SEPARATION OF METAL IONS BY ION-EXCHANGE CHROMATOGRAPHY FROM THE MEDIUM OF TRIETHYLENETETRAMINE - N, N, N', N", N''', N''' - HEXAACETIC ACID

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Procedures for the separation of metal ions on the column of strong acid cation exchanger Dowex 50W X8 were worked out. They are based on the already determined distribution coefficients of 20 metal ions in the medium of triethylenetetramine-N,N,N',N",N'''.N'''-hexaacetic acid. Some of the procedures were applied for the analyses of inorganic materials.

The effect of triethylenetetramine-N,N,N',N",N''',N'''-hexaacetic acid (TTHA) on the sorption of metal ions on strong acid cation exchanger Dowex 50 W X8 was studied in the previous paper[1]. Distribution coefficients and their functions on pH were determined for Cu^{2+}, Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Zn^{2+}, Cd^{2+}, Al^{3+}, In^{3+}, Tl^+, Th^{4+}, Pb^{2+}, Bi^{3+}, Cr^{3+}, UO_2^{2+}, Mn^{2+}, Fe^{3+}, Co^{2+} and Ni^{2+}. Based on those values, procedures for the mutual separation of some of the studied metals by ion--exchange chromatography are presented in this paper.

EXPERIMENTAL

Apparatus and Reagents

The determination of metals by atomic absorption spectrometry (AAS) was carried out on a Perkin-Elmer 306, spectrophotometric measurements on a Unicam SP 800 instruments. Fluorimeter H 960 (Hilger and Watts) and polarograph PO 4 (Radiometer) were used to determine berylium and thalium respectively. Columns with sintered glass discs, 25 cm long and 12 mm internal diameter were used for chromatographic separations. The columns were packed with such amount of an exchanger in the Na^+-form that was equivalent to 4 g of the dry (110°C) resin.

The treatment of the Dowex 50W X8 resin (50—100 mesh), the preparation of stock solutions of metal ions as well as the other used reagents were described in the previous paper[1]. Methods of determination of individual elements were also described in the previous paper[1] and the determination of uranium in the presence of excess thorium in reference[2]. Polarographic determination of Tl^+ in the medium of acetate buffer and EDTA was described by Weiss[3].

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Procedures for the Separation of Binary Mixtures

Separation factor, *i.e.* the ratio of distribution coefficients of two metals is the value that determines the theoretical possibility of the separation of these ions on the ion-exchange column. A successful separation can be achieved[4] when the separation factor is higher than 30 while the distribution coefficient of a weakly retained ion is less than 10. Separation factors for selected pairs of metals were calculated and are presented in Table I.

Following techniques were used to separate the individual pairs of metals:

a) *Selective sorption.* All solutions were prepared by the same way as solutions for the determination of distribution coefficients[1], *i.e.* the concentration of separated ions was kept 0·001M, pH was adjusted by the buffer action of 0·05M monochloroacetic acid (pH 2—3·5), acetic acid (pH 3—5) and at pH > 5 directly by TTHA. The ionic strength 0·1 was maintained by the addition of known amount of 1M-NaClO$_4$. Such solutions were passed through the column of an ion exchanger at the rate 30—50 ml/hour. Weakly retained ion was eluted by 150—200 ml of the eluent (0·001M-TTHA of the same ionic strength and pH). The retained ion was then stripped by 50—100 ml 2M-HCl or 4M-HNO$_3$.

b) *Selective elution.* Both elements were applied at the top of the column from the solution of given pH and ionic strength, but not containing TTHA. Then 150—200 ml 0·003M-TTHA of the given ionic strength and pH was allowed to flow through the column. After the weakly retained ion had been completely eluted, the final stripping was carried out by the solution of an acid.

In all cases the effluents were collected in 10—25 ml portions and analyzed for both separated metals in order to determine the course of elution diagrams and hence to find the efficiency of the separation process.

TABLE I

Calculated Values of Separation Factors
The ion having the higher value of its distribution coefficient is listed as the first.

Separated ions	pH	Separation factor	Separated ions	pH	Separation factor
Mn^{2+}—Fe^{3+}	2·0	3 000	Al^{3+}—Th^{4+}	2·0	>10 000
Mn^{2+}—Fe^{3+}	2·5	5 600	Al^{3+}—In^{3+}	2·0	5 400
Mn^{2+}—Ni^{2+}	2·5	2 300	Al^{3+}—Fe^{3+}	2·0	4 900
Mn^{2+}—Co^{2+}	2·5	48	Cr^{3+}—Fe^{3+}	2·0	900
UO_2^{2+}—Th^{4+}	2·0	>10 000	Be^{2+}—Al^{3+}	4·0	> 5 000
UO_2^{2+}—Bi^{3+}	2·2	840	Be^{2+}—UO_2^{2+}	4·0	35
UO_2^{2+}—Pb^{2+}	3·5	> 300	Cd^{2+}—Cu^{2+}	2·0	120
Tl^+—In^{3+}	2·5—4·5	1 100	Pb^{2+}—Cu^{2+}	2·0	130
Ba^{2+}—Ca^{2+}	7·0	240	Mn^{2+}—Cu^{2+}	2·5	3 400
Ba^{2+}—Mg^{2+}	7·0	160	Ca^{2+}—Zn^{2+}	4·0	4 100
Ba^{2+}—Sr^{2+}	7·0	28	Mg^{2+}—Zn^{2+}	4·0	2 400
Pb^{2+}—Bi^{3+}	2·0—2·2	93	Co^{2+}—Ni^{2+}	2·0	50

c) *Batch method.* Solution of both elements containing 0·001M excess TTHA and adjusted to a given pH and *I* of 0·1 was agitated for 12 hours with such amount of an ion-exchanger in the Na^+-form which is equivalent to 1 g of the dry resin. The slurry was then transferred into the column fitted with a sintered glass disc, the liquid phase was collected and the ion-exchanger eluted with 2M-HCl.

For mixtures where a very sharp separation had been achieved further experiments were aimed at the separation of both metals in various concentration ratio. If the actual concentrations are not specifically mentioned further in the text, the concentration of one of the metals was kept 0·001M while the ratio was changed by decreasing the concentration of the other metal. The 0·001M-TTHA excess, pH and ionic strength were maintained, if not mentioned otherwise.

For very small contents of the strongly retained ion, the column was washed by 100 ml 0·5M--HNO_3 prior to the final elution. This helps to rid the column of the excess Na^+ ions so that the final eluate may then be concentrated by evaporation for the actual determination.

RESULTS

Separation of Binary Mixtures

Binary mixtures of the studied metal ions were separated by the described techniques and the following results were obtained:

a) *Separation of manganese and iron* was studied at pH 2·0 − 2·5. Ferric ions were quantitatively eluted by 150 ml of the eluent while Mn^{2+} ions by 2M-HCl. Under these conditions the separation up to the ratio 1 : 100 can be carried out. The separation process is still effective when the Fe^{3+} concentration is increased up to 0·04M and TTHA concentration up to 0·05M. After the elution by 150 ml 0·001M-TTHA of pH 2 followed by 100 ml 0·5M-HNO_3 the eluate contained less than 0·02% of the original amount of iron and total manganese. The separation was satisfactory even in the ratio 1 : 5000.

b) *Separation of manganese from nickel and manganese from cobalt* was studied at pH 2·5. In both cases a very good separation was obtained; the resulting eluate contained all Mn^{2+}. The separation was also efficient even in the concentration ratio 1 : 100.

Manganese separation from the mixture of iron, nickel and cobalt in the ratio 1 : 2000 : 500 : 500 was tested at pH 2·5 in the solution containing 0·02M-Fe^{3+}, 0·005M-Ni^{2+} and 0·005M-Co^{2+} at the TTHA concentration 0·04M. After the elution by 150 ml 0·001M-TTHA $\left(pH\ 2·5,\ I = 0·1\right)$ followed by 100 ml 0·5M-HNO_3 the final eluate contained 99·5% of the original amount of Mn^{2+}.

c) *Separation of uranium from thorium, bismuth and lead.* The most favourable pH for the separation of UO_2^{2+} and Th^{4+} is 2·0. All Th^{4+} is in 150 ml of the effluate while the 2M-HCl eluate contains 99·9% UO_2^{2+}. The quantitative separation up to the concentration ratio 1 : 1000 may be achieved if the conditions are modified $\left(Th^{4+}\right.$ and TTHA concentrations increased, the column washed by 0·5M-$HNO_3\right)$.

The separation of UO_2^{2+} and Bi^{3+} at pH 2·2 is also quantitative.

The separation factor for UO_2^{2+} and Pb^{2+} has its maximum at pH 3·5, the actual separation was, nevertheless, not complete. Only 80 ml of the eluent was required to elute not only all Pb^{2+} but also more than 50% of UO_2^{2+}.

d) Separation of thalium and indium can be carried out in the wide range of pH 2·5 − 4·5. All indium was in 100 ml of the effluent while 99% Tl^+ was found in 100 ml of the 2M-HCl eluate. The separation can successfully be carried out up to the ratio 1 : 1000.

e) Separation of barium from calcium and barium from magnesium is efficient when the technique of the selective elution at pH 7·0 is employed. The column with the sorbed ions was eluted by 100 ml 0·001M-TTHA (pH 7·0, I 0·1). The eluate contained all Ca^{2+} and Mg^{2+} ions respectively. Ba^{2+} was then stripped by 100 ml 4M-HNO$_3$. After the amounts of the sorbed calcium and magnesium had been increased and the column washed by 0·01M-TTHA, barium was separated even in the ratio 1 : 1000. In all experiments, more than 98% barium was found in the final eluate $(4M\text{-}HNO_3)$.

The separation of barium and strontium is less effective. The final eluate contains not only all barium but also approximately 10% of the original amount of strontium. Sr^{2+} ions pass into the final eluate even if the columns containing smaller amount of an ion-exchanger $(0·5 − 1 \text{ g})$ are used.

f) Separation of lead and bismuth was followed at pH 2·0 − 2·2. Total Bi^{3+} is eluted by 80 ml 0·001M-TTHA while the Pb^{2+} ions are in 100 ml of the 2M-HCl eluate. The technique of the selective sorption makes possible to separate lead and bismuth up to their ratio 1 : 1000 under modified conditions (concentrations of Bi^{3+} and TTHA increased, the column washed by 0·5M-HNO$_3$).

g) Separation of aluminium from thorium and aluminium from indium. Both separations may be carried out by the selective elution of Th^{4+} and In^{3+} ions respectively from the column of an ion-exchanger by 0·001M-TTHA of pH 2·0.

h) Separation of aluminium from iron and chromium from iron was tested by various techniques but it was not found satisfactory due to the mutual contamination of individual fractions. Best results were achieved by the batch method with solutions of pH 2·0. The final eluate of 2M-HCl contained 95% Al^{3+} and 0·6% Fe^{3+}. Similarly in the separation of chromium and iron, 96% Cr^{3+} and 0·6% Fe^{3+} was found in the final eluate.

i) Separation of berylium from aluminium and berylium from uranium. Berylium may be separated from aluminium by the selective sorption at pH 4·0. Important is to boil the solution before the sorption process to enhance the complexing of Al^{3+}. The final eluate contains 98% Be^{2+} together with 0·8% of the original Al^{3+}. The medium of pH 4·0 is also suitable for the separation of berylium from uranium. 150 ml

of the eluent contains 99·7% UO_2^{2+} while 0·4% UO_2^{2+} and 99·5% Be^{2+} was found in the 2M-HCl eluate.

j) *Separation of cadmium, lead and manganese from copper.* Separation of cadmium and copper was carried out at pH 2·0. All Cu^{2+} ions are eluted by 100 ml 0·001M-TTHA while 99·4% Cd^{2+} was found in the 2M-HCl eluate. For the quantitative separation of lead and copper, pH 1·5 had to be used. The final eluate contained 99·7% Pb^{2+} and only 0·1% Cu^{2+}. The separation of manganese and copper was carried out at pH 2·5. The eluate contained all Mn^{2+} and also 0·09% Cu^{2+}.

k) *Separation of calcium and magnesium from zinc.* Both separations can be most favourably carried out at pH 4·0. After the elution by the eluent, the final 2M-HCl eluate contained 100% Ca^{2+} as well as 0·4% Zn^{2+} and 99·3% Mg^{2+} as well as 0·5% Zn^{2+} respectively.

l) *Separation of cobalt and nickel.* Best results were obtained when the pH of the starting solution was lowered to 1·7. 150 ml of the eluent $(0·001M$-TTHA, pH 1·7, I 0·1$)$ contained all Ni^{2+} ions and 1·4% Co^{2+} while the remaining 98·6% Co^{2+} was found in the 2M-HCl eluate.

Analytical Applications

It results from the above outline that some of the studied separation processes are highly effective and reliable even in very inconvenient concentration ratios of both elements. Several analytical applications for the determinations of trace components in inorganic materials have been worked out.

a) *Determination of traces of uranium in thorium compounds.* Measure 25 ml aliquots of the stock solution of 0·1M-Th(NO$_3$)$_4$. 5 H$_2$O (Merck, containing less than $1 . 10^{-4}$% U) and add the series of 5, 4, 3, 2 and 1 ml $1 . 10^{-4}$M solution of a UO_2^{2+} compound. Further measure 5 ml 0·5M monochloroacetic acid, 15 ml 0·1M-TTHA and adjust pH to 2·0 by the addition of 1M-NaOH. Maintain the ionic strength I 0·1 by the calculated addition of 0·5M-NaClO$_4$ and make up the volume to 50 ml. Pass the solution through the column of Dowex 50W X8 in the Na$^+$-form at the rate 40—50 ml/hour. Wash the column by 150 ml of the eluent (0·01M-TTHA, 0·05M monochloroacetic acid, pH 2·0, I 0·1) followed by 100 ml 0·5M-HNO$_3$ and 50 ml water. Elute the sorbed UO_2^{2+} ions by 50 ml 2M-HCl and determine their concentration spectrophotometrically using Arsenazo III (ref.[2]).

If uranium is determined in thorium sulphate or acetate, both elements are first transferred to nitrates by their precipitation by dilute (1 + 1) NH$_4$OH, dissolving the precipitate in 5 ml concentrated HNO$_3$, evaporation almost to dryness and by diluting by water. Further procedure was identical as already described.

The results of the determination are shown in Table II.

b) *Determination of barium in limestone.* Add 3 ml water to 0·25 g of the sample on the PTFE dish. Further add 15 ml hydrofluoric acid and after the evolution of CO$_2$ has ceased, 1 ml HClO$_4$. Evaporate the contents of the dish till white fumes of HClO$_4$ appear, then add 2 ml of saturated solution of H$_3$BO$_3$ and evaporate to dryness. Dissolve the residue in hot 2 ml concentrated HNO$_3$

and 10 ml water. Transfer the solution into a 150 ml beaker, add 30 ml 0·1M-TTHA, 5 ml 0·5M acetic acid and adjust pH to 5·5 by the addition of 1M-NaOH. Pass the solution through the column of Dowex 50W X8 in the Na^+-form at the rate 30—40 ml/hour. Wash the column by 100 ml of the eluent (0·01M-TTHA, pH 7·0) followed by 100 ml 1M-HCl and 50 ml water. Elute the retained Ba^{2+} ions by 100 ml 4M-HNO_3, add 1 ml 30% H_2O_2 and evaporate to dryness. Dissolve the residue in 0·5 ml concentrated HNO_3 and 5 ml water and measure the absorbance using atomic absorption spectrometer with a three-slot burner fed by the acetylene–air mixture at 553 nm.

The results of the barium determination in three samples of limestones from Bohutín and their comparison with the results obtained by other method[5] are presented in Table III.

TABLE II

Determination of Uranium in Thorium Compounds

Th^{4+} added mg	U(VI) added mg	U(VI) found %
580	23·8	115·0[a]
580	47·6	110·0[a]
580	71·4	101·7[a]
580	95·2	101·2[a]
580	119·0	101·0[a]
232	23·8	110·0[b]
232	71·4	101·6[b]
232	119·0	100·4[b]
232	23·8	109·5[c]
232	71·4	101·5[c]
232	119·0	100·6[c]

Analysed compound: Thorium: [a] nitrate, [b] sulphate, [c] acetate.

TABLE III

Determination of Barium in Limestones

Sample	Found % Ba	Standard method[5] % Ba
Limestone I	0·063	0·064
Limestone II	0·020	0·019
Limestone III	0·0046	0·0044

c) *Determination of manganese in steel.* Dissolve 0·1 g sample of steel in 25 ml boiling dilute (1 : 1) HCl with the addition of 0·3 ml 30% H_2O_2. Make up the volume of the dissolved sample to 100 ml in a volumetric flask. Measure 10 ml aliquot part of the sample, add 5 ml 0·1M-TTHA, 5 ml 0·5M monochloroacetic acid, adjust pH 2 by the addition of 1M-NaOH and maintain the ionic strength I 0·1 by the addition of the calculated amount of 0·5M-NaClO$_4$. Make up the volume to 50 ml and pass the solution through the column of Dowex 50W X8 in the Na$^+$-form at the rate 40—50 ml/hour. Wash the column by 100 ml of the eluent (0·01M-TTHA, 0·05M mono-chloroacetic acid, pH 2·0, $I = $ 0·1) followed by 100 ml 0·5M-HNO$_3$ and 50 ml water. Elute the retained Mn^{2+} ions by 100 ml 2M-HCl. Evaporate the solution, make it up to an appropriate volume (10—25 ml) and measure the absorbance by AAS using a acetylene–air mixture at 279 nm.

The main advantage of this procedure is the elimination of the interference of Fe^{3+} ions and it is therefore possible to prepare standard solutions simply by the dilution of the stock solution of Mn^{2+}.

The method was applied to the determination of manganese in the Czechoslovak standard sample of steel No 3-2-02 with the certified content of 0·74% Mn. The presented procedure gave the result of 0·75% Mn.

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