Second United Nations
International Conference
on the Peaceful Uses of
Atomic Energy

A/CONF.15/P/1832
U.S.A.
June 1958

ORIGINAL: ENGLISH

ION EXCHANGE PROPERTIES OF HYDROUS OXIDES

By

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During the last decade ion exchange has become an established separations technique. It has found application not only in water purification, the original major application, but also in analytical chemistry, in separation and isolation of new elements, in hydro metallurgy, and of course in many specialized fields related to the utilization of atomic energy.

The largest fraction of recent ion exchange literature has dealt with the synthetic organic resins. Their ready availability and stability is probably largely responsible for the present popularity of ion exchange as a separations tool. The inorganic zeolites, with which all early ion exchange work was carried out, have with the years become less popular for separations, presumably because they are unstable, both in strongly acidic and strongly basic media.[1a] While other inorganic materials have also been used either for ion exchange or adsorption processes, their application has been primarily to chromatography of organic compounds in non-aqueous media and to separations involving non-electrolytes.

Several years ago the authors began a re-examination of the adsorptive properties of inorganic materials from the point of view of possible ion exchange utilization.[2,3,4] Siliceous materials were excluded because of their acid and base lability and because development of new adsorbents was a primary objective.

The time for systematic re-examination of adsorptive properties of inorganic materials seemed overdue because through the availability of radioactive tracers of most elements many cumbersome analytical problems had become greatly simplified. Detailed knowledge of adsorptive properties of inorganic materials had become of considerable importance in many fields such as geochemistry, heterogenous catalysis and corrosion. Utilization of adsorption processes in the rapidly expanding atomic energy field had created a demand for materials stable in intense radiation fields and at high temperatures. Most inorganic adsorbents are expected to have radiation stability and some of these might also have high temperature stability. In addition, because of

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* Oak Ridge National Laboratory, operated by Union Carbide Corporation for the U. S. Atomic Energy Commission.

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the wide variety of materials to choose from, there was a high probability that compounds with unusual selectivities would be found.

The very large class of insoluble hydrous oxides seemed to us an ideal starting point for a general investigation of adsorption and ion exchange with inorganic materials, and the present paper summarizes some of our findings. Adsorptive properties of hydrous oxides are well known[5,6] and relatively detailed studies have been carried out with one of these, hydrous aluminum oxide. Various chromatographic processes based on aluminum oxide have been described[1-b,7-14] and ion exchange properties have been attributed at times to this[15-19] and other oxides.[20-22] We shall attempt description of adsorptive properties in terms of ion exchange terminology. Though in part a semantic device, this is considered useful because it permits direct adaptation of the extensive available information on ion exchange technology and theory to new adsorbents.

An ion exchanger is usually pictured as a matrix to which charged, or potentially charged, groups are affixed. If the counter-ions which are necessary to give the material over-all electrical neutrality are negatively charged, one speaks of an anion exchanger, and if they are positively charged, of a cation exchanger. In a useful exchanger these counter-ions should be readily diffusible. In the organic exchangers the diffusion medium is generally the imbibed water or electrolyte; in many inorganic materials the diffusion medium is probably the solution surrounding the solid particles or crystallites.

Most organic exchangers are considered related to high molecular weight poly-electrolytes, though cross-linked into an insoluble matrix. One is tempted to propose a similar picture for hydrous oxides. During the hydrolysis of many metal ions, positively charged polymers are formed on the acid side of the iso-electric point and negatively charged polymers have been reported (iso-poly acids) on the alkaline side. If these polymeric aggregates are arranged into an insoluble 3-dimensional network, i.e., by a generalized cross-linking procedure, anion and cation exchangers should result. The insoluble "hydroxides" or "hydrous oxides" might be considered such 3-dimensional networks. Without anionic or cationic impurities they would be reminiscent of weakly acidic cation exchangers in the hydrogen form or weakly basic exchangers in the free base form. The networks would become charged on treatment with acids or bases.

Of course, not all elements form insoluble hydrous oxides (phosphorus, arsenic) and others form oxides which are too dispersible for use in columns (Mo(VI), W(VI)). The oxides of these elements are very acidic and hence are expected to form cation exchangers if incorporated into an insoluble matrix. This can be done[3b,4,23] by precipitating certain amorphous insoluble salts, e.g., zirconium phosphate, zirconium tungstate. An excess of the acidic oxide is needed to produce cation exchange activity. Because of the presence of excess acid in the acid washed precipitates we shall refer to these materials by the generic term "acid salts." They are included in the present paper because of the implied relation to hydrous oxides and because otherwise a comparative discussion of ion exchange properties of hydrous oxides would be arbitrarily limited by solubility considerations.

Treatment of hydrous oxides with an amount of acid insufficient to dissolve them often yields so-called basic salts, though not necessarily with simple stoichiometric composition. Presumably hydrogen ions of the added acid react with some of the attached hydroxide ions of the solid to yield water molecules which remain attached to the metal. The network acquires a positive charge. The anions of the acid become included in the solid as counter-ions giving it electrical neutrality. These counter-ions, if not built into the network, should be readily diffusible and hence these basic salts are expected to be anion exchangers.

If the metals on which the hydrous oxides are based are sufficiently acidic, one might expect the networks to react with, or coordinate, hydroxide ions and assume a negative charge. The cations of the base which simultaneously become incorporated in the solid should retain a high degree of diffusibility and a cation exchanger should result.

In some intermediate pH region a given solid might show both anion and cation exchange activity and thus in a sense be a giant zwitter-ion. At the pH at which both effects are equal (iso-electric or iso-ionic point) salt pickup predominates. In this model adsorption of a salt is directly related to the anion and cation exchange properties of the solid and does not result from an entirely different mechanism.

The model was discussed in terms of cross-linked polymers, which implies amorphous solids. However, crystalline materials should, except for adsorptive capacities, have similar properties provided, of course, no phase changes occur during the adsorption process. Reversible reactions would be expected to occur only on the surfaces of these crystals. The large crystals with their relatively small surfaces should have low capacities. The capacity of microcrystalline materials might approach those of amorphous materials, where adsorption would be pictured as occurring on the "surfaces" of chains or sheets.

In some cases reactions of the solids with acids might result in substitution of a hydroxide ion by the anion of the acid, i.e., in formation of first coordination sphere complexes, rather than charged hydrated surfaces. With this mechanism unique selectivities reflecting unique complexing properties of the metals would be expected. The exchange reactions would be rapid if the complexes formed on the surface are in rapid equilibrium with the ions in solution, which presumably would be the case with most metals.

The seat of exchange activity assumed here for the hydrous oxides is quite different from that usually assumed for zeolites and clay minerals where exchange activity is attributed to substitution in a fixed lattice of ions with lower positive charge for ions with higher charge. In the hydrous oxides exchange activity would be imparted to the solid through an essentially reversible reaction with the medium.

However, irrespective of possible mechanisms or models certain basic questions appeared to need experimental resolution before adsorption on hydrous oxides could usefully be described in terms of ion exchange terminology and used in typical ion exchange technology.

1. Are reactions of acids and bases with oxides rapidly reversible?

2. Are the adsorbed anions and cations rapidly exchangeable for other ions of the same type? In particular, are rates sufficiently fast for column operation?

3. Are changes in properties (hysteresis) sufficiently slow so that prediction of properties can be made with confidence?

4. Are capacities sufficiently high for applications?

5. How far can idealized ion exchange relationships be applied to the adsorption reactions? As a corollary, are the adsorptive properties reasonably independent of loading?

Some of these questions had previously been answered affirmatively for hydrous aluminum oxide. As we shall demonstrate with typical results, we have found additional affirmative answers for other hydrous oxides and "acid-salts" sufficient to imply that these classes of compounds indeed are suitable for ion exchange applications.

PREPARATION

The adsorbents were prepared by suitable precipitation reactions.[3,4] In the precipitation of metals which are soluble in the common mineral acids (Cr(III), Zr(IV), Sn(IV), Th(IV), etc.), acidic solutions were treated with base (usually NH_3) until precipitation was complete. In the case of Nb(V), precipitation was carried out from HF-HNO_3 solutions. For Ta(V), solutions in base were prepared from the products of carbonate fusions (tantalate) and the hydrous oxides precipitated by addition of acid. Similarly, vanadium(V) was precipitated by addition of acid to a vanadate solution.

Since some of the most acidic oxides are readily dispersible (e.g., Mo(VI), W(VI)), or soluble (e.g., P_2O_5, As_2O_5), their expected ion exchange characteristics could be utilized only by the more devious technique of precipitating a suitable metal (e.g., Zr(IV)) with an excess of appropriate reagent (Na_2WO_4, H_3PO_4, etc.). The resulting solids shall be referred to as zirconium tungstate, zirconium phosphate, etc. The other solids shall be referred to as hydrous oxides. These designations will be used whether or not the solids have simple stoichiometric composition or special crystal structure.

The usually flocculent or gelatinous precipitates were collected by centrifugation or filtration, dried at room temperature, ground in a mortar, and sized by screening and decantation. For column operation materials of mesh size ca. 150 were usually selected. In some cases, portions of the solids were dried or fired overnight at controlled elevated temperatures.

No attempt was made to prepare true gels, although in a few instances (particularly with zirconium tungstate) gels happened to form. It is expected that, in general, dried ground gels (or beaded gels) would have better packing characteristics in columns than the materials obtained from flocculent precipitates, that they would have slower equilibration (diffusion) rates but otherwise have similar adsorptive properties.

REVERSIBILITY OF ADSORPTION REACTIONS

In the precipitation of hydrous oxides or hydroxides pure compounds are rarely obtained. The precipitates frequently retain some of the anions of the solution or cations of the precipitating base. These "impurities" are usually difficult to remove by washing with water. This is expected from an ion exchange point of view (electro neutrality) since the concentration of hydrogen and hydroxide ions available for replacing the ionic "impurities" is very small in the wash water. Usually, the impurities may be removed readily by treatment with excess acids or excess base. During this treatment, however, new "impurities", the anions of the acid or the cations of the base, may be introduced.

As a typical example consider hydrous zirconium oxide. The solid precipitated with ammonia from a concentrated solution of zirconium oxychloride, after drying and washing with water, was found to release approximately 0.3 moles of chloride ions per kg. of solid on treatment with excess base. If the base used is sodium hydroxide, containing radioactive sodium tracer (e.g., Na^{22}), it can be readily demonstrated that the resulting solid contains substantial amounts of sodium ions. The extent of base pickup, as well as acid pickup (see also Ref. 24), seems to depend principally on the composition of the solution (pH and salt concentration) as also recently pointed out by Amphlett and coworkers.[22] Through suitable analyses a composition-pH diagram may be constructed. Typical diagrams of this type (titration curves) which are standard for characterization of organic ion exchange resins are illustrated in Fig. 1 for Zr(IV) and Sn(IV). These titration curves were obtained at essentially constant ionic strength (0.1 $\underline{M}$) using NaCl-HCl and NaCl-NaOH mixtures.

For both Zr(IV) and Sn(IV) the chloride content of the solid decreases continuously with increasing pH, becoming essentially negligible in basic solutions. Conversely the sodium content of the solids is negligible in acidic solutions and increases continuously with pH. These titration curves are quite reproducible for a given solid, i.e., they do not differ substantially after several cycles of acid and base treatment. They are also reasonably reproducible for solids prepared in approximately the same way and dried at the same temperature.

Further proof of reversibility may be obtained by studying the equilibrium acidity as a function of supporting electrolyte concentration. If the composition of the solid is kept constant, the activity coefficients in the solid are independent of solution composition and hence, at equilibrium, the activity $\underline{a}$ of the adsorbed electrolyte is also constant. We have attempted to check this relationship by studying the acidity of various NaCl solutions in equilibrium with a hydrous zirconium oxide sample containing ca. 0.7 moles of Cl^- per kg. of solid and no significant amounts of sodium ions. As expected from the equation

$$\underline{a}_{HCl} = \underline{m}_H \underline{m}_{Cl} \gamma_{\pm}^2 = \text{constant} \quad (1)$$

the equilibrium acidity $\underline{m}_H$ was found to decrease with increasing chloride concentration $\underline{m}_{Cl}$. Indeed eq. 1 was verified to better than ±5% in the chloride concentration range 10^{-3} to 1 $\underline{M}$.

A still more stringent test of reversibility is a study of acid and base adsorption as a function of temperature.[25] The studies again were carried out at constant loading of the solid with respect to HCl or NaOH and a typical set of data is illustrated in Fig. 2. From this plot of log $\underline{m}_H$ (or log $\underline{m}_{OH}$) vs. 1/T, where T is the absolute temperature, the values of ΔH of adsorption in the temperature range studied were found to be -6.9 and -3.8 kcal per mole of HCl and NaOH respectively. Repetitive runs on the same sample did not exactly reproduce the equilibrium acidities shown in Fig. 2, presumably because of an ageing process accelerated at higher temperatures. Acidities found at a given temperature for the rising and falling branches of a temperature cycle differed at most by a factor of 2; this corresponds to an extremely small change in the composition (loading) of the solid. In any case, the slopes of the lines, particularly those obtained with decreasing temperatures, were quite reproducible.

In one case, adsorption of HNO_3 by hydrous zirconium oxide, the study was carried to 150° C. After ageing for several hours at 150° C equilibrium acidities were measured with decreasing temperature. A plot of log $\underline{m}_H$ vs. 1/T was a straight line over the whole temperature range. The value of ΔH of adsorption (-8.4 kcal) was in reasonable agreement with that found in the lower temperature studies for HCl.

We shall give here one additional example illustrating reversibility. Bromide tracer was added to a column (0.2 $cm.^2$ x 5.0 cm.) of hydrous zirconium oxide in the nitrate form (nitric acid washed). The adsorbed tracer was eluted with 0.1 $\underline{M}$ KNO_3 at a flow rate of 0.8 cm./min. and the effluent analyzed radiometrically for bromide ions. The resulting elution curve is reproduced in Fig. 3. It has the typical Gaussian shape expected for rapid ion exchange chromatography, proving that rates of adsorption and desorption are sufficiently rapid even for standard column operation.

APPARENT CAPACITIES

Acid base titration curves like those of Fig. 1 give directly the apparent capacities of the exchangers (e.g., as moles per kg. adsorbent). In a given medium the relative anion exchange (chloride uptake) and cation exchange (sodium uptake) capacities of different oxides may differ substantially. Thus, in acidic solutions Zr(IV) is able to hold more chloride ions than Sn(IV) and, conversely, in basic solutions Sn(IV) holds more sodium ions than Zr(IV). In a study of a large number of hydrous oxides it became apparent that the relative importance of the anion and cation exchange branches may differ widely and in some cases one or the other branch may be absent. Thus no detectable anion exchange branch was observed for very acidic oxides such as Mo(VI), W(VI), U(VI) and V(V) and only small cation exchange branches for such basic oxides as Th(IV) and Bi(III).

While the capacities determined by acid base titration (see Fig. 1) are quite large in terms of moles per kg. of solid or moles per liter of bed, considerably higher apparent capacities could have been realized if the solids had been treated with more acidic or more basic solutions or with anions which are more strongly adsorbed. Thus fluoride uptake as high as 4 moles per kg. has been realized for hydrous zirconium oxide, which corresponds to almost 1 mole of F^- per mole of Zr(IV).

Similarly, high capacities were observed in acid-base titrations of "acid salts". For example, a zirconium phosphate sample, dried at 25° C was titrated in 0.1 M CsCl with 0.2 M CsOH containing Cs^{134} tracer. Apparent capacities, determined radiometrically from the cesium content of the solid rose from about 1 mole Cs per kg. near pH 1.5 to about 4.5 moles per kg. near pH 9.5 (see Fig. 4). The higher figure corresponds to almost 1 mole Cs/mole PO_4 (or 2 moles Cs/mole Zr(IV)) which would be one-half of the value expected if the solid had the composition $ZrO(H_2PO_4)_2$, i.e., had 4 replaceable hydrogen ions per mole of zirconium or 2 replaceable hydrogen ions per mole of phosphate.

Acid-base titrations of zirconium tungstate or zirconium molybdate are complicated because at sufficiently high pH loss of the anion from the solid becomes serious with a resulting decrease in the capacities computed per kg. of original solid (see Fig. 5). However, the maximum ratios of moles Cs per mole molybdenum or tungsten on the solid are also not much less than 1:1.

EFFECT OF DRYING TEMPERATURE

Increase in the drying temperature of the solids generally causes a decrease in the apparent capacity. In a few cases, such as zirconium tungstate, drying at temperatures as low as 100° C causes essentially complete destruction of the cation exchange properties. However, for most hydrous oxides the data shown in Table I, which were obtained for hydrous zirconium oxide, are typical.

The chromate uptake data were obtained by measuring breakthrough curves of chromate with Cr(VI) solutions containing at least 2 moles of acid (HNO_3 or HCl) per mole of Cr(VI). Exhaustion of the column can be followed visually since the chromate (or dichromate) forms a sharp, strongly colored band. If chromium tracer has been added (Cr^{51}) quantitative breakthrough curves may be established quickly by radiometric methods. This chromate exhaustion technique was found to be a reliable and convenient method for comparing the anion exchange capacities of oxides.

Increase in drying temperature usually causes a decrease in apparent capacity. In a few cases slight increases in capacity were found after drying at 100 or 200° C, presumably because with loss of excess water the number of moles of metal oxide per kg. of solid had been substantially increased. The loss in capacity which occurs on drying at higher temperatures is almost surely caused by a growth in the size of crystallites which causes a decrease in the effective surface area per mole of oxide. This crystallite growth was independently confirmed by the sharpness of the diffraction lines observed in x-ray crystallographic examinations.

TABLE I

Effect of Drying Temperature on Cr(VI) Uptake
by Hydrous Zirconium Oxide
(Column Breakthrough Method with Acidic Cr(VI) Solutions)

Temp. °C	Moles Cr(VI) / kg. solid	Moles Cr(VI) / liter bed	% H_2O	Moles Cr(VI) / mole Zr(IV)
32	1.38	0.85	46.4	0.32
105	1.25	1.12	19.4	0.19
202	0.91	0.87	15.4	0.13
320	0.45	0.47	7.0	0.06
500	0.14	0.18	1.1	0.02
800	0.05	0.07	(0)[a]	0.006

(a) Assumed value

ION EXCHANGE IDEALITY

Ion exchange equilibria may be written[2b] in the form

$$aB^{\pm b} + bA^{\pm a}_{(r)} \rightleftharpoons bA^{\pm a} + aB^{\pm b}_{(r)} \qquad (2)$$

with the equilibrium constant

$$\underline{K}_{AB} = \frac{\underline{m}^{a}_{B(r)}\ \underline{m}^{b}_{A}}{\underline{m}^{a}_{B}\ \underline{m}^{b}_{A(r)}}\ \frac{\gamma^{a}_{B(r)}\ \gamma^{b}_{A}}{\gamma^{a}_{B}\ \gamma^{b}_{A(r)}} = \underline{K}^{m}_{AB}\ \Gamma_{AB} \qquad (3)$$

where $\underline{m}$ is the concentration of the ion indicated by subscript, subscript (r) denotes the exchanger phase, no subscript the aqueous phase. $\underline{K}_{AB}$ is the equilibrium constant, which with proper choice of standard states may be set equal to unity, $\underline{K}^{m}_{AB}$ is the concentration quotient and Γ_{AB} the appropriate activity coefficient quotient. Eq. 3 is general for two phase equilibria although in some cases the activity coefficients may assume quite unpredictable values. It will be useful as an ion exchange equation if the activity coefficients in the solid (exchanger) phase do not vary rapidly, at least under some limiting conditions.

With organic exchangers the activity coefficient ratio $\gamma^{a}_{B(r)}/\gamma^{b}_{A(r)}$ for the exchanger phase is essentially constant, if exchange reactions are carried out in moderately dilute electrolyte solutions, if one of the adsorbed ions ($B^{\pm b}$) occurs at trace concentrations, and if no complexing or hydrolytic reactions occur. The composition of the exchanger ($\underline{m}_{A(r)}$) is then essentially independent of the concentration of the adsorbed tracer ion and eq. 3 simplifies to

$$\underline{D}_{B}\underline{m}_{A}^{b/a}\ \frac{\gamma_{A}^{b/a}}{\gamma_{B}} = \text{constant} \qquad (4)$$

where the distribution coefficient, $\underline{D}_B$, is defined by

$$\underline{D}_B = \frac{\underline{m}_{B(r)}}{\underline{m}_B} \qquad (5)$$

According to eq. 4 a plot of log $\underline{D}_B$ vs. log $\underline{m}_A$ should, except for activity coefficient corrections in the aqueous phase, be a straight line with slope -b/a. This relationship has been verified for several exchange reactions involving tracer ions adsorbed on hydrous oxides as illustrated in Figs. 6 and 7.

For ion exchange terminology to be generally useful, deviations from ideality should also not be excessive when adsorption experiments are carried out as a function of loading. Equivalently, $\underline{K}^m_{AB}$ should not change rapidly as $\underline{m}_{B(r)}$ increases and $\underline{m}_{A(r)}$ decreases, under conditions where the sum $(\underline{m}_{B(r)} + \underline{m}_{A(r)})$ (apparent capacity) is approximately constant. This aspect of ideality has been checked in a few cases. Typical is the exchange of Cs^+ and NH_4^+ ions on zirconium tungstate where $\underline{K}^m$, though not independent of $\underline{m}_{Cs(r)}$, varied by less than a factor of two, as $\underline{m}_{Cs(r)}$ increased from zero (trace concentration) to one-half of apparent capacity. There was no evidence for a small number of "active sites" as so often proposed in adsorption studies.

Since adsorbabilities closely follow the ideal dependence on ionic strength and loading, there seems little doubt about the general usefulness of applying ion exchange terminology to these adsorption reactions. Of course it must be remembered that these ideal relationships can be found only with certain simple ions which do not undergo complexing, polymerization or hydrolytic reactions in the media of interest.

SELECTIVITY AND SEPARATIONS

One of the most attractive features of hydrous oxide adsorbents, compared with standard organic ion exchange resins, is their unusual and sometimes unique selectivity. The examples which shall be discussed have been selected to illustrate this point. For this reason complexing reactions in the aqueous phase were avoided although these are standard devices for enhancing separations with organic exchangers. As long as the inorganic solids are not dissolved by the complexing agents, the improvement in separations should be similar for organic and inorganic exchangers.

1. Adsorption of polyvalent anions - Most hydrous oxides seem to have unusual selectivities for polyvalent anions as compared with monovalent anions. This property was implied in our proposal to use adsorption of chromate as a standard technique for evaluating anion exchange capacities. Since many heavy metals occur normally in solution as polyvalent anions (e.g., Mo(VI), W(VI), V(V)), the hydrous oxides might find application in problems involving concentration or recovery of these elements. Other ions which are strongly adsorbed include borate, sulfate, phosphate, arsenite, and arsenate.

Since the polyvalent anions are so strongly adsorbed, their removal from the exchangers may at times be difficult. Probably the most effective eluents are strong bases such as NaOH, although weaker bases such as ammonia (and in some cases carbonate, acetate, etc.) may be satisfactory. While displacement of weakly adsorbed anions from the exchangers can usually be achieved essentially quantitatively (see Fig. 3) elution, even by bases, of strongly adsorbed anions may be incomplete. For example, columns loaded with chromate and then eluted either with ammonia or NaOH, frequently retain a yellow cast which can be removed only by prolonged treatment with strong base. The per cent chromate lost in a rapid elution cycle, however, is usually small (< 5%) and seems relatively independent of the amount of chromate originally adsorbed, i.e., approximately the same fraction is retained with tracers as with macro quantities. This small "irreversibility" probably results from changes in the structure of the solids as they are treated with strong bases, and presumably involves covering of exchange sites by the products of slowly reversible hydrolysis reactions.

2. Special anion selectivities - Whenever unusual complexing properties of the metals can be utilized, the adsorbents should have special selectivies. This effect was illustrated by the enormous capacity of zirconium oxide for fluoride ions which is expected from the fact that Zr(IV) is strongly complexed by this anion. Adsorbents prepared from certain transition elements, which are strongly complexed by the higher halides, should have special selectivity for these anions. For this reason studies have been carried out on the adsorption properties of bismuth oxide for higher halide ions and the anticipated special selectivity was confirmed. Since Bi_2O_3 readily undergoes phase changes (oxy-halides, etc.) when treated with acids, the flow characteristics of columns prepared from Bi_2O_3 often deteriorate rapidly. However, this difficulty can be avoided and selectivity sometimes even improved if mixed oxides are prepared by co-precipitating Bi(III) with other metals (e.g., Sn(IV)).

3. Separation of negatively charged complexes - The remarkable selectivity of exchange resins for certain negatively charged metal complexes has become the basis of many separations processes.[26] Although there is ample reason to presume that this special selectivity is related to properties of the organic network, it was nevertheless of interest to investigate whether negatively charged complexes could also be adsorbed by and separated on hydrous oxides.

Some adsorption of negatively charged complexes on hydrous oxides has been observed. While it is quite modest compared with that found for organic exchangers, it is sufficient to allow some separations. An example, separation of Ag(I) and Au(III) in HCl, where they are well-known to form strong negatively charged complexes, is given in Fig. 8. This separation almost surely involves anion exchange of metal complexes since hydrous zirconium oxide in strongly acidic solution is almost exclusively an anion exchanger, and since adsorbability of both elements increases with decreasing HCl concentration approximately as expected from anion exchange-mass action considerations.

4. Separation of alkali metals - Cation exchangers prepared from acidic oxides (e.g., zirconium phosphate, tungstate or molybdate), when

largely in the hydrogen form, were found to have remarkable selectivity for the various alkali metals. Adsorbability increases sharply with atomic number and is extremely high for cesium in acidic solutions. Under these conditions cesium is so strongly adsorbed that it may be isolated essentially uniquely from all other elements in the periodic table. It has been removed, for example, from acidic solutions of lithium chloride (13.6 M) and of aluminum nitrate (2 M). It may also, as a further example, be removed from uranyl sulfate solutions.

Complete separation of the alkali metals from each other has been achieved with relatively small columns as illustrated in Fig. 9. The elements were adsorbed on zirconium tungstate. Elution was carried out with ammonium chloride solutions whose concentrations were increased after each element had been removed to compensate (mass-action law) for the high adsorbabilities of the higher alkali metals and obtain them in narrow bands.

With some adsorbents the elution order of the alkali metals may be reversed, e.g., Cs^+ may be eluted before Na^+. This occurs, for example, with hydrous titanium oxide in base and, interestingly, with uranium (VI) oxide.

Such reversal of selectivity is also implied, to some extent, by the decrease of selectivity which occurs when the insoluble "acid salts" are neutralized with ammonia (converted from the hydrogen to the ammonium form). Indeed, after complete conversion to the ammonium form, zirconium phosphate, for example, has essentially no selectivity left for the alkali metals and they may readily be eluted as a group from a column (see also section 6).

5. Separation of alkaline earths - The "acid salts" have been found to have excellent selectivity for the alkaline earths. As demonstrated in Fig. 10, the elements from calcium to radium may be completely separated from each other with a relatively small column of zirconium molybdate. Because of the large differences in adsorbability, a stepwise elution technique was chosen, as in the separation of the alkali metals. Particularly interesting is the extremely large difference in the adsorbability of barium and radium, which by this technique can be separated with columns only a few centimeters in length.

6. Separation of alkali metals from alkaline earths - The extreme versatility of hydrous oxides and "acid salts" for separations may be illustrated by the large variety of techniques which can be used for separation of two elements (Cs and Ba) representative of these groups.

In strongly acidic solutions, for example, Cs^+ is strongly held by zirconium phosphate. Under these conditions Ba^{++} is essentially not adsorbed, and separation of these elements can be achieved rapidly with a column less than a centimeter long. The separation is sufficiently rapid to permit complete isolation of the short-lived Ba^{137} from its long-lived parent by a milking procedure involving flushing a column containing Cs^{137} with acid.

The elution order may be inverted and separations carried out equally rapidly and effectively by using a salt form (NH_4^+) of the exchanger and using an ammonium salt as eluent. A group separation involving various alkali metals and alkaline earths which is based on this principle is demonstrated in Fig. 11.

Techniques for separation of alkali metals and alkaline earths can, of course, also be developed with other hydrous oxides. If these separations are carried out in neutral or weakly acidic solutions Ba^{++} is usually much stronger adsorbed than Cs^{+}. The latter can be eluted from short columns with moderately concentrated salt solutions (e.g., NH_4Cl). More concentrated or acidic solutions are necessary for removal of Ba^{++}. Separations based on this procedure have been carried out with hydrous oxides such as ZrO_2 and SnO_2. Interestingly, uranium(VI) oxide may also be used, as illustrated in Fig. 12, though solubility considerations limit the acid range which is suitable for elution.

7. Other separations - In our discussion of cation exchange separations we have so far concentrated on the alkali metals and alkaline earths. This was done because ambiguities regarding adsorption mechanisms could thus best be avoided. These elements do not undergo extensive hydrolytic reactions in the media considered, and questions regarding species in solution normally do not arise. However, separations with hydrous oxides as adsorbents are of course not limited to these elements.

For example, rare earths can be adsorbed on hydrous oxides from basic, neutral and even moderately acidic solutions. With eluents of controlled pH and proper electrolyte concentration they may be separated from alkali metals and alkaline earths. Fig. 13, involving separation of Eu^{+++} and Cs^{+} with hydrous zirconium oxide is a typical illustration.

Another example, separation of Co(II) and Fe(III) is presented in Fig. 14. Both elements are strongly adsorbed by zirconium tungstate from moderately acidic or neutral solutions. Cobalt can be eluted at some intermediate acidity where iron remains strongly adsorbed. It may then be eluted either at very high acidity or by taking advantage of complexing reactions.

Extremely interesting is the strong adsorption of copper by hydrous oxides (e.g., hydrous zirconium oxide) from ammoniacal solutions. The intense blue color of the adsorption band indicates that Cu(II) is held as the characteristic ammonia complex. Effective capacities are high. Elution can be achieved with acid, though it is difficult to remove in this manner the last traces of copper. Nevertheless, many interesting separations processes involving transition elements may be based on this ability of the oxides to adsorb ammonia complexes.

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We have endeavored in this brief summary of our work on ion exchange properties of hydrous oxides to demonstrate the great promise these and other inorganic materials hold for chemical separations. The studies have so far been limited to compounds containing a few types of metals and anions. No doubt, other interesting separations will be found as the studies are extended to other metals and anions, particularly those with strikingly different complexing properties. However, aside from separations, we believe that adsorption studies of the type discussed are particularly intriguing because with their simplicity and high sensitivity they should develop into powerful tools for equilibrium and kinetic studies of surfaces and for comparative studies of amorphous and microcrystalline materials.

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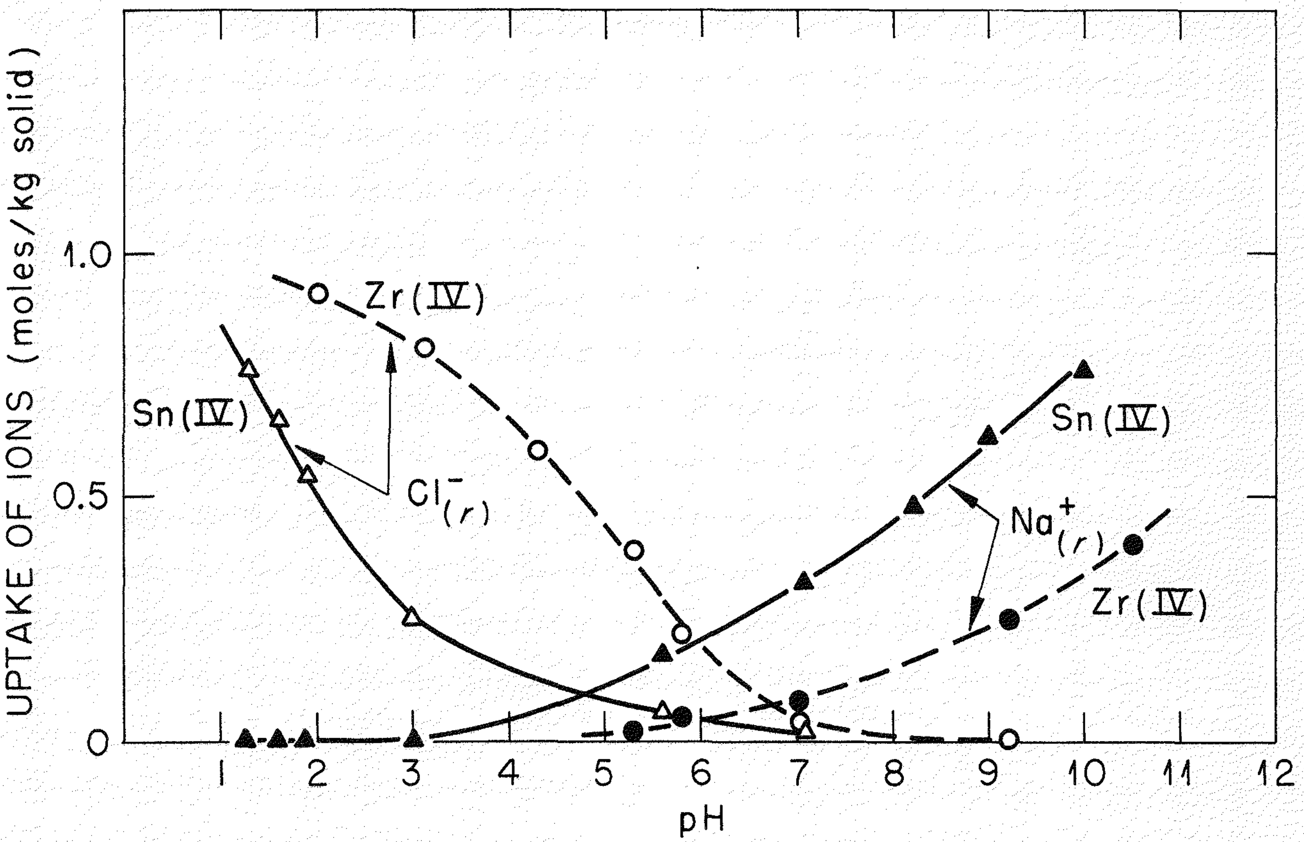

Figure 1

ANION AND CATION EXCHANGE PROPERTIES OF HYDROUS Zr(IV) AND Sn(IV) OXIDES

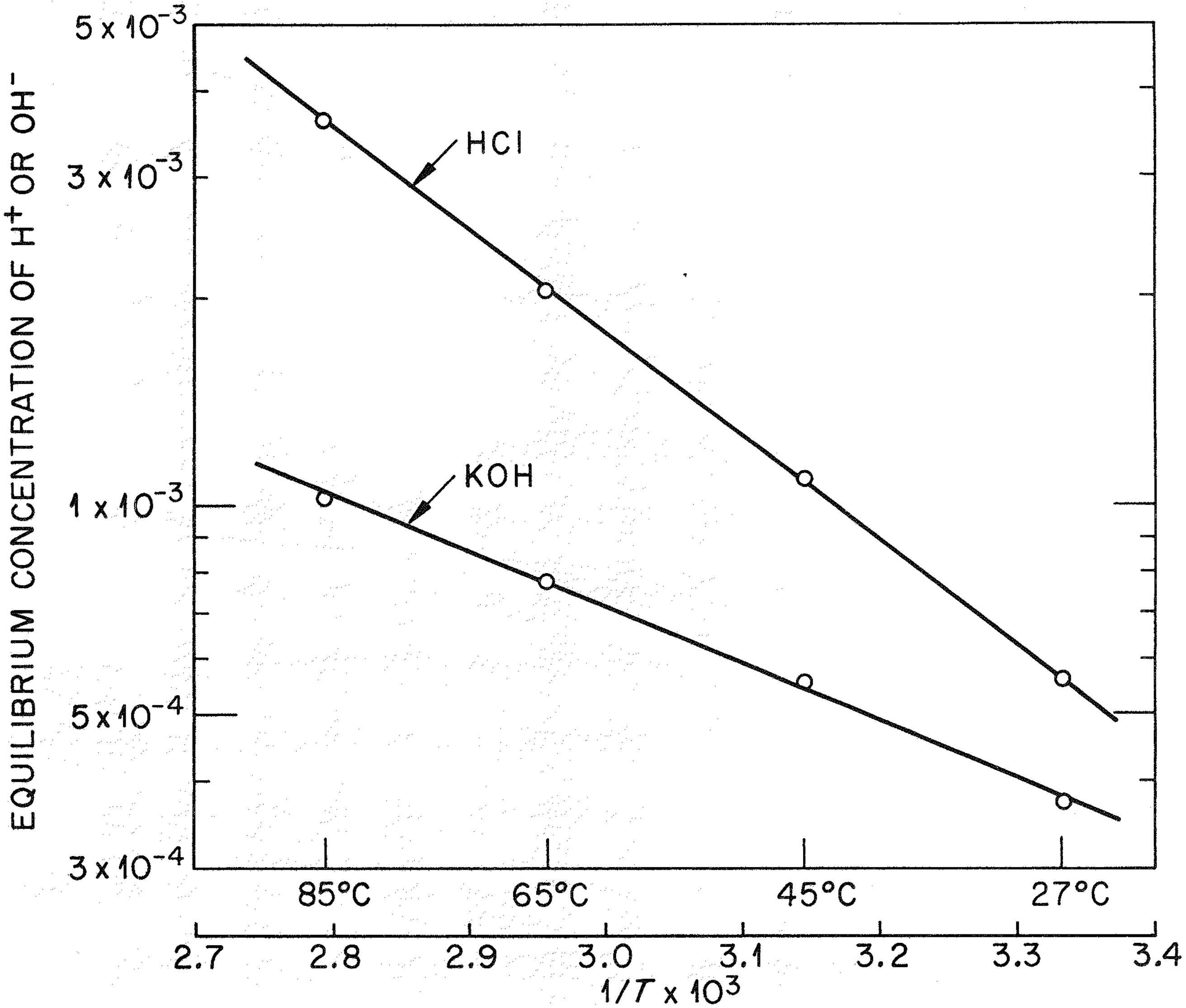

Figure 2

TEMPERATURE DEPENDENCE OF HCl AND KOH ADSORPTION BY HYDROUS ZIRCONIUM OXIDE

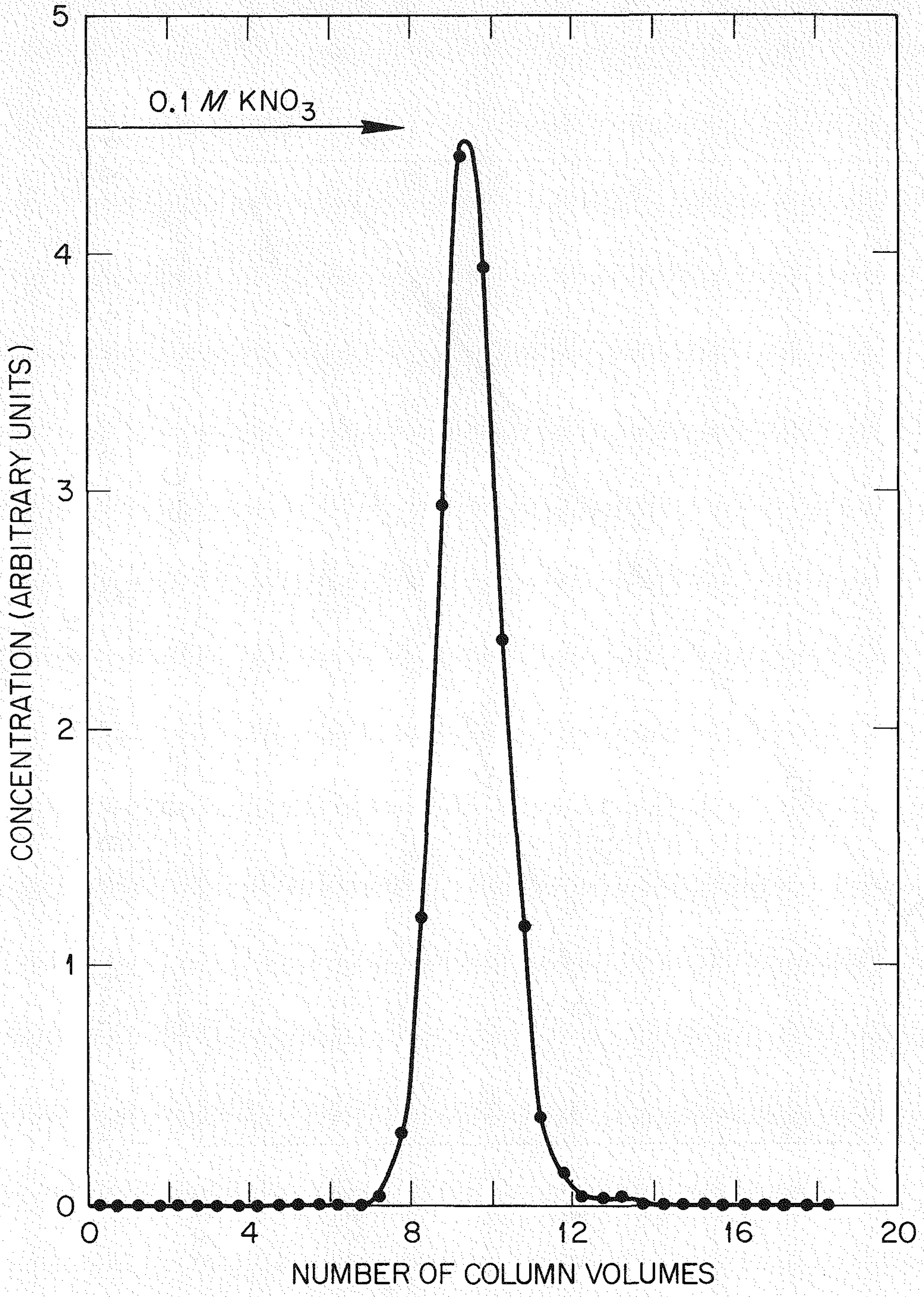

Figure 3
ELUTION OF Br^- FROM A HYDROUS ZIRCONIUM OXIDE COLUMN
(Drying Temp. 200°C, 5.0 cm x 0.20 cm^2 Column, Flow Rate 0.8 cm/min.)

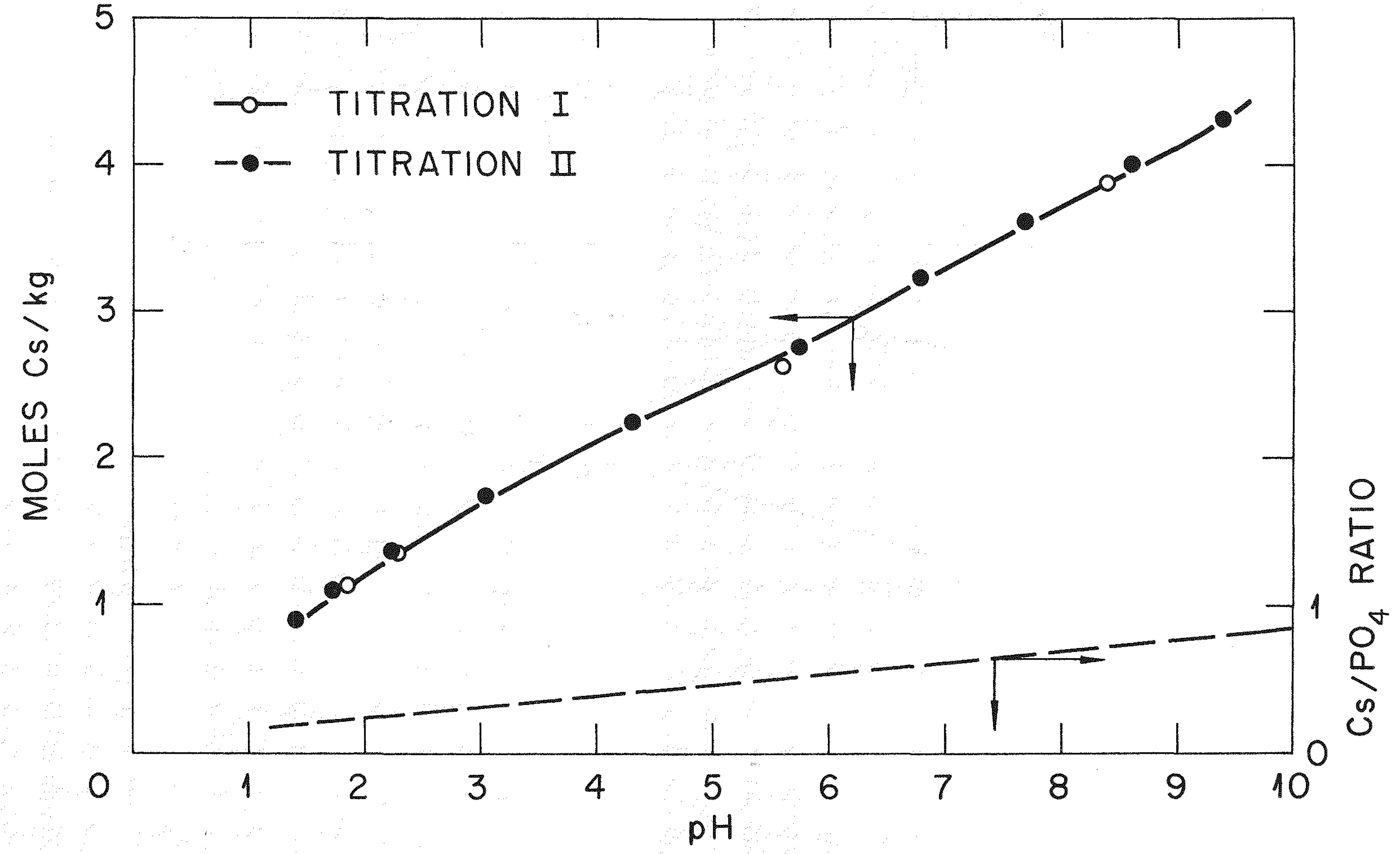

Figure 4

CESIUM UPTAKE BY "ZIRCONIUM PHOSPHATE"

Drying Temperature: 25°C
Pretreatment: 1 *M* HCl - H_2O
Medium: 0.1 *M* CsCl
Titrant: 0.2 *M* CsOH

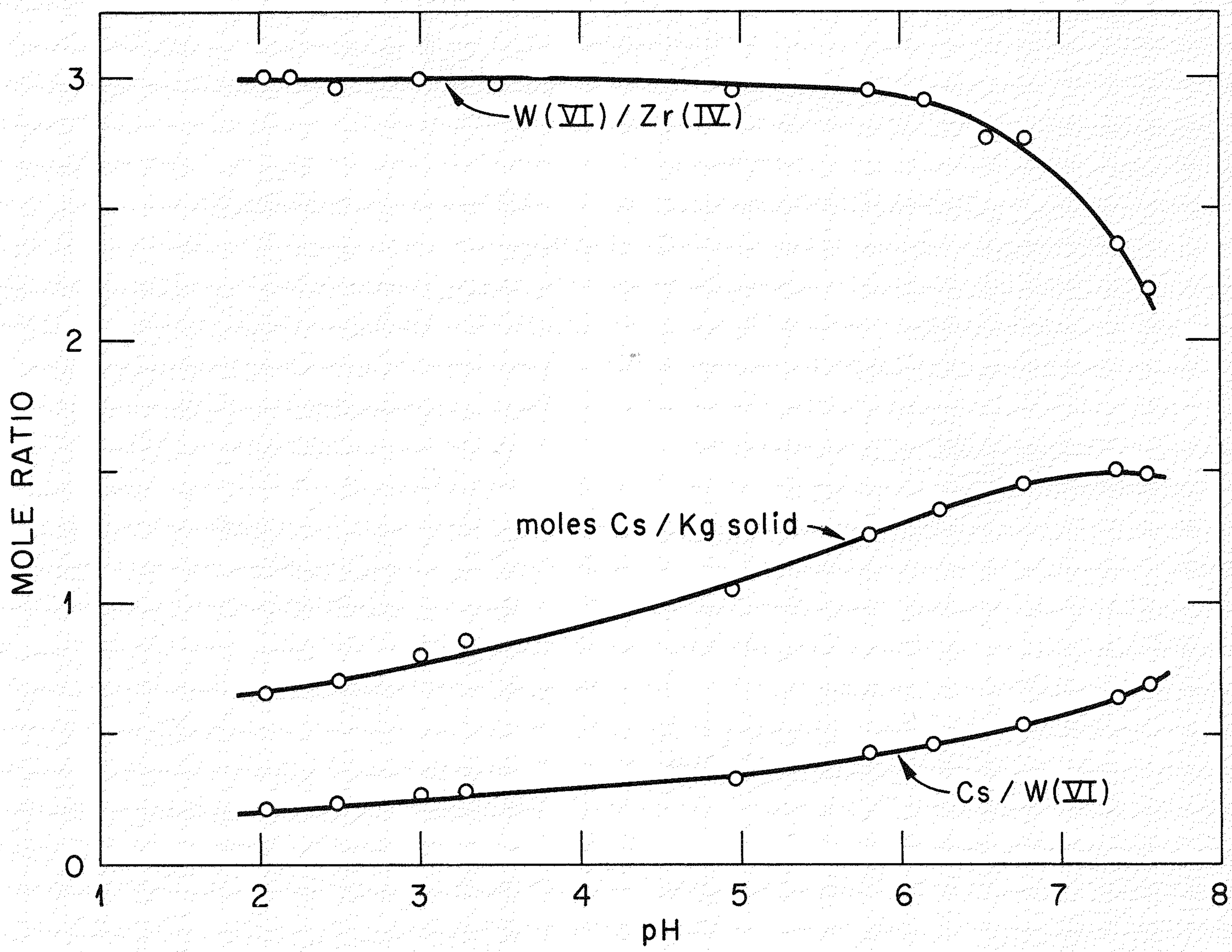

Figure 5

STABILITY AND ION EXCHANGE PROPERTIES OF Zr(IV) - W(VI) PRECIPITATES

(Ammonia Titration in 1 *M* NH_4Cl, Followed by Cs^+-NH_4^+ Exchange, Drying Temp. 25°C)

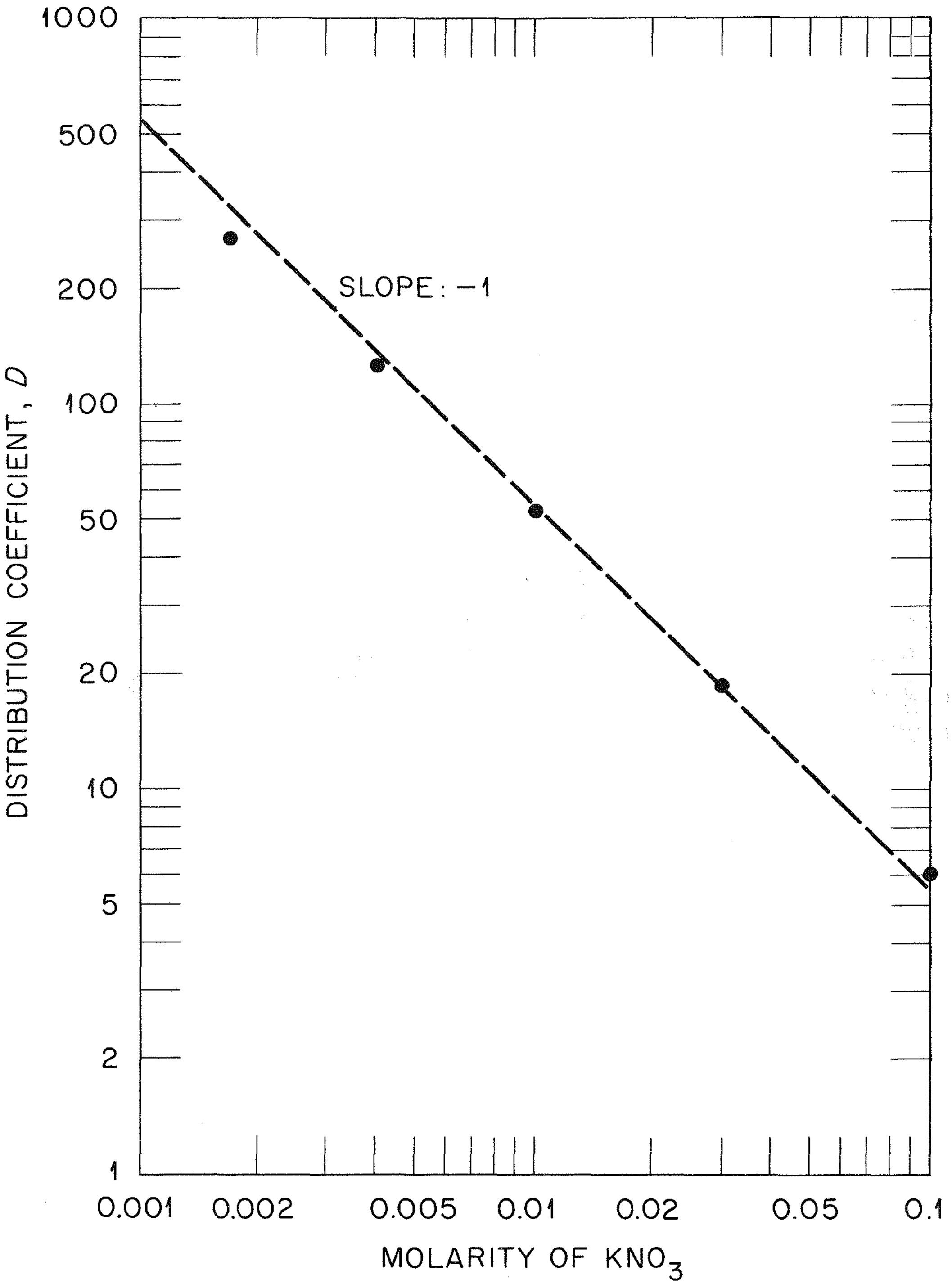

Figure 6
BROMIDE-NITRATE EXCHANGE WITH HYDROUS ZIRCONIUM OXIDE
(Drying Temperature 200°C)

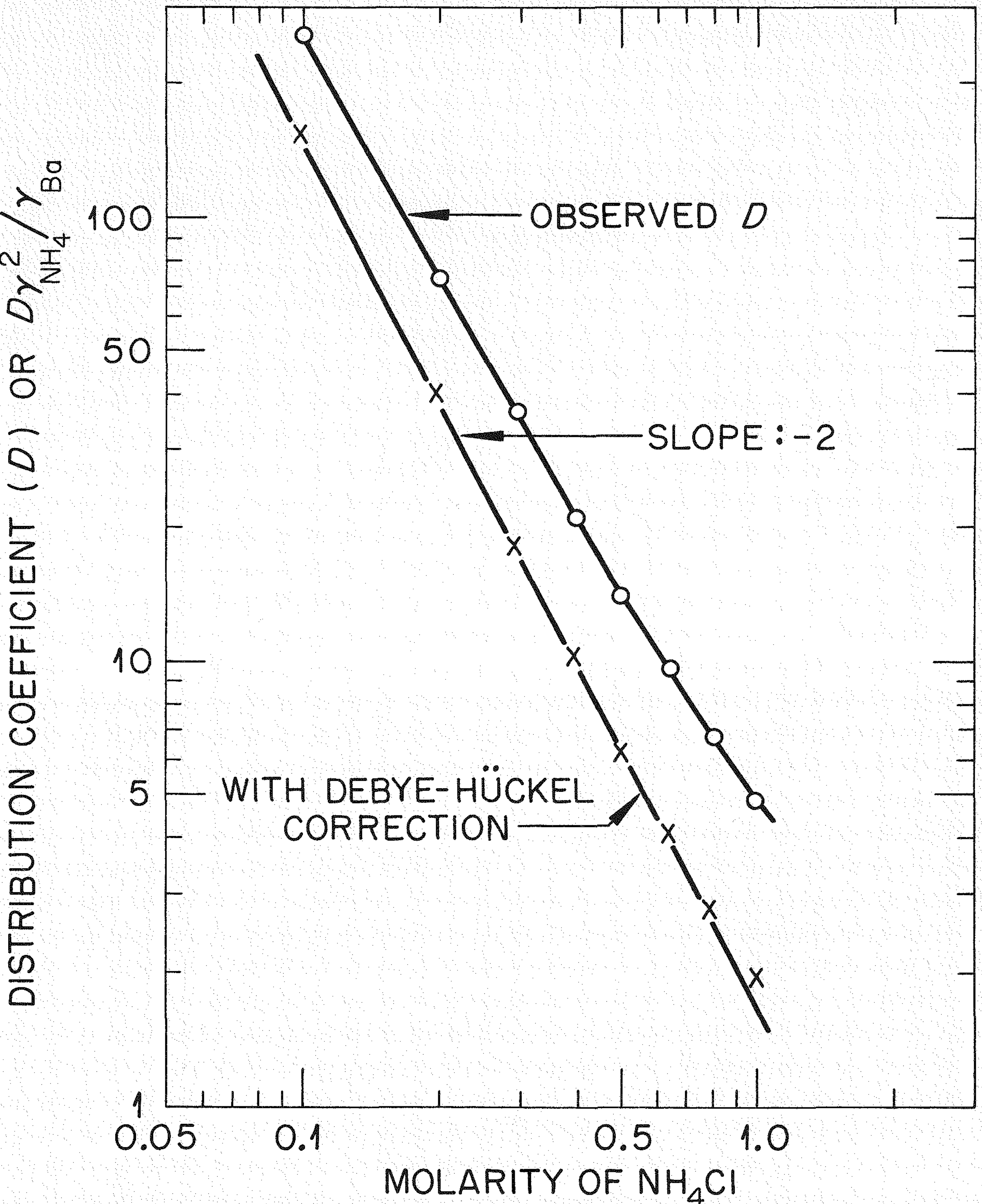

Figure 7
ADSORPTION OF TRACE Ba^{++} ON ZIRCONIUM TUNGSTATE

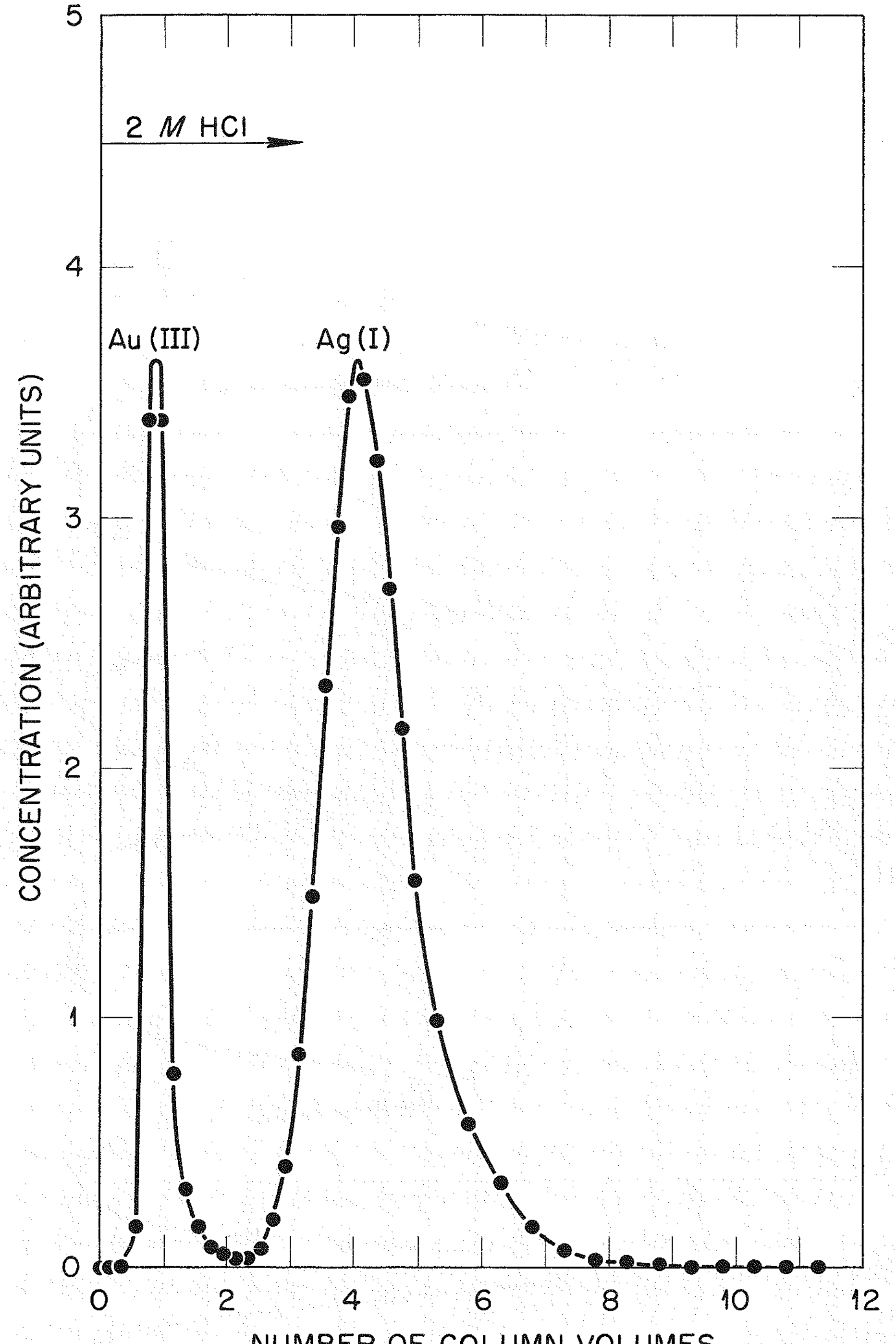

Figure 8

SEPARATION OF Au(III) AND Ag(I) WITH HYDROUS ZIRCONIUM OXIDE

(Drying Temp. 200°C, 3.6 cm x 0.28 cm^2 Column, Flow Rate 0.5 cm/min.)

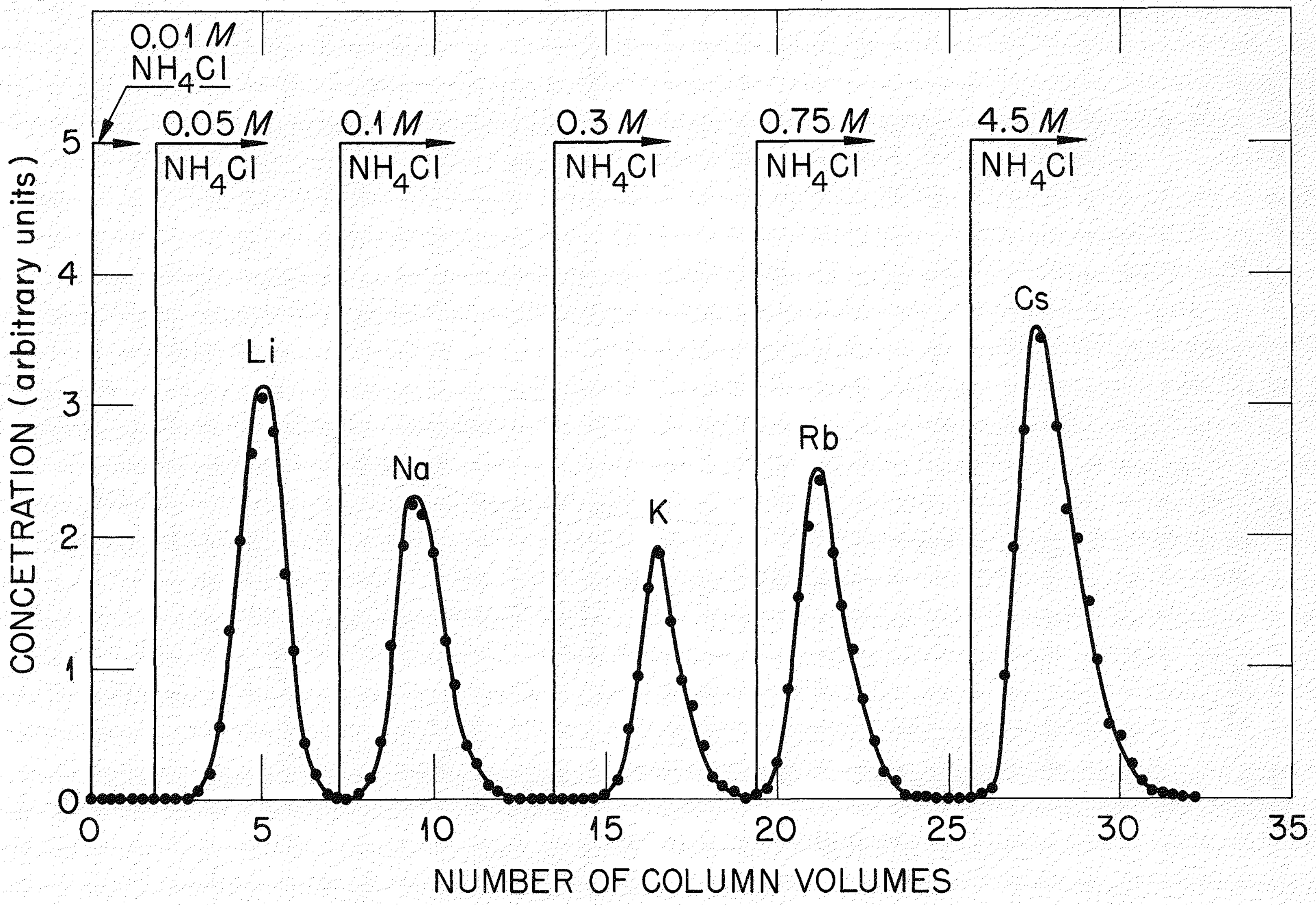

Figure 9

SEPARATION OF THE ALKALI METALS

(Zirconium Tungstate, 12.3 cm x 0.13 cm^2 Column, Flow Rate ca. 0.75 cm/min.)

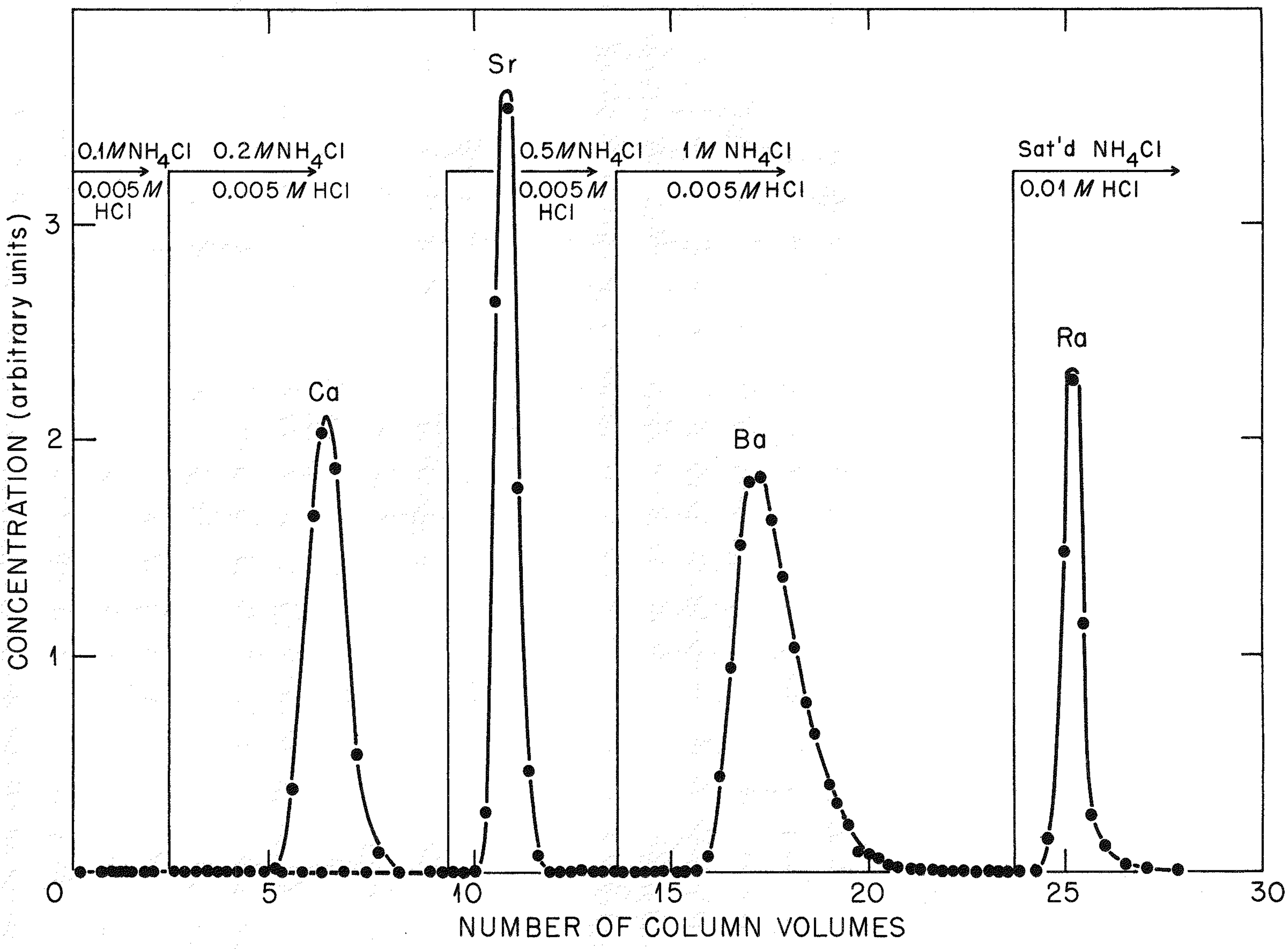

Figure 10

SEPARATION OF ALKALINE EARTHS WITH ZIRCONIUM MOLYBDATE
(Drying Temp. 25°C, 0.19 cm^2 x 10.0 cm Column, Flow Rate 1.1 cm/min.)

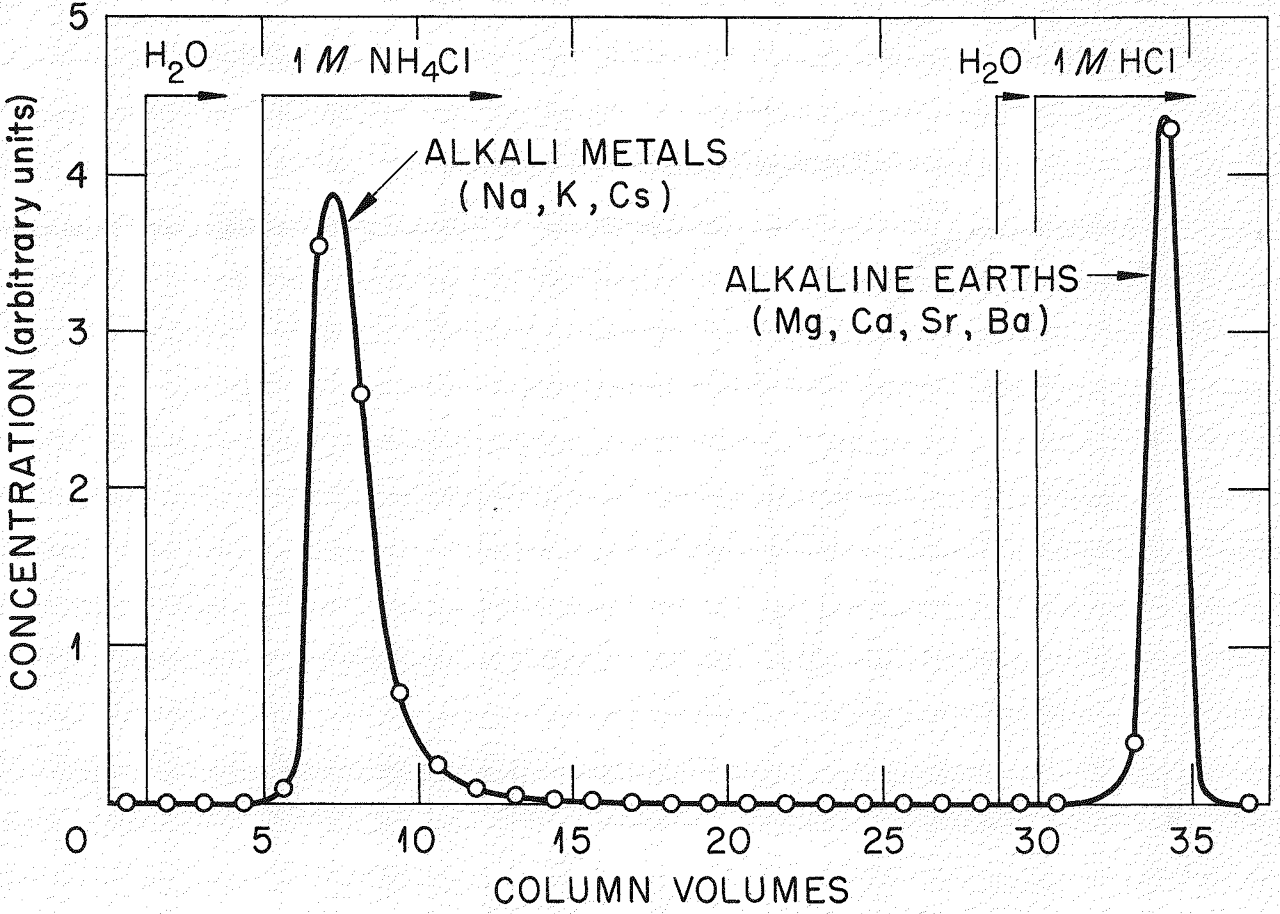

Figure 11

GROUP SEPARATION OF ALKALI METALS AND ALKALINE EARTHS WITH ZIRCONIUM PHOSPHATE

Drying Temperature: 25°C
Pretreatment: 1 M NH_3
Column: 0.2 cm^2 x 2.0 cm
Flowrate: 1.1 cm/min
Loading: 0.025 eqv/kg/elements

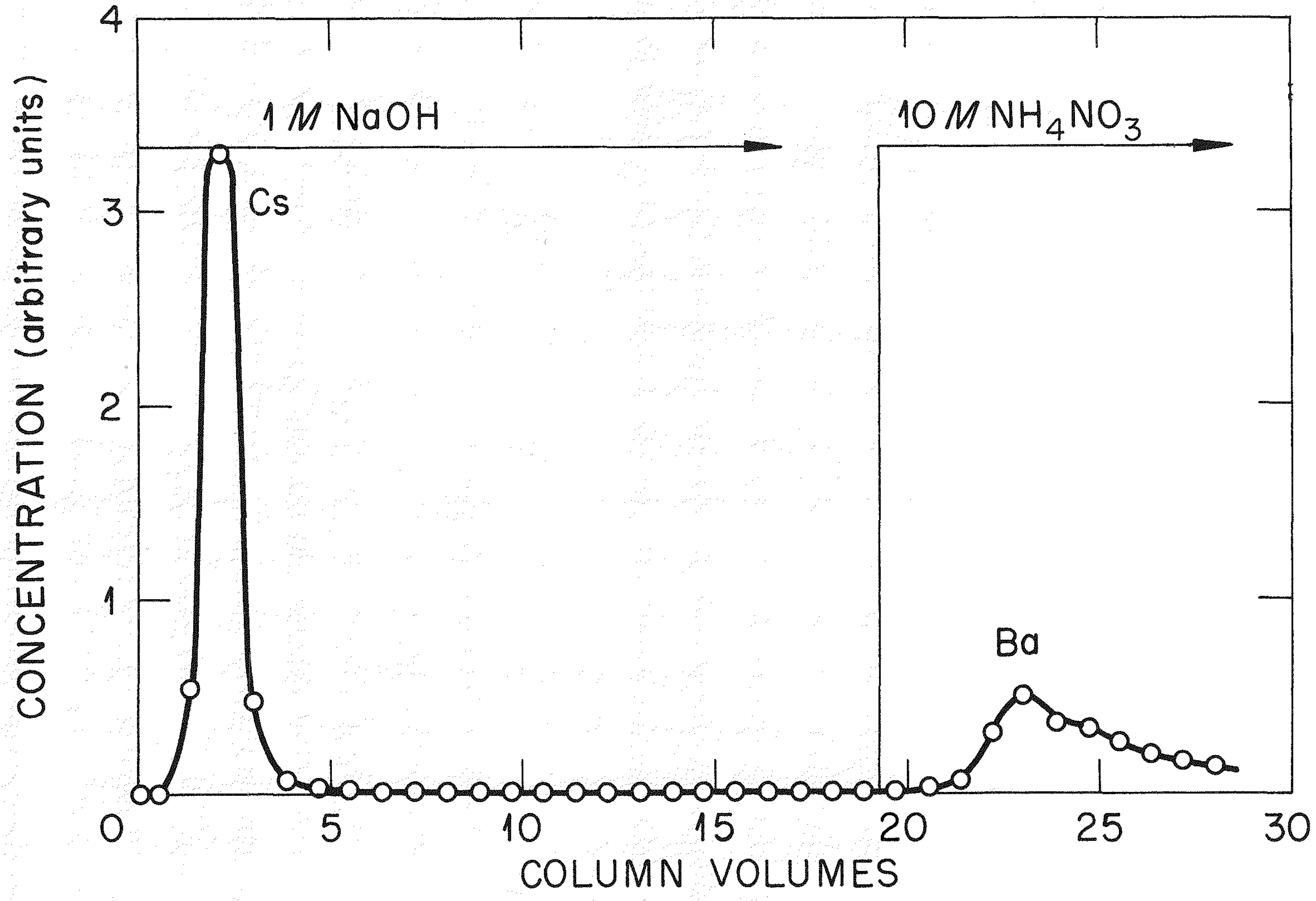

Figure 12

CATION EXCHANGE SEPARATION OF Cs^+ AND Ba^{++} WITH URANIUM (VI) OXIDE

(Drying Temp. 25°C, Column 0.2 cm^2 x 3 cm, Flow Rate 1 cm/min)

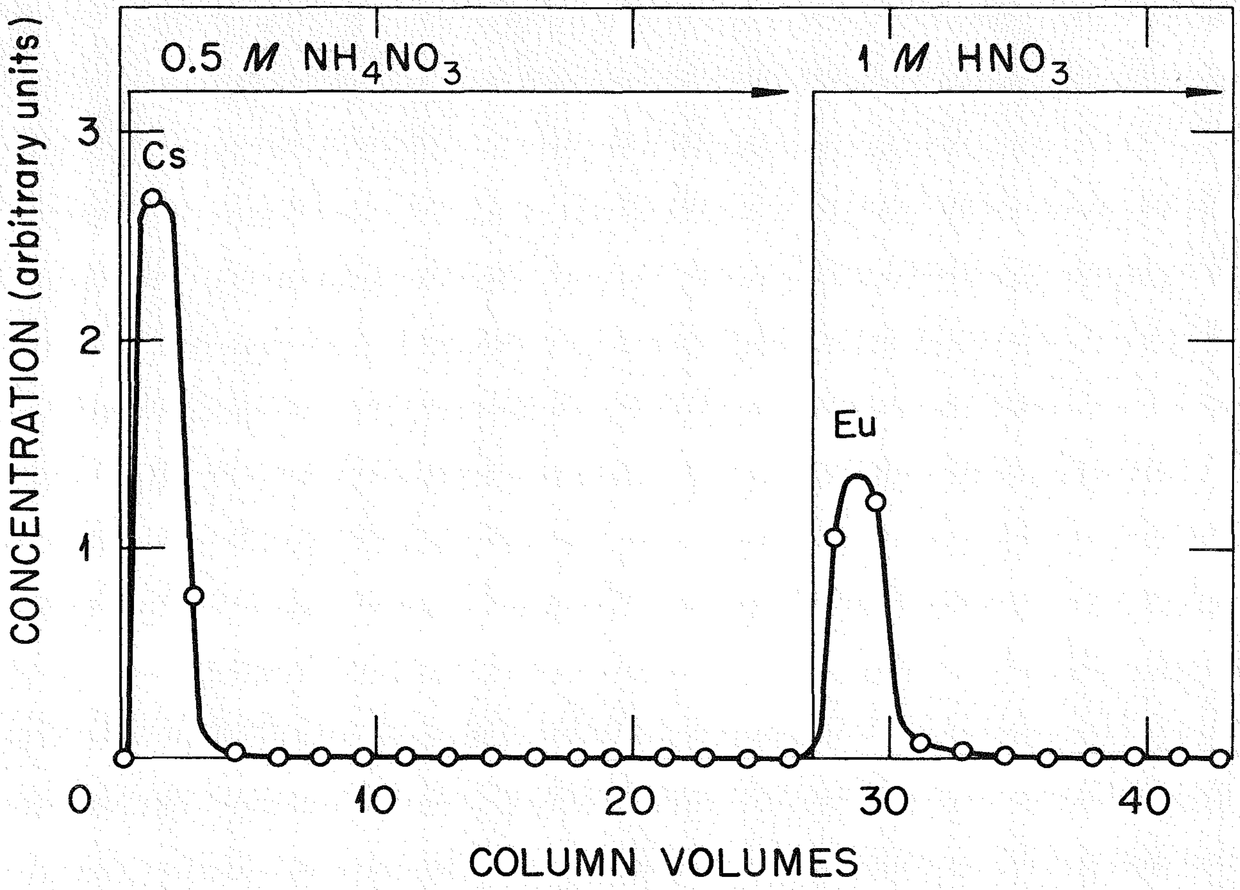

Figure 13

SEPARATION OF ALKALI METALS FROM RARE EARTHS WITH ZIRCONIUM OXIDE

Drying Temperature: 300°C
Pretreatment: NaOH
Column: 0.2 cm^2 x 1.5 cm
Flowrate: 1.3 cm/min

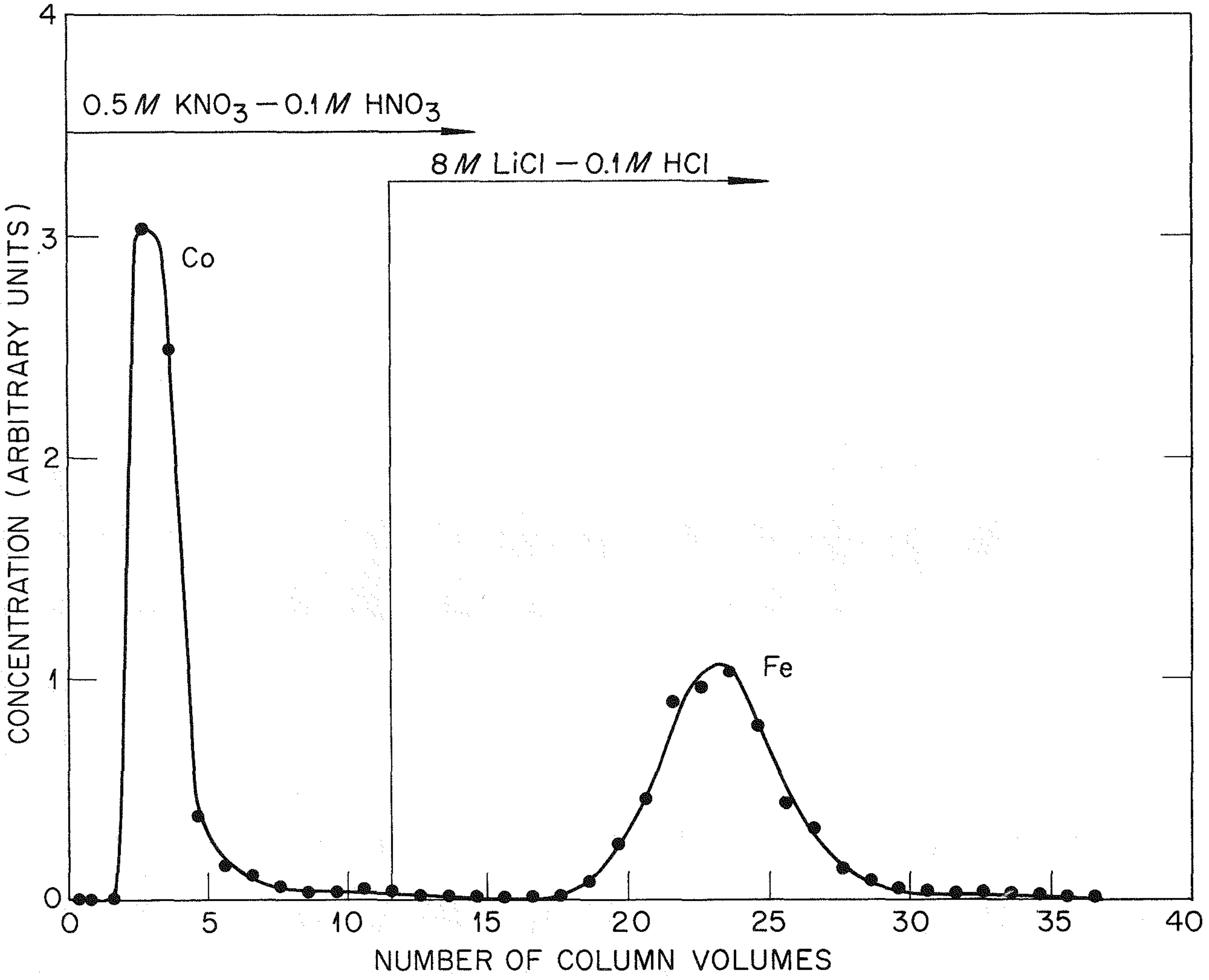

Figure 14

SEPARATION OF Co(II) AND Fe(III)

(Zirconium Tungstate, Drying Temp. 25°C, 5.5 cm x 0.09 cm^2 Column, Flow Rate 0.5 cm/min.)

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