A Systematic Ion Exchange Separation of Metallic Elements. I. Group Separation of Metallic Elements by Anion Exchange with Hydrochloric Acid

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A number of systematic separation methods of metallic elements using an ion exchange resin have been reported. Tompkins, Khym and Cohn[1], and Kimura, Minami and Honda[2] have reported systematic procedures for the separation of fission products by means of cation exchange. Minami, Fujimoto and Kakihana proposed a method[3,4] for the analysis of major ionic species in natural water using a cation exchange resin. Takiyama and Suito[5] reported a group separation of cations using anion exchange resins of various forms as precipitants, according to the principle of the usual qualitative analysis. Kraus and his co-workers[6] separated transition metals from each other by anion exchange in a hydrochloric acid medium. They have also carried out an extensive study[7] of the anion exchange adsorption of a number of elements from the same acid and other media. Jentsch and Pawlik[8] have also studied the adsorption from hydrochloric acid. A few years ago, the present authors reported an ion exchange method for silicate analysis[9]. The present authors are now interested in a systematic method for the isolation of all metallic elements in the usual quantity by ion exchange, without any other separatory operation. In systematic separation procedures, it is usual first to separate these elements into several groups, instead of isolating them one by one from the start. For an eluant employed in a group separation as the first stage of systematic procedure by ion exchange, it is necessary that it not produce an insoluble compound with most metals, and that it can be easily removed by heating or other simple operations after elution, since a large excess of eluant may make the subsequent separation troublesome. From this point of view, hydrochloric acid may be considered to be one of the most suitable eluants. In this experiment, the group separation was carried out by elution with various concentrations of hydrochloric acid through an anion exchange column, based on the Kraus' method. Some of the metallic elements which form insoluble or volatile compounds with hydrochloric acid, or which occur rarely in nature, and which form complicated compounds of various oxidation states, were excepted.

Experimental

Resin.—The anion exchanger used in this work was a "Dowex 1-X8". The commercial chloride resin (100～200 mesh) was previously washed with water by means of suspension. The water, together with the resin of the finest mesh, was removed several times by decantation. Ten and forty milliliters columns of this chloride resin were used in the preliminary test and the separation experiment respectively. Each column was washed in turn with concentrated and dilute hydrochloric acids and water, and just before the addition of a sample solution it was treated with 10.5～11 M hydrochloric acid.

Solutions.—Hydrochloric acid as an eluant was of special grade and was used without further purification. Solutions of metal elements were prepared by dissolving their chlorides or oxides in water or hydrochloric acid except in the following cases: solutions of lead, bismuth and uranium were the acidified aqueous solutions of their nitrates: the solution of thallium(III) was prepared by treating thallous nitrate with a mixture of hydrochloric acid and nitric acid and then dissolving it in hydrochloric acid after the volatilization of nitric acid; the solution of arsenic(III) was prepared from arsenous acid, and the solution of arsenic(V) was obtained by oxidizing arseneous acid.

Procedure for Separation Experiments.—Each solution, usually containing about 5～10 mg. of an element, was evaporated to small volume, and concentrated hydrochloric acid was added so that the sample

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[1] E. R. Tompkins, J. X. Khym and W. E. Cohn, *J. Am. Chem. Soc.*, **69**, 2769 (1947).

[2] K. Kimura, E. Minami and M. Honda, *Japan Analyst*, **3**, 335 (1954).

[3] H. Kakihana, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **71**, 481 (1950).

[4] E. Minami, M. Fujimoto and H. Kakihana, ibid., **74**, 740 (1953).

[5] K. Takiyama and E. Suito, *Japan Analyst*, **4**, 8 (1955).

[6] K. A. Kraus and G. E. Moore, *J. Am. Chem. Soc.*, **75**, 1460 (1953).

[7] K. A. Kraus and F. Nelson, "Anion Exchange Studies of the Fission Products", Peaceful Uses of Atomic Energy, Proceedings of the International Conference in Geneva, Vol. 7, p. 113 (1955) (United Nations).

[8] D. Jentsch and I. Pawlik, *Z. anal. Chem.*, **146**, 88 (1955).

[9] J. Yoshimura and H. Waki, *Japan Analyst*, **6**, 362 (1957).

solution might be adjusted to a volume of 10 ml. and to a hydrochloric acid concentration of 10.5~11 M. This solution was immediately added on the top of the column (Dowex 1, 40 ml., ϕ 1.2 cm.), and at the same time the effluent began to collect. When the sample solution was passed through the resin bed and no liquor was found on the top of the bed, a small volume of 11 M hydrochloric acid was added after washing the inside wall of the vessel used and the glass column, and the elution by 11 M hydrochloric acid was kept continuously by a connection with a separating funnel. When 40 ml. of the effluent was obtained, the elutriant was altered by 6.5 M hydrochloric acid, and the effluent was collected in another vessel. When 80 ml. of the effluent for 6.5 M was obtained, the elutriant was altered by 3 M hydrochloric acid. One hundred milliliters of the effluent for 3 M was collected. The metal elements still remaining in the resin bed after elution with 3 M hydrochloric acid were desorbed with extremely dilute hydrochloric acid below 0.5 M or with other elutriants appropriate for individual cases. The flow rate was 0.5 ml./min. for 11 M and 3 M hydrochloric acids, and 0.8 ml./min. for 6.5 M. All elutions were done at room temperature. In each elution the metal element in each fraction of the effluent was detected or determined, mostly by a usual method. Also, in the preliminary test, a similar procedure was employed, though a smaller column and smaller volumes of sample solution and of elutriant were used.

Results and Discussion

In the preliminary test in which a 10 ml. column was used, results* were obtained as expected from Kraus' experiments. Most metallic elements seemed to be classified experimentally into four groups from their behavior in elution with hydrochloric acid using an anion exchange resin, though each group was not enough separated from the others. The four groups were those not adsorbed even from concentrated hydrochloric acid, those adsorbed from the concentrated hydrochloric acid and desorbed with the 6 M acid, those desorbed by the acid below 6 M to 3 M, and those eluted with difficulty by 3 M hydrochloric acid. Besides, there were also some elements which have behavior intermediate between the first two groups.

The use of a longer column leads to the possibility of the more quantitative separation for these elements, and this may be required when considerable amounts of sample are treated. From this point of view, the column of 40 ml. was employed as well as in the silicate analysis[9]. The second elution was done by preferance with 6.5 M hydrochloric acid, since the use of hydrochloric acid less than 6 M might cause a partial effluence of cobalt into the part of the second group.

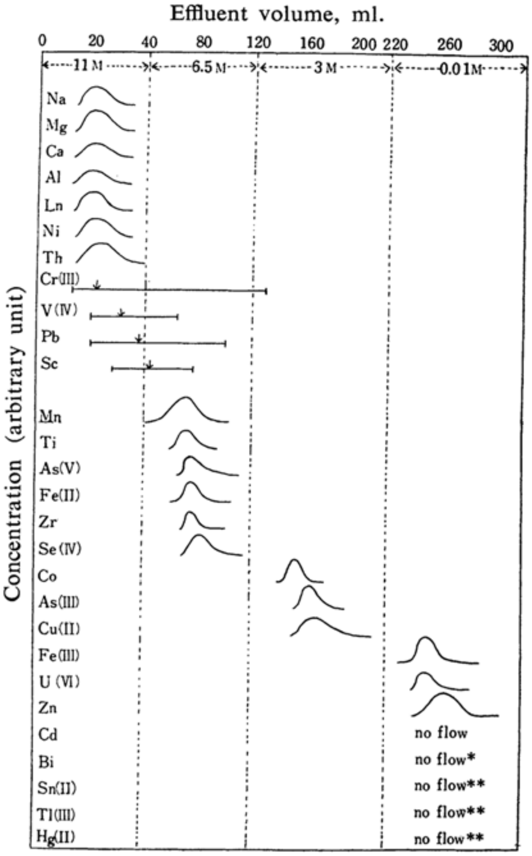

Fig. 1. Elution curves of metallic elements from the 40 ml. column of "Dowex 1-X8" with hydrochloric acid solutions of various concentrations.

|—| : Range where an metal element was detected
↓ : Point of maximum metal concentration in the effluent
* Test by 0.1 M HCl
** Test by 0.5 M HCl

As shown in Fig. 1 which gives an individual elution curve obtained by quantitative or semi-quantitative analysis of the effluent, the metallic elements investigated, except scandium, lead, vanadium(IV) and chromium(III), were quantitatively separated into four groups using the column of 40 ml. Scandium was found in the second section of effluent for the most part, although also in the first section of effluent in some portions. In order to separate it perfectly from non-adsorbed elements, 13 M hydrochloric acid must be employed[10]. But this may be of no practical use as an elutriant. Chromium(III)

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* Elution curves have not been shown in this paper to avoid duplication, since they were like in tendency to those in the separation experiment where a 40 ml. column was used.

10) J. Yoshimura, Y. Takashima and H. Waki, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **79**, 1169 (1958).

TABLE I. CLASSIFICATION OF METALLIC ELEMENTS

Group I				Group II			Group III		Group IV	
Li	Be	Al	Th	Mn	Fe(II)	Se	Co	As(III)	Fe(III)	Zn
Na	Mg	Y			As(V)			Cu(II)	U(VI)	Cd
K	Ca	La-Lu			Ti					Sn(II)
Rb	Sr				Zr					Tl(III)
Cs	Ba				Hf					Hg(II)
	Ni									Bi(III)
	Cr(III)		V(IV)	Sc	Pb					

Group I is eluted by 1 column volume of 11 M HCl.
Group II is eluted by 2 column volume of 6.5 M HCl.
Group III is eluted by 2.5 column volume of 3 M HCl.
Group IV is still held by the resin column after elutions by 11 M, 6.5 M and 3 M HCl.

and vanadium(IV) were found for the most part in the first section of effluent, but some portions of them were in the second one. Chromium can not be concentrated in a small volume of the effluent by hydrochloric acid because, it is considered, chromium has variously stable complex forms in the chloride solution. Lead extended half-and-half over the two sections. The elution favorable for only these elements may, conversely, be unsuitable for the group separation of most other metallic elements.

The classification of metallic elements based on the preliminary test and the separation experiment are tabulated in Table I. Some elements not described in this paper will be added to this table later in further studies. Especially, the assignment of more elements to group IV may be expected from Kraus' distribution data[7].

The use of a longer column and the careful selection of eluting conditions employing more kinds of chloride concentration might permit a further separation of the moderately adsorbable elements (groups II and III). However, much more time and a delicate technique may be required for them. Consequently, other eluants may be preferable for isolation inside these groups. Among the elements in group IV, the separation of Fe, U-Zn-Cd can be done easily using hydrochloric acid of extremely low concentration. However, such an dilute acid must be used prudently, since a number of strongly adsorbable elements tend to be hydrolyzed in dilute acid. The subdividing of this group by more dilute hydrochloric acid can be formalized only with difficulty unless the elution behaviors of these elements are known extensively. For the desorption of group IV in this experiment, hydrochloric acid of an arbitrary concentration below 0.5 M, water, perchloric acid, nitric acid and other elutriants were selected according to individual cases. The use of a smaller column leads to a poor separation between group I and manganese, and at least a near-40 ml. column is needed for a quantitative separation. If a sample contains no manganese, a somewhat smaller column may be used.

These classifications can not be interpreted in terms of the stability constant[11] of a chloro-complex in the solution phase. To explain the adsorbability of a metal ion on an anion exchange resin, the form and the stability of the complex in the resin phase must also be taken into account. Although these are not clear in general at present, the features of the four groups may be given an outline as described below.

Group I contains alkali metals, alkaline earth metals, aluminum, yttrium, lanthanide elements, thorium and nickel. These elements do not form any anionic complex species in either hydrochloric acid solution or resin, and pass through the resin column even with concentrated hydrochloric acid. They are collected in only one column volume of the effluent by 10.5~11 M.

Group II contains manganese, titanium, iron(II), zirconium, arsenic(V), selenium(IV) and also probably hafnium*, which are collected in the next two column volumes of the effluent by 6.5 M. These elements form anionic chloro-complexes in the resin phase for the concentrated hydrochloric acid medium, while they do not form presumably anionic chloro-complexes in any appreciable amount in the solution phase over the whole range of chloride concentration. An exception is arsenic(V), which appears to exist not as a chloro-complex anion but as an arsenate ion. Among non-metallic ions, sulfate and phosphate fall into both groups I and II.

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[11] J. Bjerrum, G. Schwarzenbach and L. G. Sillén, "Stability Constants, Part II—Inorganic Ligands", London (1958).

* It was confirmed that the adsorption of hafnium was not stronger than that of zirconium, although hafnium was not eluted by 10 M hydrochloric acid.

TABLE II. ANALYSES OF MIXED SOLUTIONS

Sample No.	Element	Taken	Found I	Found II	Found III	Found IV
1	Ni	5.97 mg.	5.94 mg.			
	Mn	2.00 mg.		2.02 mg.		
	Co	0.0840 mmol.			0.1591 mmol.	
	Cu(II)	0.0771 mmol.				
	Fe(III)	9.92 mg.				9.80 mg.
2	Th	7.42 mg.	7.08 mg.			
	Zr	3.97 mg.		3.90 mg.		
	U(VI)	89.4 mg.				89.3 mg.
3	Ni	59.7 mg.	59.5 mg.			
	Cu(II)	49.0 mg.			49.4 mg.	
	Zn	0.0708 mmol.				0.1120 mmol.
	Cd	0.0419 mmol.				

I : Effluent by 11 M HCl
II : Effluent by 6.5 M HCl
III : Effluent by 3 M HCl
IV : Effluent by extremely dilute HCl

Group III contains cobalt, arsenic(III) and copper(II), which are collected in the next two and a half column volumes of the effluent by 3 M. These elements form anionic chloro-complexes not only in the resin phase, but also in the solution phase for the concentrated hydrochloric acid medium.

Group IV contains iron(III), uranium(VI), zinc, cadmium, bismuth, tin(II), mercury(II), thallium, etc., which remain in the column after the elution with 3 M. Most elements in group IV form stable anionic chloro-complexes in both phases, even in a dilute hydrochloric acid medium. Iron(III) and uranium(VI) may be rather like the elements in group III in this point. However, they are conveniently classified in group IV, since their concentration regions of adsorption are as wide as those of other elements in this group.

The separation data on mixed solutions which consist of a few elements are shown in Table II. Sample 1 contains the elements situated in one end of each group with respect to the effluence. Samples 2 and 3 are those which contain a large quantity of special elements. Furthermore, a successful quantitative group separation can be expected in a mixed solution containing more elements in ordinary combination except in the following cases: 1) when an element undergoes a change in valency during the separatory process by reaction with other elements or with hydrochloric acid, 2) when a sample solution contains an element which is apt to produce a volatile compound in hydrochloric acid, 3) when the quantity of metal elements included is beyond a limit permissible from the column exchange capacity, and 4) when a sample solution of 10 ml. of concentrated hydrochloric acid can not be prepared in the case where a metal element of small solubility in the acid is treated in a relatively large amount.

For case 3 or 4, an increase in the resin bed volume and the volume of sample solution may be required.

Summary

1) As the first stage in the systematic separation of metallic elements by ion exchange, a group separation on an ordinary scale was tried using an anion exchanger "Dowex 1-X8", with hydrochloric acid, a method based on Kraus' method.

2) Most metallic elements usually treated in the chemical analysis can be separated into four groups by the elution through a 40 ml. column using 11 M, 6.5 M and 3 M hydrochloric acid as elutriant. Satisfactory results were obtained on analysis for a mixed solution.

3) These classifications may be explained in terms of the formation of a chloro-complex of a metal, not only in the solution phase but also in the resin phase.

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