Separation of transition and heavy metals on an amidoxime complexing sorbent

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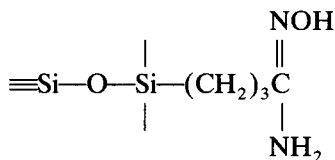
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Abstract

A silica gel-based sorbent with chemically bonded amidoxime functional groups was applied to the determination of transition and heavy metals. The sorbent has both complexing and anion-exchanging properties. The separation of transition and heavy metals showed high selectivity. Solutions of complexing acids (oxalic and dipicolinic) were used as eluents. The dependence of metal retention on pH and the concentration and nature of the complexing agents was studied. For Mn^{2+}, Cd^{2+}, Pb^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cu^{2+} and Hg^{2+} selective separation was achieved by gradient elution with oxalic acid as the eluent on a 100×3 mm I.D. column in 10 min. The interference of Fe^{3+} was completely eliminated, as this metal is very strongly retained on the sorbent. UV detection with postcolumn reaction with 4-(2-pyridylazo)resorcinol was used.

1. Introduction

The use of complexing sorbents in ion-exchange chromatography has led to considerable progress in the analysis of transition and heavy metals. Sorbents with iminodiacetic [1–3] and dithiocarbamate [4] functional groups have been successfully used for metal separations. In this work, a silica gel-based sorbent with chemically bonded amidoxime functional groups was applied to the determination of transition and heavy metals. The sorbent structure is

$$\equiv Si - O - \underset{\displaystyle |}{\overset{\displaystyle |}{Si}} - (CH_2)_3 \underset{\displaystyle NH_2}{\overset{\displaystyle NOH}{\underset{|}{\overset{\|}{C}}}}$$

Previously this sorbent was used only for the sorbent was used only for the sorption and separation of Fe^{3+}, V^{5+}, Cu^{2+} and Mo^{5+} cations [5–7]. The amidoxime NH_2 groups are responsible for both the sorbent's anion-exchange and complexing ability. An amidoxime complexing sorbent can be applied to the selective ion chromatographic (IC) determination in waters of Mn^{2+}, Pb^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cu^{2+} and Hg^{2+}.

2. Experimental

The chromatographic system consisted of a double-piston pump (Dokba, Russian Federation), a reagent-delivery module for postcolumn derivatization and a UV–Vis detector (LCD 2563; Prague, Czech Republic). Sample injection was carried out with a Rheodyne (Berkeley, CA,

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USA) Model 7125 valve equipped with a 100-μl loop. The separation was carried out on 50 × 3 mm I.D. and 100 × 3 mm I.D. stainless-steel columns packed with Amidoxim (Elsiko, Russian Federation) amidoxime-based sorbent.

Solutions of 5 mM oxalic acid with several pH values, solutions of 5–15 mM oxalic acid and a solution of 8 mM oxalic acid–0.5 mM dipicolinic acid were used as eluents. The pH of the oxalic acid solutions was adjusted by the addition of sodium hydroxide. The eluent flow-rate was maintained at 1.0 ml/min. After leaving the analytical column, the eluate stream was mixed with a postcolumn reagent, which was delivered by nitrogen pressure providing of flow-rate of 0.3 ml/min. The postcolumn reagent contained 0.5 mM sodium 4-(2-pyridylazo)resorcinol (PAR) in 3 M ammonia solution and 1 M acetic acid. The coloured complexes of metal ions were monitored for absorption at 540 nm. All solvents were of analytical-reagent grade.

3. Results and discussion

Solutions of tartaric, citric, oxalic and dipicolinic acid were tried as eluents. It was found that tartaric and citric acid did not provide a good simultaneous separation of the transition metal cations. The low selectivity of separation with these eluents is analogous to that obtained with 3 mM HNO$_3$ (Fig. 1). As can be seen, only Cu^{2+} cations show sufficiently strong retention on this sorbent; Zn^{2+}, Ni^{2+}, Co^{2+}, Cd^{2+} and Pb^{2+} are weakly retained on the amidoxime sorbent under these conditions. However, all these metals are separated on the amidoxime sorbent-packed column using an eluent containing 5 mM oxalic acid or a mixture of 8 mM oxalic and 0.5 mM dipicolinic acid. This presumably occurs because of the higher stability of the anionic metal complexes produced by these acids in the eluent than the stability of such complexes in the case of tartaric and citric acid. The anionic metal complexes are sorbed by the amidoxime basic groups and are separated (Fig. 2). The eluent pH exerts affects the degree of separation and the order of elution.
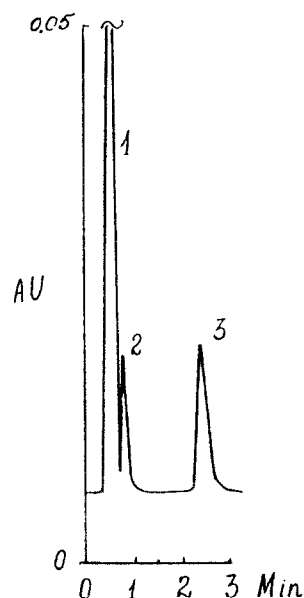

Fig. 1. Chromatogram of transition metals on the Amidoxim column with nitric acid as eluent. Column, 50 × 3 mm I.D. packed with Amidoxim sorbent; eluent, 3 mM HNO$_3$ (pH 2.5); flow-rate, 1 ml/min; detection, UV–Vis; postcolumn reaction with PAR. Peaks: 1 = Cd^{2+}, Ni^{2+}, Co^{2+}, Pb^{2+}; 2 = Zn^{2+}; 3 = Cu^{2+}.

The graphs for the dependence of some transition metal retention times on oxalic acid eluent pH value are shown in Fig. 3. The sorbent's chelating properties and its anion-exchange properties contribute to the retention of the metals. With a decrease in pH, the chelating ability of the sorbent and oxalate also decreases, which leads to a decrease in the metal retention times. With an increase in pH, the anion-exchange capacity of the sorbent decreases and the eluting ability of oxalate increases, which also leads to a decrease in the metal retention times. These facts explain the presence of maxima on the curves (Fig. 3).

The eluent pH exerts a very strong influence on the retention time of Cu^{2+}, which may be due to the especially powerful complexing ability of Cu^{2+}. As Fig. 3 shows, the best and fastest separation of the metals is achieved using an eluent of pH 3.6. The separation under these conditions is shown in Fig. 4. An increase in eluent concentration produces a decrease in the
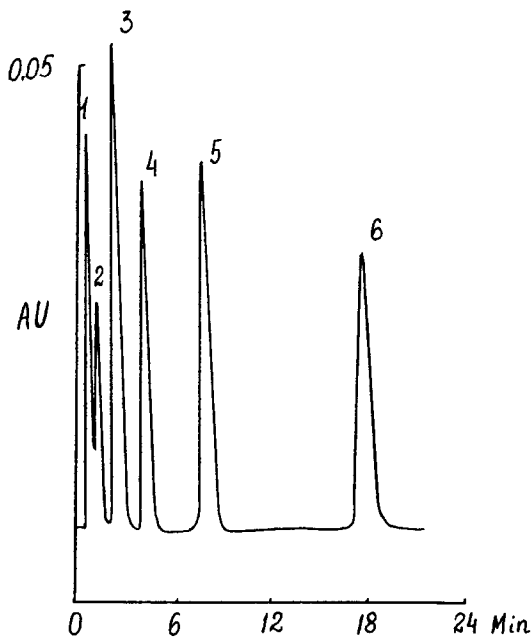
Fig. 2. Separation of transition metal ions on the Amidoxim column using oxalic acid as eluent. Eluent, 5 mM oxalic acid (pH 2.2); other conditions as in Fig. 1. Peaks: 1 = Cd^{2+}; 2 = Pb^{2+}; 3 = Co^{2+}; 4 = Zn^{2+}; 5 = Ni^{2+}; 6 = Cu^{2+}.
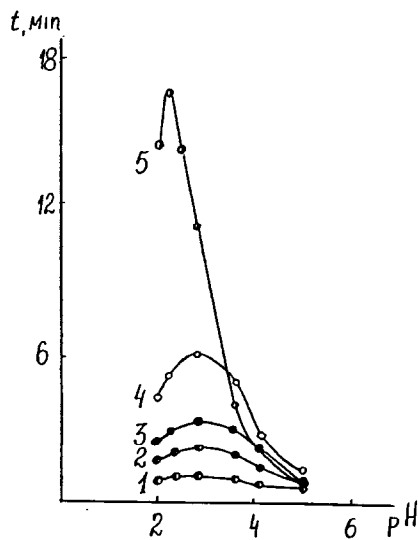

Fig. 3. Graphs of retention time *versus* oxalic acid eluent pH for some transition metals. Column, 50 × 3 mm I.D. packed with Amidoxim sorbent; eluent, 5 mM oxalic acid with various pH values; flow-rate, 1 ml/min; detection, UV–Vis; postcolumn reaction with PAR. 1 = Cd^{2+}; 2 = Co^{2+}; 3 = Zn^{2+}; 4 = Ni^{2+}; 5 = Cu^{2+}.
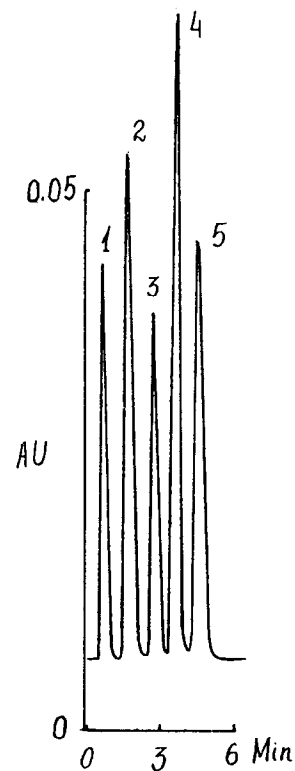

Fig. 4. Separation of transition metals on the Amidoxim column with sodium oxalate as eluent. Eluent, 5 mM sodium oxalate (pH 3.6); other conditions as in Fig. 1. Peaks: 1 = Cd^{2+}; 2 = Co^{2+}; 3 = Zn^{2+}; 4 = Cu^{2+}; 5 = Ni^{2+}.

retention times of the anionic metal complexes. For this reason, on acceptable retention time for the Hg^{2+} cation, which is very strongly retained on the amidoxime sorbent, can be obtained (Fig. 5).

The application of gradient elution noticeably decreases the analysis time, preserving the multicomponent character of the analysis.

One of the specific features of the amidoxime sorbent is the weak affinity to Mg and Ca and the very strong affinity to Fe. This makes it possible to eliminate their interference in the determination of Zn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Hg^{2+}.

The amidoxime sorbent-filled column has a long lifetime. The degree of separation on the amidoxime column increases on adding dipicolinic acid to the oxalic eluent, as more stable
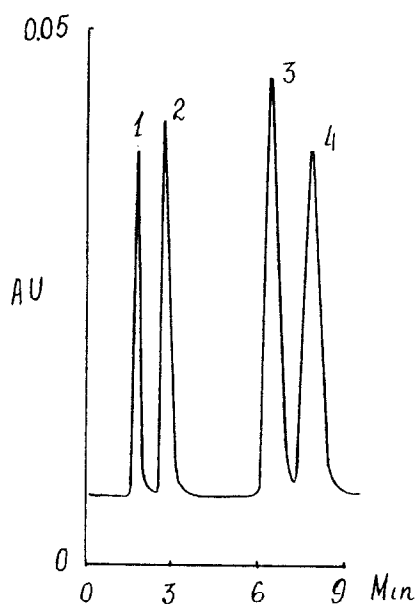
Fig. 5. Determination of Hg^{2+} on the Amidoxim column with oxalic acid as eluent. Eluent, 15 mM oxalic acid (pH 1.8); other conditions as in Fig. 1. Peaks: $1 = Zn^{2+}$; $2 = Ni^{2+}$; $3 = Cu^{2+}$; $4 = Hg^{2+}$.
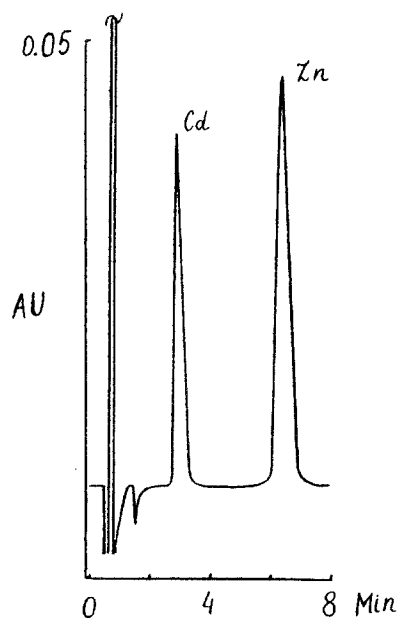

Fig. 6. Determination of Cd^{2+} and Zn^{2+} on the Amidoxim column using oxalic acid–dipicolinic acid as eluent. Eluent, 4 mM oxalic acid–4 mM sodium oxalate–0.5 mM dipicolinic acid (pH 3.4); detection, UV at 254 nm; other conditions as in Fig. 1.

and strongly retained metal dipicolinic complexes are formed. In this instance direct UV detection of the separated metal complexes at 254 nm was applied (Fig. 6).

The elution conditions developed may be used for quantitative analysis. For example, the results for Cu^{2+} determination were certified value 5.0 ppm and found (mean ± S.D.) 5.1 ± 0.1 ppm ($n = 5$). Chromatographic conditions for the rapid separation and determination of Zn^{2+}, Co^{2+}, Pb^{2+}, Cd^{2+}, Hg^{2+} and Cu^{2+} in water samples were established. The technique involves the application of standard spectrophotometric conditions for the detection of metals with postcolumn reaction with PAR.

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