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Retention of Heavy Metals and Their Separation on Silica Gel Modified with Calconecarboxylic Acid

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Abstract

Sorption of 35 metal ions on silica gel impregnated with a mixture of Aliquat 336 and calconecarboxylic acid was investigated. It was found that the complexation of metals is relatively rapid, and the relative capacity of the sorbent is different for various metals and increases with pH. Only alkali metals are not retained on the sorbent, and alkaline earth metals are retained from solutions of pH > 4, contrary to other metal ions. The retained metals can be eluted from the sorbent with dilute solutions of hydrochloric or perchloric acid without elution of the chelating reagent. The sorbent was used for the preconcentration of trace amounts of heavy metals from aqueous solutions in the presence of macroamounts of sodium, potassium, calcium, and magnesium as well as for the separation of some metal ion mixtures by extraction chromatography.

INTRODUCTION

The determination of trace amounts of heavy metals in various materials often requires their preliminary concentration and their separation from macroamounts of other metals for elimination of the matrix effect. Besides commercial chelating resins used for these purposes, other chelating sorbents have recently found increasing popularity (*1*), and especially interesting are silica gels modified with various chelating reagents (*2–5*). Although the synthesis of chelating sorbents is rather difficult, many of them can be obtained in a simple manner by impregnating silica gel with a mixture of liquid anion exchanger and sulfonated chelating reagent (*6*). Silica gels impregnated with a mixture of Aliquat 336 and nitroso-R-salt (*7*, *8*), thorin (*9*), or Eriochrome Black T (*10*, *11*) were used for preconcentration of metal ions from dilute aqueous solutions for the separation of metal ion mixtures by column extraction chromatography or for additional purification of some analytical grade reagents before their determination by atomic absorption spectrometry or anodic stripping voltammetry.

It was earlier found that calconecarboxylic acid (CCA), known also as Patton-Reeder indicator (*12*), is very strongly extracted into Aliquat 336 in chloroform, forming stable ion-pairs with alkylammonium cations (*13*). Although only the reaction of calcium with CCA in alkaline media has been described (*14*), the structure of the reagent suggests that other metal ions should also form complexes with it, and we therefore decided to prepare silica gel modified with CCA and to investigate its properties.

EXPERIMENTAL

Materials

Aliquat 336 (General Mills Chemicals, USA) was purified from iron by washing a chloroform solution of this salt with 0.1 *M* HCl and then several times with doubly distilled water. Calconecarboxylic acid [(2-hydroxy-4-sulfo-1-naphtylazo)-3-naphtoic acid]-Ind. (POCh, Poland) was used without further purification.

Silica gel 100, 0.063–0.2 mm (Merck, F.R.G.), previously fractionated (the fraction of particle size 0.1–0.2 mm being collected) and purified from iron in the manner described previously (*7*), was used as a support for the stationary phase.

Aqueous metal ion solutions were prepared by dilution of Titrisol standard metal salt solutions (Merck, F.R.G.) or were prepared from appropriate analytical grade reagents [nitrates of Ag, Hg(I), U(VI), Ga, In, Bi, La, Th, or $K_2Cr_2O_7$ and K_2TeO_3].

Working solutions were freshly prepared from standard metal salt solutions by dilution with doubly distilled water and adjusted to an appropriate pH with a mixture of HCl and KCl (pH 1 and 2), tartrate buffer (pH 3–6), or borax buffer (pH 9).

Solutions of perchloric and hydrochloric acids (Suprapur, Merck, F.R.G.) were used as eluants.

Apparatus

A single beam AAS 1N (Zeiss, G.D.R.) atomic absorption spectrophotometer was used for determination of Ca, Mg, Sr, Cu, Fe, Co, Ni, Zn, Cd, Mn, Ag, Pb, and Hg; barium, sodium, and potassium were determined by flame emission spectrometry. Other metals were determined spectrophotometrically with a UV-VIS VSU 2P spectrophotometer (Zeiss, G.D.R.). pH measurements were made with a Mera-Elwro N 517 (Poland) direct reading pH meter with a glass-calomel electrode assembly.

Procedure

The impregnating solution was prepared by shaking an appropriate volume of 0.01 *M* solution of Aliquat 336 in freshly distilled chloroform with 5 volumes of 0.001 *M* aqueous solution of CCA. After separating the phases, the organic phase was filtered through a cellulose filter to remove the remaining aqueous solution. Silica gel was impregnated with a chloroform solution of Aliquat 336 + CCA in the following manner. 200 mL of the organic solution (containing 1 mmol CCA and 2 mmol Aliquat 336) was mixed with 8.59 g silica gel. The diluent was then evaporated with a vacuum evaporator on a water bath. 1 g of the chelating sorbent obtained contained 0.1 mmol CCA and 0.2 mmol Aliquat 336.

Small glass columns (110 × 5 mm) dry packed with 0.4 g sorbent were used for the determination of the relative capacities of the sorbent toward metal ions. 50 mL of the solution containing 5 mg of the metal ion to be tested was passed during 5 minutes through the column, and unretained metal was determined in the eluate by AAS or spectrophotometrically.

Glass columns (290 × 8 mm) dry packed with 5 g of the sorbent were used for the separation of metal ion mixtures as well as for the preconcentration of traces of Zn, Cu, and Fe(III) in the presence of macroamounts of alkali and alkaline earth metals. Chromatographic separations were performed in the following manner. After the column had been washed with 10 mL of pH 5 buffer solution, a 100-mL volume of the synthetic solution of pH 5 containing 0.1 mg of each metal ion separated was passed through the column. The metals were eluted with perchloric acid solution, 5 mL fractions being collected using fraction collector 301 (Premed, Poland). Metals were determined in single fractions by AAS or spectrophotometrically.

The influence of the contact time on the relative capacity of the sorbent toward some chosen metal ions was investigated by the static method. 0.4 g of the sorbent was then shaken with 5 mL of the metal salt solution (previously adjusted to an appropriate pH) containing 0.3 mg of the metal ion investigated. The mixture was subsequently centrifuged, and the metal ion in the solution was determined.

The influence of the flow rate on the capacity of the sorbent was investigated by using small columns packed with 0.4 g of the sorbent. 5 mL of the solution containing 0.3 mg of the metal ion being tested was then passed through the column, and unretained metal was determined in the eluate. The flow rate was regulated by using a syringe pump.

In a similar manner column experiments were performed under conditions where the relative capacity of the sorbent was somewhat higher than the amount of metal ion in the solution being passed through the column. Columns packed with 0.5 g of the sorbent were then used, and 5 mL volumes of the solution containing 0.15 mg of each metal ion being tested were passed through the column.

RESULTS AND DISCUSSION

In preliminary experiments it was found that calconecarboxylic acid is very strongly bound with Aliquat 336 on the surface of silica gel, and elution of the complexing agent requires high concentrations of mineral acids to be passed through the column. CCA was only partially eluted with 2 *M* perchloric acid or 10 *M* hydrochloric acid, which confirmed earlier predictions (*13*) about the high stability of the ion-pair composed of quaternary alkylammonium cation and an anion of CCA.

The relative capacities of the sorbent toward the metal ions increased with the pH of the solution passed through the column (see Table 1). Only alkali metal ions were unretained even at pH 9, whereas some metal ions were retained from distinctly acidic solutions [Ga, In, Tl, Bi, Sb, Ti, V(IV), W(VI), and Fe(III)]. Alkaline earth metals were retained at pH > 4.0, but the relative capacities of the sorbent toward these metal ions in alkaline media were relatively high. It should be added that the maximum capacities of the sorbent toward some metal ions should be somewhat higher than the values given in Table 1 since the capacities were estimated at high elution rates (10 mL/min).

All metals can be eluted from the sorbent with dilute solutions of mineral acids (0.1 *M* $HClO_4$ or 1 *M* HCl) which did not elute CCA from the sorbent, which makes it possible to repeat the sorption–elution

TABLE 1
Relative Capacities of the Sorbent

	Sorption capacity (μmol/g) at pH									Elution	
Metal	1	2	3	4	4.5	5	5.5	6	9	HCl (*M*)	$HClO_4$ (*M*)
Mg	0	0	0	0	0.9	4.6	10.1	14.7	28.4	0.001	0.0001
Ca	0	0	0	0	0.7	3.2	9.2	12.6	22	0.001	0.0001
Sr	0	0	0	0	0.5	3.1	6.2	9.4	17	0.001	0.0001
Ba	0	0	0	0	0.3	2.4	5.8	8.2	15.3	0.001	0.0001
Al	0	0	2.5	4.1	—	—	—	6.3	[a]	0.1	0.01
Ga	2.4	5.1	[a]	[a]	—	—	—	[a]	[a]	1.0	0.1
In	0.6	1.1	2.3	[a]	—	—	—	[a]	[a]	1.0	0.1
Tl(I)	1.2	2.3	4.3	7.2	—	—	—	10.5	16.2	1.0	0.1
Pb	0	0	2.1	3.6	—	—	—	5.6	9.3	—	0.01
As(III)	0	0	1.4	2.8	—	—	—	4.6	6.8	0.1	0.01
Sb(III)	1.3	[a]	[a]	[a]	—	—	—	[a]	[a]	1.0	0.1
Bi	1.5	[a]	[a]	[a]	—	—	—	[a]	[a]	1.0	0.1
Se(IV)	0	0.8	4.2	5.3	—	—	—	7.6	12.1	0.1	0.01
Te(IV)	0	1.2	3.1	4.2	—	—	—	5.8	9.8	0.05	0.005
Ti(IV)	1.4	2.7	4.7	5.9	—	—	—	7.2	16.4	0.05	0.005
V(V)	1.8	2.3	3.5	4.1	—	—	—	5.8	9.7	0.05	0.005
Cr(III)	0	0.8	4.4	6.2	—	—	—	8.2	12.1	0.05	0.005
Cr(VI)	0	0.9	4.8	6.4	—	—	—	9.0	14.3	0.05	0.005
Mo(VI)	0	2.3	6.3	7.6	—	—	—	9.8	16.2	0.05	0.005
W(VI)	1.2	2.1	4.4	6.1	—	—	—	9.2	16.4	0.5	0.05
Mn(II)	0	0	8.2	9.4	—	—	—	11	21.4	0.1	0.01
Fe(III)	8.2	[a]	[a]	[a]	—	—	—	[a]	[a]	1.0	0.1
Co	0	1.1	3.9	5.7	—	—	—	8.7	15.3	0.1	0.01
Ni	0	1.3	5.6	7.8	—	—	—	11.2	17.4	0.1	0.01
Cu(II)	0	2.2	8.2	9.9	—	—	—	12.4	23.2	0.1	0.01
Ag	0	0.6	1.6	2.2	—	—	—	3.1	9.2	—	0.01
Zn	0	0	0.8	3.1	—	—	—	6.2	13.4	0.01	0.001
Cd	0	0	0.7	2.7	—	—	—	5.4	10.2	0.01	0.001
Hg(I)	0	0	0.6	1.4	—	—	—	2.2	4.3	—	0.05
Hg(II)	0	0	0.9	1.7	—	—	—	2.8	5.1	0.5	0.05
La	0	0	1.3	2.0	—	—	—	3.8	5.4	0.1	0.01
Th	0	0	1.6	2.7	—	—	—	4.2	9.3	0.1	0.01
U(VI)	0	0	1.2	2.2	—	—	—	3.5	8.4	0.1	0.01

[a] Hydrolysis or metal hydroxide precipitate.

process many times in the same column. On the other hand, the concentrations of acids quantitatively eluting the metals from the sorbent were different for various metals.

Although in the experimental conditions used some metals could be retained by a sorbent containing an excess of quaternary alkylammonium chloride relative to the amount of CCA also in the form of simple anions (TeO_3^{2-}, SeO_3^{2-}, MoO_4^{2-}, and $Cr_2O_7^{2-}$ or CrO_4^{2-}) or chloride complexes, some metals were retained from solutions of pH 1 and 2 buffered with a mixture of HCl and KCl [Fe(III), Bi, Sb, and In]. The increase of the relative capacity of the sorbent with pH for other metal ions indicates their retention in the form of metal complexes with CCA.

The sorption kinetics of some chosen metal ions were investigated by static and dynamic methods (Fig. 1).

The relative capacities of the sorbent changed with time in a different manner for various metals (Fig. 2). The maximum values for calcium, magnesium, chromium, and cadmium were reached rapidly whereas the complexation of copper and especially of aluminum required a longer shaking time (30 or 60 min). It should be added that experiments performed for metals at other pH values (4 or 9) gave similar results—only the maximum values of the capacities were different.

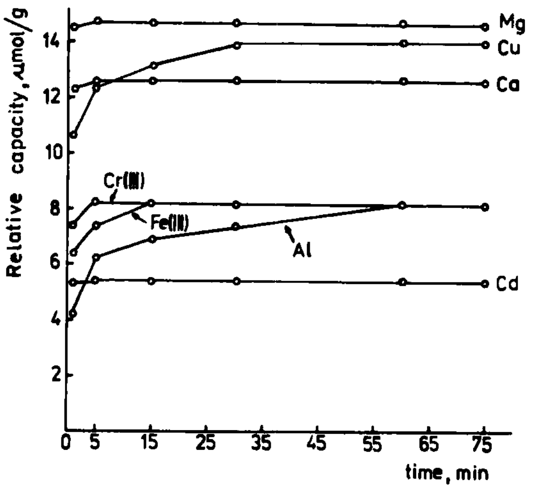

FIG. 1. Relative capacities of sorbent toward metal ions [determined by the static method at pH 6 except for iron(III) which was determined at pH 1] as a function of shaking time.

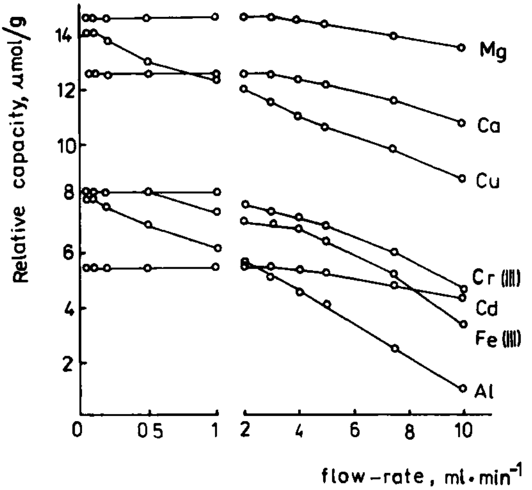

FIG. 2. Relative capacities of sorbent toward metal ions as a function of the flow rate of solution (pH 6 except for iron which was determined at pH 1) passed through the column.

These observations have been confirmed by experiments performed with the dynamic method. The relative capacities for magnesium and calcium decreased only insignificantly with an increase of the flow rate of the solution passed through the column, whereas they distinctly decreased for copper and especially for aluminum (Fig. 3), which confirms the slow complexation kinetics of these metals.

Since the capacity of the sorbent in a column used for the concentration of a metal should be higher than the amount of metal ion present in the solution passed through the column, several experiments were carried out under these conditions. The results obtained are illustrated by Fig. 4 in the form of the percentage of metal ion recovery as a function of the flow rate of the solution. Metal ions relatively slowly complexed with CCA (aluminum) were quantitatively retained by the sorbent at a flow rate of 5 mL/min.

The different pH values required for the sorption of various metals from aqueous solutions suggested the possibility of the concentration of heavy metals and their separation from macroamounts of alkali and alkaline earth metals. To verify this supposition, a 100-mL volume of the synthetic aqueous solution was adjusted to pH 4.0 with tartrate buffer. It contained 1% Na, 0.14% Mg, 0.04% Ca and K, and 5 × 10^{-5} % of Zn, Cu,

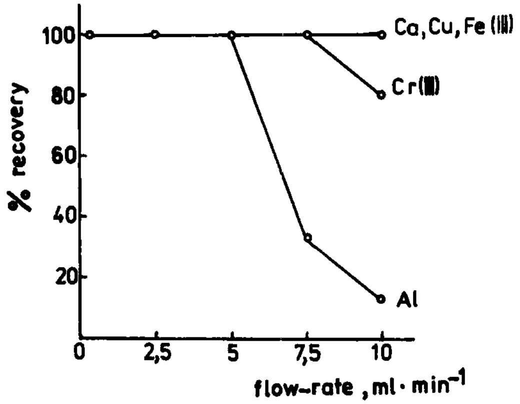

FIG. 3. Percent recovery of some metals vs flow-rate relationships.

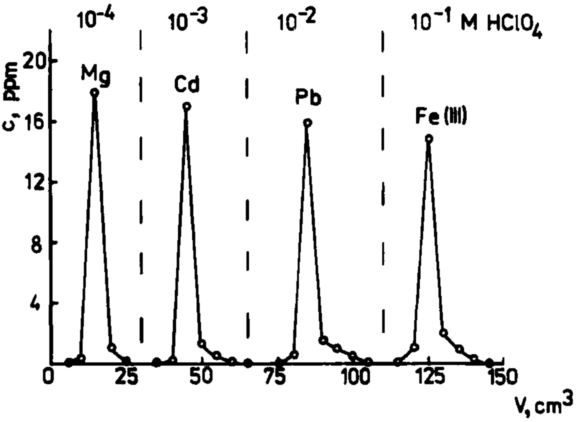

FIG. 4. Separation of the synthetic mixture Mg-Cd-Pb-Fe(III) containing 100 μg of each metal ion separated on silica gel treated with a mixture of Aliquat 336 and CCA. Mean flow rate: 1 mL/min.

and Fe(III), and was passed through the column. After the column had been washed with 15 mL of doubly distilled water, all unretained metals (Ca, Mg, Na, and K) were found in the collected eluates. The retained metals (Zn, Cu, and Fe) were then eluted with 5 mL of 0.5 *M* $HClO_4$ and determined in the eluate by AAS. Recoveries higher than 98% were found for each retained metal ion. Thus, in the authors' opinion, the proposed sorbent can be utilized for the preconcentration of traces of heavy metals from aqueous solutions and for the elimination of the matrix effect of alkali and alkaline earth metals in the determination of heavy metals by conventional analytical methods. It should be added that a column packed with the proposed sorbent can be used many times in sorption–elution processes owing to the very high concentrations of mineral acids required for the elution of CCA from the sorbent. This supposition was verified in sorption–elution processes for iron, chromium, zinc, and magnesium performed several times with use of the same column since reproducible results in the determination of metals in eluates were obtained.

Different concentrations of mineral acids required for elution of some metal ions from the sorbent can be utilized for the separation of some metal ion mixtures. Examples of some extraction–chromatographic separations performed by stepwise elution with perchloric acid solutions are illustrated by Figs. 4–7. It should be added that all chromatographic bands were relatively sharp, even for metals [Fe(III), Sb, Bi] which should hydrolyze in the pH 5 solutions introduced into the column.

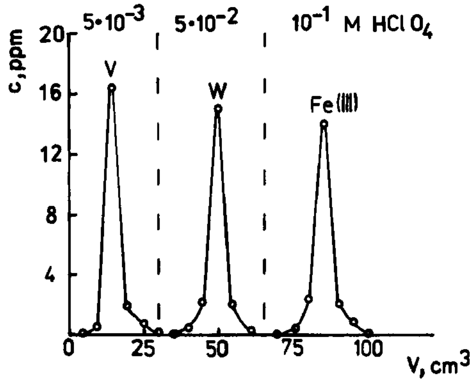

FIG. 5. Separation of the mixture V(V)-W(VI)-Fe(III). Separation conditions as in Fig. 4.

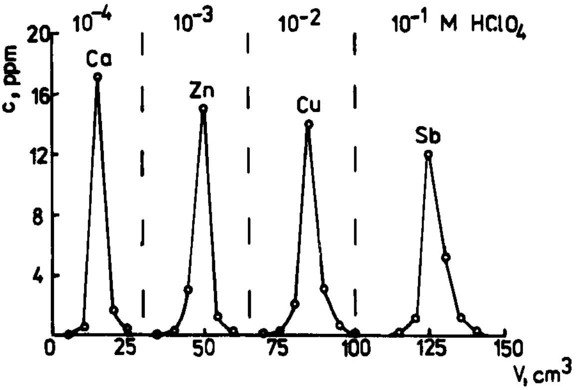

FIG. 6. Separation of the mixture Ca-Zn-Cu-Sb. Separation conditions as in Fig. 4.

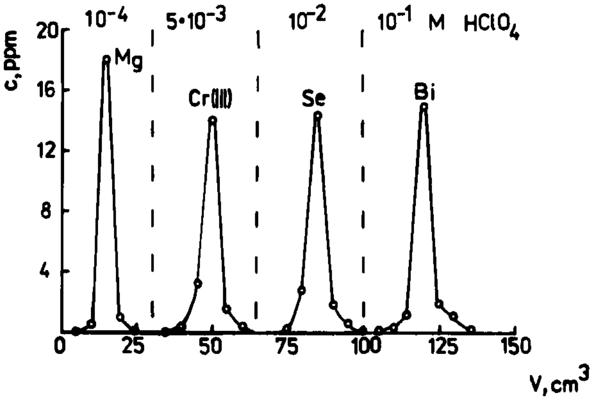

FIG. 7. Separation of the mixture Mg-Cr(III)-Se(IV)-Bi. Separation conditions as in Fig. 4.

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