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SHORT COMMUNICATION

ADDITIONAL PURIFICATION OF ALKALI OR ALKALINE EARTH SALTS BY USING SILICA GEL MODIFIED WITH PYROCATECHOL VIOLET AS A SORBENT

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Summary—Sorption of 14 metal ions on silica gel impregnated with a mixture of Aliquat 336 and Pyrocatechol Violet was investigated. It was found that alkali metals and calcium are not retained on the sorbent, magnesium is retained from solutions of $pH > 6$, contrary to other metal ions. The sorbent was used for purification of some salts from trace amounts of heavy metals and magnesium. Some metals ion mixtures have also been separated by using column extraction chromatography stepwise elution with perchloric acid solutions.

Modern analytical separations and on-line preconcentration of metal ions are very useful tools in analytical chemistry. Selective precolumns have been used for on-line concentration with selective elution of interfering matrix components.[1] Column switching, reinjection and suppressor techniques have been employed for the separation and matrix elimination of metals.[2]

Chelating sorbent used in analysis of metals can be obtained in a very simple manner by impregnation of silica gel with a mixture of Aliquat 336 (methyltricaprylammonium chloride) and a sulfonated chelating reagent.[3] The sorbents containing some sulfonated hydroxyazo dyes [Eriochrome Black T,[4] Calconecarboxylic Acid,[5] Chromotrop 2B,[6] Calcon,[7] Calmagit][8] and other chelating reagents [Nitroso-R-Salt,[9] Titan Yellow][10] 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) 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 Pyrocatechol Violet—are described.

EXPERIMENTAL

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

Reagents

Pyrocatechol Violet (POCh Gliwice, Poland) was purified by recrystalization from methanol). Other reagents and aqueous metal salt solutions were the same as described previously.[7]

Procedure

The impregnating solution was prepared by shaking an appropriate volume of a 0.025 mol/l solution of Aliquat 336 in freshly distilled chloroform with 2.5 volumes of a 0.005 mol/l aqueous solution of Pyrocatechol Violet.

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 + Pyrocatechol Violet in the following manner: 100 ml of the organic solution containing 1.19 g (0.0025 mol) of Aliquat 336 and 0.49 g (0.00125 mol) of Pyrocatechol Violet was mixed with 10.8 g silica gel. The diluent was then evaporated with a vacuum evaporator on a water bath. One gram of the chelating sorbent obtained contained 0.1 mmol Pyrocatechol Violet and 0.2 mmol Aliquat 336. Other procedures and apparatus used were the same as described previously.[7]

RESULTS AND DISCUSSION

Pyrocatechol Violet is a common reagent used in the spectrophotometric determination of many metal ions, as well as the indicator in complexometric analysis.[11] The preliminary experiments performed in our laboratory indicated the strong extraction of Pyrocatechol Violet from aqueous solutions into Aliquat in chloroform.[2]

The high stability of this ion-pair was confirmed by the relative high concentration of hydrochloric (>0.5 mol/l) or perchloric (>0.005 mol/l) acid required for a partial elution of this dye from silica gel impregnated with a mixture 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.

The relative capacities of silica gel modified with Pyrocatechol Violet toward metal ions investigated increase with pH of the solution passed through the column (Table 1).

Calcium ions (contrary to other chelating sorbents obtained earlier in our laboratory) also alkali metal ions were not retained even at pH 9, whereas some metal ions (Fe(III), Bi) were retained from distinctly acidic solutions and magnesium was retained at pH ⩾6. The concentration of acids eluting the retained metals are differentiated: elution of metals forming stable complexes with Pyrocatechol Violet [Bi[13]] require relatively high concentrations of HCl (>0.1 mol/l) or $HClO_4$ (0.01 mol/l) whereas magnesium is easily eluted with very dilute solutions of hydrochloric, or perchloric acids (0.0001 mol/l).

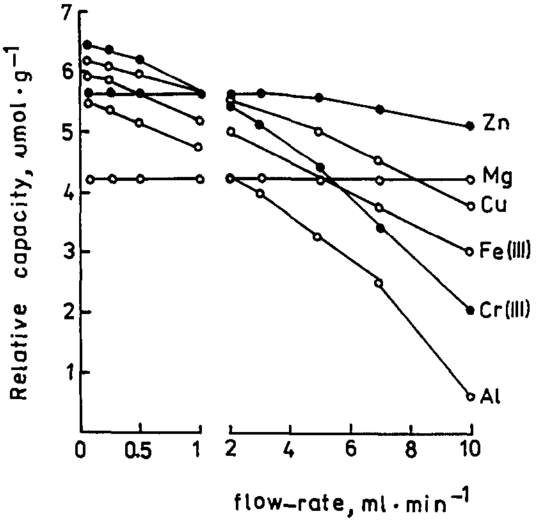

Fig. 1. Relative capacities of the sorbent toward metal ions as a function of the flow rate of the solution passed through the column (pH 6 except for iron which was determined at pH 3).

Table 1. The relative capacities of the sorbent toward metal ions (µmol/g) and minimal concentrations of acid (mol/l) required for elution of metal ions (1 g of the chelating sorbent contained 0.1 mmol Pyrocatechol Violet and 0.2 mmol Aliquat 336)

	Solution at pH					Elution	
Metal	1	3	5	6	9	$HClO_4$	HCl
Mg	0	0	0	4.2	6.2	0.0001	0.0001
Al	0	0.8	3.2	4.2	9.4	0.001	0.005
Cu	0	2.1	4.2	5.6	7.8	0.001	0.005
Fe(III)	1.1	5.2	*	*	*	0.01	0.1
Co	0	3.8	6.4	8.6	10.2	0.001	0.01
Ni	0	1.2	3.1	4.3	16.4	0.001	0.01
Zn	0	1.6	3.8	5.6	8.3	0.001	0.01
Cd	0	0	1.1	2.4	5.6	0.0005	0.001
Pb	0	0	2.0	4.6	8.1	0.0005	—
Cr(III)	0	0	3.1	5.6	9.2	0.001	0.005
Bi	3.2	6.6	*	*	*	0.01	0.1

*Hydrolysis.

The relative capacities of silica gel modified with Pyrocatechol Violet toward aluminium and chromium distinctly decreased with increasing flow rates of the solutions passing through the column (see Fig. 1); however the effect of the flow rate on the capacity of sorbent for zinc and magnesium was negligible. The investigations performed using a static method (sorbent shaken with aqueous metal salt solutions) confirmed the low rate of complexation for inert aquo complexes (or polymeric hydroxy species) formed in the pH range 5–6 for chromium and aluminium: maximum values of the relative capacities for these metals were reached only at very long shaking times (70 min).

Different concentrations of minimal acids required for elution of metals 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 in Fig. 2.

It should be added that a column packed with proposed sorbent can be used many times in sorption-elution processes owing to the relative high concentrations of mineral acids required for the elution of Pyrocatechol Violet from the sorbent. This supposition was verified in sorption-elution processes for zinc, cadmium, lead and copper performed five times with use of the

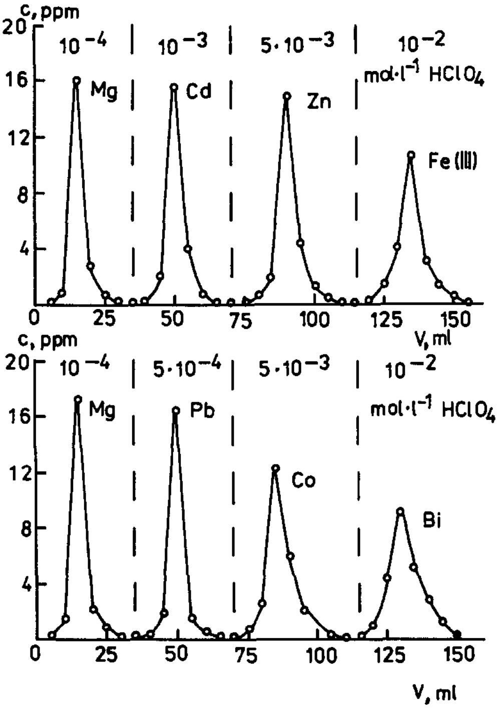

Fig. 2. Separation of metal ion mixtures containing 100 μg of each metal ion, separated on silica gel treated with a mixture Aliquat 336 and Pyrocatechol Violet. Columns packed with 5 g of sorbent. Mean flow rate 1 ml/min.

same column since reproducible results in the determination of these metals in eluates were obtained.

Since all metals except alkali and alkaline earth metals are retained from aqueous solutions at pH < 6 on silica gel impregnated with a mixture of Aliquat 336 and Pyrocatechol Violet, it was expected that the sorbent could be used for additional purification of alkali, alkaline earth metals or ammonium salts from heavy metals. Therefore, several anodic stripping voltammetric measurements for aqueous solutions of these salts and the same solutions passed through the column packed with proposed sorbent have been performed. Although calcium chloride solution contained considerable amounts of copper, lead, cadmium and zinc, after passing the solution through the column packed with silica gel modified with Pyrocatechol Violet, these metals were almost completely removed. On the other hand, it is expected that the sorbent could be useful for preconcentration of traces of heavy metals from aqueous solutions (e.g. drinking water or sea water) and elimination of matrix effect from alkali and alkaline earth metals (especially from calcium) in the determination of heavy metals by AAS.

Since calcium ions are not retained by silica gel modified with Pyrocatechol Violet, the sorbent can be also used for purification of calcium salts from impurities of magnesium. This supposition was confirmed experimentally in determination of magnesium in solutions of calcium salts—after passing these solutions through the columns packed with sorbent, magnesium was almost completely removed.

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REFERENCES

1. A. Siriraks, H. M. Kingston and J. M. Riviello, *Anal. Chem.*, 1990, **62**, 1185.
2. V. B. Conrad and W. D. Brownlee, *Anal. Chem.*, 1988, **60**, 365.
3. S. Przeszlakowski, E. Soczewiński, R. Kocjan, J. Gawecki and Z. Michno, *Polish Patent*, 128 743, November 1985.
4. S. Przeszlakowski and R. Kocjan, *Analyst*, 1985, **110**, 1077.
5. S. Przeszlakowski and R. Kocjan, *Sep. Sci. and Technol.*, 1989, **24**, 291.
6. R. Kocjan, *Chem. Anal.* (Warsaw), 1991, **36**, 473.
7. R. Kocjan and S. Przeszlakowski, *Talanta*, 1992, **39**, 63.
8. R. Kocjan, *Sep. Sci. and Technol.*, 1992, **27**(3), 408.
9. S. Przeszlakowski and R. Kocjan, *Chromatographia*, 1982, **15**(11), 717.
10. R. Kocjan, *Analyst*, 1992, **117**, 741.
11. Z. Marczenko, *Spektrofotometryczne Oznaczanie Pierwiastkow (Spectrophotometric Determination of Elements)*. Warsaw, 1979.
12. M. Garbacka, *Diploma Dissertation*, Medical Academy, Lublin, 1992.
13. J. Inczedy, *Równowagi Kompleksowania (Complex Equilibria in Analytical Chemistry)*, PWN, Warsaw, 1979.