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Additional Purification of Some Salts by Using Silica Gel Modified with Calmagit as a Sorbent

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Abstract

Sorption of 35 metal ions from aqueous solutions in the pH range between 1 and 9 by silica gel impregnated with a mixture of Aliquat 336 and Calmagit was investigated. The retained metals can be eluted with dilute solutions of hydrochloric or perchloric acids. The sorbent was used for purification of some potassium, sodium, and ammonium salts from trace amounts of zinc, lead, cadmium, and copper. The effectiveness of purification was confirmed by anodic stripping voltammetry. Some metal ion mixtures have also been separated by using column extraction chromatography and stepwise elution with perchloric acid solutions.

INTRODUCTION

Silica gels modified with some sulfonated hydroxyazo dyes [Eriochrome Black T (*1*, *2*), calconecarboxylic acid (*3*), and Chromotrop 2B (*4*)] and obtained in a simple manner by impregnation of silica gel with a mixture of Aliquat 336 and chelating reagent have been proposed as chelating sorbents for the preconcentration of heavy metals from dilute aqueous solutions and their separation from macroamounts of alkali and alkaline earth metals as well as for separation of metal ion mixtures by column extraction chromatography. In this paper some properties of a new chelating sorbent—silica gel modified with Calmagit—are described. The sorbent was prepared mainly for additional purification of some high purity alkali metal salts used as supporting electrolytes in polarography and especially in anodic stripping voltammetry since the very high sensitivity of the latter method is decreased through trace amounts of zinc, lead, cadmium, and copper present in supporting electrolyte solutions.

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EXPERIMENTAL

All experiments were done at room temperature (21 ± 2°C).

Materials

Calmagit (Aldrich-Chemie, FRG) was used as supplied without further purification. Other reagents and aqueous metal salt solutions were the same as described previously (*3*).

Apparatus

A single beam AAS 1N (Zeiss, GDR) atomic absorption spectrophotometer was used for the determination of Ca, Mg, Sr, Cu, Fe, Co, Ni, Zn, Cd, Mn, Ag, Pb, and Hg; Ba, Na, and K were determined by flame emission spectrometry. Other metals were determined spectrophotometrically with a UV-VIS VSU 2P spectrophotometer (Zeiss, GDR). A voltammetric analyzer UPE-2a (Radius, Poland) was used for the determination of traces of lead, cadmium, zinc, and copper in aqueous solutions of potassium, sodium, and ammonium salts by anodic stripping voltammetry. A graphite electrode, impregnated with epoxy resin and coated with mercury film *in situ,* was used as a working electrode with a working area of 12.5 mm^2. The details of the preparation of this electrode were described by Sykut et al. (*5*).

Procedure

The impregnating solution was prepared by shaking an appropriate volume of a 0.01-*M* solution of Aliquat 336 in freshly distilled chloroform with 5 volumes of a 0.001-*M* aqueous solution of Calmagit. After separating the phases, the organic phase was filtered through a cellulose filter. Silica gel was impregnated with a chloroform solution of Aliquat 336 + Calmagit in the following manner: 200 mL of the organic solution was mixed with 8.7 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 Calmagit and 0.2 mmol Aliquat 336. Voltammetric determination of metals was performed in the following manner: 10 mL volumes of solutions of potassium or ammonium chlorides (analytical grade) were passed through a column packed with 5 g of the sorbent. The columns packed with 1 g sorbent were used only when doubly distilled water or a solution of sodium chloride Suprapur (Merck, FRG) was purified. Mercuric nitrate was subsequently added into each solution [the concentration of $Hg(NO_3)_2$ in the solution was 10^{-4} *M*]. Into one previously purified potassium chloride solution, 2 μL volumes of standard Cu^{2+}, Cd^{2+}, Pb^{2+}, and Zn^{2+} ions of 100 ppm concentration were introduced (concentration of each metal ion

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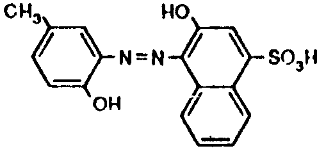
added to the solutions was then 20 ppb). Oxygen was removed from the analyzed solutions with a stream of argon of special purity. The solutions were electrolyzed for 3 min at −1.2 V. Anodic oxidation of metals was subsequently performed at an amplitude of 1.2 V and a speed of potential change of 10 mV/s. Other details of the procedure and the column packings were analogous to those described previously (*3*).

RESULTS AND DISCUSSION



Calmagit, a popular indicator in the complexometric determination of calcium and magnesium (*6*, *7*), has also been proposed for the spectrophotometric determination of these metals (*8*, *9*) as well as of aluminum (*10*), thorium (*11*), and rare earth elements (*12*). Preliminary experiments performed in our laboratory indicated a very strong extraction of Calmagit from aqueous solutions into Aliquat 336 in chloroform. The partial elution of this reagent from silica gel coated with a mixture of Aliquat 336 and Calmagit required relatively high concentrations of perchloric (>0.07 *M*) and especially of hydrochloric (>5 *M*) acids.

The relative capacities of silica gel modified with Calmagit toward metal ions are collected in Table 1. The capacities increase with pH for all the metal ions investigated, but in a somewhat different manner. Some metals are retained on columns packed with this sorbent even at pH 1 [Ga, In, Tl, Bi, Sb, Fe(III), and Cu]; all other metals are retained at pH 3 except Ca and Mg, which are retained at pH $\geq$ 4. The concentrations of acids eluting the retained metals are differentiated: elution of metals forming stable complexes with Calmagit [Fe(III), Cu, Tl, Ga, In] requires relatively high concentrations of HCl (>0.5 *M*) or $HClO_4$ (>0.1 *M*) whereas alkaline earth metals are easily eluted with very dilute solutions of hydrochloric (0.001 *M*) or perchloric (0.0005 *M*) acids.

The relative capacities of silica gel modified with Calmagit toward aluminum and chromium distinctly decrease with the flow rates of solutions passed through the column (see Fig. 1); however, an inconsequential effect of the flow rate on the capacity of sorbent was observed for zinc, calcium, and magnesium. The investigations performed using the static method (sorbent shaken with aqueous metal salt solutions) confirmed the low speed of complexation for inert aquo complexes of chromium and aluminum.

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TABLE 1

The Relative Capacities of the Sorbent toward Metal Ions (μmol/g) and Minimal Concentrations of Acid (mol/L) Required for Elution (1 g of the chelating sorbent contained 0.1 mmol Calmagit and 0.2 mmol Aliquat 336)

	Sorption at pH								Elution	
Metal	1	2	3	4	4.5	5	6	9	HCl (*M*)	$HClO_4$ (*M*)
Na	0	0	0	0	—	—	0	0	—	—
K	0	0	0	0	—	—	0	0	—	—
Mg	0	0	0	0	0.7	3.1	16.1	29.2	0.001	0.0001
Ca	0	0	0	0	0.6	3.2	15.4	28.6	0.001	0.0001
Sr	0	0	0	0	0.4	2.8	14.1	26.1	0.001	0.0001
Ba	0	0	0	0	0.3	2.5	12.8	24.3	0.001	0.0001
Al	0	0	2.6	4.4	—	—	6.8	11.4	0.1	0.01
Ga	2.2	4.3	^{a}	^{a}	—	—	^{a}	^{a}	1.0	0.1
In	0.5	0.9	2.1	^{a}	—	—	^{a}	^{a}	1.0	0.1
Tl	0.9	1.7	3.6	6.1	—	—	9.8	15.4	1.0	0.1
Pb	0	0	1.9	3.4	—	—	6.6	9.1	—	0.01
As(III)	0	0	1.3	3.6	—	—	4.4	6.4	0.1	0.005
Sb(III)	1.1	^{a}	^{a}	^{a}	—	—	^{a}	^{a}	1.0	0.1
Bi(III)	1.2	^{a}	^{a}	^{a}	—	—	^{a}	^{a}	1.0	0.1
Se(IV)	0	0.6	3.6	5.1	—	—	7.4	11.8	0.1	0.01
Te(IV)	0	1.3	3.0	4.1	—	—	5.6	10.0	0.05	0.01
Ti(IV)	1.1	2.3	4.5	5.8	—	—	7.1	15.7	0.05	0.01

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V(V)	1.3	2.1	3.6	3.9	—	—	5.8	9.6	0.05	0.01
Cr(III)	0	0.8	4.2	6.0	—	—	8.0	11.7	0.05	0.005
Cr(VI)	0	0.9	4.6	6.2	—	—	8.6	14.4	0.05	0.005
Mo(VI)	0	2.2	6.2	7.5	—	—	9.4	16.0	0.5	0.005
W(VI)	0.9	2.0	4.2	5.9	—	—	8.9	16.1	0.1	0.05
Mn(II)	0	0	6.5	8.2	—	—	11.2	23.1	0.05	0.01
Fe(III)	4.3	[a]	[a]	[a]	—	—	[a]	[a]	0.5	0.1
Co	0	0.9	3.6	5.4	—	—	10.1	16.7	0.1	0.01
Ni	0	1.1	3.8	7.3	—	—	11.1	17.0	0.1	0.01
Cu	0.8	2.4	6.6	8.3	—	—	14.5	25.0	0.5	0.05
Ag	0	0.7	1.7	2.1	—	—	2.9	8.2	—	0.01
Zn	0	0	1.0	2.8	—	—	6.2	12.5	0.01	0.005
Cd	0	0	0.9	2.6	—	—	5.3	10.2	0.01	0.005
Hg(I)	0	0	0.5	1.3	—	—	2.0	3.8	—	0.01
Hg(II)	0	0	0.8	1.6	—	—	2.5	4.8	0.1	0.01
La	0	0	1.2	1.7	—	—	3.7	5.2	0.1	0.01
Th	0	0	1.6	2.7	—	—	4.0	9.1	0.1	0.01
U(VI)	0	0	1.1	2.1	—	—	3.2	8.0	0.1	0.01

[a] Hydrolysis or metal hydroxide precipitate.

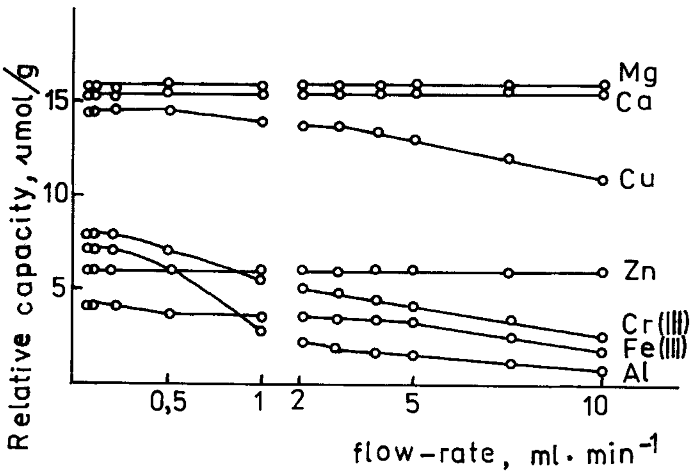

FIG. 1. Relative capacities of sorbent toward metal ion as a function of the flow rate of the solution (pH 6 except for iron which was determined at pH 1) passed through the column.

Maximal values of the relative capacities for these metals were reached only at very long shaking times (75 min).

When the sorbent capacity was somewhat higher than the amount of metal ion present in the solution passed through the column, quantitative

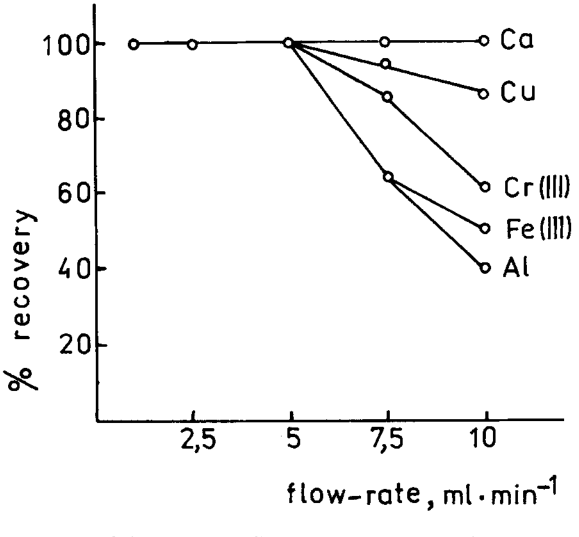

FIG. 2. Percent recovery of the metals vs flow rate relationships (the amounts of the metals in solutions were 25% lower than the maximal relative capacity of the sorbent).

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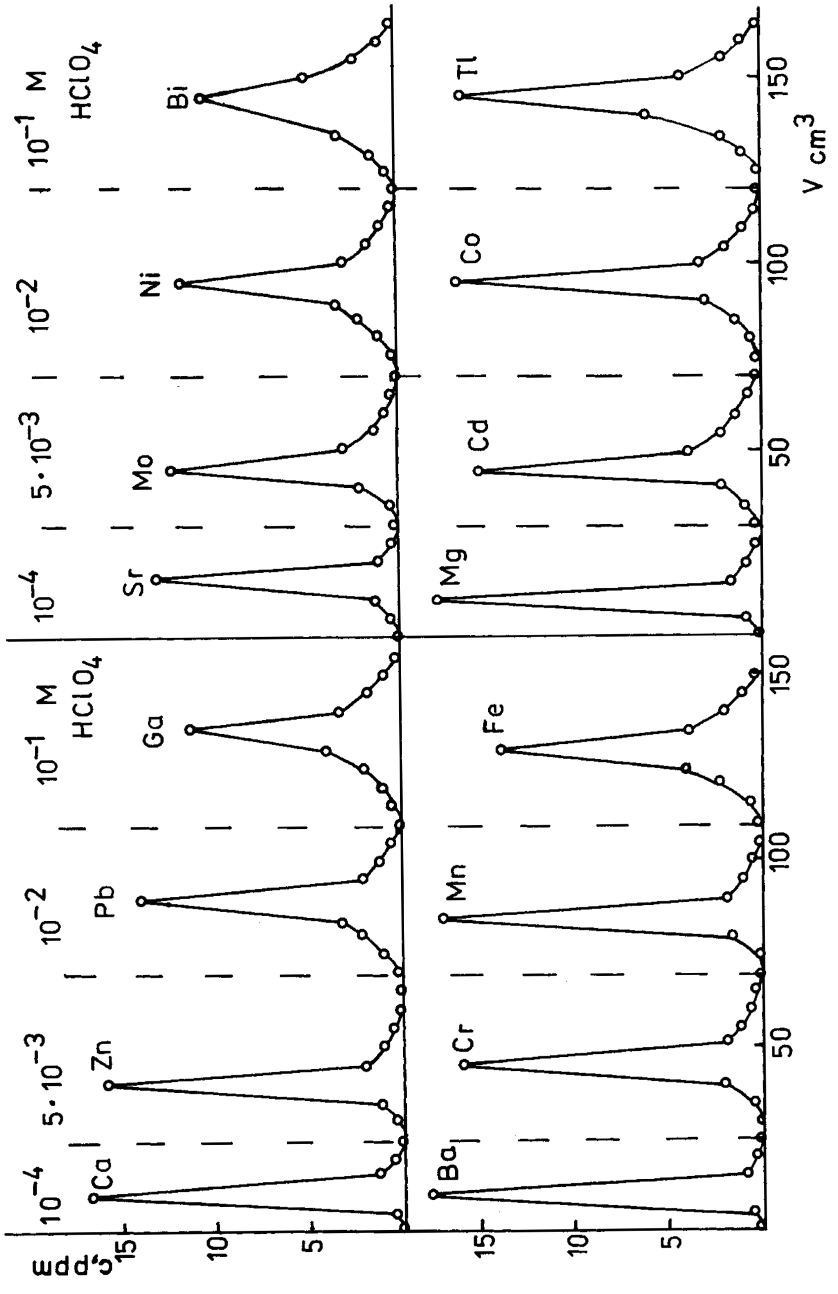

FIG. 3. Separations of metal ion mixtures containing 100 μg of each metal ion to be separated. Columns packed with 5 g silica gel modified with Calmagit.

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sorption was reached at relatively high flow-rates (5 mL/min) even for aluminum and chromium (Fig. 2).

Silica gel modified with Calmagit can be used for the separation of metal ion mixtures by column extraction chromatography by utilizing the different concentrations of perchloric acids eluting various metals. Some examples of the chromatographic separations performed are illustrated by Fig. 3.

Since all metals except the alkali metals are retained from aqueous solutions at pH ≥ 4 by silica gel impregnated with a mixture of Aliquat 336 and Calmagit, it was expected that this sorbent could be used for additional purification of alkali metals or ammonium salts (especially from heavy metals). Therefore, several anodic stripping voltammetric measurements for aqueous solutions of these salts and for the same solutions passed

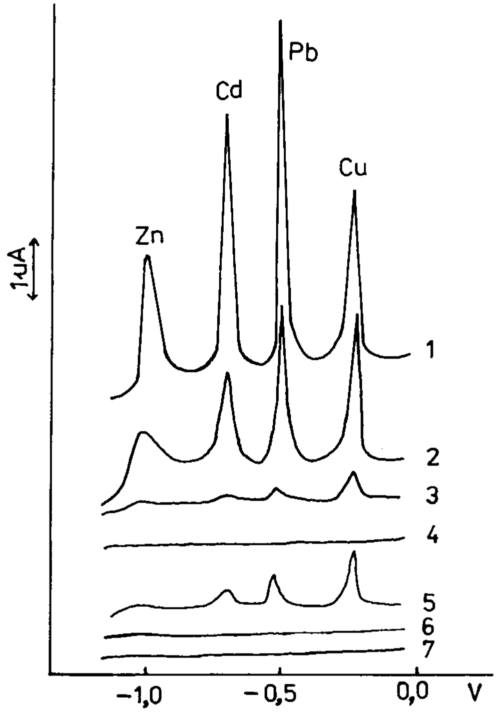

FIG. 4. Voltammograms for 10 mL volumes of aqueous metal salt solutions. 1: 0.5 *M* KCl (analytical grade) to which Zn, Cd, Pb, and Cu was added (concentration of each metal ion, 20 ppb). 2: 0.5 *M* KCl (analytical grade). 3: 9 mL of 0.1 *M* NaCl Suprapur + 1 mL of 0.5 *M* KCl previously purified. 4: Sample 3 passed through the column with a sorbent. 5: 9 mL of 0.1 *M* NH_4Cl of analytical grade + 1 mL of purified 0.5 *M* KCl. 6: Sample 5 passed through the column. 7: Sample 2 passed through the column packed with a sorbent.

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through columns packed with the proposed sorbent have been performed.

The voltammograms illustrated by Fig. 4 confirm this supposition. Although the potassium chloride and ammonium chloride (analytical grade) solutions contained considerable amounts of copper, lead, cadmium, and zinc (traces of these metals were also found in 0.1 *M* sodium chloride Suprapur solution), these metals were completely removed after passing these solutions through columns packed with silica gel modified with Calmagit. In the author's opinion, the proposed sorbent could also be useful for additional purification of alkali metals or ammonium salts solutions used as supporting electrolytes in some electrochemical methods of analysis, especially in anodic stripping voltammetry, since the theoretically extremely high sensitivity of this method ($\sim 10^{-12}$ mol/L) is limited in practice by impurities of metal ions present in supporting electrolytes and even in doubly distilled water.

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