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HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY OF METALS ON SORBENTS WITH GRAFTED TнIAZOLYLAZO-COMPOUNDS

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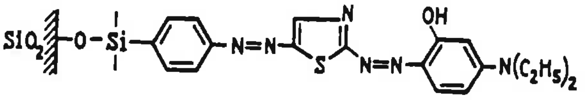
Chromatographic behavior of Cu(II), Co(II), Cd(II), Zn(II), Pb(II), and Mn(II) on columns packed with silica gel with grafted 2(2'-thiazolylazo)dimethylaminophenol or 2-(2'-thiazolylazo)resorcinol (TAR) groups under conditions of HPLC is studied. Aqueous solutions of citric acid or N,N,N',N'-tetracetic ester of β,β'-diaminodiethylglycol (GEDTA) with variable acidity and concentration was used as the mobile phase.

One of the promising areas in high-performance liquid chromatography (HPLC) of ions of the transition and heavy metals is utilization of silicas modified chemically by complex-forming organic compounds serving as a fixed phase. As compared with the traditionally used ion-exchange agents, complex-forming sorbents are advantageous in many respects and allow improving, predicting, and varying the separation selectivity by optimizing composition of the mobile phase with due regard for the stability constants of the appropriate metal complexes, dissociation constants of immobilized functional groups on the surface of the sorbent and the components constituting the mobile phase. When choosing compounds covalently tied to the silica surface a postulate about insignificant changes in the acid-base and complex-forming properties of the grafted ligand, as compared to its homogeneous analog, is usualy utitized [1]. In HPLC of transition metals silicas with grafted organic reagents whose properties are studied fairly well (8–oxyquinoline [2,3], dithizone [2], iminodiacetic acid [4], propylamidoxime [5], β-diketones [2,6], phenylhydrazono-2-pyridinecarboxyaldehyde [7]) are employed.

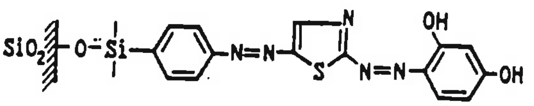
In the present work application of silicas with grafted 2-(2'-thiazolylazo)-5-diethylaminophenol (TAAP) and 4-(2'-thiazolylazo)resorcinol (TAR) as a fixed phase in HELC of metals is discussed. The above thiazole azocompounds can readily be synthesized and purified and were used earlier in analytical practice as chelate-forming reagents for extraction-photometric determination of a number of transition and heavy metals [8] and also as adsorption modifiers for ion-exchange resins [9, 10] and silicas [11] to obtain selective sorbents.

EXPERIMENTAL

Silasorb-Si-Silica-600 with the specific surface area of 600 m^2/g and mean particle size of 10 μm was used as a matrix for sorbent synthesis. The sorbents were synthesized according to the following scheme. The silica surface was treated with n-aminophenyltrimethoxysilane. The amino-groups were then diazotized and azo-combined with diethylaminophenol or resorcinol. By this way intensely colored sorbents of the following structure were obtained [12]:



(SiO$_2$–TAAP)



(SiO$_2$–TAR)

To evaluate the static sorption capacity of the sorbents 0.1 g samples were introduced into solutions with a known Cu(II) content, the solution was shaken during 1 h and then filtered. The needed value was found from the difference in the copper content before and after sorption. The copper content in the solution was measured by atomic-absorption spectroscopy (AAS). At pH 6.5 the static sorption capacity was 30±5 μmol/g for SiO_2–TAAP. The chromatographic studies were performed in the isocratic regime employing a liquid-phase chromatograph consisting of a "Beckman 114 M" high-pressure pump, "Rheodyn 7125" sample meter with a loop 20 μl in volume, LSD 2563 spectrophotometric detector with changeable light filters, and after-column derivatization unit [3]. A $2{\cdot}10^{-4}$ M 4-(2′-pyridylazo)resorcinol (PAR) solution in ammonia buffer with pH 9.5 was used as a reagent. The chromatographic peaks of the metals were detected by absorption of metal complexes with PAR at 546 nm. Direct photometric detection at 227 and 254 nm was carried out in a number of experiments. Stainless steel columns (250 × 4.6 mm) were packed with the sorbent employing the suspension technique at 400 atm. Aqueous solutions of citric acid and N,N,N′,N′-tetracetic ester of β,β'-diaminodiethylglycol (GEDTA) were utilized as a mobile phase. The solution acidity was changed by adding 2 M NaOH solution. Solutions of metals of a 10 mg/l concentration were prepared by dissolving precisely weighed samples of appropriate nitrates in 0.01 M HNO_3. All the solutions used in the study were filtered through a membrane filter with a pore diameter of 0.45 μm. The efficiency of columns with TAAP-SiO_2 and TAR-SiO_2 calculated from the toluene and anthracene chromatographic peaks obtained with a hexane mobile phase was 8500 and 2400 theoretical plates.

RESULTS AND DISCUSSION

TAAP-SiO_2 and TAR-SiO_2 were selected as the fixed phase for HELC of transition metals based on the previous studies of the sorption characteristics (Fig. 1) and taking into account the sorption kinetics, sorption capacity, selectivity of the functional groups with respect to metals, and sorption reversibility [12].

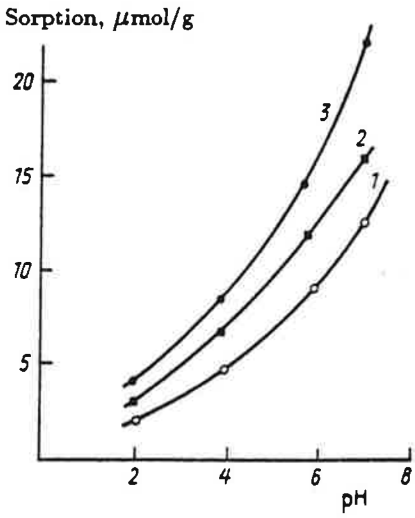


Fig. 1

Ion sorption of: *1*, zinc(II); *2*, copper(II); *3*, lead(II) ions from aqueous solutions on a sorbent with grafted TAAP molecules as a function of pH.

Preliminary studies of metal complexation on a sorbent surface suggest that in the dynamic regime 1:1 complexes are predominantly formed. Hence, these sorbents satisfy in all parameters the requirements imposed on the HELC complex-forming sorbents [4]. It follows from the procedure of TAAP-SiO_2 and TAR-SiO_2 synthesis that of the total number of grafted groups about 80% are aminophenyl ones and about 20% are grafted thiazolylazo-compound molecules. The presence of functional groups of a different nature on the fixed-phase surface may exert a negative influence on separation of metals, however the contribution of aminophenyl groups to metal retention is insignificant [2]. Of importance is independence of the molecular form of sorbents with grafted TAAP and TAR molecules from the mobile-phase acidity in the pH 3.5–7 range, which results from the fact that the protonation constant of the TAAP diethylaminophenyl group is $pK = 3.2$ [13], while dissociation of the TAAP and TAR oxy-groups becomes appreciable at pH > 8.5. This means that variations in the metal-separation selectivity depend on changes of the complexation parameters in the mobile phase. The reason why solutions of aminopolycarbonic acids (GEDTA and EDTA) and citric acid are used as a mobile phase in separation of a number of transition metals is a possibility of direct photometric detection of the chromatographic peaks by absorption of the appropriate metal complexes in the UV spectral region [5, 14]. In addition, the multistage dissociation of these acids allows pH of the mobile phase to be maintained at a constant level without employing buffer solutions. We studied the dependence of the retention times for Mn(II), Co(II), Cu(II), Cd(II), Pb(II), and Zn(II) ions on the concentration of a complex-forming agent and the mobile-phase acidity. It follows from the data listed in Table 1 that the metal retention time drops as the concentration grows, however such strongly retained ions as Cu(II) and Co(II) may be eluted at the given pH by a 0.05 M citric acid solution only.

Table 1

Retention Times (t_R, min) for Metal Ions on a Column with TAAP-SiO_2 as a Function of the Citric-Acid Concentration in the Mobile Phase (pH 4.0, flow rate of the mobile phase 1.0 ml/min)

Metal ion	Concentration of citric acid in the MP, M		
	0.05	0.2	0.01
Mn(II)	1.70	1.70	1.80
Cd(II)	2.05	2.35	2.95
Pb(II)	3.6	4.2	5.25
Zn(II)	12.0	15.8	19.2
Co(II)	26.0	40	–
Cu(II)	39.0	50	–

The following order of metal elution: Mn(II) < Cd(II) < Pb(II) < Zn(II) < Co(II) < Cu(II), was observed. This order correlates well with the stability constants of the metal complexes in homogeneous solutions found for 2-(2′-thiazolylazo)dimethylaminophenol (a TAAP analog) [15] and TAR [16]. This fact may be considered as an indirect proof of the key role played by metal complexation with immobilized reagents in chromatographic separation of metals. It is worth noting that a comparison of the chromatographic properties of the columns packed with TAAP-SiO_2 and TAR-SiO_2 did not reveal great differences and allowed us to estimate the contribution of the protonated TAAP diethylaminophenyl-groups to ion-exchange interaction of the immobilized reagent with citrate anionic-metal complexes as insignificant. The further investigation was performed with the more efficient column with TAAP-SiO_2. The metal retention time versus mobile-phase acidity dependence exhibits a more complex behavior (Fig. 2). As pH grows the multibase acids (citric and GEDTA) dissociate, their complexing ability increases, and the ratio of the contributions of the two competing metal-ion complexation reactions in the chromatographic system changes (on the sorbent surface and in the mobile phase). As is obvious from these dependences, the retention times for the majority of the ions diminish as pH grows, except for Pb(II), which, in a weakly acidic and neutral pH regions, shows formation of polynuclear hydroxo-complexes capable of being adsorbed on the modified-silica surface. In the latter case specific interactions with the residual silanol-groups cannot be ruled out either. This statement is supported by the asymmetric shape of the chromatographic peak for Pb (the asymmetry factors are 1.82 and 1.02 for Pb and Cd, respectively) (Fig. 3). Apart from pH of the mobile phase, of

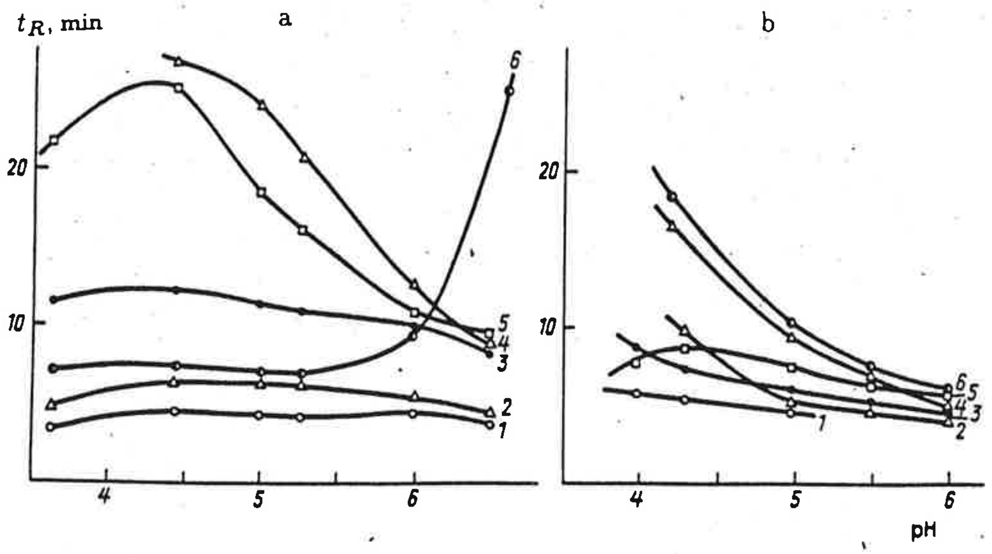


Fig. 2

Metal retention time versus mobile-phase acidity for a column with TAAP-SiO_2: *1*, Mn(II); *2*, Cd(II); *3*, Zn(II); *4*, Cu(II); *5*, Co(II); *6*, Pb(II); *a*, 0.05 M citric acid solution; *b*, 0.001 M GEDTA solution. The mobile-phase flow rate is 1 ml/min.

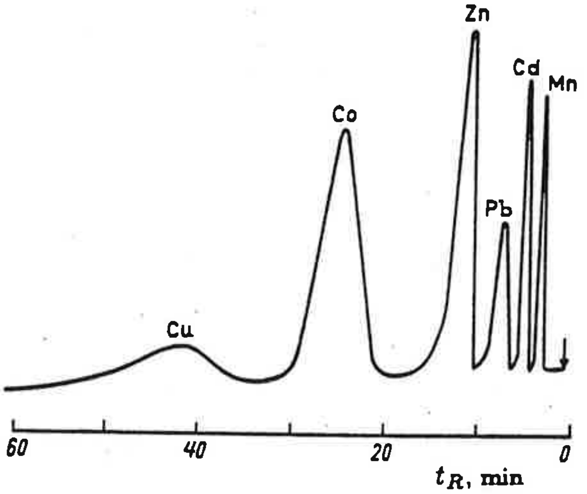


Fig. 3

Chromatogram of metal-mixture separation. Column 250 × 4.6 mm, sorbent TAAP-SiO_2, mobile phase 0.05 M citric acid solution, pH 3.62, photometric detector with an after-column reactor, $2 \cdot 10^{-4}$ M PAR, 546 nm.

importance for variations in the metal separation efficiency is a nature of the complexing agent. When 10^{-3} M·GEDTA solutions were used as a mobile phase, decrease in the retention times and a change of the order of metal emergence were observed, however the separation selectivity in this case turned out to be low. The above version of metal ion separation, which may be referred to as "complex-forming sorbent" – "complex-forming eluent" offers great opportunities of variation of the separation selectivity and may be used to elaborate techniques for detecting transition and heavy metals.

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