A Separation Scheme for the Analysis of Metal Ions Using Column Extraction Chromatography. Grouping of Nineteen Metal Ions into Six Fractions[1]

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A new scheme for the quantitative group separation of 19 common cations by reversed-phase extraction column chromatography has been devised. The following six columns, in which the organic solvent was adsorbed on Daiflone(polytrifluorochloroethylene), were prepared: a TBP–2N HCl column for Fe(III), Hg(II), and Sn(IV); a TOA(CCl_4)–2N HCl column for Ag(I), Bi(III), Zn(II), and Cd(II); a TBP–6N HCl column for Sb(III); an AcAc($CHCl_3$)–pH 5.0 column for Cr(III) and Al(III); a TTA(MIBK)–pH 5.0 column for Cu(II), Co(II), Ni(II), Pb(II), Mn(II), and Mg(II), and a TTA(MIBK)-pH 7.0 column for Ca(II), Sr(II), and Ba(II). After a test solution had been passed through the six columns successively in the above order, the metal ions are grouped and entirely retained on the specified columns.

Most of the investigations of the mutual separation of metal ions have been mainly concerned with the specific problems involved in separating some desired elements from their mixture, or in separating an important element from many other unimportant ones; therefore, a more general separation method for each ion from a mixture of various metals, of any composition, is much to be desired.

We aimed to establish a systematic scheme for the separation of many metals in macro to trace amounts; as the first report on our continuing study, this paper will present a quantitative grouping scheme for 19 common metals by reversed-phase extraction chromatography using six different columns.

A sequential separation scheme for the quantitative analysis of many different metal ions had been the object of much searching; recently, among the many kinds of separation techniques, the solvent extraction technique has been preferred for this purpose; there having been several reports on it, including those by Chalmers *et al.*[2–4] and more recently by Morsches and Tölg.[5]

Unless the distribution coefficients of metal ions differ remarkably from each other, multiple extraction steps such as counter-current extraction are required for any quantitative separation, and this is tedious. If reversed-phase extraction-column chromatography, which is closely related to liquid-liquid extraction in the batch system, could be adopted for the purpose, the multiple extraction would take place successively in the column; the extraction column technique can be used for trace to macro levels with a very simple apparatus, and this apparatus can, if necessary, be automatized. There have been a few reports in which the extraction chromatography has been used for the separation of a mixture involving many metals. Among these, one described the use of a α-benzoinoxime–$CHCl_3$–polytetrafluoroethylene bed,[6] and others, the use of a di(2-ethylhexyl)orthophosphoric acid–Kieselguhr column,[7,8] both being combined with an ion-exchange column; the metals were thus separated into several groups suitable for their gamma spectrometry. Recently, a comprehensive separation scheme has been devised by Fritz and Latwesen[9] for the separation of 27 metal ions with trioctyl phosphine oxide, isopropyl ether, and isobutylmethyl ketone columns in combination with an ion-exchange column; it seems an excellent work in our field of investigation. The procedure of Deing *et al.*,[10] involving extraction with a tri-*n*-butylphosphate and di(2-ethylhexyl)orthophosphoric acid column, has also been proposed for the separation of fission products of irradiated uranium. The present paper will describe the systematic and quantitative group separation of 19 common metal ions using six columns based on reversed-phase extraction chromatography; tri-*n*-butylphosphate(TBP)–6 N HCl, TBP–2 N HCl, tri-*n*-octylamine(TOA)–CCl_4–2 N HCl, acetylacetone(AcAc)–$CHCl_3$–pH 5.0, 2-thenoyltrifluoroacetone(TTA)–methyl isobutyl ketone–(MIBK)–pH 5.0, and TTA–MIBK–pH 7.0 columns. These columns were named the TBP-(1) column, the TBP-(2) column, the TOA column, the AcAc column, the TTA-(1) column, and the TTA-(2) column respectively. The grouping metal ions from a complex mixture of various metals in varying concentrations is the first step to a quantitative separation of each metal alone from the respective column.

The Selection of The Extraction System and The Construction of a Separation Scheme. It is necessary to select a good extractant, a suitable solvent, and the optimum conditions for the purpose from the wide variety of extraction systems which have been reported. The authors chose the extraction systems described above for those reasons. Extraction systems should

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[3] R. A. Chalmers and D. M. Dick, *ibid.*, **32**, 117 (1965).

[4] R. A. Chalmers and G. Svehla, "Solvent Extraction Chemistry," eds. D. Dyrssen et al, p. 600, North-Holland, Amsterdam, 1967.

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[9] J. S. Fritz and G. L. Latwesen, *Talanta*, **17**, 81 (1970).

[10] R. Denig, N. Trautmann, and G. Herrmann, *J. Radioanal. Chem.*, **6**, 331 (1970).

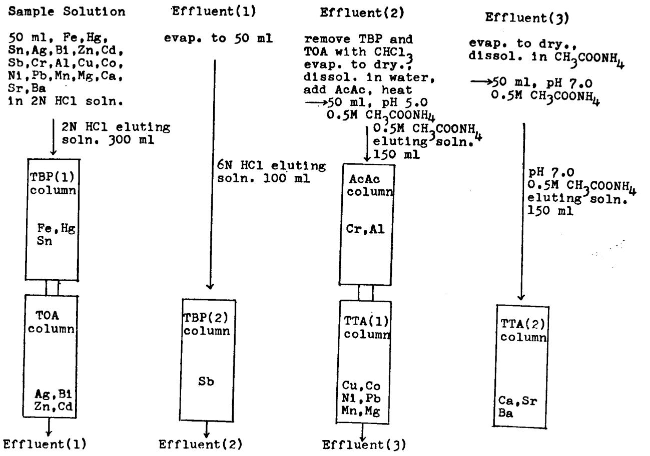

Fig. 1. Scheme of group separation.

be selective; that is, the extractability of the metal ions to be separated must be high enough for them to be retained on the upper part of the extraction column. The distribution of each metal ion should be markedly dependent on the acidity or pH of the aqueous medium; if so, the metal ions retained on the column can be eluted easily by varying the acidity or pH of the eluting solution. A simple medium in which no masking agent or nonvolatile salt exists is also preferred as an eluant, for its use will facilitate the subsequent determination of metals and the simple isolation of the compound.

The scheme shown in Fig. 1 was prepared for the group separation of 19 common cations by reversed-phase extraction column chromatography, with reference to sufficient information about the behavior of each element in the extraction system, taking the following points into consideration: (1) the extractions of the metal ions, readily hydrolyzable in a weakly acidic solution, were done in the earier stage of the separation process; (2) two columns in which eluting solutions of an identical acidity or pH could be used were joined together, and (3), the separation conditions were set up so as none of the retained metals could be released from the column even when a sample solution of a large volume flowed through.

Experimental

Reagents and Materials. *Daiflon*: Daiflon (a trade name of polytrifluorochloroethylene) M-300 moulding powder was purchased from the Daikin Kogyo Co.; 42-to 80-mesh powder was used.

Metals: Chlorides and nitrates of metals of an analytical reagent grade were dissolved in hydrochloric, nitric acid, or redistilled water.

Organic Reagents and Solvents: TTA, MIBK, chloroform, TOA, carbon tetrachloride, AcAc, and TBP were all of a chemically pure grade.

Radiochemicals: Several radionuclides were employed in order to ascertain the behavior of individual ions in the chromatography: Fe-59, Hg-203, Sn-113, Bi-207, Ag-110m, Zn-65, Cd-115m, Sb-124, Co-60, Ni-63, Sr-90, and Ca-45 were employed. The radiochemical purity of these nuclides was examined by measuring their half-lives, γ-ray spectra, and β-ray adsorption curves with aluminum foils.

Organic Solvent Solutions Available for the Stationary Phase of the Column. In each case the organic solvent solution used for the stationary phase should be in equilibrium with the eluting solution which comes in contact with the column.

100% TBP Solution for the TBP(1) and TBP(2) Columns: The TBP was equilibrated with 2 N (or 6 N) HCl.

20% TOA–CCl$_4$ Solution for the TOA Column: This solution was equilibrated with an equal volume of 2N HCl.

50% AcAc–CHCl$_3$ Solution for the AcAc Column: This solution was equilibrated with an equal volume of an 0.5 M ammonium acetate solution of pH 5.0 which had been saturated with an AcAc–CHCl$_3$ solution.

1.5 M TTA–MIBK Solution for the TTA(1) and TTA(2) Columns: This solution was equilibrated with an equal volume of an 0.5 M ammonium acetate solution of pH 5.0 (or 7.0) which had been saturated with MIBK.

Eluting Solutions. Each eluting solution was equilibrated with a proper organic solvent solution placed in the column.

Eluting Solution for the TBP(1) and TBP(2) Columns: 2 N (for Column 1) or 6 N (for Column 2) HCl which had been saturated with a small amount of TBP was used.

Eluting Solution for the TOA Column: 2 N HCl saturated with a TOA–CCl$_4$ solution was used.

Eluting Solution for the AcAc Column: Fifty milliliters of AcAc were placed in a 1-l separating funnel, and then 300 ml of water saturated with CHCl$_3$ and 125 ml of a 2 M ammonium acetate solution which had been saturated with CHCl$_3$ were added. The funnel was shaken, and a very small amount of the undissolved AcAc was rejected; then the aqueous phase was transferred into a measuring flask, and its volume was made up to 500 ml with water saturated with CHCl$_3$. The pH of this solution was then adjusted to 5.0 by adding 0.5 M acetic acid saturated with CHCl$_3$.

Eluting Solution for the TTA(1) Column: A TTA reagent (3.1 g) was dissolved, with shaking for 30 minutes, in 900 ml of a 0.5 M ammonium acetate solution which had been saturated with MIBK, then the pH of the solution was adjusted to 5.0 by adding 0.5 M acetic acid saturated with MIBK. The total volume was made up to 1 l with a solution of 0.5 M ammonium acetate solution saturated with MIBK.

Eluting Solution for the TTA(2) Column: With a TTA reagent (3.2 g), the eluting solution was prepared in the manner described just above, but the pH was adjusted to 7.0.

The amount of a TTA reagent to be dissolved in the eluting solution was determined in accordance with Reference 11.

Test Solutions. Stock solutions, each containing 0.5 mg of the metal ion in question per ml, were prepared. A test solution was prepared by diluting the stock solution so as it contained 1.0 mg of each element per 100 ml; in some cases, a radioactive tracer was added to the test solution. Fifty milliliters of the test solution were used for the column experiment. It is often desirable, but not in all cases, that the test solution have a composition similar to that of the eluting solution except for the metal ion. According to the variety of the metal ion in the sample solution to be tested, some part of the scheme shown in Fig. 1 may be omitted. Therefore, in such a case a test solution should have a composition similar to that of the eluting solution for the column from which the systematic separation starts.

The "test solution used for the AcAc column" was prepared as follows: Two milliliters of a stock solution (if necessary, with a radioactive tracer) were placed in a beaker and

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11) I. Akaza, M. Kozaka, and T. Imamura, *Bunseki Kagaku*, **14**, 825 (1965).

diluted to about 20 ml with water saturated with AcAc–CHCl$_3$. The pH was adjusted to 5.0 by adding 0.5 M acetic acid or aqueous ammonia, both saturated with CHCl$_3$; 5 ml of AcAc were then added to this solution. The beaker was heated gently for an hour, and then cooled. Twenty-five milliliters of a 2 M ammonium acetate solution saturated with AcAc–CHCl$_3$ were added to this solution, and the pH was adjusted to 5.0 by adding 0.5 M acetic acid or aqueous ammonia, both saturated with CHCl$_3$. Finally, the solution was transferred into a measuring flask and its volume was made up to 100 ml with water of pH 5.0 which had been saturated with the AcAc–CHCl$_3$ solution.

Experimental Procedure. Column Preparation. A glass chromatographic column, 0.94 cm in diameter and 30 cm long, and with a coarse frit at the bottom, was used. The Daiflon powder (5.5 g) was placed in an Erlenmyer flask fitted with a stopper, and then a definite volume of a proper "organic solvent solution for the stationary phase" (described above) was poured in. The preferable volumes of the organic solvent are 6.0 ml of TBP, 7.0 ml of 20% TOA–CCl$_4$, 5.0 ml of 50% AcAc–CHCl$_3$ and 6.5 ml of 1.5 M TTA–MIBK for each 5.5-g portion of Daiflon; these volumes were derived from the results of other preliminary experiments, in which the adsorbable amount of each organic solution on Daiflon had been determined. The stoppered flask was shaken gently by hand and was then left to stand over three hours. A small volume of an adequate eluting solution was added, and the slurry was poured into the chromatographic column. Every time a small portion of slurry was added, the column bed was gently pressed with a glass rod; the bed length eventually reached about 20 cm. About 50-ml portion of an adequate eluting solution was passed through the column in order to remove any contaminant.

In such a way, the six columns were prepared.

Basic Chromatographic Procedure. Fifty milliliters of a test solution prepared as above were percolated through the column at the rate of about 0.3 ml per minute, and then an eluting solution of a definite composition was passed through at a flow rate of about 0.5 ml per minute. The effluent was taken in a fraction collector or in beakers.

In the chromatographic process, some metal ions in the test solution were retained on the column, while others passed through the column and went into the subsequent column.

Systematic Procedure for the Group Separation. One systematic procedure for the group separation of 19 common cations from their mixtures is based on the scheme shown in Fig. 1, in compliance with the basic chromatographic procedure described above. The following descriptions of the individual columns show that the method may be applicable for the grouping of 19 cations when the entire course of the scheme is followed. Nevertheless, if some part of the scheme is omitted when the ions which would be retained in the omitted column are known to be absent in a sample solution, the test solution should be prepared as described in the appropriate paragraph discussing the test solutions.

The test solution(a) for the TBP(1) column was fed into the TBP(1) column, which was joined with the TOA column. A 300-ml portion of the "eluting solution for the TBP(1) column" was run through both columns. The effluent(1) from the lower column was collected in a beaker and evaporated to a small volume, and then the volume was make up to 50 ml with water saturated with TBP (test soln. (b)). The test solution (b) was fed into the TBP(2) column, and then 100 ml of "the eluting solution for the TBP(2) column" was run through this column. The effluent (2) was collected, 1 ml of concentrated nitric acid was added, and then the solution was shaken, together with a small volume of chloroform, for a minute in order to remove the small amount of dissolved TBP and TOA from the aqueous solution. After that, the aqueous phase was collected and evaporated to dryness under an infrared lamp in order to expel the free nitric acid and hydrochloric acid. The residue was dissolved in about 20 ml of water saturated with AcAc–CHCl$_3$ solution. After the pH of this solution had been adjusted to 5.0, 2.5 ml of AcAc was added to this solution; then the mixture was heated gently for an hour until the completion of the formation of the AcAc-chelates with metal ions. After cooling, 12.5 ml of a 2 M ammonium acetate solution saturated with CHCl$_3$ was added to the solution, and the pH of the solution was adjusted again to 5.0. Finally, the volume was made up to 50 ml with water saturated with the AcAc–CHCl$_3$ solution (test soln. (c)). The test solution (c) was poured into the upper column of the combined set of AcAc and TTA(1) columns, and 150 ml of "the eluting solution for the AcAc column" was run through these combined columns. The effluent (3) from the lower column was collected in a beaker and evaporated to dryness. The residue was dissolved again in "the eluting solution for the TTA(2) column," and the volume was made up to 50 ml with the solution (test soln. (d)). The test solution (d) was placed in the TTA(2) column, and then 150 ml of "the eluting solution for the TTA(2) column" was run through the column in order to wash it (effluent (4)). Finally, the columns were separated from one another, and the metal ions retained on each column were eluted with a suitable solution or were removed from the column, together with the stationary phase, by washing the column with ethanol. The metal ions thus released were determined as will be described below.

Determination of Metal Ions. In general, the metal ions in the effluent from each column were determined colorimetrically, radiometrically, or flamephotometrically. The

TABLE 1. THE ANALYTICAL METHODS USED FOR THE DETERMINATION OF THE METAL IONS

Metal	Method
Fe	Radiometric (Fe-59)
Hg	Radiometric (Hg-203)
Sn	Radiometric (Sn-113)
Bi	Radiometric (Bi-207)
Ag	Radiometric (Ag-110 m)
Zn	Radiometric (Zn-65)
Cd	Radiometric (Cd-115 m)
Sb	Radiometric (Sb-124)
Cr	Spectrophotometric as dichromate (440 mμ)
Al	Spectrophotometric as oxinate (390 mμ)
Cu	Spectrophotometric as diethyldithiocarbamate (435 mμ)
Co	Radiometric (Co-60)
Ni	Radiometric (Ni-63)
Pb	Spectrophotometric as dithizonate (510 mμ)
Mn	Spectrophotometric as permanganate (520 mμ)
Mg	Spectrophotometric as oxinate (380 mμ)
Ca	Atomic adsorptiometric Radiometric (Ca-45) Flamephotometric (554 mμ)
Sr	Radiometric (Sr-90) Flamephotometric (460.7 mμ)
Ba	Flamephotometric (515 mμ)

analytical method used for the determination of each metal ion is described in Table 1. In the case of colorimetric methods, MIBK, chloroform, and carbon tetrachloride were apt to be present in the effluent; they had to be removed by evaporation. A small amount of TBP and TOA in the effluent did not interfere with the colorimetric method, but TTA and AcAc did. When TTA or AcAc was present in the effluent, concentrated nitric acid was added to the solution and then the solution was evaporated to dryness to decompose the organic matter.

When the effluent was fractionated in the tubes of a fraction collector, each fraction was submitted to the determination of the metal ions. On the other hand, the whole effluent from one column was collected and evaporated to a small volume under an infrared lamp; then the final solution was made up to 50 ml with a suitable acidic solution. An aliquot of this solution was also pipetted out for the determination of the metal ions.

When a radioactive tracer was employed, each metal ion in the effluent or on the column was checked not only by means of its radioactivity, but also by means of its specific reagent.

Visuable colored bands appearing on a column during the elution (for example, on the AcAc and TTA(1) columns) generally provided a good measure for the column separation: TBP(1) column–Fe(yellow), Sn(yellow); TBP(2) colun–Sb(yellow); AcAc column–Cr(light violet-brown); TTA(1) column–Cu(green), Co(red-brown), Ni(light yellow-green), Pb(light yellow), Mn(orange-yellow).

Results and Discussion

Chromatographic Behavior of Metal Ions. If separation proceeds chromatographically on the basis of only the partition phenomenon, the chromatographic behavior of each metal ion on the column can be predicted by means of this equation: $E=D\cdot B+F$, where D is the batch distribution ratio, which has been otherwise obtained under conditions corresponding to those in the column extraction; E, the volume of the effluent before the emergence of the solute in a maximal concentration in the column; B, the volume of the stationary phase, and F, the volume of the mobile phase in the column.

Actually, the behavior of each metal ion was in good agreement with that predicted from the distribution ratio in the batch extraction. For example, in the TBP-HCl system, the extraction behavior of many metal ions against the concentration of HCl has been investigated in batch extraction by Ishimori *et al.*[12] and with reversed-phase thin layer chromatography by Bark *et al.*[13]; their extraction mechanisms have been also discussed by the latter. Their data, shown by the values of D or R_f, and the results we have obtained here are given in Fig. 2. The behavior of the metal ions in this reversed-phase chromatography agreed with those predicted from the data of the batch extraction and the thin-layer chromatography in relation to the concentration of HCl of the aqueous phase.

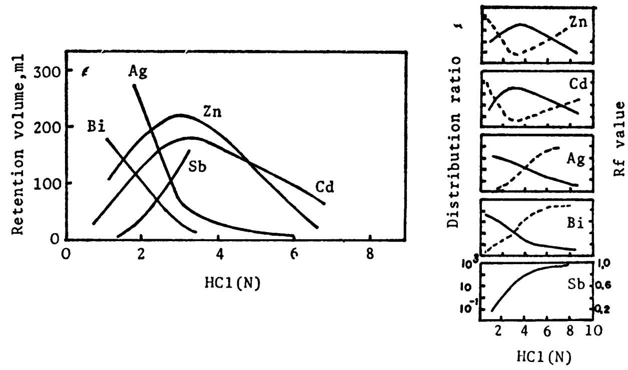

Fig. 2. The retention volume of TBP column and distribution ratio or R_f value as a function of HCl concentration.
—— Ishimori's data by liq.-liq. extraction.
---- Bark's data by reversed-phase thin layer chromatography.

Retention of Individual Ions on the Column. To examine quantitatively the retention of each metal ion on a column, a 50-ml portion of a test solution containing a metal ion was first fed into the column, and then a 100-ml portion of an adequate eluting solution was passed through the column. The amounts of both the metal ion retained on the column and that in the effluent were determined, and the percentages of retention were calculated. No loss of metal ions was found in any column experiment; more than 99% of them could be recovered. The results obtained are illustrated in Table 2. Iron, mercury and tin were perfectly retained on the TBP(1) column from 2 N HCl, and Bi, Ag, Zn, and Cd were also retained on the TOA column from 2 N HCl; Sb was completely retained on the TBP(2) column from 6 N HCl. Chromium and aluminum were retained on the AcAc

Table 2. The retention of individual ions on the columns, conducted separately

Metal	Retained %					
	TBP(1) column	TOA column	TBP(2) column	AcAc column	TTA(1) column	TTA(2) column
Fe(III)	100	100	100			
Hg(II)	100	100	100			
Sn(IV)	100	100	100			
Bi(III)	1.0	100	0			
Ag	0.9	100	0			
Zn	43.2	100	2.1			
Cd	1.6	100	35.8			
Sb(III)	0	9.2	100			
Cr(III)	0	0	0	100		
Al	0	0	0	100		
Cu	0	0	0	0.5	100	
Co	0	0	0	0	100	
Ni	0	0	0	0	100	
Pb	0	0	0	0	100	
Mn(II)	0	0	0	0	100	
Mg	0	0	0	0	100	
Ca	0	0	0	0	0	100
Sr	0	0	0	0	0	100
Ba	0	0	0	0	0	100

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[12] T. Ishimori, K. Watanabe, and E. Nakamura, This Bulletin, **33**, 636 (1960).

[13] L. S. Bark, G. Duncan and R. J. T. Graham, *Analyst*, **92**, 347 (1967).

column, and Cu, Co, Ni, Pb, Mn, and Mg on the TTA column from a 0.5 M ammonium acetate buffer solution of pH 5.0. Calcium, strontium, and barium were perfectly retained on the TTA column from a 0.5 M ammonium acetate solution of pH 7.0. The bismuth, silver, zinc, and cadmium on the TBP(1) column ($D=10$), Sb on the TOA column ($D=5$), Zn and Cd on the TBP(2) column ($D=15$) and Cu on the AcAc column ($D=8$) were not completely washed down from the column because of their relatively higher distribution ratios; they still remained on the lower part of the column. These metal ions could, however, be eluted from the column by the subsequent passing of an adequate eluting solution through the column.

The Bahavior of the Metal Ions in a Mixed Solution on Each Column. In achieving the group separation of cations, it is also necessary to examine the chromatographic behavior of the metal ion in question as well as that of all the other ions by passing mixed solutions through the respective columns in the scheme of group separation. Fig. 3 summarizes the features of the chromatographic behavior of each metal ion in the presence of all the others. This has been constructed of the data collected by many experiments carried out with 50-ml portions of test solutions containing all the metal ions except the metal ion in question. In such a case, the behavior of all the metal ions can not be defined simultaneously; therefore, only the behavior of the desired metal ion was followed by the use of its radioactive tracer, or by other methods, in the presence of all the others.

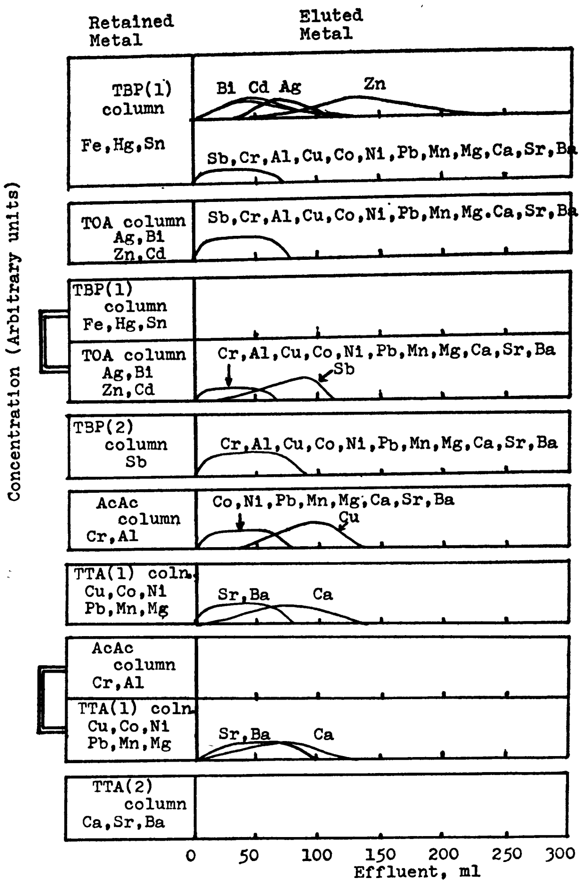

Fig. 3. The behavior of the 19 metal ions on each column. Sample solution: 50 ml, containing each 0.5 mg of cations.

As is shown at the left-hand side in Fig. 3, Fe, Hg, and Sn on the TBP(1) column, Ag, Bi, Zn, and Cd on the TOA column, Sb on the TBP(2) column, Cr and Al on the AcAc column, Cu Co, Ni, Pb, Mn, and Mg on the TTA(1) column, and Ca, Sr, and Ba on the TTA(2) column were retained completely on the upper part of the column, even after 300 ml of the eluting solution had been passed through. On the other hand, most of the other cations passed through each column easily; these data were represented by the elution curves. These results are in good agreement with those shown in Table 2; the results on the TTA(2) column are also in good agreement with those obtained in the previous paper.[14]

A Combined Column Consisting of the TBP(1) and the TOA Columns in Fig. 3: As has been mentioned above, the eluting solutions for both the TBP(1) and TOA columns were of the same acidity. Therefore, if the TBP(1) column could be joined to the top of the TOA column, the separation procedure would become simpler. Fifty milliliters of a test solution containing 19 cations were fed into the combined columns. After a 300-ml portion of the "eluting solution for the TBP(1) column" had been run through the two columns, the metal ions were determined in each fraction of the effluent. Finally, the two columns were disjoined and the metals retained on each column were determined respectively. The result was in good agreement with that obtained with a single column. Therefore, when both the TBP(1) and TOA columns must be employed, a combined column should always be used in the separation process.

The Combined Columns Consisting of the AcAc and TTA (1) Columns in Fig. 3: The acetylacetone column was joined to the top of the TTA(1) column for the same reason as in the case of the TBP(1) and TOA columns. Fifty milliliters of the test solution for the AcAc column were fed into the combined column, and then 200 ml of "the eluting solution for the AcAc column" was run through the column; each fraction of the effluent from the lower column was submitted to a determination of the metal ions. The columns were then disjoined from each other, and the retained metal ions were determined. The results agreed with those obtained in the experiment using the two columns were separately. Thus, it is possible to effect the group separation by using a combination of the AcAc column and the TTA column.

The Group Separation of 19 Common Cations. On the basis of the scheme shown in Fig. 1, the group separation of 19 common cations from their mixtures was carried out without a fraction collector in order to prove the practical usefulness of the method. After the entire course of the scheme had been finished, each column was separated from the other and the metal ions retained on each column were determined.

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[14] I. Akaza, This Bulletin, **39**, 980 (1966).

The actual separation into the six groups was successfully achieved; the results agreed well with the expectations mentioned in the previous paragraph. Consequently, it was clarified that the scheme devised by the present authors was useful and effective for the group separation of 19 common cations, and might also be useful for the practical analysis of a sample solution containing these cations.