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ANALYTICAL APPLICATION OF LiCHROPREP RP-8 MODIFIED WITH ERIOCHROME BLACK T

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ABSTRACT

The new chelating sorbent for metal ions was prepared by impregnation of chemically modified silica LiChroprep RP-8 with ion pairs composed of cation of Aliquat 336 and anion of Eriochrome Black T. A hypothesis for binding this ion pair by the surface of the applied carrier was presented. The sorbent was compared with an analogous sorbent with a plain silica carrier containing the same ion pairs. A higher stability of the sorbent in comparison with that of the plain silica chelating sorbent was demonstrated. The sorbent obtained was applied for additional purification of aqueous solutions of alkali metals from trace amounts of heavy metals and for chromatographic separations of some chosen mixtures of some metal ions. The multiple use of the sorbent based on RP-8 in sorption–desorption processes of metal ions without deterioration of their sorption capacities was demonstrated.

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Key Words: Eriochrome Black T; LiChroprep RP-8; Chelating sorbent; Purification of alkali metal salts; Extraction chromatography

INTRODUCTION

The analysis of microtraces of metals is now possible thanks to modern instrumental methods, among which the leading positions of those based on atomic absorption or emission should be mentioned. In spite of the marked specificity and sensitivity of these and other methods, the separation of the analyte from the matrix and/or their preconcentration is still frequently the prerequisite of exact analysis. Therefore, separation methods—extraction [also in the form of solid phase extraction (SPE)] and especially chromatography, owing to their rapidity, simplicity, and selectivity—still play an important role.

In the trace analysis of metal ions, an important role is played by the chelating sorbents (1). The introduction of chelating functional groups into the matrix of a solid ion exchanger capable of providing specific interactions with metal ions permits the preparation of selective chelating resins (2). Besides commercial chelating resins used for these purposes, other chelating sorbents have found increasing popularity recently (3), and especially interesting are silica gels modified with various chelating reagents (4).

The chelating sorbents can be obtained in a very simple manner by modification of silica gel with ion pairs formed by an alkylammonium cation of a liquid anion exchanger such as Aliquat 336 (methyltrioctylammonium chloride) and the anion of a sulfonated chelating reagent (5).

It was found that liquid anion exchangers are strong extractants of sulfonated chelating reagents from aqueous solutions because they form generally stable ion pairs and their stability depend on the type of chelating reagent and ion exchanger. It was found that Aliquat 336 is the best extractant maintaining its extraction ability also in alkaline media (6).

It was also found that the stability of the ion pairs formed is greater for more hydrophobic sulfonated chelating reagents; therefore, Eriochrome Black T, a relatively hydrophobic reagent was chosen for our investigations. The application of a chelating sorbent obtained by impregnation of silica with a mixture of Aliquat 336 and Eriochrome Black T to trace analyses for some metals was reported in a previous paper (7).

In analytical chemistry, including trace analysis of metal ions, chemically modified silicas have found wide application (8).

Our earlier data indicated the high stability of sorbents formed by impregnation of chemically modified silica (RP-8 and RP-18) with mixtures of

Aliquat 336 and sulfonated chelating reagents (9). Therefore, we decided to study the sorbent by modification of RP-8 with Eriochrome Black T and to compare this with common silica gel modified with Eriochrome Black T, as in Fig. 1.

Eriochrome Black T is commonly used as an indicator in complexometric titrations and as chromogenic reagent for the spectrophotometric determination of some metals (10).

EXPERIMENTAL

All experiments were performed at room temperature (20 ± 1°C).

Reagents and Solutions

LiChroprep RP-8 and LiChroprep RP-18 (0.040–0.063 mm) (Merck, Darmstadt, Germany) were used as support for the stationary phase.

Eriochrome Black T (POCh, Gliwice, Poland) was used without further purification.

Aliquat 336—methyltrioctylammonium chloride (Merck, Germany) was purified from iron by washing a chloroform solution of this salt with 10^{-1} mol L^{-1} hydrochloric acid and then several times with doubly distilled water.

Aqueous solutions of metal salts were prepared by dilution of Titrisol standard metal salt solutions (Merck). Working solutions were freshly prepared from standard metal salt solutions by dilution with doubly distilled water (previously adjusted to an appropriate pH value with 1 mol L^{-1} hydrochloric acid, acetate buffer, or tetraborate buffer).

Freshly distilled chloroform of analytical-reagent grade was used as diluent of Aliquat 336.

Solutions of $HClO_4$ and HCl Suprapur grade (Merck, Germany) were used as eluents.

KCl of analytical-reagent grade (POCh, Poland) and Suprapur grade (Merck, Germany) were used for purification from heavy metals.

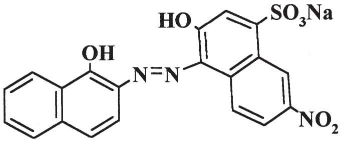

Figure 1. Formula of Eriochrome Black T.

Apparatus

A Pye Unicam (Cambridge, UK) single-beam atomic absorption spectrometer was used for the determination of the metal ions.

Eriochrome Black T was determined with a Spekol 11 visible spectrophotometer (Zeiss, Jena, Germany).

All pH measurements were performed with a Mera–Elwro N517 direct-reading pH meter (Wroclaw, Poland), with a glass-silver/silver chloride combination electrode.

A UPE-2a voltammetric analyzer (Radius, Gdańsk, Poland) was used in the determination of trace amounts of Pb^{2+}, Cd^{2+}, Cu^{2+}, and Zn^{2+} in KCl by anodic stripping voltammetry. A graphite electrode, impregnated with epoxy resin and coated with a mercury film in situ was used as working electrode having a working area of 12.5 mm^2.

Procedure

The impregnating solution was prepared by shaking an appropriate volume of 0.01 $mol\,L^{-1}$ solution of Aliquat 336 in freshly distilled chloroform with 10 volumes of 0.001 $mol\,L^{-1}$ aqueous solution of Eriochrome Black T. After separating the phases, the organic phase was passed through a cellulose filter to remove the residual aqueous phase.

LiChroprep RP-8 was impregnated with a chloroform solution of a mixture of Aliquat 336 and Eriochrome Black T in the following manner. Amounts of 10 g of the sorbent were prepared by mixing a 100 mL portion of the organic solution containing 1 mmol of Eriochrome Black T (0.461 g) and 1 mmol of Aliquat 336 (0.442 g) with 9.07 g of LiChroprep RP-8. The diluent (chloroform) was then evaporated using a vacuum evaporator on a water bath. A 1 g amount of the chelating sorbents obtained contained 0.1 mmol of Eriochrome Black T and 0.1 mmol of Aliquat 336.

Elution of Eriochrome Black T from the sorbent with aqueous solutions of mineral acids was performed in the following manner. A 0.1 g amount of the obtained sorbent was shaken for 10 min with 5 mL of an appropriate acid solution in small tubes. The solution was subsequently centrifuged and the dye was then determined by spectrophotometry at 334 nm with reference to a calibration graph.

Small polypropylene columns (55 mm × 13 mm) (J. T. Baker, Phillipsburg, NJ) were packed with 0.1 g of dry sorbent and used to measure the relative capacity of the sorbent towards different metal ions. A 5 mL portion of each solution (previously adjusted to an appropriate pH), containing 0.3 mg of the metal to be determined, was passed through each column for 5 min.

Columns (65 mm × 13 mm) packed with 5 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 7, 10 mL of the synthetic solution at pH 7, containing 100 μg of each metal ion, were passed through the column. The metals were then eluted with $HClO_4$ solutions, and the eluate was collected in 5 mL fractions.

Each percolate was analyzed by AAS with flame atomization to determine the residual metal ion concentrations.

Voltammetric determination of the metals was performed in the following manner. Volumes of 10 mL of 0.5 mol L^{-1} KCl analytical grade to which mercuric nitrate was subsequently added [the concentration of $Hg(NO_3)_2$ in the resulting solution was 10^{-4} mol L^{-1}] were passed through columns packed with 1 g of the sorbent. Into one previously purified KCl solution 2 μL volumes of standard solutions of Cu^{2+}, Cd^{2+}, Pb^{2+}, and Zn^{2+} ions of 100 ppm concentration were introduced (the concentration of each metal ion added in the solution 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 -1.3 V. Anodic oxidation of the deposited metals was subsequently performed with an amplitude 1.2 V and potential change of 10 mV sec^{-1}.

RESULTS AND DISCUSSION

As discussed in the Introduction, chelating sorbents can be obtained by impregnation of silica gel with mixtures of Aliquat 336 and sulfonated chelating reagents.

During the preparation of such sorbents a double molar excess of the tetraalkylammonium salt (Aliquat 336) had to be used relative to the stoichiometric 1:1 amount of sulfonated chelating reagent. It was found experimentally many times that the use of excess amounts of Aliquat 336 improved the quality of sorbents so that they became more resistant to loss of the chelating reagent or the whole ion pairs by aqueous acid solutions (5).

The problems are: how the ion pairs are bound by the silica surface; what is the role of the double excess of Aliquat 336; and what is the cause of the increased stability of the sorbents prepared with this excess.

Hansen et al. (11), in their paper on dynamically modified silica, have demonstrated that the Br^- anion from the tetraalkylammonium bromide binds the hydrogen ions from the surface silanol groups of silica; the H^+ ions are substituted by the tetraalkylammonium cation.

Present experiments on the preparation of sorbent were carried out on the basis of modified silica–RP-8 and the earlier investigated ion pair composed of Aliquat 336 and sulfonated chelating reagent Eriochrome Black T (the dye used alone, without Aliquat 336, to impregnate RP-8 did not give good results: it was easily lost from the column by bidistilled water).

The investigations of such sorbent have shown that in this case the double excess of Aliquat 336 (as in the case of plain silica carrier) is not necessary.

The alkyl chains ("brush") on the RP-8 surface, bind directly the Aliquat–Eriochrome Black T ion pairs according to Fig. 2.

The chelating sorbent thus prepared is more stable in comparison to those formed on the basis of plain silica. This is shown in Fig. 3, which represents the amounts of lost Eriochrome Black T (in the form of anion or whole ion pairs) plotted against the concentration of the acid applied.

The higher stability of the sorbent based on RP-8 could be explained by the fact that acidic solutions do not displace the ion pairs as in the case of sorbent prepared on plain silica carrier. The cause of greater stability of the sorbent based on RP-8 in comparison to plain silica is probably the lesser number of sites sensitive to breaking under the influence of chemical reagents. In the case of silica-based sorbent, there are three such sites: the place of binding the first layer of Aliquat 336 to the silica surface, the area of binding the second Aliquat 336 layer to the first, and the binding of Eriochrome Black T molecule to the second Aliquat 336 layer. In the case of sorbent based on RP-8 adsorbent, there are only two such places: binding of Aliquat 336 to the "brush" of RP-8 and the bond between Eriochrome Black T to Aliquat 336.

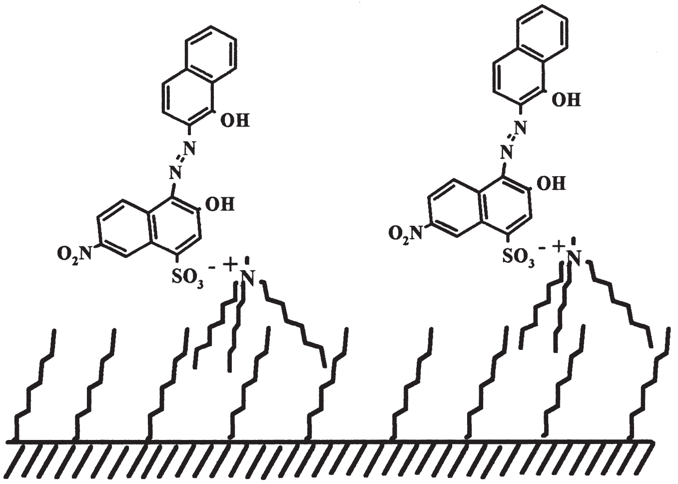

Figure 2. LiChroprep RP-8 modified with ion pairs composed of cation of Aliquat 336 and anion of Eriochrome Black T.

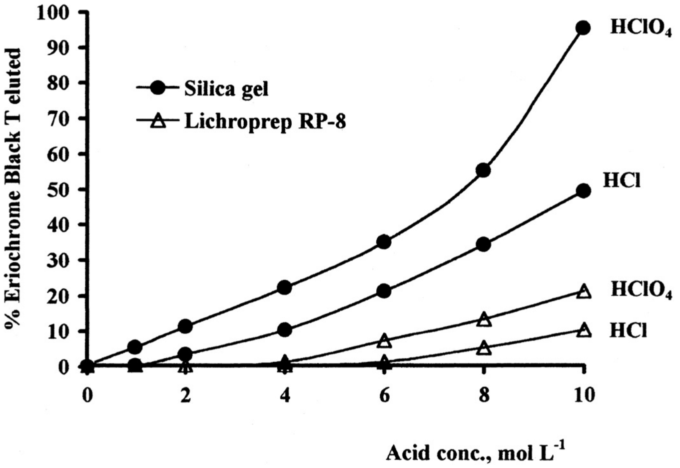

Figure 3. Percent of Eriochrome Black T eluted from silica and LiChroprep RP-8 modified with a mixture of Aliquat 336 and Eriochrome Black T as a function of concentration of $HClO_4$ or HCl acids used as eluents. A 0.1 g amount of the sorbent was shaken for 10 min with 5 mL of $HClO_4$ or HCl solution.

The strong retention of Eriochrome Black T is important for the elution of metals from the column and for regeneration of the sorbent with dilute solutions of mineral acids.

The capacities of the sorbent for the metals investigated are different and increase for larger pH values of the aqueous solution and they were comparable to those obtained with a silica carrier (7). This is understandable taking into account the equal amounts of chelating reagent (Eriochrome Black T) per gram of each sorbents.

The sorbent prepared was applied successfully to analytical problems analogous to those described earlier for Eriochrome Black T sorbent based on plain silica.

The different retention of the metals investigated, depending on pH of the aqueous solution, can be used for extraction chromatographic separation of several metal ion mixtures.

Figure 4 represents the separation of a synthetic mixture of some metal ions by column extraction chromatography using stepwise gradient elution with a solution of perchloric acid. The sequence of elution of the separated metal ions is in agreement with the increasing values of logarithm of stability constants of Eriochrome Black T and the metals investigated ($\log \beta$) : $Mg^{2+} = 7.0$; $Cd^{2+} = 12.74$; $Co^{2+} = 20.0$; $Cu^{2+} = 21.38$. The recovery of the separated metals was in the range of 98–99%.

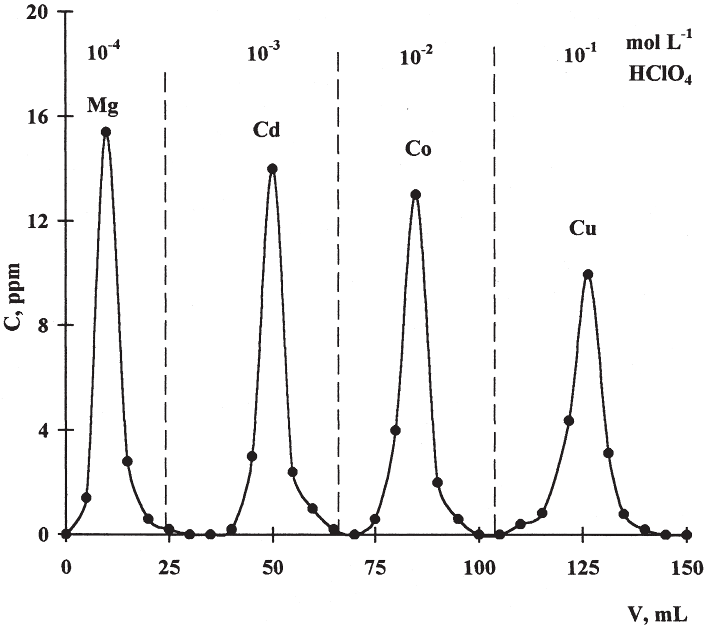

Figure 4. Separation of metal ion mixtures containing 100 μg of each metal ion, on LiChroprep RP-8 treated with a mixture of Aliquat 336 and Eriochrome Black T. Column packed with 5 g of sorbent. Mean flow rate: 1 mL min^{-1}.

It was found that alkali metal and ammonium ions are not retained on LiChroprep RP-8 coated with the mixture of Aliquat 336 and Eriochrome Black T in a wide pH range (1–9), whereas other metal ions are retained at pH $>$ 3.

Therefore, the proposed sorbent can be applied to remove trace amounts of heavy metals from aqueous solution of sodium, potassium, and ammonium salts.

Voltammograms for potassium chloride solutions shown by Fig. 5 confirmed this supposition. It was found that analytical grade potassium chloride solution contained considerable amounts of Cu, Cd, Pb, and Zn (traces of these metals, especially Pb and Cu, were also found in KCl Suprapur solution). After the passage of these solutions through a column packed with the sorbent, these metals were almost completely removed.

As discussed earlier, the sorbent containing ion pairs from Eriochrome Black T–Aliquat 336 deposited on RP-8 is considerably more stable than an analogous sorbent based on plain silica. It has been demonstrated experimentally that in the case of the silica sorbent the repeated use of a column for five times caused the sorption capacity to decrease gradually owing to loss of Eriochrome

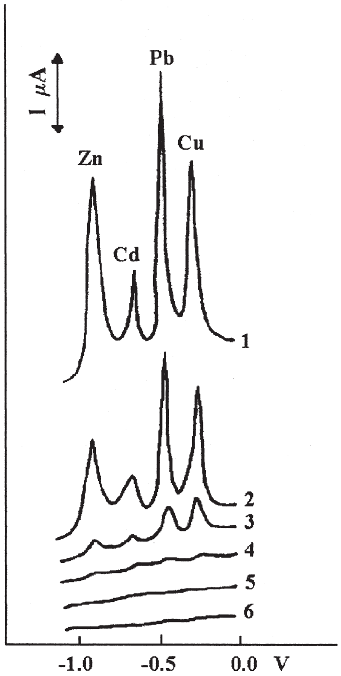

Figure 5. Voltammograms for 10 ml volumes of 0.5 mol L^{-1} KCl solutions after 3 min electrolysis at −1.3 V. Curves: (1) unpurified solution of analytical grade KCl to which Zn^{2+}, Cd^{2+}, Pb^{2+}, and Cu^{2+} ions were added (the concentration of each metal ion was 20 ppb); (2) unpurified solution of analytical grade KCl; (3) unpurified solution of Suprapur grade; (4) sample one after passing through the column packed with LiChroprep RP-8 modified with Eriochrome Black T; (5) sample two after passing through the column; and (6) sample three after passing through the column.

Black T, so that the results were not quite reproducible. On the other hand, sorbent with RP-8 shows practically no changes under these conditions.

The reproducibility of the sorbent obtained in several repeated preparations was high and the differences for analogous experiments were lower than 1–2%.

CONCLUSIONS

In conclusion, it can be stated that chelating sorbent with Eriochrome Black T on the basis of RP-8 has much better properties and better chances of practical use than the analogous sorbent with silica carrier.

It can be successfully applied in trace analysis of various metal ions—as sorbent for SPE and as stationary phase in column chromatography.

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