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Silica Gel Modified with Methylthymol Blue for Separation and Preconcentration of Trace Amounts of Heavy Metals from Some Salts

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ABSTRACT

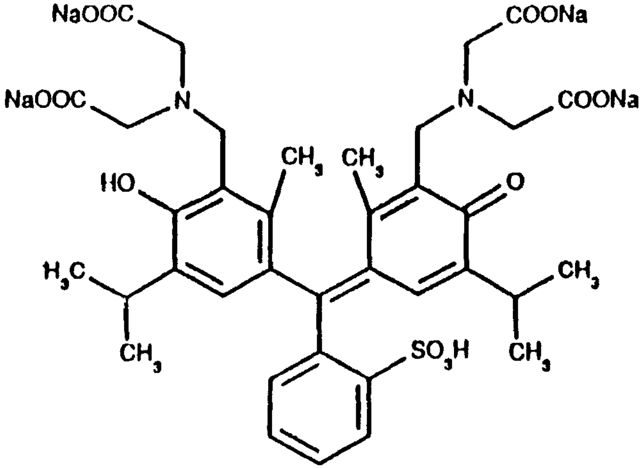
The sorption of 16 metal ions on silica gel impregnated with a mixture of Aliquat 336 and Methylthymol Blue was investigated. It was found that the sorption behavior depends upon the species and the pH of the loading solution. Alkali-metal ions were not retained under any of the investigated conditions. The retained metals can be eluted from the sorbent with dilute solutions of hydrochloric or perchloric acid without significant elution of the chelating reagent. The method was used for the purification of some salts from trace amounts of zinc, lead, cadmium, and copper. The effectiveness of the purification was confirmed by anodic stripping voltammetry. Some metal-ion mixtures were also separated by using column-extraction chromatography and stepwise elution with perchloric-acid solutions.

INTRODUCTION

Much attention has been paid in recent years on chelating sorbents which are utilized for selective or nonselective concentration of metal ions from aqueous solutions as well as for separation of metal-ion mixtures (1–3). Especially interesting for these purposes are silica gels modified with various chelating reagents (4).

A chelating sorbent can be obtained simply by impregnation of silica gel with a mixture of Aliquat 336 (methyltricaprylammonium chloride) and a sulfonated chelating reagent (5). Sorbents containing some sulfonated hydroxyazo dyes such as Eriochrome Black T (6), Calconecarboxylic acid

(7), Chromotrop 2B (8), Calcon (9), Calmagit (10), and other chelating reagents such as Nitroso-R-Salt (11) and Titan Yellow (12) have been proposed as sorbents for preconcentration of trace amounts of heavy metals from aqueous solutions (before determination of these metals by atomic absorption spectrometry or other conventional methods). They can also be used to separate trace metal ions from macroamounts of alkali and alkaline earth metals, as well as to separate metal ion mixtures by column-extraction chromatography. This paper describes properties of a new chelating sorbent-silica gel modified with Methylthymol Blue {3,3′-bis[*N*,*N*-di(carboxymethyl)aminomethyl]thymol sulfonephtalein sodium salt}:



EXPERIMENT

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

Materials

The Methylthymol Blue (POCh, Gliwice, Poland) was purified by recrystallization from methanol. The other reagents and aqueous metal salt solutions were the same as previously described (7).

Apparatus

A single-beam, Pye Unicam atomic absorption spectrometer was used to determine the metals, except for aluminum, which was determined spectrophotometrically using Alizarin Red S and a Specol 11 VIS spectrophotometer (Zeiss, Germany). Measurements of pH were made with a Mera-Elwro N 517 (Poland) direct-reading pH meter using a glass–silver chloride electrode assembly. A voltammetric analyzer UPE-2a (Radius, Poland) was used to determine trace amounts of copper, lead, cadmium, and zinc dissolved in a potassium chloride solution by anodic stripping voltammetry. A graphite electrode, impregnated with epoxy resin and coated in situ with a mercury film [the concentration of mercury(II) ions in the sample solution was 10^{-4} mol/L^{-1}], was used as a working electrode having a working area of 12.5 mm^2. The details of the preparation of this electrode were previously described by Sykut et al. (13).

Procedure

The impregnating solution was prepared by shaking an appropriate volume of a 0.025-M solution of Aliquat 336 in freshly distilled chloroform with 2.5 volumes of a 0.005-M aqueous solution of Methylthymol Blue.

After separating the phases, the organic phase was filtered through a cellulose filter to remove any residual aqueous solution. Silica gel was soaked in a chloroform solution of Aliquat 336 + Methylthymol Blue in the following manner: 100 mL of the organic solution containing 1.19 g (0.0025 M) of Aliquat 336 and 1.06 g (0.00125 M) of Methylthymol Blue was mixed with 10.25 g of silica gel, and the solvent was evaporated using a vacuum evaporator on a water bath. Under those conditions, 1 g of the chelating sorbent contained 0.1 mmol of Methylthymol Blue and 0.2 mmol of Aliquat 336.

Small polypropylene columns 55 mmL × 5 mmϕ (Baker, USA) were packed with 0.25 g of dry sorbent and used to determine the relative capacity of the sorbent toward different metal ions. Five milliliters of each solution containing 0.5 mg of the metal to be tested (previously adjusted to an appropriate pH) were flowed through each column for 5 minutes. Each treated solution was tested to determine the residual metal ion concentrations. The influence of the flow rate on the sorbent capacity was investigated using small columns packed with 0.25 g of the sorbent. Five milliliters of the solution containing 0.25 g of the metal ion being tested was then flowed through the column at different rates, and the eluate was analyzed for the metal ion being tested. The flow rates were regulated by using a syringe pump.

Columns (65 mmL × 13 mmϕ) packea with 4 g of dried sorbent were used to study the separation of metal ion mixtures. After conditioning the column with 1 mL of buffer solution at pH 9, 10 mL of the synthetic solution of pH 9 containing 100 μg of each metal ion separated was flowed through the column. The metals were then eluted with perchloric acid solutions, and the eluate was collected in 5-mL fractions.

Voltammetric determination of metals was performed by flowing 10 mL 0.5 mol/L^{-1} potassium chloride solution containing mercury(II) nitrate through columns packed with 1 g of the sorbent. Standard solutions of Cu^{2+}, Cd^{2+}, Pb^{2+}, and Zn^{2+} ion were also introduced (the concentration of each metal ion added in the solution was then 20 ppb). The solutions were electrolyzed for 3 minutes at −1.3 V. Anodic oxidation of the metals was subsequently performed at an amplitude of −1.3 V and a change of potential of 10 mV/s^{-1}. Oxygen was removed by bubbling the solutions with high-purity argon.

Stripping of Methylthymol Blue from the organic phase with aqueous solutions of mineral acids was performed in the following manner. Five milliliters of the organic solution was shaken for 10 minutes with an equal volume of aqueous appropriate acid solution. The aqueous phase was subsequently centrifuged, and the dye was then determined spectrophotometrically at 444 nm on the basis of a calibration graph. A tenth of a gram of the sorbent obtained was shaken for 10 minutes with 5 mL of an appropriate acid solution in small tubes. The solution was subsequently centrifuged, and the concentration of the eluted chelating reagent was determined as described above.

RESULTS AND DISCUSSION

Phthaleins and sulfophaleins comprise an important group of chelating reagents. Many of them are complexons (aminopolycarboxylic-type chelating compounds) such as Methylthymol Blue.

Methylthymol Blue is a popular reagent used in the spectrophotometric determination of many metal ions (14). It is also used as an indicator in complexometric analyses in a wide range of pHs.

This paper describes the properties of silica gel modified with Methylthymol Blue as a sorbent for metals. Our preliminary experiments indicated the strong extraction of Methylthymol Blue from aqueous solutions into Aliquat 336 in chloroform (15). The high stability of this ion pair was confirmed by the high concentrations of hydrochloric (>1 M) or perchloric acid (<0.05) required to partially elute the Methylthymol Blue from the silica gel impregnated with a mixture of Aliquat 336 and Methylthymol Blue (Fig. 1).

The prepared sorbent contained as excess of Aliquat 336 to ensure the higher resistance of the chelating reagent bound with Aliquat 336 toward strong mineral acids used as eluents for metals.

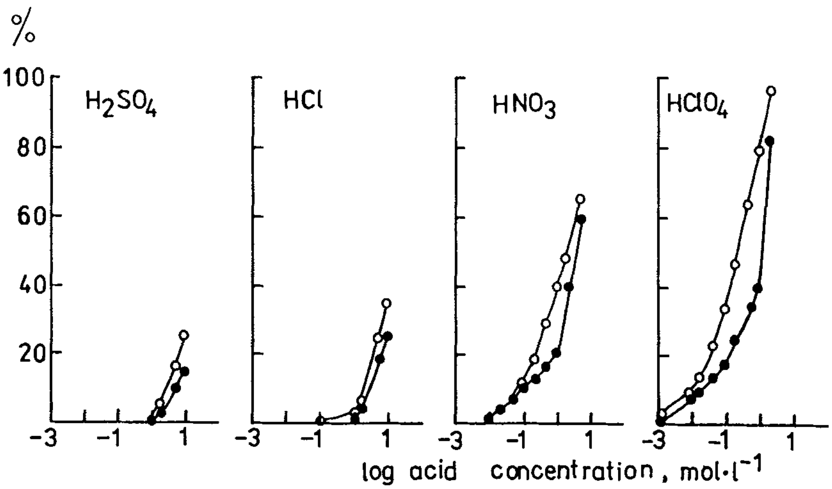


FIG. 1 Percentage of Methylthymol Blue eluted from silica gel impregnated with a mixture of Aliquat 336 and Methylthymol Blue (●) or reextracted from the organic phase as a function of the concentration of mineral acids used as eluants or reextractions.

The relative capacities of silica gel modified with Methylthymol Blue toward the metal ions investigated increase with an increased pH of the solutions passed through the column (Table 1).

Although in the experimental conditions used some metals could be retained by a sorbent containing an excess of quaternary alkyl-ammonium chloride relative to the amounts of dye also in the form of chloride complexes [some metals retained from solutions of pH 1 buffered with a mixture of HCl and KCl are Fe(III) and Bi], 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 the dye.

Alkali metal ions were unretained even at pH 9 whereas some metal ions were retained from acidic solutions [Fe(III), Bi]. Alkaline earth metal ions were retained at pH > 5. The elution of metal ions forming stable complexes with Methylthymol Blue [Fe(III), Bi] (16) requires relatively high concentrations of HCl (>0.1 M) or $HClO_4$ (0.01 M) whereas alkaline earth metals are easily eluted with very dilute solutions of hydrochloric or perchloric acids (0.0001 M). The relative capacities of the sorbent toward aluminum and chromium decreased with increasing loading rates (Fig. 2). However, the effect of the flow rate on the capacity of sorbent for calcium, zinc, and magnesium was negligible. The investigations performed using a batch method (sorbent shaken with aqueous metal salt

TABLE 1
Relative Capacities of the Sorbent toward Metal Ions (μmol/g) and Acid Concentrations (mol/L) Required for the Elution of Several Metal Ions[a]

Metal	Sorption at pH					Elution	
	1	3	5	6	9	$HClO_4$ (M)	HCl (M)
Ca	0	0	0	1.4	5.1	0.0001	0.0001
Mg	0	0	1.2	3.4	8.3	0.0001	0.0001
Al	0	2.4	4.2	5.7	10.2	0.001	0.005
Cu	0	4.7	8.4	10.2	16.8	0.005	0.01
Fe(III)	1.2	6.8	[b]	[b]	[b]	0.01	0.1
Co	0	3.4	7.6	10.1	15.3	0.001	0.01
Ni	0	2.3	6.5	9.1	14.3	0.001	0.01
Zn	0	1.1	4.1	6.1	9.2	0.001	0.005
Cd	0	0	1.3	3.6	6.2	0.001	0.01
Pb	0	0	2.2	6.3	9.4	0.001	
Cr(III)	0	0	3.4	7.1	10.2	0.001	0.005
Bi	2.1	4.3	[b]	[b]	[b]	0.01	0.1

[a] One gram of the chelating sorbent contained 0.1 mmol Methylthymol Blue and 0.2 mmol Aliquat 336.

[b] Hydrolysis.

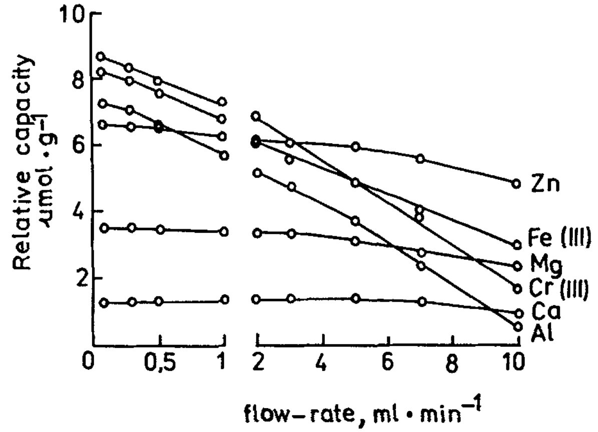


FIG. 2 Relative capacities of the sorbent toward metal ions as a function of the flow rate of the solution passed through the column (pH 6, except for iron, which was determined to have a pH of 3).

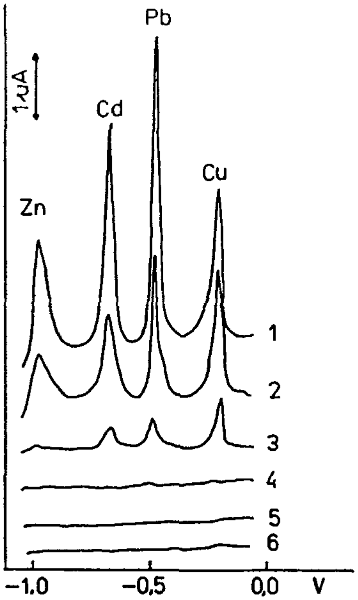


FIG. 3 Voltammograms for 10 mL volumes of aqueous potassium chloride solutions after 3-minute electrolysis at − 1.3 V. Curves: (1) 0.5 M KCl (analytical grade) to which Zn, Cd, Pb, and Cu were added (the concentration of each metal ion is 20 ppb); (2) 0.5 M KCl (analytical grade); (3) 0.5 M KCl (Suprapur); (4) sample 3 after treatment; (5) sample 2 after treatment; (6) sample 1 after treatment.

solutions) confirmed the slow complexation of aluminum or chromium inert aquo complexes (or polymeric hydroxy species) in the pH range 5–6. Equilibrium capacities for these metals were reached only at very long shaking times (70 minutes).

Since all metals except alkali and alkaline earth metals can be retained from aqueous solutions at pH < 5, it is conceivable that this sorbent could be used for additional purification of alkalies, alkaline earth metals, or ammonium salts from heavy metals. To prove this concept, three different solutions, as described in Fig. 3, were flowed through columns filled with sorbent.* As shown in Fig. 3, copper, lead, cadmium, and zinc were almost completely removed.

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* The after-treatment solutions were analyzed for residual heavy metals using anodic stripping voltammetry. Figure 3 shows the voltammetric analysis of the three solutions before and after treatment.

Increased concentrations of mineral acids can be used to separate some metal ion mixtures previously loaded in the sorbent. Examples of some extraction chromatographic separations performed by stepwise elution with perchloric acid solutions are illustrated in Fig. 4.

It was found that a column packed with the sorbent can be reused many times due to the high concentrations of mineral acids required to remove the Methylthymol Blue from the sorbent. This supposition was verified in repetitive sorption–elution process tests using zinc, cadmium, lead, and copper. Tests performed five times with the same column showed reproducible results. The extremely high sensitivity of the anodic stripping

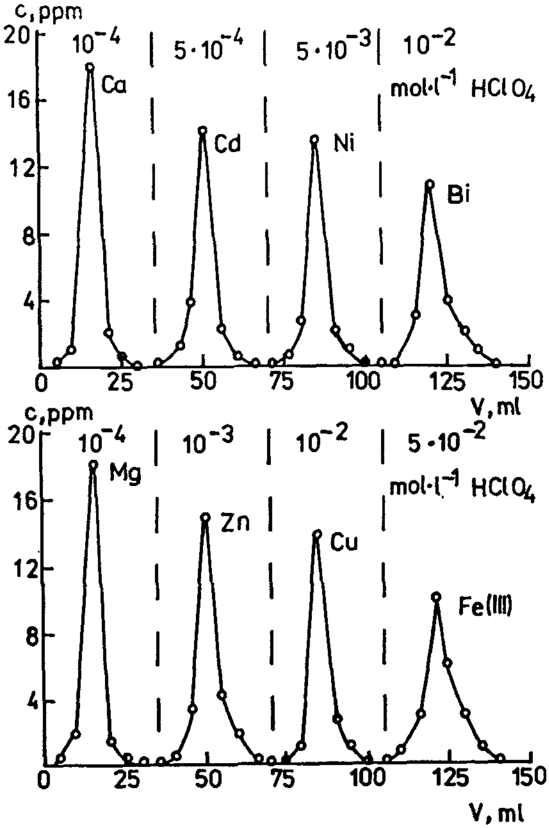

FIG. 4 Separation of metal ion mixtures containing 100 μg of each metal ion, using silica gel soaked with a mixture of Aliquat 336 and Methylthymol Blue. Columns packed with 5 g of "dry" sorbent. Mean flow rate: 1 mL/min^{-1}.

voltammetry ($\sim 10^{-12}$ mol/L^{-1}) is, in practice, limited by the impurities in the supporting electrolytes. The proposed sorbent could be used to purify those solutions in order to achieve the maximum sensitivity. Similarly, the sorbent could be useful to preconcentrate traces of heavy metals from aqueous solutions (e.g., drinking water or seawater) and to eliminate matrix effects of alkali and alkaline earth metals in the determination of heavy metals by atomic absorption spectrometry.

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REFERENCES

1. G. V. Myasoedova and S. B. Savvin, *Khelatoobrazuyushche sorbenty*, Nauka, Moscow, 1984.
2. A. Mizuike, *Enrichment Techniques for Inorganic Trace Analysis*, Springer Verlag, Berlin, 1983.
3. M. Marhol, *Ion Exchangers in Analytical Chemistry*, Academia, Prague, 1982.
4. M. A. Marshall and H. A. Mottola, *Anal. Chem.*, *57*, 729 (1985).
5. S. Przeszlakowski, E. Soczewiński, R. Kocjan, J. Gawecki, and Z. Michno, Polish Patent 128,743, November 1985.
6. S. Przeszlakowski and R. Kocjan, *Analyst*, *110*, 1077 (1985).
7. S. Przeszlakowski and R. Kocjan, *Sep. Sci. Technol.*, *24*, 291 (1989).
8. R. Kocjan, *Chem. Anal.* (*Warsaw*), *36*, 473 (1991).
9. R. Kocjan and S. Przeszlakowski, *Talanta*, *39*, 63 (1992).
10. R. Kocjan, *Sep. Sci. Technol.*, *27*(3), 409 (1992).
11. S. Przeszlakowski and R. Kocjan, *Chromatographia*, *15*(11), 717 (1982).
12. R. Kocjan, *Analyst*, *117*, 741 (1992).
13. K. Sykut, I. Cukrowski, and E. Cukrowska, *J. Electroanal. Chem.*, *115*, 137 (1980).
14. Z. Marczenko, *Spectrophotometric Determination of Elements*, Warsaw, 1979.
15. M. Garbacka, Diploma Dissertation, Medical School, Lublin, 1992.
16. J. Inczedy, *Complex Equilibria in Analytical Chemistry*, PWN, Warsaw, 1979.

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