left(\frac{(0.049 \text{ cm/s})(613 \text{ s})}{4.06 \text{ cm}} - 1 \right) = 0.64$$

The specified outlet concentration C divided by total concentration C_0 at the peak in the elution curve is (18):

$$C/C_0|_{\max} = 0.5$$

The value of X at $C/C_0 = 0.5$, $Y/X = 0.64$, and $v/X = 3 \times 10^{-4}$ is 4.0 (15).

Solving for D_p in Eq. (43) gives:

$$D_p = \frac{X}{1.21 \times 10^8} = 3.3 \times 10^{-8} \text{ cm}^2/\text{s} \quad (48)$$

The concentration gradient $(C_s - C_c)/C_s$ reduces to 10^{-3} at $F_0 = 0.2$ (16) where:

C_s = surface concentration (arbitrary units)

C_c = center concentration (arbitrary units)

($C_c = 0$ at $t = 0$)

and F_0 is defined as:

$$F_0 = \frac{D_p t}{4b^2} \quad (49)$$

The time needed for the electrolyte to diffuse into the pores is:

$$t_{\text{diff}} = \frac{(0.2)(4)b^2}{D_p} \quad (50)$$

Substitution of the values of D_p and b into Eq. (50) yields:

$$t_{\text{diff}} = \frac{(0.2)(4)(3.7 \times 10^{-3} \text{ cm})^2}{3.3 \times 10^{-8} \text{ cm}^2/\text{s}} = 330 \text{ s}$$

The peak front contacts the particle in approximately 3 column volumes so:

$$t_{\text{contact}} = \frac{(N_{\text{cv}})V_{\text{bed}}}{Q} = \frac{(3 \text{ beds})(1.15 \text{ cm}^3/\text{bed})}{(0.5 \text{ cm}^3/\text{min})(\text{min}/60 \text{ s})} = 415 \text{ s}$$

where

$$t_{\text{contact}} = \text{contact time.}$$

Therefore, $t_{\text{contact}} > t_{\text{diff}}$; so there are no pore-diffusion limitations. For carbon impregnated with ZrP, the flow rate is $0.13 \text{ cm}^3/\text{s}$, or one-fourth of the oxidized-carbon flow rate. The contact time is then four times as great, and pore diffusion problems are even less of a concern.

10.6 Location of Original Data and Equipment

Original data are located in Databook A-9185-G, pp. 57-100 and Databook A-9911-G, pp. 86-94, on file at the MIT Practice School, Bldg. 1505, Oak Ridge National Laboratory. The three ion-exchange columns are under the supervision of J. S. Johnson, Jr., ORNL.

10.7 Statistical Calculations for Distribution Coefficients

10.7.1 Low Distribution Coefficient

The elution with $0.3 \text{ M NH}_4\text{Cl}$ for a sodium tracer on an unoxidized carbon bed was performed by the same procedure five times, with results

of $D_{Na} = 0.85, 0.8, 0.8, 0.85, \text{ and } 0.89$. The average value is $D_{ave} = 0.84$. The standard deviation is (20):

$$\sigma = \sqrt{\frac{\sum (D - D_{ave})^2}{N_0 - 1}} \quad (51)$$

where

σ = standard deviation

N_0 = number of data points.

Substitution of the above values yields

$$\sigma = 0.026$$

Use of the t-test for $\alpha = 0.05$ (95% confidence), two-tail, and $v = N - 1 = 4$ gives:

$$t = 2.776 \text{ (20)}$$

The 95% confidence limit becomes (20):

$$D = D_{ave} \pm t' \sigma = 0.84 \pm 0.072 \quad (52)$$

The 95% confidence limit falls within a range of $\pm 0.072/0.84 = \pm 8\%$.

10.7.2 High Distribution Coefficient

The elution for a 0.1 M NH_4OH and 0.1 M NH_4Cl electrolyte with sodium tracer on an oxidized carbon column was performed three times, with the following values of D : 26.1, 25.9, 25.7, which average 25.9. Proceeding as before:

$$N = 2$$

$$\sigma = 0.2$$

$$t' = 4.303$$

This leads to a 95% confidence limit of:

$$D = 25.9 \pm 0.9$$

or a range of $0.9/25.9 = 4\%$.

10.7.3 Pure-Zirconium-Phosphate Distribution Coefficients

If we use the equation:

$$D_{zp} = \frac{D_e - f_c D_c}{f_{zp}} \quad (53)$$

where

$$\begin{aligned} f_c &= 0.7 \\ f_{zp} &= 0.3 \end{aligned}$$

the 95% confidence ranges are applied to the values of D_e and D_c to determine ranges of error in D_{zp} . For 0.1 M HCl electrolyte on ZrP-impregnated carbon, $D_e = 250 \pm 4\%$, and D_c (oxidized carbon) = $28.7 \pm 4\%$. If we ignore errors in the weight-fraction measurements, then the ranges of values of D_{zp} are:

$$\text{Maximum } D_{zp} = \frac{(250)(1.04) - (0.7)(28.7)(0.96)}{0.3} = 802$$

$$\text{Minimum } D_{zp} = \frac{(250)(0.96) - (0.7)(28.7)(1.04)}{0.3} = 731$$

$$\text{Average } D_{zp} = \frac{250 - 0.7(28.7)}{0.3} = 766$$

The 95% confidence range is 766 ± 36 or $\pm 5\%$. A similar procedure was followed for all the data points.

10.8 Cesium Equilibration

The effect of equilibrating the bed with cesium ions before introduction of cesium tracer was investigated. Nonradioactive cesium of concentration 10^{-5} M was added to the electrolytic solution for equilibration of the bed and the glass wool and for the remainder of the test run with 0.1 M NH_4OH and NH_4Cl on oxidized carbon. The presence of cesium in the electrolyte had no effect on the distribution coefficient.

10.9 Glass-Wool Calibration

The possibility of adsorption of ions by the glass wool was tested. The distribution coefficient for a column packed only with glass wool was calculated using 0.3 M NH_4Cl as the electrolyte with sodium tracer. The column eluted so rapidly that an accurate distribution coefficient could not be calculated, but one can conclude it is approximately zero. The effect of adsorption by the glass wool was ignored. The data for the test are shown in Table 7.

Table 7. Glass-wool calibration

5-drop samples = 0.29 ml
bed volume = 0.45 ml
void volume = 0.4 ml

Sample	Gamma counts/min
Background	1,126
1	2,517
2	26,423
3	10,695
4	4,831

10.10 Nomenclature

a_i	Activity of specie i
b	Particle radius, cm
$C_{\max}$	Maximum counts
C_o	Electrolyte concentration, moles/liter
D_{ave}	Average distribution coefficient, g/g bed/g/ml solution
D_i	Distribution coefficient of species i, g/g bed/g/ml solution
D_e	Experimentally measured distribution coefficient, g/g bed/g/ml solution
D_{zp}	Distribution coefficient of pure zirconium phosphate, g/g bed/g/ml solution
D_c	Distribution coefficient of oxidized carbon, g/g bed/g/ml solution
D_p	Pore diffusivity, cm^2/s
D_L	Film diffusivity cm^2/s
f_{zp}	Weight fraction zirconium phosphate
f_c	Weight fraction oxidized carbon
K_{eq}	Equilibrium constant
K_f	Mass transfer coefficient, $\text{cm}^3 \text{ bed}/\text{cm}^2 \text{ s particle}$
K_i^M	Selectivity coefficient of species i
m	$\frac{\epsilon}{1 - \epsilon}$
$M_i _s$	Mass of i adsorbed on bed, g
$M_i _{\text{aq}}$	Mass of i in solution, g
M_b	Mass of bed
ΔM	Mass difference before and after water saturation, g
N_{cv}	Number of column volumes
$N_{\text{cv}} _{\max}$	Number of column volumes at peak effluent concentration

N	Sample number
N_i	Number of theoretical plates for separation
N_T	Total number of plates
N_{Cs}	Number of plates for cesium
N_{Na}	Number of plates for sodium
N_0	Number of experiments repeated
q_0	Ion exchange capacity, meq/g
$\dot{Q}$	Volumetric flow rate, cm^3/min
R_f	Film resistance, s
R	Column radius, cm
Re	Reynolds number, $\rho_L d_p V \epsilon / \mu_L$
Sc	Schmidt number, $\mu_L / \rho_L D_L$
S	Selectivity ratio
t	t-test parameter
t_{contact}	Contact time, s
t_{diff}	Diffusion time, s
t_e	Elution time, s
V_s	Volume of electrolyte, cm^3
V_b	Volume of bed, cm^3
V_{sa}	Sample volume, cm^3
V_w	Glass-wool void volume, cm^3
V_v	Bed void volume, cm^3
V_{TT}	Tube-plus-tip volume, cm^3
V	Interstitial flow velocity, cm/s
X	Diffusivity parameter
Y/X	Time parameter

Z	Bed length, cm
B	Band width, cm ³
ϵ	Bed void fraction
v/X	Film-diffusion parameter
μ_L	Film viscosity, g/cm s
ρ_L	Film or liquid density, g/cm ³
σ	Standard deviation
ρ_{H_2O}	Water density, g/cm ³
ρ_b	Bed density, g/cm ³
Superscripts	
+	Solution quantity
-	Adsorbed quantity

10.11 References

1. Marinsky, J. A. and Y. Marcus, eds., Ion Exchange and Solvent Extraction: A Series of Advances, Vol. 5, pp. 5-110, Marcel Dekker, New York, 1973.
2. Nagy, L. G., J. Radioanal. Chem., **58**(1-2), 215 (1980).
3. Tamashita, H. Bull. Chem. Soc. Japan, **53**(5), 1331 (1980).
4. Keller, O. L., "Chemistry Division Annual Progress Report for Period Ending July 31, 1981," pp. 141-145, ORNL-5817 (1982).
5. Clearfield, A., J. Inorg. Nucl. Chem., **35**, 1099 (1973).
6. Clearfield, A. and A. S. Medina, J. Phys. Chem., **75**(24), 3750 (1971).
7. Amphlett, C. D., Inorganic Ion Exchangers, pp. 36-102, Elsevier, New York, 1964.
8. Shiao, S. Y., J. S. Johnson, Jr., and C. G. Westmoreland, J. Inorg. Nucl. Chem., in press, 1982.
9. Inoue, Y. and M. Tsuji, Bull. Chem. Soc. Japan, **51**(2), 479 (1978).

10. Johnson, J.S., Personal communication, ORNL, March 1982.
11. Yoe, I. I. and T. B. Koch, eds., Ion Exchange, Wiley, New York, 1957.
12. Chemical Rubber Company, Cleveland, Ohio, CRC Handbook of Chemistry and Physics, p. F-126, 1977.
13. Hamer, W. J., "Theoretical Mean Activity Coefficients of Strong Electrolyte in Aqueous Solutions from 0 to 100°F," NSRDS-NB524, U.S. Govt. Printing Office, Washington (December 1968).
14. Kim, H. W. and L. B. Road, "The Use of Ion Exchange for the Removal of Nuclides Present in Liquid Streams Associated with Nuclear Power Plants," ORNL/MIT-155, October 24, 1972.
15. Rosen, J. B., Ind. and Eng. Chem., 46(8), 1690 (1952).
16. Beek, W. J. and K. M. K. Muttzall, Transport Phenomena, Wiley, New York, 1975.
17. Kullberg, L. and A. Clearfield, J. Phys. Chem., 85, 1578 (1981).
18. Shiao, S. Y. personal communication, ORNL, February 1982.
19. Satterfield, C. N., Mass Transfer in Heterogeneous Catalysis, M.I.T. Press, Cambridge, Mass., 1970.
20. Blank, Leland, Statistical Procedures for Engineering, Management, and Science, pp. 54, 497, 630, McGraw Hill, New York, 1980.