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Studies on the Adsorption of Traces of Zirconium on Manganese Dioxide from Acid Solutions

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Abstract

The adsorption of zirconium on manganese dioxide from nitric and perchloric acid solutions has been investigated at different concentrations of electrolyte, adsorbent, and adsorbate. The effect of other cations and anions on adsorption has been studied. Fluoride, citrate, oxalate, molybdate, tartrate, carbonate, phosphate, Fe(III), Sr(II), Zn(II), Cr(III), and Mg(II) drastically reduce adsorption. Adsorption of other metal ions on the oxide has been measured under identical conditions. Based on these data, separation of zirconium from a number of elements, including cobalt, zinc, caesium, neodymium and lutetium, can be achieved. Zirconium adsorption follows Freundlich's equation $C_{\text{Ads}} = AC_{\text{Bulk}}^{1/n}$ with the values of $1/n = 0.92$ and $A = 40 \text{ mmol/g}$. Thus manganese dioxide can be used for the separation and preconcentration of zirconium from dilute solutions.

INTRODUCTION

Zirconium is an important material in chemical and nuclear engineering and in metallurgy because of its anticorrosion and desirable mechanical properties and low thermal neutron cross-section (0.185 b). The minerals of zirconium usually contain 1-2% hafnium. The properties of zirconium are affected by its hafnium content. For example, the presence of 1-2% hafnium in zirconium could raise its thermal neutron

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cross-section from 0.185 to 1 barn because of a high thermal neutron cross-section of hafnium (1) (102 b). Therefore, it is essential that zirconium should be free from hafnium or within tolerable limits. Because of their similar chemical and physicochemical properties, their mutual separation has always been a problem for analytical chemists in nuclear technology.

Inorganic ion-exchangers, showing specific selectivity for certain metal ions, have been widely used for their separation and concentration from very dilute solutions (2, 3). Manganese dioxide, one of such useful ion-exchangers, has been studied in our laboratory for the adsorption of a number of elements like cobalt (4), strontium (5), caesium (6), cadmium (7), europium (8), and mercury (9). The adsorption of zirconium and hafnium on manganese dioxide has been studied separately in detail in order to evolve a set of conditions where their mutual separation can be achieved. This paper describes the adsorption behavior of zirconium ions on manganese dioxide from acid solutions.

EXPERIMENTAL

Reagents and Radiotracers

Manganese dioxide (Product No. 11015), B.D.H. microanalytical reagent, black in color, 10–20 mesh was used as such. The BET surface area determined by adsorbing nitrogen was found to be 113 m²/g. The porosity was found to be 2.17 cm³/g, and average pore diameter was 0.17 μ m. The solid phase density was determined to be 6.63 g/cm³.

⁹⁵Zr tracer was obtained by irradiating zirconium metal (Johnson & Matthey) in a PARR-I research reactor of this institute for 48 h at a thermal flux of 2×10^{13} n/cm² · s. The metal was then dissolved in a 1:9 mixture of concentrated sulfuric acid and hydrofluoric acid, heated nearly to dryness, more concentrated sulfuric acid was added, and then dried completely. The tracer was kept in 2 M nitric acid solution and then was made in 0.1 M nitric acid solution, as per requirement. The concentration of zirconium in the solution was determined spectrophotometrically (10) using the xylenol orange method against a calibration curve drawn by using standard zirconyl chloride solutions. These solutions were standardized by EDTA titrations using salicylic acid as an indicator (11). All other tracers used in this study were produced locally, and their radiochemical purity was checked by gamma spectroscopy.

All solutions were made from doubly distilled deionized water and analytical reagents.

Procedure

Distribution coefficients (K_D) were determined radiometrically using the batch technique at room temperature ($23 \pm 2^\circ\text{C}$). A solution (4.5 cm^3) having a specified concentration of zirconium or other element and nitric or perchloric acid was shaken with a known amount of manganese dioxide for equilibration and then centrifuged for phase separation. The initial and equilibrated activity of the radiotracer solution was assayed, and K_D values were computed in the usual manner (6). All measurements were the average of at least triplicate runs.

Instruments

The surface area of manganese dioxide was measured with a BET Quantasorb Sorption System model No. QS-11. The pore size analysis and density determination were performed with a mercury porosimeter, Micromeritics Auto Pore 9200 model. Gross gamma measurements were carried out with the aid of a Nuclear Chicago model 8725 well-type scintillation counter using a 58-cm^2 NaI(Tl) crystal. Gamma ray spectroscopy was done with the help of a semiplanner 30 cm^3 Ge(Li) detector (Canberra Inc.) coupled with a Nuclear Data 4410 computerized multichannel analyzer having an 8K memory. A Bausch and Lomb Spectronic 2000 spectrophotometer was used for spectrophotometric analysis.

RESULTS AND DISCUSSION

Experiments were conducted to determine the optimum shaking time for the adsorption of zirconium on manganese dioxide from aqueous solutions of varying concentrations of nitric or perchloric acid. For these studies 100 mg oxide was used whereas the concentration of zirconium was arbitrarily kept constant at $9.6 \times 10^{-5}\text{ M}$ for all three concentrations (0.1, 1, and 6 M) of the acids employed. Perchlorate and nitrate ions show very little tendency to form complexes with zirconium (1, 12), and no evidence is available of their complexes, at least at $\geq 2\text{ M}$ acid concentration (12). Therefore, nitric acid and perchloric acid solutions were

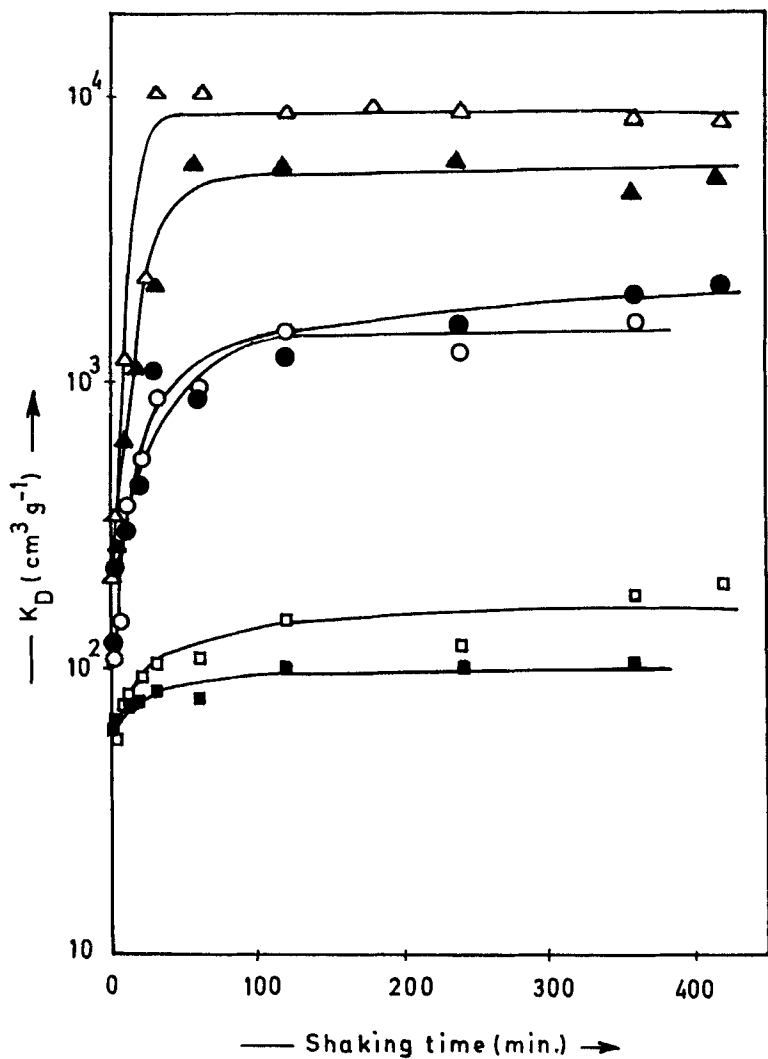


FIG. 1. Adsorption of zirconium as a function of shaking time from acid solutions. $[\text{Zr}] = 9.6 \times 10^{-5} \text{ M}$, Manganese dioxide = 100 mg . (Δ) 0.1 M HClO_4 , (\blacktriangle) 0.1 M HNO_3 , (\circ) 1 M HClO_4 , (\bullet) 1 M HNO_3 , (\square) 6 M HClO_4 , (\blacksquare) 6 M HNO_3 .

selected as suitable media for adsorption studies of zirconium. Figure 1 shows the distribution coefficient (K_D) of zirconium as a function of shaking time in the range of 2 min to 7 h from nitric acid or perchloric acid solutions of fixed concentrations. In general, the distribution coefficient increases with increasing shaking time and then attains a constant value where adsorption equilibrium is established. Moreover, K_D values increase with decreasing acid concentration in the order $6\text{ M} < 1\text{ M} < 0.1\text{ M}$ for both perchloric and nitric acid solutions and are in agreement with our previous observations (4, 5, 8, 9) regarding the adsorption of other metal ions on manganese dioxide. Comparative K_D values from 0.1 and 6 M perchloric acid solutions are higher than the corresponding values from nitric acid solutions of similar concentrations throughout the entire shaking time investigated, whereas distribution coefficients from 1 M nitric acid solutions are more than the comparative values obtained from 1 M perchloric acid solutions. Because of the highest K_D values obtained at 0.1 M acidity, these solutions of both the acids were found most suitable as electrolytes for further studies. In the case of 0.1 M perchloric acid solutions, the equilibrium is usually achieved in 30 min whereas from 0.1 M nitric acid solutions this is almost obtained in 40 min. Therefore, for further studies, 30 and 40 min shaking times were selected for 0.1 M solutions of perchloric and nitric acid, respectively. After these respective equilibrium times, the percentage adsorption of zirconium from 0.1 M solutions of both acids is almost quantitative and more than 99%.

To check the dissolution of manganese dioxide, 50 mg was shaken with 4.5 cm³ of the appropriate solution of nitric or perchloric acid for 40 min and 6 h separately. The solution was then filtered through a 0.2- μ m pore size sinter (ACE Bectan Dickinson & Co., U.S.A.). The amount of manganese due to dissolution was then measured colorimetrically (13) at 545 nm as its permanganate after its oxidation with potassium periodate. The results are shown in Table 1. It is evident from Table 1 that the dissolution of the oxide increases with an increase in acid concentration and shaking time. The extent of dissolution in both acids is almost the

TABLE 1
Percent of Manganese Dioxide Dissolved

Shaking time	HNO ₃ (M)				HClO ₄ (M)			
	0.1	1	3	6	0.1	1	3	6
40 min	0.10	0.36	0.53	0.82	0.14	0.37	0.53	1.18
6 h	0.17	0.50	1.01	1.12	0.25	0.45	0.99	1.26

same and is independent of the nature of the acids. Within an equilibrium time of 40 min, selected for further experiments, the dissolution in 0.1 *M* acid solution is $\leq 0.14\%$. No correction due to the dissolution of a minute amount of the oxide has been applied when estimating the distribution coefficients.

Another parameter which usually affects adsorption is the amount of adsorbent. Under the selected conditions of shaking time and electrolyte concentration, the adsorption of zirconium was studied for different amounts of manganese dioxide in the range of 10 to 250 mg from both

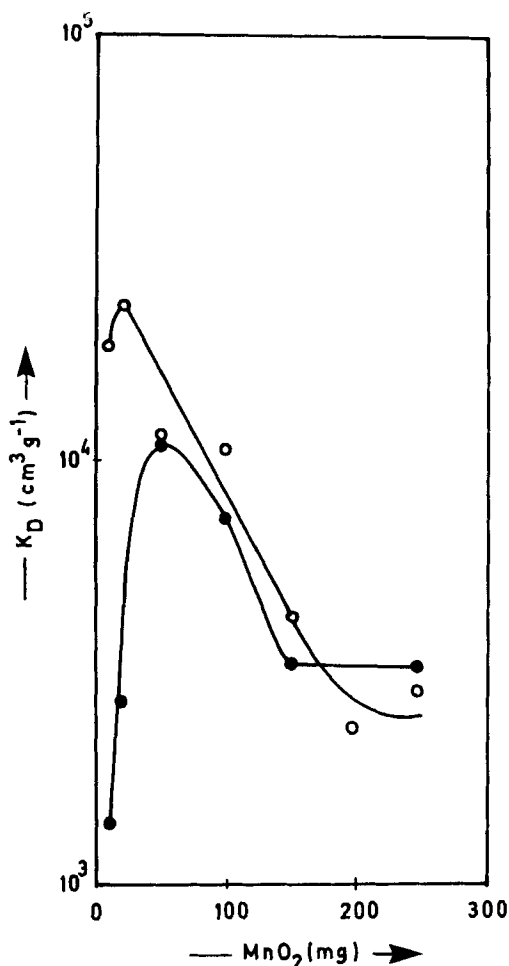


FIG. 2. Influence of the amount of manganese dioxide on the adsorption of zirconium from (○) 0.1 *M* HClO₄ and (●) 0.1 *M* HNO₃.

acid solutions independently. The results are shown in Fig. 2. The adsorption behavior from both acids is somewhat different. From 0.1 *M* nitric acid solution, the distribution coefficient increases with an increasing amount of the adsorbent, attains a maximum value at 50 mg of the oxide, and then starts decreasing up to 150 mg. With a further increase in the amount of manganese dioxide, it acquires a constant value. Therefore, 50 mg of the oxide was selected for further adsorption studies. However, in the case of 0.1 *M* perchloric acid solution, the profile of the distribution coefficient with varying amounts of the adsorbent shows an increase in K_d values up to 20 mg where a maximum is observed. The distribution coefficient starts decreasing with a further increase in the amount of adsorbent. The adsorption behavior of zirconium with varying amounts of manganese dioxide from 0.1 *M* nitric acid and perchloric acid solution is similar to what was observed earlier for the adsorption of cobalt (4), strontium (5), caesium (6), and cadmium (7). For further studies, 50 mg of the oxide was used for both the acid solutions (0.1 *M*).

The adsorption of zirconium on manganese dioxide was also studied in the wide concentration range of 10^{-5} to 10^{-3} *M* to determine the extent of adsorption at different concentrations from both acid solutions. The results are given in Fig. 3. It is concluded from the results that the adsorption of zirconium is strongly dependent on its concentration in the aqueous solution. Adsorption at low concentrations ($<10^{-4}$ *M*) increases with increasing concentration of adsorbate, attains a maximum value at around 2×10^{-4} *M* concentration, and then starts decreasing with a further increase in zirconium concentration. The adsorption behavior of zirconium with respect to its own concentration is almost identical from both acid solutions. However, the distribution coefficient is somewhat greater from perchloric acid as compared to that from nitric acid solution up to 10^{-4} *M*, whereas the reverse is true at lower zirconium concentrations. The extent of adsorption at maximum from both media is $>99\%$. The adsorption trend of zirconium with respect to its own concentration in solution is quite similar to what was observed earlier for mercury (9) adsorption on manganese dioxide. The extent of adsorption of zirconium is related to Langmuir and Freundlich adsorption isotherms. The data fit very well with the linear form of Freundlich's isotherm (14) (Fig. 4).

$$\text{Log } C_{\text{Ads}} = \text{log } A + \frac{1}{n} \text{log } C_{\text{Bulk}}$$

over the entire range of zirconium concentration investigated, where C_{Ads} is the absorbed concentration in mol/g, and C_{Bulk} is the bulk concentration in *M* (mol/dm³), and *A* and *n* are characteristic constants for the

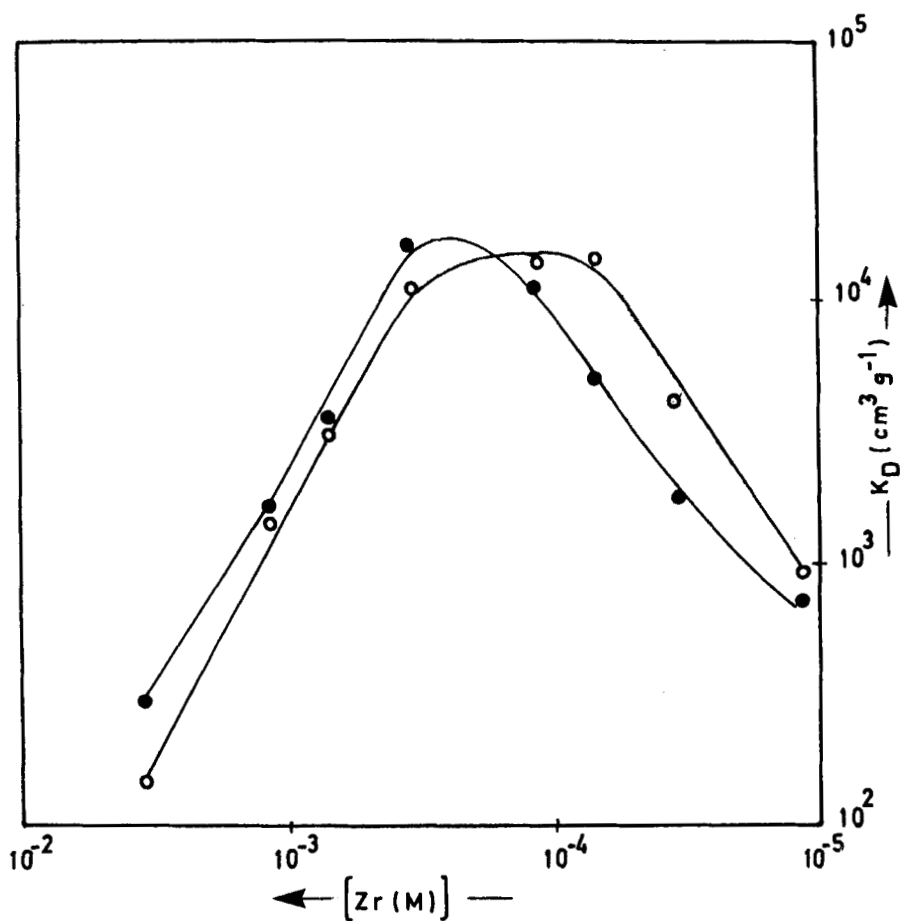


FIG. 3. Effect of zirconium concentration on its adsorption from (●) $0.1 M HClO_4$ and (○) $0.1 M HNO_3$.

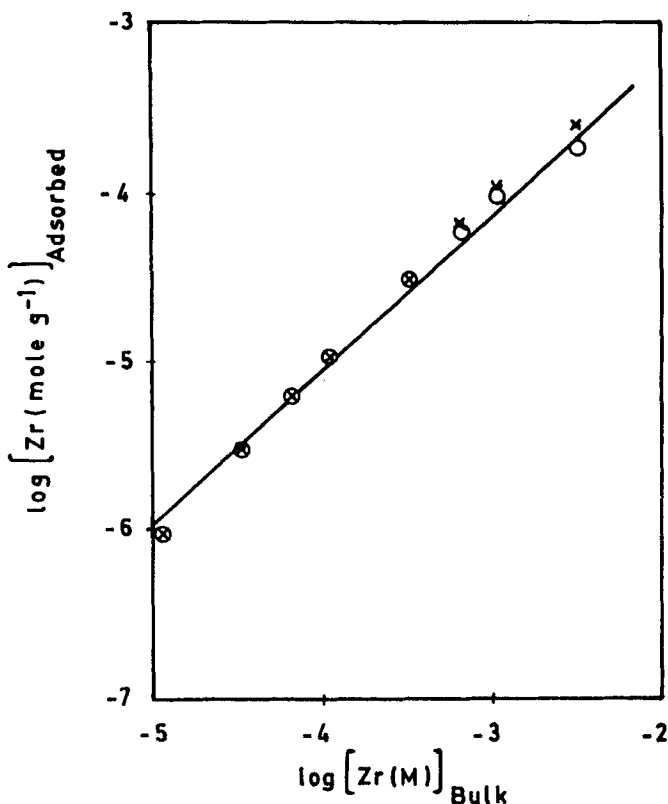
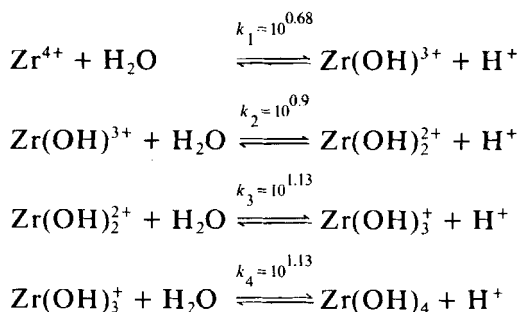


FIG. 4. Freundlich-type adsorption isotherm of zirconium on manganese dioxide: (O) 0.1 M HNO₃ and (X) 0.1 M HClO₄.

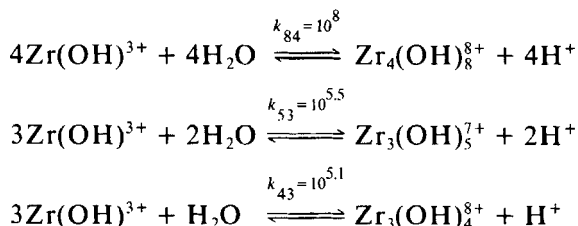
adsorption system. The values of $1/n = 0.92$ and $A = 40$ mmol/g have been estimated for this system from the slope and intercept, respectively.

The behavior of zirconium ions in aqueous solution is very complicated. Their state depends on the predominance of one or another process like hydrolysis, polymerization, and complex formation occurring under different conditions in solution. Zirconium may be present as ions of different composition and show different degrees of activity. Therefore, it is necessary to ascertain the nature of zirconium ions in solution in order to understand their adsorption behavior toward manganese dioxide. Zirconium compounds in aqueous solution are characterized by their high degree of hydrolysis, which depends on the

concentration of hydrogen ions. The following equilibria (15) are expected in aqueous solution:



Moreover, zirconium tends to form different polymers. Higher polymerization is indicated at higher concentrations and at lower acidities (1). However, when 0.1 *M* perchloric acid or nitric acid solution is used, polymers exist even at very dilute solutions (of the order of 10^{-4} *M*). Three significant polymeric species are envisaged via the following reactions starting from monomer Zr(OH)^{3+} (16):



In the 0.1, 1, and 6 *M* acid solutions used for the initial experiments, the possible species of zirconium (hydrolyzed or polymeric) have been estimated by using successive equilibrium constants (15) and respective formation constants (16) for the polymeric species given above. The dominant species at 0.1 *M* H^+ concentration were found to be Zr(OH)_4 (~46%), $\text{Zr}_4(\text{OH})_8^{8+}$ (30%) and $\text{Zr}_3(\text{OH})_5^{7+}$ (19%) as suggested (1, 17). However, at 1 *M* acid solution the dominant species would be neutral Zr(OH)_4 (64%), cationic species Zr^{4+} (17%), Zr(OH)^{3+} (9%), Zr(OH)_2^{2+} (5%), and Zr(OH)_3^+ (<5%) as per observations (1). At 6 *M* acidity the dominant species are expected to be unhydrolyzed Zr^{4+} (56%), Zr(OH)^{3+} (19%), Zr(OH)_4 (12%), Zr(OH)_2^{2+} (<8%) and Zr(OH)_3^+ (~5%). No polymeric species of zirconium at higher acidity (≥ 1 *M*) and low concentration were expected to be present in zirconium solution. These estimates are in conformity with the observation that the number of hydroxyl groups

increases at low hydrogen ion concentration, and at higher acidities the solution contains Zr^{4+} ions. At 0.1 *M* acid concentration, where neutral $Zr(OH)_4$ and polymeric species $Zr_4(OH)_8^{8+}$ and $Zr_3(OH)_5^{7+}$ are the dominant species, maximum adsorption has been noticed. It is concluded that polymeric or neutral species tend to adsorb more strongly than the cationic species formed at higher acid concentrations (1 and 6 *M*).

The effect of various anions on the adsorption of zirconium from both acid solutions has been examined under optimum conditions. The anions were mostly added as sodium salts, and their concentration was 0.1 *M*. The results are listed in Table 2. It is obvious that fluoride, citrate, oxalate, molybdate, tartrate, carbonate, and phosphate drastically reduce the adsorption from both solutions. However, the adsorption of zirconium in the presence of iodide ions from both acid solutions and in the presence of thiocyanate ions only from perchloric acid is enhanced significantly. This shows that anionic complexes of these two ions with zirconium are more strongly adsorbed on the oxide surface than the zirconium ions themselves. Severe interference of above-mentioned anions in the adsorption may possibly be explained by the destruction of adsorbable polymeric forms of zirconium, and zirconium is not carried

TABLE 2
Influence of Foreign Anions on the Adsorption of Zirconium on Manganese Dioxide from 0.1 *M* Solutions of Nitric Acid and Perchloric Acid

Anion ^a	K_D (cm ³ /g)	
	0.1 <i>M</i> HNO ₃ ^b	0.1 <i>M</i> HClO ₄ ^c
Nil	14,210	3,689
Acetate	897	468
Carbonate	88.6	151
Chloride ^d	9,994	1,876
Citrate	8.4	10.8
Fluoride	4.9	6.0
Iodide ^d	13,224	99,120
Molybdate	35.6	18.6
Oxalate	10.4	10.8
Phosphate	286	1,032
Tartrate ^d	85.8	140
Thiocyanate ^d	2,727	122,572
Vanadate	974	890

^aAnions were added as sodium salts, and their concentration was 0.1 *M*.

^b[Zr] = 1.15×10^{-4} *M*.

^c[Zr] = 6.9×10^{-4} *M*.

^dPotassium salts used.

to the manganese dioxide surface as its respective anion complexes. These anions can readily enter the coordination sphere of zirconium and substitute hydroxyl groups, and thus can break the polymeric species of zirconium (1). Strong complexes of zirconium with oxalate, citrate, tartrate, thiocyanate, and fluoride have been reported (1, 12, 16), and evidence of an anionic complex of zirconium with carbonate is also available (12).

The influence of various cations of different valence states on adsorption has been investigated under optimum conditions. The cations were added in the form of their nitrates, and their concentration was kept at 0.1 *M*. The results are given in Table 3. In 0.1 *M* perchloric acid solution, all the cations tested except Ca(II) suppress the adsorption of zirconium, whereas in nitric acid solution, Na(I), K(I), and Al(III) enhance the adsorption while other cations reduce the adsorption to some extent, Mg(II), Zn(II), Sr(II), Cr(III), and Fe(III) drastically. Therefore, it is necessary that all the interfering cations and anions be removed from solution before adsorption of zirconium on the oxide. The influence of cations in perchloric acid medium is somewhat more pronounced compared to that in nitric acid.

TABLE 3
Effect of Foreign Cations on the Adsorption of Zirconium on Manganese Dioxide from 0.1 *M* Solutions of Nitric Acid and Perchloric Acid

Cation ^a	K_D (cm ³ /g)	
	0.1 <i>M</i> HNO ₃ ^b	0.1 <i>M</i> HClO ₄ ^c
Nil	14,210	3,689
Na(I)	43,671	2,920
	—	3,222 ^d
K(I)	20,807	1,769
Mg(II)	2,934	621
Ca(II)	11,807	4,928
Co(II)	6,413	3,065
Zn(II)	1,542	324
Sr(II)	1,409	2,272
Al(III)	32,802	772
Cr(III)	2,402	89.4
Fe(III)	101	23.6
La(III)	9,102	1,057
Ce(III)	13,860	489

^aCations were added as nitrates, and their concentration was 0.1 *M*.

^b[Zr] = 1.15×10^{-4} *M*.

^c[Zr] = 6.9×10^{-4} *M*.

^dAdded as perchlorate.

TABLE 4
Distribution Coefficient of Other Metal Ions from 0.1 *M* Nitric Acid and 0.1 *M* Perchloric Acid Solution on Manganese Dioxide

Metal ion	Metal ion concentration (<i>M</i>)	K_D (cm ³ /g)	
		0.1 <i>M</i> HNO ₃	0.1 <i>M</i> HClO ₄
Cs(I)	1.51×10^{-4}	25.9	16.7
Co(II)	1.73×10^{-4}	3.8	6.4
Zn(II)	1.44×10^{-4}	8.0	—
Sc(III)	1.07×10^{-4}	91.3	46.0
Nd(III)	2.26×10^{-4}	13.9	812
Sm(III)	1.78×10^{-4}	40.4	74.0
Eu(III)	8.89×10^{-5}	57.4	43.0
Gd(III)	1.61×10^{-4}	61.3	46.6
Tb(III)	5.65×10^{-4}	49.1	40.6
Tm(III)	4.82×10^{-5}	37.6	26.6
Yb(III)	4.62×10^{-5}	39.8	40.7
Lu(III)	3.83×10^{-4}	28.8	19.1
Se(IV)	1.35×10^{-4}	754	—
Hf(IV)	1.58×10^{-4}	193	186
Zr(IV)	3.45×10^{-4}	11,258	16,673

In order to compare the adsorption behavior of zirconium with other metal ions and to determine the selectivity of manganese dioxide, K_D values for different elements, at 10^{-5} to 10^{-4} *M* concentration from both nitric acid and perchloric acid solutions, were measured under similar experimental conditions and are shown in Table 4. This table indicates complete adsorption of zirconium from both media whereas higher K_D values (>100 cm³/g) are observed for Se(IV) and Hf(IV) from both the electrolytes and for Nd(III) only from 0.1 *M* perchloric acid solutions. Interestingly, Nd(III) has a low distribution coefficient (13.9 cm³/g) from 0.1 *M* nitric acid solution. In other words, Nd(III) can be adsorbed on manganese dioxide from 0.1 *M* perchloric acid solution and can be eluted with 0.1 *M* nitric acid solution. Although partial adsorption of certain metal ions has been noticed, large separation factors have been obtained between zirconium and Cs(I), Co(II), Zn(II), Lu(III), Tm(III), and Yb(III). These separation factors are notably better for Co(II), Nd(III), and Sm(III) from nitric acid solution whereas they are higher for the rest of the elements from perchloric acid solution. The adsorptivity can be attributed to the pore size cavity of the oxide which provides an entrance pathway for ions to be diffused and to the binding force between the oxide surface and the metal ions.

For elution studies, $2 \times 0.5 \text{ cm}^3$ of 0.1 M nitric acid solution containing $580 \mu\text{g}$ zirconium and ^{95}Zr tracer was loaded onto a column of 700 mg of MnO_2 ($3.5 \text{ cm} \times 1 \text{ cm } \phi$). The elution was started after 40 min with 3 M nitric acid at a flow rate of 0.67 to $0.8 \text{ cm}^3/\text{min}$. Fractions of 2 cm^3 were collected and assayed radiometrically for their zirconium content. About 41% zirconium was removed from the column in a 50-cm^3 solution. In another experiment on a $1 \text{ cm} \times 1 \text{ cm } \phi$ manganese dioxide column (200 mg), $150 \mu\text{g}$ zirconium was loaded in 0.1 M nitric acid solution and then eluted similarly with 6 M nitric acid solution and analyzed for zirconium. In 50 cm^3 , $\sim 50\%$ zirconium was eluted from the oxide. It appears that elution of adsorbed zirconium is partial and that an increase in the concentration of the eluting nitric acid solution does not enhance desorption efficiency appreciably.

These data indicate the possibility that adsorption of zirconium on manganese dioxide can be exploited for its enrichment from very dilute solutions, for the separation of zirconium from certain metal ions, and for the storage and removal of its activity from low and medium active solutions for waste disposal.

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