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ION-EXCHANGE PROPERTIES OF ACTIVATED CARBON FILLED WITH HYDROUS Zr(IV) AND Zr(IV)-P(V) OXIDES*

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SUMMARY

Filling the pores of activated carbon with hydrous oxides allows one to take advantage of the attractive ion-exchange properties of the oxides and to avoid difficulties of column operation with the hydrous oxides alone arising from particle size, particle uniformity, and dispersibility. Procedures are outlined for incorporation of useful amounts of hydrous Zr(IV) oxide and mixed oxides of Zr(IV) and P(V) in high surface area charcoals. A dilute solution of Zr(IV) salt in solutions of moderate acid concentration is first contacted with the carbon and the Zr(IV) taken up precipitated with ammonia. More than one cycle may be desirable. Higher Zr(IV) oxide contents may be attained by pretreating the charcoal with nitric acid at elevated temperature. The rates of exchange between filled carbons and solution are adequate for column separations.

INTRODUCTION

The excellent separations capabilities of organic ion exchangers are difficult to exploit in many environments of interest. Temperature limitations may not be as restrictive as often assumed; anion exchangers, at least, have given good results at least to 150°C¹. However, high radiation fields and aggressive chemical environments do preclude use in some desirable applications. This is one of the reasons that there has been continuing interest in inorganic adsorbents. Another has been the remarkable selectivities of many inorganic materials. For example, in acidic media some hydrous oxides^{2,3}, have high distribution coefficients for anions (such as chromate or tungstate). Others are very selective between alkali metal ions and between alkaline

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earth ions; this discrimination is common in amorphous or microcrystalline preparations comprised of mixtures of hydrous oxides of acidic and basic ions (frequently referred to as, *e.g.*, "zirconium phosphate" or "thorium tungstate", although no definite stoichiometry is implied).

In spite of these attractive properties, hydrous oxides appear not to have been used to any great extent, at least in industrial applications. One probable reason is the difficulty of preparing them in forms suitable for column use. It is sometimes difficult to prepare particles of the desired size and of a narrow range of dimensions. Further, hydrous oxides, although frequently of adequately low solubility, have a tendency to peptize in many chemical environments.

A possible remedy for these difficulties is incorporation of inorganic adsorbents in other solid materials. Kraus and co-workers have shown that by filling the pores of activated carbons with hydrous Fe(III) oxide⁴ and Sn(IV) oxide⁵, advantage could be taken of both the excellent chromatographic properties of the charcoal and of the adsorptive properties of the inorganic material. The same approach worked well with zinc sulfide⁶ and silver chloride⁷, which remove by metathesis ions from solution that form more insoluble sulfides (*e.g.*, silver) or silver salts (*e.g.*, iodide). The kinetics of exchange of ions between solutions and filled solids is rapid enough for operation of columns at good flow-rates.

Hydrous oxides of Fe(III) and Sn(IV) illustrate alternative approaches to attaining acceptably high loadings in pores. With Fe(III), advantage is taken of the high distribution of this ion on the solid from several molar hydrochloric acid solutions, a property of activated carbon paralleling adsorption by organic ion exchange resins⁴. With Sn(IV), the high solubility of SnCl₄ allows high loading simply by filling the pores with a concentrated aqueous solution. In either case, the hydrous oxide is precipitated by exposing the carbon after loading with Fe(III) or Sn(IV) to ammonia gas. The solid then contains two to three moles of the hydrous oxide per kg charcoal.

Filling charcoal by hydrous Zr(IV) oxide would be of particular interest. Its solubility is exceptionally low. Its isoelectric point is in the neutral pH region, and it behaves as an anion exchanger in acidic solutions and as a cation exchanger in alkaline solutions. It has to an exceptional degree the desirable properties previously mentioned of high selectivities for polyvalent anions and of formation of mixed hydrous oxides with acidic ions. However, in earlier attempts we have experienced difficulty in attaining loadings of hydrous Zr(IV) oxide comparable to those of Fe(III) or Sn(IV). The solubility of Zr(IV) compounds under conditions practical for precipitation after saturating the pores is relatively limited. Further, we found that much of the oxide tends to precipitate on the surface when we tried preparation by the technique used for Sn(IV). These difficulties have led us to investigate the adsorption of Zr(IV) on activated carbons over a wide range of aqueous compositions in hope of finding conditions under which distribution coefficients are high enough to effect useful loadings by the approach successful with Fe(III).

Nagy *et al.*⁸ have described preparation of activated carbons with amorphous zirconium phosphate on the surface by treating with phosphoric acid, drying, exposing to Zr(IV) in hydrochloric acid, washing and heat treating. Capacities for cation adsorption were increased over those of their original carbon by an order of magnitude, but were not very high; that for Cs(I), for example, was reported to be about 0.1 moles/kg, and for Sr(II) considerably less.

We describe here results of our survey to locate conditions giving high loadings of activated carbon with hydrous Zr(IV) oxide. We also report preparation of activated carbon with zirconium phosphate in the pores, and preliminary evaluation of its chromatographic properties.

EXPERIMENTAL

Activated carbon

The coconut charcoal used was high surface area, nominally 1000 m²/g, material from Barnebey Cheney. It was crushed and screened (-100 mesh, +200 mesh) to isolate the lot for these studies. This material has an uptake from 0.01 M Na⁺ solution of about 0.01 equiv./kg solid at pH 5 and about 0.3 equiv./kg at pH 11. Its uptake can be greatly increased by treatment with oxidizing agents. For tests here, as received material was exposed to 90% (fuming) nitric acid at 70°C for 35 min in some cases, followed by water wash and drying at 110°C. This procedure increased Na⁺ uptake to about 0.5 equiv./kg at pH 5 and 1.5 equiv./kg at pH 11. In other cases, exposure was to 70% nitric acid at 60°C for 2 h. Further details on the charcoal and oxidative treatment are given elsewhere⁹ (this as-received material is designated BC-2 in ref. 9).

Distribution coefficients and uptake

Equilibria between solid and solution phases were determined either by batch equilibration or by use of columns. In batch equilibrations, solutions were analyzed before and after equilibration with the use of radioactive tracers. The amount on solids was computed by material balance from the decrease in solution tracer concentration after contact with solids. Tracers used were ⁹⁵Zr and ²²Na.

Columns were comprised of beds of charcoal supported on glass-wool plugs in 0.6-cm I.D. glass tubes; the heights of the beds were between 3 and 4.5 cm, and they contained about 0.5 g (dry) of adsorbent. The bed was pre-equilibrated with the medium of interest by passage of twenty bed volumes through the column. The tracer (²²Na or ¹³⁷Cs, ca. 10⁻⁹ M) was then introduced at the top of the column in a 0.075-ml volume, or less than 10% of the bed volume. A thin plug of glass wool at the top of the bed eliminated disturbance of the adsorbent from turbulence caused by introduction of samples. Passage of the supporting electrolyte solution by gravity-driven flow was restarted, and samples of about a quarter to two thirds of a bed volume were collected on a sample changer. They were counted with a sodium iodide-thallium scintillation counter. Flow-rates were 0.13 ml/min (0.46 cm/min) through a column of charcoal filled with hydrous Zr(IV)-P(V) oxide, 0.5 ml/min (1.8 cm/min) through oxidized carbon, and 0.8 ml/min (2.5 cm/min) through unoxidized carbon. The flow-rates in cm/min refer to superficial velocity, or to total bed volume divided by the column cross-sectional area. The average flow-rate through the bed is therefore this value divided by fractional volume of voids between particles, estimated to be 0.6. In the separation tests, 0.075 ml of each tracer were added, and the counting was carried out on a Canberra multichannel analyzer capable of distinguishing Cs and Na.

With tracer loadings a small fraction of ion-exchange capacity having a much higher distribution coefficient than the bulk can lead to erroneous evaluations of

performance in separations with macro concentrations. To guard against this possibility, the pre-equilibration solutions contained $10^{-5} M$ of non-radioactive sodium ions. This precaution was not generally followed with Cs, but a test with dead Cs gave the same results as without. Adsorption on glass wool and on glass walls was shown to have negligible effect on results. Counting rates were corrected for background; peak counts were 50–200 times background.

For a symmetrical peak, the number (N_{\max}) of (geometrical) bed volumes (V_b) needed to reach the center of the peak in the eluent is related to the distribution coefficient D (amount adsorbed per kilogram of solid divided by the amount per liter of solution, units l/kg or ml/g) by the relation^{10,11}

$$D = \frac{N_{\max} - i}{(w/V_b)} \quad (1)$$

where i is the fraction of bed volume occupied by interstitial solution, w is weight (g) of solid in the bed, and $V_{\max} = N_{\max}V_b$ is the volume (ml) of eluting solution needed to reach the center of the eluting peak. (In obtaining D , small corrections were made for other volumes besides interstitial hold up in the column.)

Reproducibility of the column method was tested for a low distribution coefficient, D_{Na} from 0.3 M ammonium chloride, and for one in the high range, D_{Na} in ammonia–ammonium chloride, 0.1 M . Values of 0.85, 0.80, 0.80, 0.85 and 0.89 were obtained for the first. For the second, values were 26.1, 25.9 and 25.7.

Filling of carbon with hydrous Zr(IV) oxide

Optimizing the procedure was the main objective, and details will be described in the results. A typical procedure involves contacting a 0.05 M ZrOCl_2 solution in 1 M hydrochloric, sulphuric, or nitric acid with charcoal with a volume–mass ratio of 100 ml/g, separation of the solid by filtration with a Buchner filter, and exposure to gaseous ammonia. This cycle was in some cases carried out three times. The solid was washed and dried for evaluation of adsorptive properties. Hydrous oxide content of the charcoal was determined from the weight before and after exposure to 500–600°C, corrected for carbon ash, measured on samples of non-filled carbon (about 10% of the weight of the carbon). The zirconium solid after the heat treatment was taken to be ZrO_2 .

Zirconium phosphate

An activated carbon filled with a mixed Zr(IV)–P(V) oxide was formed by first equilibrating carbon with 0.05 M ZrOCl_2 in 1 M nitric acid, and then passing 1 M phosphoric acid through a column made up of this Zr-form carbon.

X-ray diffraction of the filled carbon, carried out by the ORNL Analytical Chemistry Division, indicated no presence of zirconium phosphate crystals of the sort seen in many preparations of zirconium phosphates¹². The implied amorphous or microcrystalline distribution of the mixed hydrous oxide is considered advantageous for ion-exchange purposes, from the point of view of capacity and rapidity of exchange reactions. From X-ray fluorescence intensities of the material, also measured by the ORNL Analytical Chemistry Division, in comparison with intensities of commercial Biorad zirconium phosphate ion exchanger, it is estimated that the filled carbon was about 30% by weight Zr–P material and that the P–Zr ratio was about 2.3; the ratio for the Biorad material was about 2.1.

RESULTS AND DISCUSSION

As we indicated in the introduction, attempts to fill carbons with hydrous Zr(IV) oxide by the method used with SnCl_4 , *i.e.*, by contacting with concentrations as high in Zr(IV) as we could prepare, did not give satisfactory products. On treating with ammonia, substantial amounts of hydrous oxide precipitate were formed on the outside of the particles and tended to peptize or otherwise be removed when the solids were used for ion-exchange purposes. Consequently, we carried out a survey of distribution between dilute solutions or Zr(IV) and activated carbons as a function of acidity, loading of the solid with Zr(IV) and of other anions present.

Distribution coefficients of tracer Zr(IV)

In general, the distribution coefficient of Zr(IV) at negligible loading of the solids increased rapidly with decreasing acid concentration. We illustrate with measurements of D_{Zr} (l/kg, measured by batch equilibration) from sulfuric acid (Fig. 1). For Barnebey Cheney charcoal, values of D are seen to fall by about three orders of magnitude as the acid concentration is increased to 4 *M*. There was little difference between nitric-acid-treated charcoal and as-received material, which had been subjected to an outgassing procedure (24 h at 500°C under vacuum) sometimes used before oxidation. (The outgassing affected the ion-exchange properties significantly, but after nitric acid treatment there was little difference between samples which had and had not been subjected to this step⁹). Measurements on a Fisher coconut charcoal are included for comparison; values of D for it were lower.

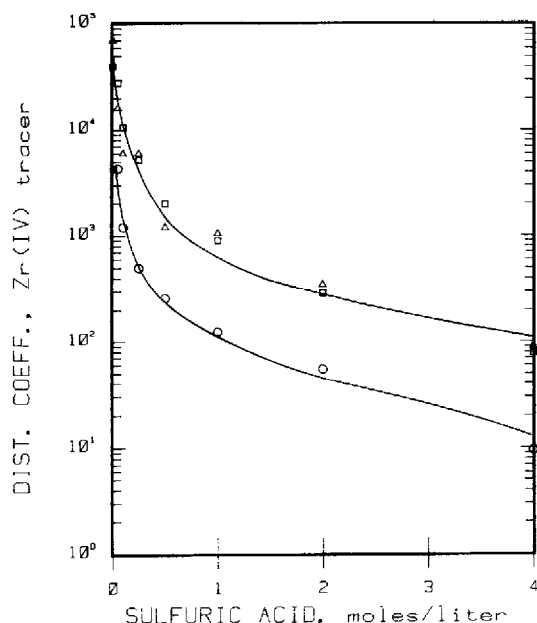


Fig. 1. Adsorption of Zr(VI) at tracer concentration from sulfuric acid solutions on various activated carbons. Δ , Barnebey Cheney, degassed; \square , Barnebey Cheney, degassed and nitric-acid-treated; \circ , coconut charcoal.

Values of D_{Zr} measured from nitric acid media decreased roughly as sharply over the range investigated (up to 3 *M* nitric acid). In hydrochloric acid, the D values dropped from about 5000 at low hydrochloric acid to about 2000 on oxidized Barnebey Cheney and to about 1000 for degassed-only material at 1 *M* hydrochloric acid, and scattered about these values out to the highest concentration of the measurements, 12 *M* hydrochloric acid. Fisher charcoal values of D were also lower, both in nitrate and chloride systems, than values for Barnebey Cheney.

Effect of loading of solid with Zr(IV) on distribution

Although high values of D should be favorable to incorporation of greater amounts of hydrous oxide in the porous structure, the possibility of non-linear isotherms or loading effects implies that the greatest amount does not necessarily correlate with the highest distribution coefficient of Zr(IV) at tracer concentration. This is illustrated in Fig. 2 by measurements of D as a function of loading of Zr(IV) on the solid for several different nitric acid concentrations. Values of tracer D rise with decreasing acid concentration (except for a slight reversal between 0.05 and 1 *M*). However, at loadings in the range 0.05 to 0.5 moles Zr(IV)/kg, values of D decline precipitously for the lower two acid concentrations. Consequently, greater amounts on the solid can be attained at intermediate acidities.

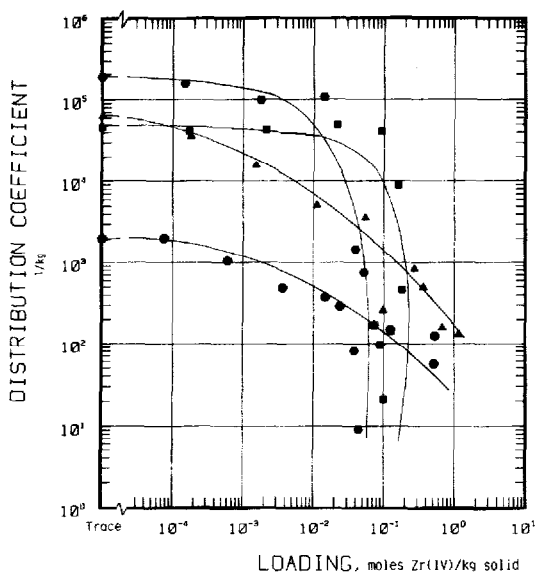


Fig. 2. Effect of loading on distribution coefficients of Zr(IV) on oxidized charcoal. Oxidation conditions: 90% nitric acid, 70°C, 35 min. ○, 0.01 *M* HNO₃; ■, 0.05 *M* HNO₃; ▲, 1 *M* HNO₃; ●, 4 *M* HNO₃.

Similar patterns were seen with the other anions. A factor which might contribute to these observations is the hydrolysis of Zr(IV). Hydrolytic polymers become in some media rather large [in the range of tens of Zr(IV) per aggregate¹³] at the lower acidities and higher Zr(IV) concentrations. These complex species may become too large for the micropores of the carbon, or in any case may shift the equilibria toward higher concentrations in the solution phase.

Fluoride is a strong complexer of Zr(IV), and might be expected to limit the hydrolysis to smaller species. Loading was measured at several ratios of F-Zr(IV) from 0.5 to as high as 8. The effect on the Zr(IV) loading attained is illustrated in Fig. 3 for hydrochloric acid solutions. In this case there is a substantial increase in maximum loading for solutions containing one mole of fluoride per mole of Zr(IV) over those for no fluoride and a decrease if F-Zr ratios were higher. However, in no case tested were loadings substantially higher than the approximately 1 mole Zr(IV)/kg obtained from 1 M nitric acid (Fig. 2), and the relative simplicity of the latter composition led us to focus on this medium for filling of carbon. It is possible that with other acid concentrations not tested, *e.g.* 1 M hydrochloric acid, addition of fluoride might be advantageous.

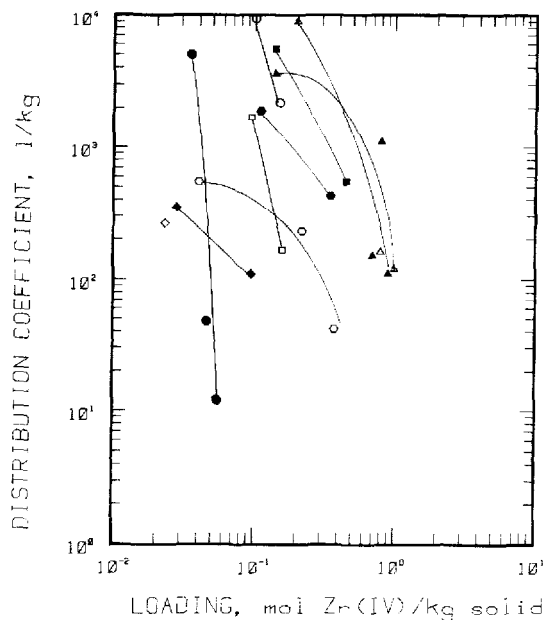


Fig. 3. Adsorption of Zr(IV) on nitric-acid-treated activated carbon from hydrochloric acid solutions, as a function of F-Zr mole ratio. ●, 0.01 M hydrochloric acid, F-Zr = 0; ○, 0.1 M hydrochloric acid, F-Zr = 0; ▲, 0.01 M hydrochloric acid, F-Zr = 1; △, 0.1 M hydrochloric acid, F-Zr = 1; ■, 0.01 M hydrochloric acid, F-Zr = 2; □, 0.1 M hydrochloric acid, F-Zr = 2; ●, 0.01 M hydrochloric acid, F-Zr = 4; ○, 0.1 M hydrochloric acid, F-Zr = 4; ◆, 0.01 M hydrochloric acid, F-Zr = 8; ◇, 0.1 M hydrochloric acid, F-Zr = 8.

Filling of carbon

On the basis of the preceding survey, 1 M nitric acid solutions were selected for filling with hydrous Zr(IV) oxide. Activated carbon was treated with 0.05 M ZrOCl₂ in 1 M nitric acid, the ratio of solid to liquid being 1 g/100 ml. The solid was then exposed to ammonia. It was then again contacted with the zirconium solution, exposed to ammonia, contacted with the zirconium solution, and again to ammonia. The amounts of hydrous Zr(IV) oxide contained in the carbon after each of these three cycles is summarized in Table I. About 0.6 moles Zr(IV)/kg was reached with as-received activated carbon, and about 0.8 moles/kg for that contacted with 90%

TABLE I
INCORPORATION OF HYDROUS Zr(IV) OXIDE IN ACTIVATED CARBON*

	<i>Mole Zr(IV)/kg charcoal</i>
<i>As-received Barnebey Cheney charcoal</i>	
First filling of ZrO ₂	0.385
Second filling of ZrO ₂	0.426
Third filling of ZrO ₂	0.612
<i>Oxidized degassed Barnebey Cheney charcoal**</i>	
First filling of ZrO ₂	0.665
Second filling of ZrO ₂	0.694
Third filling of ZrO ₂	0.814

* 10 grams of Barnebey Cheney activated carbon were soaked in 1 l of 0.05 M ZrOCl₂ in 1 M nitric acid in each cycle.

** Exposed to 90% nitric acid at 70°C for 35 min.

nitric acid for 35 min at 70°C. Although these loadings are less than those attained with Fe(III) and Sn(IV) and are also (for reasons not altogether clear) less than might have been hoped from the patterns in Fig. 2, they are high enough to be useful.

Ion uptakes of filled carbons

Hydrous oxides are weak electrolyte ion exchangers². In contact with solutions of acidic pH, they tend to be anion exchangers, and in contact with basic solutions, cation exchangers. Anion exchange "capacity," if defined as the concentration of exchangeable ions other than hydroxide on the solid, will tend to increase with increasing acidity; cation capacity or uptake will increase with increasing pH. The pH at which the two are equal is frequently referred to as the isoelectric point. It will vary for a given oxide with the types of ions present because equilibria between protons and salt cations and between hydroxides and salt anions are involved. Also because of these equilibria, uptake can be expected to vary with salt concentration in the solution phase^{2,14}.

We report here measurements as a function of pH of uptake of sodium ions by charcoal filled with hydrous Zr(IV) oxide. It should be remembered that the objective of incorporation of the oxide is not to increase the ion-exchange capacity of the charcoal, which at least after oxidative treatment is rather high in any case. Instead, the purpose is to take advantage of the selectivities of the hydrous oxide in a form suitable for use in columns.

Fig. 4 compares uptakes of sodium ions after no, one, two and three fillings of as-received charcoal. A trend to higher uptakes after successive cycles is apparent through considerable scatter. Fig. 5 compares as-received and oxidized material with the same charcoals after three filling cycles. The uptake of the oxidized carbon is seen to be somewhat less after the hydrous oxide is incorporated than before. However, the uptakes are substantially higher than the filled as-received material, that ratio being about 2:1 in comparison to about 4:3 ratio of incorporated hydrous oxide (Table I). In both cases, the uptakes are higher than those on hydrous Zr(IV) oxide alone^{2,14}. It appears that there is still a substantial contribution of sites on the carbon to uptake.

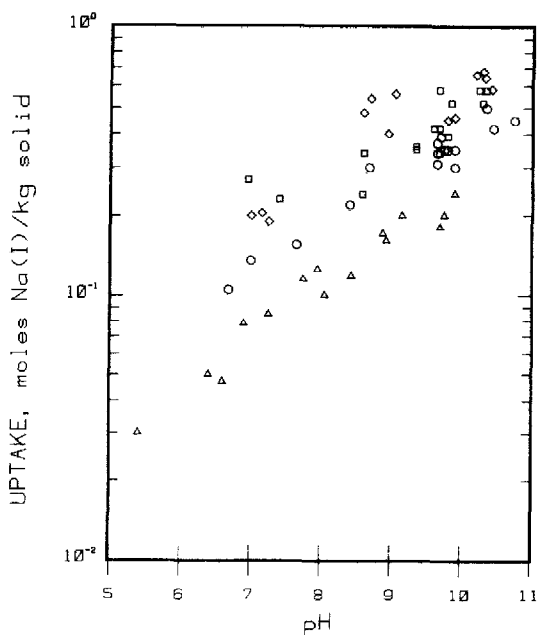


Fig. 4. Sodium ion uptake on as-received Barneby Cheney activated carbon from 0.01 *M* sodium chloride. Filling with hydrous Zr(IV) oxide. Δ , None; \circ , first; \square , second; \diamond , third.

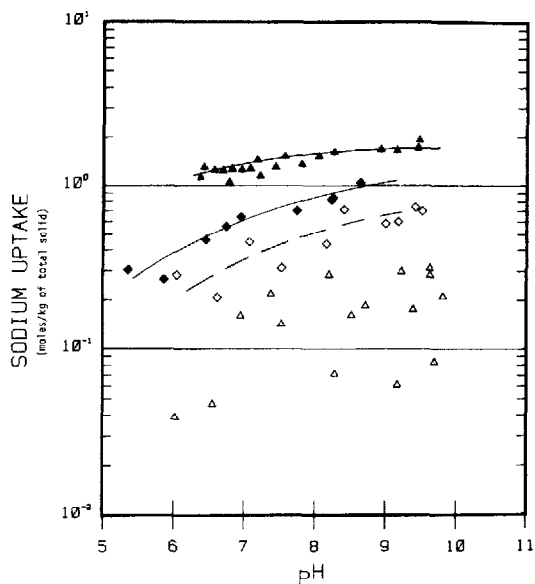


Fig. 5. Sodium ion uptake on charcoal filled with hydrous Zr(IV) oxide (from 0.1 *M* sodium chloride; charcoal oxidation conditions: 70% nitric acid, 60°C, 2 h). Δ , As received, no Zr(IV); \blacktriangle , oxidized, no Zr(IV); \diamond , as received, third filling; \blacklozenge , oxidized, third filling.

Fig. 6 summarizes uptakes on charcoal filled with hydrous Zr(IV)-P(V) oxide by the method described in the Experimental section. Comparison with Fig. 5 indicates an increase in uptake from 0.1 *M* sodium chloride of the oxidized Zr-P filled charcoal over that of material filled only with hydrous Zr(IV) oxide and a somewhat less marked difference between the as-received filled with the hydrous Zr(IV) oxide vs. hydrous Zr(IV)-P(V) oxide. Uptake is much greater in both cases from 0.1 *M* sodium chloride than from 0.01 *M* sodium chloride, presumably on account of the exchange between sodium ions and phosphate protons.

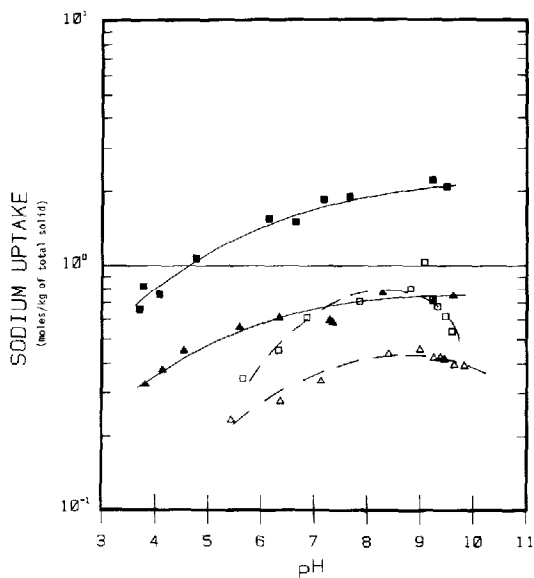


Fig. 6. Uptake of sodium ions on charcoal filled with Zr(IV)-P(V) hydrous oxides. Oxidation conditions: 70% nitric acid, 60°C, 2 h. □, As received, 0.1 *M* NaCl; ■, oxidized, 0.1 *M* NaCl; △, as received, 0.01 *M* NaCl; ▲, oxidized, 0.01 *M* NaCl.

Selectivities

Distribution coefficients of tracer Na^+ and Cs^+ as a function of ionic strength were measured by the column method on unoxidized carbon, oxidized carbon, and oxidized carbon filled with hydrous Zr(IV)-P(V) oxide. The supporting electrolytes were ammonia-ammonium chloride [the two being present in equal concentrations and the ionic strength being in effect the concentration of ammonium chloride (pH \approx 9.5)], ammonium chloride (pH \approx 5.5), and (0.1–1 *M*) hydrochloric acid. Results are collected in Table II.

The values of *D* for the as-received activated carbon are low. There is little selectivity between Na^+ and Cs^+ by this material, either at alkaline or slightly acidic pH; measurements were not carried out at acidic pH.

Distribution coefficients were higher on the oxidized material, and there appears to be some selectivity between Na^+ and Cs^+ at the pH values for which comparisons are possible, alkaline and slightly acidic. The discrimination is not great, however.

TABLE II
DISTRIBUTION COEFFICIENTS (OBSERVED FOR TOTAL SOLIDS)

X = not measured.

Carbon state	Electrolyte	pH	Sodium tracer ionic strength (M)			Cesium tracer ionic strength (M)		
			0.1	0.3	1.0	0.1	0.3	1.0
Unoxidized	Ammonia-ammonium chloride	9.5	4.4	2.3	1.5	4.6	2.2	1.6
	Ammonium chloride	5.5	1.4	0.85	0.7	2.2	1.4	0.9
Oxidized	Ammonia-ammonium chloride	9.5	25.7	16.7	9.6	18.5	5.5	1.74
	Ammonium chloride	5.5	27.2	8.2	3.2	16.5	5.2	1.5
	Hydrochloric acid (0.1-1 M)	X	X	X	X	28.7	12.6	4.7
Filled with hydrous Zr(IV)-P(V) oxide	Ammonia-ammonium chloride	9.5	45.2	23.8	11.7	26.2	11.3	3.6
	Ammonium chloride	5.5	27.5	12.7	4.6	26.2	10.5	4.6
	Hydrochloric acid (0.1-1 M)		2.9	1.6	1.4	250	77.3	30.5

Oxidized carbon filled with hydrous Zr(IV)-P(V) oxide appears more interesting. Distribution coefficients are higher, and there is a reversal in selectivity between alkaline and acidic media, illustrated in Fig. 7 for ionic strength of 0.1 M. A similar reversal has been observed for hydrous Zr(IV) oxide².

The distribution coefficients in Table II are for the total solid, carbon plus filler. As we mentioned previously, there is some evidence of a contribution by the activated carbon to the total ion-exchange capacity after incorporation of inorganic material. The observed values of D in such cases are

$$D = \sum_i (f_w)_i D_i \quad (2)$$

where $(f_w)_i$ is the weight fraction of adsorbent i and D_i the distribution coefficient for it. With the analytical value of f_w of hydrous Zr(IV) phosphate oxide, 0.3, and with the assumption that the contribution of the carbon is the same after filling as before, we have computed from the values of Table II distribution coefficients for the filler alone. These are presented in Fig. 8. For tracer loading, if there is no co-ion invasion (*i.e.*, uptake of ions of the same charge sign as the fixed charge of the ion exchange material), the concentration of the macro counterion (c_{macro}) on the solid will be essentially the ion-exchange capacity C^* . If in addition activity coefficient ratios of adsorbed species between solution and solid phases are constant, from the equilibrium constant K for the exchange, the distribution coefficient of the ion in tracer concentration should follow the equation

$$\log D_{\text{tracer}} = -\log c_{\text{macro}} + \log K + \log C^* \quad (3)$$

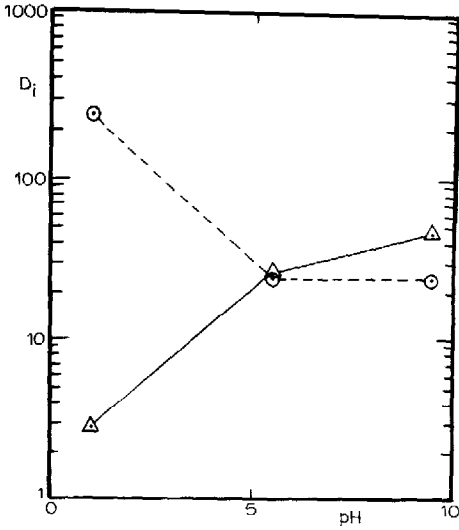


Fig. 7. Distribution coefficients of $^{137}\text{Cs}^+$ (\odot) and $^{22}\text{Na}^+$ (Δ) on activated carbon filled with hydrous Zr(IV)-P(V) oxide from 0.1 M (1,1) electrolyte.

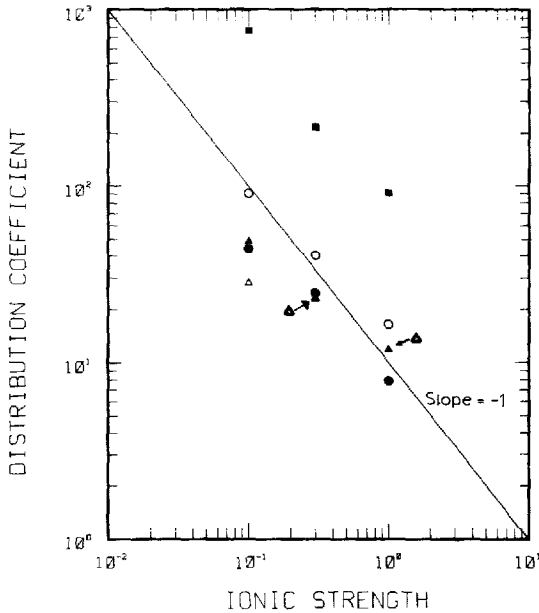


Fig. 8. Distribution coefficients of tracer Na^+ and Cs^+ on hydrous Zr(IV)-P(V) oxide, incorporated in activated carbon. \blacksquare , Cs^+ in hydrochloric acid; Δ , Na^+ in ammonium chloride; \blacktriangle , Cs^+ in ammonium chloride; \circ , Na^+ in ammonia-ammonium chloride; \bullet , Cs^+ in ammonia-ammonium chloride.

when all ions are univalent. A plot of $\log D_{\text{tracer}}$ vs. $\log c_{\text{macro}}$ should be linear, of slope -1 .

The results in Fig. 8 follow the expected pattern roughly, the slopes being not quite as steep as ideal. The differences could arise from several of the assumptions made. They are in the direction expected from the effect of co-ion invasion. We have

no measurements of chloride uptake under these conditions, but an appreciable contribution of this factor at the highest ionic strengths would not be surprising.

As with the bulk hydrous oxide^{2,15}, the ratios of D for Na^+ and Cs^+ appear favorable for column separation in acidic media; the substantial differences in D with pH imply that adsorbed ions can be readily eluted by changes in solution composition, in the manner possible with hydrous Zr(IV)-P(V) oxide not supported on activated carbon².

Separation of Cs^+ and Na^+

The feasibility of separation is confirmed by estimation of the number of theoretical plates, P_N , from the elution curve of a spike of tracer added to electrolyte solution flowing through the column, by the equation¹⁶

$$P_N = 8(V_{\max}/\beta)^2 \quad (4)$$

where β is the band width, *i.e.*, the volume of solution between the eluent concentrations of $1/e$ times the peak concentrations observed at V_{\max} . For Cs^+ tracer in 0.1 M hydrochloric acid, P_N was 5200 and for Na^+ *ca.* 12, the geometrical mean (total plates) being 250. The ratio $D_{\text{Cs}}/D_{\text{Na}} = 250/2.9 = 86$ in 0.1 M hydrochloric acid. For a 99.99% separation with 250 plates, this ratio would only need to be 1.7. It should be possible, therefore, to remove Na^+ essentially completely from the column before appreciable amounts of Cs^+ are eluted. In fact, to remove the Cs^+ in a convenient volume, change of electrolyte composition to lower its distribution coefficient will be desirable, and there should be ample discrimination to allow this. The prospects for a clean separation are favorable.

The same analysis for a Na^+ - Cs^+ separation from ammonia-ammonium chloride, 1 M , in which Cs^+ should be eluted first, gives about 19 plates and a ratio of $D_{\text{Na}}/D_{\text{Cs}} = 3.25$; a ratio of distribution coefficients of 5 would be needed for good separation. Only partial separation is predicted.

These estimates assume that film and particle diffusion do not have important effects. Analysis for the oxidized-carbon column (flow-rate 0.5 ml/min) and an assumed diffusion coefficient of the ions in water of $1.3 \cdot 10^{-5}$ cm²/sec gave, by Satterfield's method¹⁷, an external mass transfer coefficient of $8.3 \cdot 10^{-3}$ (cm³_{liq})/(cm²_{particle} sec), with a particle Reynolds number of 0.01. The resulting film resistance of $5.2 \cdot 10^{-4}$ S used in Rosen's¹⁸ model of mass transfer in a packed bed yields a film coefficient v/x of $9.3 \cdot 10^{-6}$, well below the value (0.01) indicative of the onset of film diffusion limitations. (In Rosen's development, v and x are dimensionless parameters, v being proportional to surface film resistance and x to effective bed length.) External mass transfer was not limiting in any of the columns.

The internal coefficient was estimated as $3.3 \cdot 10^{-8}$ cm²/sec based on Rosen's¹⁸ model for a distribution coefficient of 10 and $c/c_0 = 0.5$ at the peak in the elution curve. That the internal diffusion coefficient is 1/400 the external value is quite low for liquid-phase diffusion; nonetheless, the time for 99.9% of the external concentration to be reached in the particle (330 sec) is less than the 415 sec contact time of the peak front. For the cases of high D , the contact time was more than four times as great, rendering pore diffusion limitations less of a concern. Pore diffusion is the controlling step but is not limiting; the separations are not seriously compromised by kinetic factors.

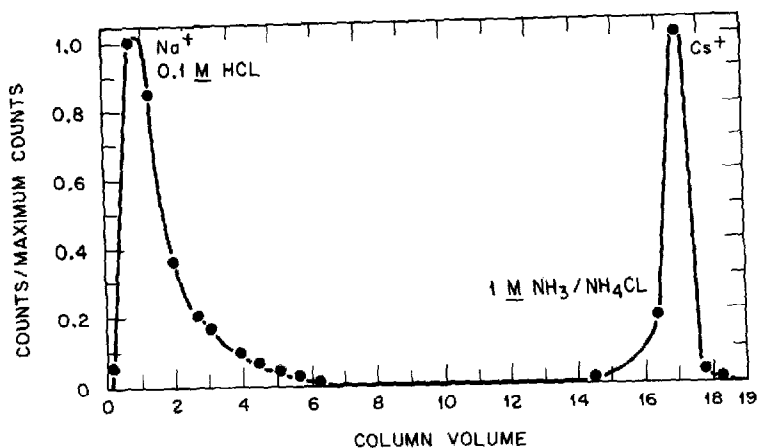


Fig. 9. Separation of Na^+ and Cs^+ by activated carbon filled with hydrous Zr(IV)-P(V) oxide. Bed height, 3.2 cm; flow-rate, 0.46 cm/min (0.13 ml/min) (visually fitted curve).

Fig. 9 shows the separation from acidic media. As the distribution coefficients indicated, clean separation is obtained, although there is some tailing of the Na^+ peak, from channeling or other causes. In order to remove the Cs^+ from the column expeditiously, the medium was changed to ammonia-ammonium chloride, 1 M, in which its distribution coefficient is low (Table II).

Fig. 10 shows the separation from ammonia-ammonium chloride, 1 M. As the distribution coefficients predict, Cs^+ is eluted first, followed by Na^+ . In agreement with the analysis above, the separation on a column of this length is not complete.

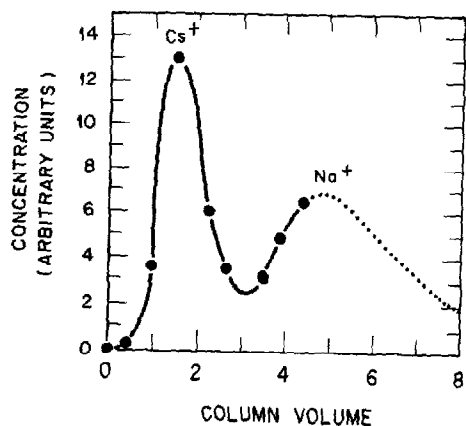


Fig. 10. Separation of mixture of Na^+ and Cs^+ tracers in ammonia-ammonium chloride, 1 M, on activated carbon filled with hydrous Zr(IV)-P(V) oxide. Bed height, 3.2 cm; flow-rate, 0.46 cm/min (visually fitted curve).

CONCLUSION

By optimizing solution composition and acidity, substantial amounts of hydrous Zr(IV) oxide can be incorporated in the pores of activated charcoal, although

we have not been able to achieve as high loading as previously attained with hydrous Sn(IV) oxide and hydrous Fe(III) oxide. A mixed hydrous oxide comprised of Zr(IV) and P(V) oxides is feasible by passage of phosphoric acid through a column of carbon earlier treated with $ZrOCl_2$. Its uptake of monovalent ions appears higher than that prepared by the procedure described by Nagy *et al.*⁸

Higher loadings are obtained by use of activated carbon treated with nitric acid before incorporating Zr(IV) oxide.

Sodium uptakes of the filled materials increase with pH, as one expects of weak-electrolyte ion exchangers. There is also an increase with concentration of the sodium ions in the solution, particularly with the Zr(IV)-P(V) material. The increase is less marked with the carbon filled with Zr(IV) oxide and is less than observed with simple hydrous Zr(IV) oxide¹⁴. Presumably, the difference reflects a contribution of the carbon itself to total Na^+ uptake, which is not very sensitive to salt concentration in the case of the oxidized charcoal⁹. The Zr(IV)-P(V) filling probably contributes a larger fraction to the total Na^+ uptake than the Zr(IV) oxide does.

The ion-exchange selectivities of carbon filled with hydrous Zr(IV)-P(V) oxide are qualitatively similar to those of the hydrous oxide in bulk form. Exact reproducibility is not to be expected, because of the sensitivity of properties to P(V)-Zr(IV) ratio, to the temperatures to which the adsorbent has been exposed, and to the extent of drying. The D_C s estimated for the *ca.* 30% mixed hydrous oxide (Fig. 8) is 765 from 0.1 M hydrochloric acid, in comparison with a literature value¹⁵ of 5700. More important for present purposes, the pattern of relative selectivities between ions in solutions between filled and bulk material is similar.

The kinetics of exchange of the filled materials is also favorable. The separation demonstrated here is comparable to that attained with bulk Zr(IV)-W(VI) material². The filled adsorbent appears to be free of some of the difficulties of preparation and stability encountered with the bulk, at the expense of lower volume capacity of the bed.

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