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A CHELATE SORBENT PREPARED BY THE MODIFICATION OF LICHROPREP RP-8 WITH TITAN YELLOW AND ITS APPLICATION

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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 Titan Yellow. The hypothetical molecular mechanism of binding this ion pair by the surface of the applied carrier was presented. The sorbent was compared with analogous sorbent with plain silica carrier containing the same ion pairs. Higher stability of the new sorbent in comparison to that of the plain silica chelating sorbent was demonstrated. The sorbent obtained was applied for chromatographic separations of some chosen mixtures of metal ions and for additional purification of aqueous solutions of alkali metals from trace amounts of heavy metals.

Keywords: Titan Yellow, chelating sorbent, LiChroprep RP-8, extraction chromatography, purification of alkali metal salts

Introduction

In the trace analysis of metal ions an important role is played by the chelating sorbents [1]. Besides commercial chelating resins used for these purposes, other chelating sorbents have recently found increasing popularity [2], and especially interesting are silica gels modified with various chelating reagents [3]. In analytical chemistry, including trace analysis of metal ions, chemically modified silicas have also found wide applications [4-6].

The chelating sorbents can be obtained in a very simple manner by the impregnation of common silica with ion pairs formed by an alkylammonium cation of a liquid anion exchanger – Aliquat 336 (methyltrioctylammonium chloride) and the anion of sulfonated chelating reagent [7]. In ref. [8] the application to trace analysis of some metals of a chelating sorbent obtained by impregnation of silica with a mixture of Aliquat 336 and Titan Yellow.

Our earlier data indicate the high stability of sorbents formed by impregnation of chemically modified silica – RP-8 with mixtures of Aliquat 336 and sulfonated chelating reagents [9,10]. Therefore we decided to prepare the sorbent by modification of RP-8 with Titan Yellow (*Fig.1*) and compare this to common unsilanized silica gel modified with Titan Yellow. The present paper relates the results of the performed investigations.

Experimental

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

Reagents and solutions

LiChroprep RP-8 (0.040-0.063 mm) (Merck, Germany) was used as support for the stationary phase.

Aliquat 336 - methyltrioctylammonium chloride (Merck, Germany) was purified by shaking a 0.1mol l^{-1} solution in chloroform with equal volume of 0.1 mol l^{-1} hydrochloric acid and subsequently five times with distilled water and then, by filtering the organic phase through a cellulose filter.

Titan Yellow (Merck, Germany), was purified as described by Nyons [11].

Aqueous metal salt solutions were prepared by dilution of Titrisol standard metal salt solutions (Merck). Working solutions were freshly prepared from standard metal salt solution 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 grade was used as diluent of Aliquat 336.

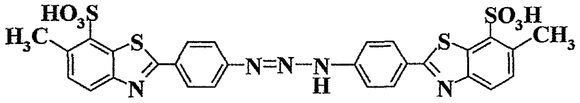


Fig.1 Titan Yellow (Thiazol Yellow G)

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

Apparatus

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

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

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

Procedure

The impregnating solution was prepared by shaking an appropriate volume of 0,01mol l^{-1} solution of Aliquat 336 in freshly distilled chloroform with 5 volumes of 0,001mol l^{-1} aqueous solution of Titan Yellow. 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 Titan Yellow in the following manner: Amount of 10 g of the sorbent was prepared by mixing a 200 ml portion of the organic solution containing 1 mmol of Titan Yellow (0.651 g) and 2 mmol of Aliquat 336 (0.884 g) with 8,465 g of LiChroprep RP-8. The diluent (chloroform) was then evaporated with the use of a vacuum evaporator on a water bath. 1 g amount of the chelating sorbent contained 0.1 mmol of Titan Yellow and 0.2 mmol of Aliquat 336.

Elution of Titan Yellow 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 337 nm with reference to a calibration graph.

Small polypropylene columns (55 mm × 5 mm) (J. T. Baker, Phillipsburg, NJ, USA) 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. Each percolate was analysed by AAS 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 or Suprapur 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 the columns packed with 1 g of the sorbent. Volumes of 2 μl of standard solutions of Cu^{2+}, Cd^{2+}, Pb^{2+} and Zn^{2+} ions of 100 ppm concentration were introduced into 10 ml of 0.5 mol l^{-1} KCl (analytical-reagent grade) (the concentration of each metal ion added in the solution was then 20 ppb). Oxygen was removed from the analysed solutions with a stream of argon of special purity. The solutions were electrolysed for 3 min. at -1.3 V. Anodic oxidation of the metals was subsequently performed at the following conditions: amplitude 1.2 V; potential change of 10 mVs^{-1}.

Results and Discussion

As discussed in the introduction, chelating sorbents can be obtained in a simple manner by impregnation of silica by ion pairs composed of methyltrioctylammonium cation and sulfonated chelating reagent anion obtained by static extraction process [7].

During the preparation of such sorbents, silica gel was impregnated with Aliquat 336 and chelating reagents from chloroform solutions in such proportions that the molar concentration of Aliquat 336 was twice as large as the concentration of the reagent containing a single sulfo group (or four times for reagents with two sulfo groups, *e.g.* Nitroso-R-Salt or Titan Yellow). It was experimentally found many times that the use of excess amounts of Aliquat 336 improved the quality of sorbents so that they became more resistant to elution of the chelating reagent or the whole ion pairs by the aqueous acid solutions.

The problem arises 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. [12] 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.

It can be presented those cations of Aliquat 336 are bound to silica surface by a similar mechanism (*Fig.2*).

The mode of binding of the ion pairs: tetraalkylammonium cation – sulfonated chelating reagent anion, with double molar excess of Aliquat 336 is probably the following: half amount of Aliquat 336 is bound to the silica surface according to *Fig.2*; the

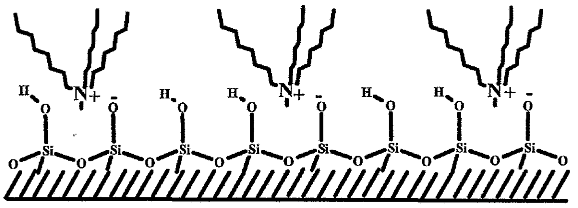


Fig.2 Silica impregnated with Aliquat 336

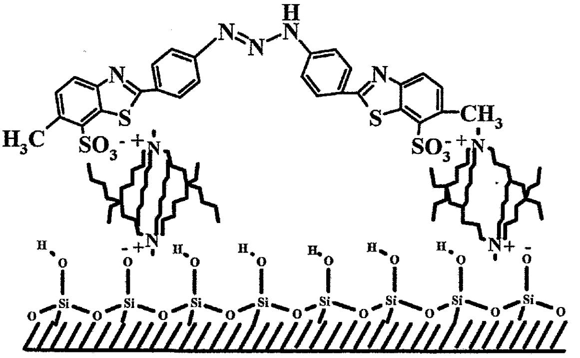


Fig.3 Silica impregnated with Aliquat 336 and modified witch ion pairs composed of cation of Aliquat 336 and anion of Titan Yellow

adsorbent surface is covered by a monomolecular layer of octyl groups from Aliquat 336 so that the surface is hydrophobized and it bounds by hydrophobic (and dispersive) interactions the second layer of Aliquat cations forming the chelating ion pairs with the sulfonated reagent. In the hydrophobic interactions the octyl groups from both tetraalkylammonium cations are involved. In effect, the carrier surface is isolated from the aqueous bulk phase and the chelating groups are outside the double layer, capable of binding metal ions in the bulk aqueous solution. The structure of the sorbent containing LiChroprep RP-8 can thus be represented as in *Fig.3*.

During elution of metal ions bound by sorbent of this type with aqueous solutions of mineral acids, the weaker or stronger accompanying elution of chelating reagents (or even whole ion pairs) is observed so that the properties of the sorbent are changed and its ion exchange capacity is decreased.

The anion of chelating reagents are displaced from the ion pairs by the anion of acids used (especially by ClO_4^- anions which have greatest affinity to the tetraalkylammonium cations).

On the other hand, the hydrogen ions from the acids applied in the eluent elute not only metal ions bound by the sorbent (which is advantageous), but also, at higher concentrations, can displace the whole hydrophobic layer in a process reverse to *Fig.2* and then the chelating sorbent is decomposed. It happens especially in cases when to elute some metal ions bound by the sorbent aqueous acid solutions of high concentrations (0.5 – 1 mol l^{-1}) are to be used. Therefore, we were looking for other carriers, which would bind the ion pairs more strongly so that sorbent of higher stability would be obtained.

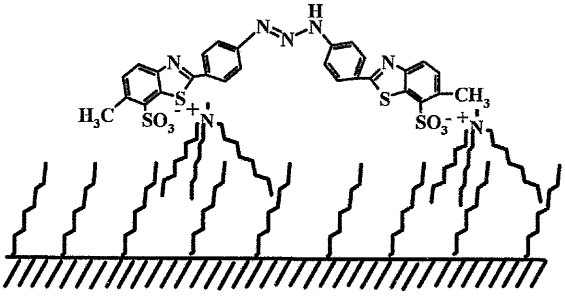


Fig.4 LiChroprep RP-8 modified with ion pairs composed of cation of Aliquat 336 and anion of Titan Yellow

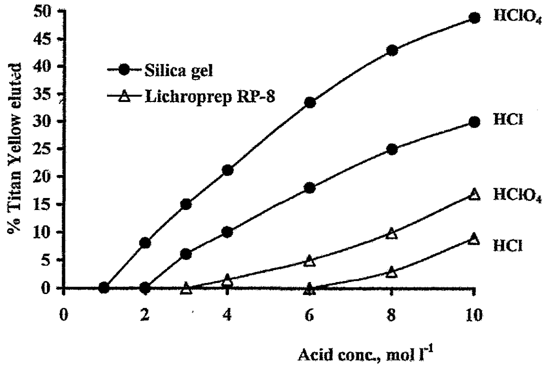


Fig.5 Percent of Titan Yellow eluted from silica and LiChroprep RP-8 modified with a mixture of Aliquat 336 and Titan Yellow as a function of concentration of $HClO_4$ and HCl acids used as eluents

We decided to prepare sorbent on the basis of modified silica – RP-8 and the earlier investigated ion pair composed of Aliquat 336 and sulfonated chelating reagent – Titan Yellow.

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 chairs ("brush") on the RP-8 surface bind directly the Aliquat – Titan Yellow ion pairs according to *Fig.4*.

The chelating sorbent thus prepared is more stable in comparison to those formed on the basis of plain silica. This is illustrated in *Fig.5* which represent the amounts of eluted Titan Yellow (in the form of anion or whole ion pairs) plotted against the concentration of the acids applied. The higher stability of sorbent on the basis of RP-8 is explained by the fact that acidic solutions do not displace the ion pairs as in the case of sorbent prepared on plain silica carrier.

Titan Yellow used alone, without Aliquat 336, to impregnate RP-8 did not give good results: it was easily eluted from the column by bidistilled water.

The ion exchange capacities of the sorbent obtained was comparable with those formed for silica carrier [8]. This is understandable tasking in to account the equal

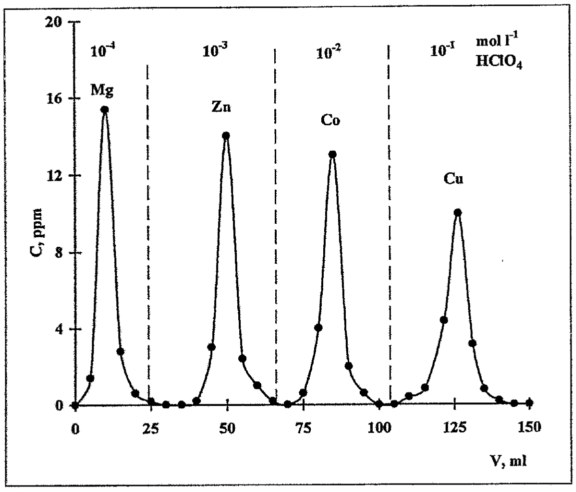


Fig.6 Separation of metal ion mixtures containing 100 µg of each metal ion, on LiChroprep RP-8 treated with a mixture of Aliquat 336 and Titan Yellow. Column packed with 5 g of sorbent. Mean flow rate: 1ml min^{-1}

amounts of chelating reagent (Titan Yellow) per 1 g of each sorbent.

Only very small differences in the concentrations of mineral acids ($HClO_4$ and HCl) necessary to elute the metal ions from the columns were also observed.

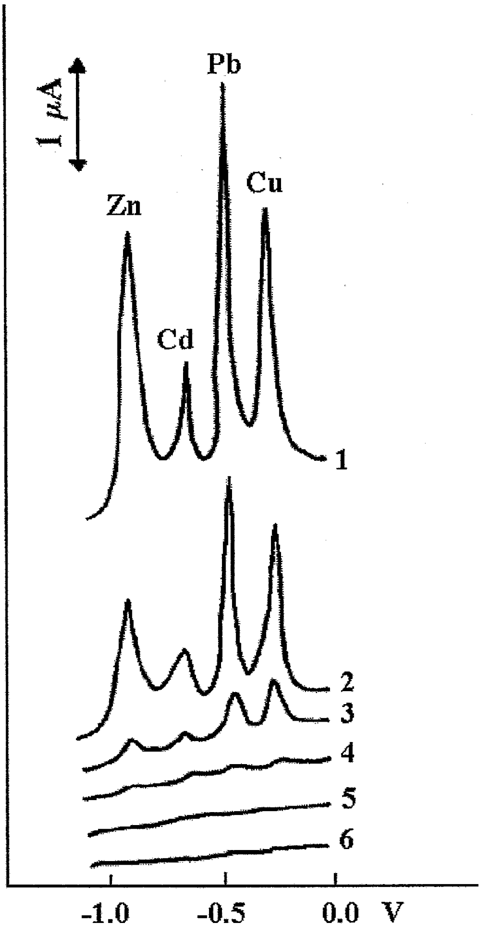
The sorbent prepared was successfully applied to analytical problems analogous to those described earlier for Titan Yellow sorbent on the basis of plain silica.

Figure 6 represents the separation of a synthetic mixture of some metal ions by column extraction chromatography using stepwise gradient elution with solution of chloric(VII) acid. The recovery of the separated metals was in the range of 97 – 99.5 %. Presumably, the practical application of the sorbent described can be found for selective preconcentration of trace amounts of iron (III) and cuprum(II). Their ions are bound even from acidic solutions (which is not observed in the case of other metals) and rather high concentrations of acids are required for their elution (Fe: 0.1 mol l^{-1}; Cu: 0.05 mol l^{-1}). In this way Cu and Fe can be separated from other ions.

On the other hand, the sorbent do not bind in a wide pH range (1-9) the ions of alkali metals and the ions of Calcium and Magnesium are bound only at pH 9, while other metals investigated were bound in the pH range 3 – 6. Therefore, the sorbent can be applied to remove trace amounts of heavy metals from aqueous solution of Sodium, Potassium, Ammonium, Calcium and Magnesium salts. Such trace amounts are present even in reagents of special "Suprapur" quality.

Figure 7 representing the voltammograms of solutions of KCl purified in the described manner confirms the useful properties of the prepared chelating sorbent.

As discussed earlier, the sorbent containing ion pairs Titan Yellow – Aliquat 336 deposited on RP-8 is considerably more stable than analogous sorbent on basis of plain silica. It has been demonstrated experimentally that in the cause of the silica sorbent the use of a column five times caused that the sorption capacity gradually decreased due to bleeding of Titan Yellow so that the results were not quite reproducible. On the other hand, sorbent with RP-8 practically did not show under these conditions any changes. Solely, during elution of iron ions (at high concentrations of acids) some small amount of Titan Yellow were eluted.



Curves: 1 - unpurified solution of analytical grade KCl to which Zn, Cd, Pb, and Cu 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 1 after passing through the column packed with LiChroprep RP-8 modified with Titan Yellow; 5 - sample 2 after passing through the column; 6 - sample 3 after passing through the column.

Fig.7 Voltammograms for 10 ml volumes of 0.5 mol l^{-1} KCl potassium chloride solutions after 3 min. electrolysis at -1.3V

To sum up, it can be said that chelating sorbent with Titan Yellow on the basis of RP-8 have much better properties and better chances of practical use that the analogous sorbent with silica carrier.

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