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### Ion-exchange adsorption of radionuclides by ferrocyanide molybdate

A number of compounds containing ferrocyanide show selective adsorption of radionuclides, especially of  $^{137}\text{Cs}$  (refs. 1-19) and some, therefore, have been used for selective adsorption of cesium from a mixture of radionuclides. BAETSLÉ *et al.* investigated the relationship between the Mo/Fe ratio in "ferrocyanide molybdate (FeMo)" and the mixing ratio of the starting materials. They clarified the crystallographic structure, and they also determined the ion-exchange behavior and some column characteristics of FeMo for several radionuclides<sup>20-23</sup>.

In work on the preparation of zinc ferrocyanide, it was found that the composition and ion-exchange behavior of a ferrocyanide were greatly dependent on the mixing ratio of the starting materials. This tendency was also observed in the preparation of nickel or copper ferrocyanide. In order to confirm the existence of such correlations among the compounds containing ferrocyanide, we prepared three varieties of FeMo by varying the mixing ratio of the starting materials. One of them (No. 3) was found to be hardly soluble in water, permitting adsorption of radionuclides in aqueous media.

In the present paper the following studies are reported: (1) comparison of the solubility or adsorption behavior of three adsorbents, (2) relationship between the distribution coefficient of No. 3 and nitric acid concentrations, (3) variation of adsorption behavior of No. 3 with or without addition of concentrated salts, (4) adsorption behavior of several radionuclides for No. 3 in sea water, and (5) isolation of  $^{137}\text{Cs}$  from sea water containing  $^{85}\text{Sr}$ ,  $^{144}\text{Ce}$ ,  $^{137}\text{Cs}$ , etc. through the column studies.

#### Experimental

*Preparation of adsorbent.* Three varieties of adsorbents were prepared by adding 0.2 M  $\text{Na}_2\text{MoO}_4$ -0.4 M HCl to 0.2 M  $\text{Na}_4\text{Fe}(\text{CN})_6$ -0.4 M HCl in the mole ratios of 0.1, 1, and 8 to 1, respectively. The resulting precipitates were numbered in series: adsorbent No. 1, No. 2 and No. 3. The adsorbents were ground, dry-sieved through a 200-300 mesh sieve, and used for batch equilibrium studies. Adsorbent No. 3 sieved through a 50-100 mesh sieve, was used for column studies. The adsorbents were analyzed by the method reported by BAETSLÉ *et al.*<sup>21</sup>.

*Batch equilibrium studies.* Distribution coefficients (ml/g),  $K_d$ , of radionuclides were determined by batch equilibrium studies. 0.1 g of adsorbent was weighed in a glass-stoppered test tube to which 5 ml of a desired solution containing a radionuclide were added. After a given period of agitation at  $25.0 \pm 0.5^\circ$ , the mixture was centrifuged at 8000 g for 1 min and the radioactivity in 2 ml of the supernatant was counted using a conventional well-type scintillation counter.

*Column studies.* Seven grams of adsorbent were slurried with about 70 ml of 0.1 M nitric acid and poured into a conventional glass column (I.D. 1 cm), pulled to a tip and plugged with glass wool at the outlet. The resultant bed was usually 10 cm high. Adsorption and elution were run at a flow rate of 5 ml/min.

All reagents used in the experiment were of reagent grade.

#### Results and discussion

*Comparison of three adsorbents.* The Mo/Fe ratio of adsorbent No. 3 was 3.4,

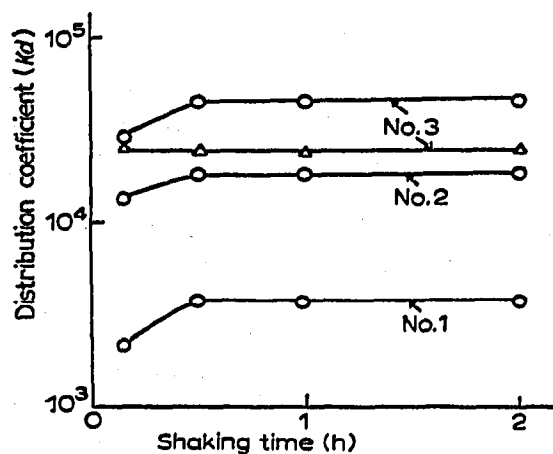


Fig. 1. Dependence of  $K_d$  values on the shaking time.  $\circ$ — $\circ$ ,  $K_d$  values in dioxane–water (1:1);  $\triangle$ — $\triangle$ ,  $K_d$  values in water.

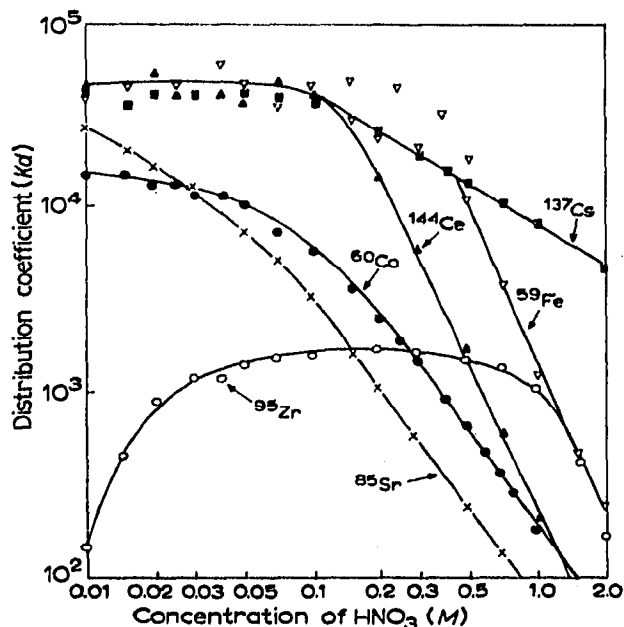


Fig. 2. Dependence of  $K_d$  values for several radionuclides on the concentrations of nitric acid.

which is lower than that reported by BAETSLÉ *et al.*<sup>21</sup>. No. 1 and 2, which were water soluble, could not yield the reliable analytical values. No. 3 was hardly soluble in water. The solubilities of No. 1 and 2 were decreased by adding an equal volume of dioxane to the aqueous phase. The  $K_d$  values increased when the shaking time was increased, with the equilibrium attained at 30 min (*cf.* Fig. 1). At equilibrium, the  $K_d$  values decreased in the following order: No. 3 > No. 2 > No. 1. Since No. 3 was hardly soluble in water, it was used for the subsequent batch and the column studies. In an aqueous medium, the adsorption equilibrium for  $^{137}\text{Cs}$  was attained at 10 min.

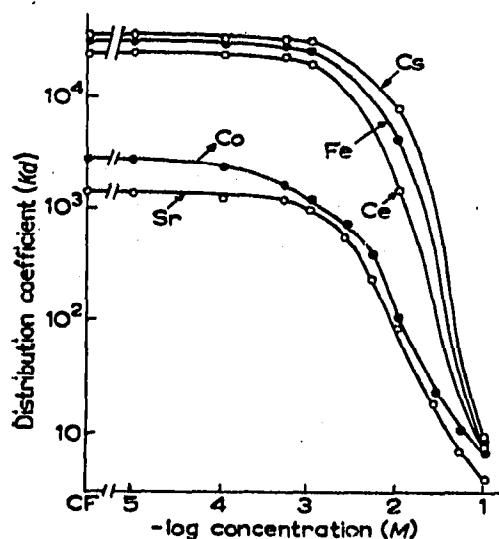


Fig. 3. Dependence of  $K_d$  values for the radionuclides on their concentrations in the initial solution. CF = radionuclides without addition of the carriers.

Subsequent batch equilibrium studies were, therefore, carried out by shaking for 10 min.

*Distribution coefficients of No. 3 and nitric acid concentrations.* The dependence of the  $K_d$  values for  $^{137}\text{Cs}$ ,  $^{59}\text{Fe}(\text{III})$ ,  $^{144}\text{Ce}(\text{III})$ ,  $^{60}\text{Co}$ ,  $^{85}\text{Sr}$  and  $^{95}\text{Zr}(\text{IV})$  on the concentrations of nitric acid is shown in Fig. 2. The individual points are an average value of 4–6 determinations. The slope is  $-1$  for  $\text{Cs}/\text{H}$ ,  $-2$  for  $\text{Co}(\text{II})/\text{H}$  and  $\text{Sr}(\text{II})/\text{H}$ , and  $-3$  for  $\text{Fe}(\text{III})/\text{H}$  and  $\text{Ce}(\text{III})/\text{H}$  over the concentration range from around 0.1 to 2  $M$  nitric acid. The observed slopes of  $^{137}\text{Cs}$  and  $^{85}\text{Sr}$  are almost consistent with those reported by HUYS AND BAETSLÉ<sup>20</sup>. The decrease in  $K_d$  values for  $^{95}\text{Zr}(\text{IV})$  observed for the lower range of nitric acid concentration might be due to the hydrolysis in the solution. Fig. 3 shows the dependence of  $K_d$  values for the radionuclides on their concentrations in the initial solution. The  $K_d$  values for the radionuclides (carrier-free) remain almost unchanged over the concentration range not exceeding ion-exchange capacity, indicating that the observed  $K_d$  values of the radionuclides are due to their own ion-exchange affinities. In the concentration range from around 0.1 to 2  $M$  nitric acid, the dependence in Fig. 2 suggests that these radionuclides are adsorbed by an ion-exchange mechanism.

TABLE I

INFLUENCE OF THE ADDITION OF CONCENTRATED SALTS ON THE DISTRIBUTION COEFFICIENTS

Nuclide	Distribution coefficient			
	0.1 $M$ $\text{HNO}_3$	0.1 $M$ $\text{HNO}_3$ + 0.5 $M$ $\text{NH}_4\text{NO}_3^a$	0.1 $M$ $\text{HNO}_3$ + 0.5 $M$ $\text{NaCl}^a$	$\text{HNO}_3$ + sea water <sup>b</sup>
$^{59}\text{Fe}$	$3 \times 10^4$	$7 \times 10^2$	$2 \times 10^3$	$1 \times 10^3$
$^{60}\text{Co}$	$5 \times 10^3$	$2 \times 10^2$	$4 \times 10^2$	$1 \times 10^2$
$^{95}\text{Zr}$	$3 \times 10^4$	$2 \times 10^3$	$3 \times 10^3$	$4 \times 10^3$
$^{85}\text{Sr}$	$2 \times 10^3$	$< 1$	5	4
$^{95}\text{Zr}$	$1 \times 10^3$	$2 \times 10^2$	$5 \times 10^2$	$7 \times 10$
$^{106}\text{RuNO}$			7	5
$^{144}\text{Ce}$	$4 \times 10^4$	$< 1$	$2 \times 10$	$1 \times 10$
$^{137}\text{Cs}$	$5 \times 10^4$	$3 \times 10^2$	$8 \times 10^3$	$5 \times 10^3$

<sup>a</sup> Dissolution of  $\text{NH}_4\text{NO}_3$  or  $\text{NaCl}$  in 0.1  $M$   $\text{HNO}_3$  to make 0.5  $M$  solutions.

<sup>b</sup> Addition of  $\text{HNO}_3$  to sea water up to a molar concentration of 0.1.

*Distribution coefficients of No. 3 in concentrated salt solutions.* Table I shows the variation in  $K_d$  values for several radionuclides on addition of concentrated salts to 0.1  $M$  nitric acid. The  $K_d$  values for  $^{85}\text{Sr}$  or  $^{144}\text{Ce}$  decrease markedly on addition of these salts to a much larger extent than expected from mutual exchange of ammonium or sodium ions. The reason for these decreases probably lies partly in the interaction of  $^{85}\text{Sr}$  or  $^{144}\text{Ce}$  and the concentrated salts. The extent of the decrease in  $K_d$  values on addition of sodium chloride is less than that on addition of ammonium nitrate. Such a minor decrease in sodium chloride may be due to the fact that the ion-exchange affinity of the adsorbent for sodium ions is lower than that for ammonium ions.

In the case of sea water,  $K_d$  values for  $^{59}\text{Fe}$ ,  $^{60}\text{Co}$  and  $^{137}\text{Cs}$  are considerably higher than those for  $^{85}\text{Sr}$ ,  $^{106}\text{RuNO}$  and  $^{144}\text{Ce}$ . The  $K_d$  values for these radionuclides in sea water are nearly equal to those in 0.5  $M$  sodium chloride. The concentration of sodium chloride in sea water corresponds to about 0.5  $M$  (ref. 24). In sea water,

the amount of sodium chloride is dominant over all the other components: magnesium, calcium, potassium, strontium, aluminum, organic materials, etc. The finding that the  $K_d$  values for the radionuclides in sea water are nearly coincident with those in 0.5 M sodium chloride may be explained by the fact that the radionuclides in extreme minority are governed by an ion-exchange property of the ferrocyanide molybdate without suffering any disturbance from the coexisting materials in large quantity. As stated above, it is noteworthy that the  $K_d$  values for  $^{85}\text{Sr}$  or  $^{144}\text{Ce}$  decreased markedly on addition of the concentrated salts. Such a decrease could not be observed when using any other compounds containing ferrocyanide such as potassium, cobalt, nickel, zinc, sodium, or potassium zinc ferrocyanide. It may, therefore, be considered to be the characteristic adsorption behavior of the ferrocyanide molybdate.

*Isolation of  $^{137}\text{Cs}$  from a mixture of radionuclides in sea water.* When 1 l of sea water spiked with  $^{85}\text{Sr}$ ,  $^{144}\text{Ce}$  and  $^{137}\text{Cs}$  was passed through a column (1 × 10 cm), the spiked  $^{137}\text{Cs}$  was quantitatively adsorbed by the column and a large portion of  $^{85}\text{Sr}$  and  $^{144}\text{Ce}$  (90%) passed through. The  $^{85}\text{Sr}$  and  $^{144}\text{Ce}$  retained were eluted with 50 ml of 1 M ammonium nitrate–0.1 M nitric acid solution. The adsorbed  $^{137}\text{Cs}$  was eluted by 4 M ammonium nitrate–4 M nitric acid solution (Fig. 4). The maximum activity

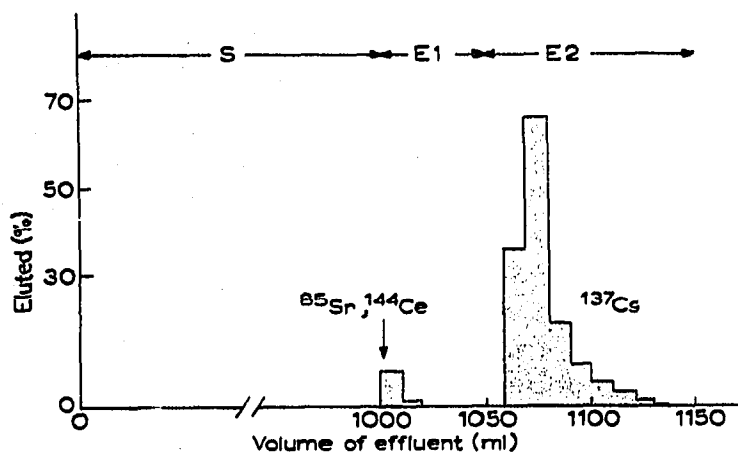


Fig. 4. Isolation of  $^{137}\text{Cs}$  in sea water containing  $^{85}\text{Sr}$ ,  $^{144}\text{Ce}$  and  $^{137}\text{Cs}$ . S = sea water containing  $^{85}\text{Sr}$ ,  $^{144}\text{Ce}$  and  $^{137}\text{Cs}$ ; E1 = 1 M  $\text{NH}_4\text{NO}_3$ –0.1 M  $\text{HNO}_3$ ; E2 = 4 M  $\text{NH}_4\text{NO}_3$ –4 M  $\text{HNO}_3$ . Column, 1 × 10 cm, 50–100 mesh.

was obtained at 30 ml of the effluent. From the whole effluent of 100 ml,  $^{137}\text{Cs}$  was recovered quantitatively. The  $\gamma$ -ray spectra characterization showed that the  $^{137}\text{Cs}$  effluent was not contaminated by  $^{85}\text{Sr}$  and  $^{144}\text{Ce}$ .  $^{59}\text{Fe}$  and  $^{60}\text{Co}$  were added to the above-mentioned sea water which was allowed to pass through the column, followed by the elution of  $^{85}\text{Sr}$  and  $^{144}\text{Ce}$  by the same procedure as mentioned above.  $^{59}\text{Fe}$  and  $^{60}\text{Co}$  along with  $^{137}\text{Cs}$  adsorbed by the column were eluted with 4 M ammonium nitrate–4 M nitric acid solution. When these radionuclides were eluted immediately after adsorption,  $^{137}\text{Cs}$  was recovered by about 100%,  $^{59}\text{Fe}$  by 60% and  $^{60}\text{Co}$  by 70%. After standing for more than one day, recovery of  $^{137}\text{Cs}$  remained the same, but a large portion of the adsorbed  $^{59}\text{Fe}$  and  $^{60}\text{Co}$  could not be eluted. Such poor recoveries may be ascribed to an isotopic exchange or an isotopic displacement occurring between the adsorbent and  $^{59}\text{Fe}$  or  $^{60}\text{Co}$ . Behavior of  $^{106}\text{RuNO}$  toward the column was similar

to that of  $^{144}\text{Ce}$  or  $^{85}\text{Sr}$ , *i.e.*, the large portion was not adsorbed and the adsorbed fraction was capable of eluting with 1 *M* ammonium nitrate–0.1 *M* nitric acid solution. Behavior of  $^{95}\text{Zr}$  in the form of zirconium fluoride was also identical to that of  $^{144}\text{Ce}$ ,  $^{85}\text{Sr}$  or  $^{106}\text{RuNO}$ , provided that it was applied in the form of zirconium fluoride.

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