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# Application of a dynamically coated sorbent and conductimetric and UV detectors to the determination of alkaline earth and transition metal cations

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## Abstract

The separation of alkaline earth and transition metal cations was performed on the reversed-phase sorbent Silasorb C<sub>18</sub> modified under static conditions with dodecylbenzenesulphonic acid and cetyltrimethylammonium bromide. Mixtures of ethylenediamine, citric acid and tartaric acid without addition of an ion-pair reagent and of dipicolinic and oxalic acid with an ion-pair reagent were used as eluents. The selective separation of twelve cations (Fe<sup>3+</sup>, Cu<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup>, Pb<sup>2+</sup>, Co<sup>2+</sup>, Cd<sup>2+</sup>, Fe<sup>2+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup> and Ba<sup>2+</sup>) in 15 min was obtained. The lifetime of this dynamically coated column was found to exceed that of a column packed with silica gel with sulphonic functional groups.

## 1. Introduction

The determination of alkaline earth and transition metals is an important part of the determination of the ionogenic content of natural and waste waters. Ion chromatography (IC) is successfully applied for this purpose and can compete with inductively coupled plasma and atomic absorption spectrometric methods for the determination of alkaline earth and transition metals [1]. Conventional reversed-phase columns and LC instruments have been increasingly used to separate metal ions [2–4].

In this paper, we propose techniques for the determination of alkaline earth and transition

metal cations using ion-pair and ion-interaction chromatography.

## 2. Experimental

The separation column for ion-interaction chromatography was prepared as follows. The reversed-phase sorbent Silasorb C<sub>18</sub> (7.5 μm) (Tessek, Prague, Czech Republic) was treated with an excess of aqueous dodecylbenzenesulphonic acid solution under static conditions. The column was filled with the resulting aqueous suspension of the sorbent with a column packing device. The column packing efficiency was evaluated by determining the number of theoretical plates per metre for the K<sup>+</sup> peak in suppressed IC. The eluent contained 5 mM HNO<sub>3</sub> and 0.2

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mM dodecylbenzenesulphonic acid. The efficiency of a well packed  $100 \times 3$  mm I.D. column was about 30 000 theoretical plates per metre. This column has been applied to the determination of alkaline earth and transition metal cations [5].

The determination of anionic complexes of transition and alkaline earth metals by ion-pair and ion-interaction chromatography was performed on a standard glass column ( $100 \times 3$  mm I.D.) containing Silasorb C<sub>18</sub> (7.5  $\mu$ m). The ion-pair reagents used included tetrabutylammonium hydroxide, sodium iodide and cetyltrimethylammonium bromide.

### 3. Results and discussion

The method for determining transition and rare earth metal cations proposed initially by Cassidy and co-workers [2,3] requires post-column reaction with 4-(2-pyridylazo)resorcinol (PAR) or Arsenazo-III and UV-Vis spectrophotometric detection. In addition, relatively high-concentration solutions of sodium tartrate, citrate and oxalate (pH 3–4) are used as the eluent. This does not permit the use of conductimetric detection and does not allow the determination of the transition and the alkaline earth metals simultaneously.

We used solutions of ethylenediamine with tartaric, citric and oxalic acid as eluents. Because of the strong eluting ability of ethylenediamine, the eluent concentration can be considerably decreased. Analogous eluents are used for the separation of metal cations on functionalized sulphonic cation exchangers. In this way the background conductivity is sufficiently low for conductimetric detection to be practicable. The alkaline earth and transition metal cations were separated on the  $100 \times 3$  mm I.D. column packed with the dynamically coated sorbent described.

With the use of the ethylenediamine-containing eluent comes the column stability is of concern. It was demonstrated experimentally that the column lifetime is more than 300 sample injections. The column's operational stability

was evaluated by the separation efficiency of the metals and by the theoretical plate number for Ca<sup>2+</sup>. The sufficiently long column lifetime can be explained by assuming that one ethylenediamine cation is sorbed by two molecules of dodecylbenzenesulphonic acid via an ion-exchange mechanism. The associate produced is strongly sorbed by the hydrophobic surface of the reversed-phase sorbent. The addition of dodecylbenzenesulphonic acid to eluent is not helpful, because its ethylenediamine salts are hardly soluble.

The addition of small amounts of 0.05 mM sodium dodecyl sulphate to the eluent and the use of guard and precolumns increases the analytical column lifetime. The precolumn filled with reversed-phase sorbent is placed between the pump and the injector for elimination of eluent contamination. The guard column is placed between the injector and the analytical column. It protects the analytical column from sample contaminants and is packed with the same sorbent.

The optimum conditions for the determination of the alkaline earth and transition metal cations on the dynamically coated sorbent were established from the results of the experimental work. A mixture of Fe<sup>3+</sup>, Cu<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup>, Pb<sup>2+</sup>, Cd<sup>2+</sup>, Co<sup>2+</sup>, Fe<sup>2+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup> and Ba<sup>2+</sup> was selectively separated using an eluent consisting of 2.5 mM ethylenediamine–2.5 mM citric acid–2.5 mM tartaric acid (Fig. 1). The most rapid separation of alkaline earth metals was obtained with 1.5 mM ethylenediamine–1.5 mM oxalic acid. Fig. 2 shows the separation of a mixture of Be<sup>2+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup> and Ba<sup>2+</sup>. The detection limit for all of the alkaline earth and transition metals using conductimetric detection is ca. 0.5 mg/l.

The technique developed for the determination of alkaline earth and transition metal cations on the dynamically coated column using indirect UV detection might be of interest. A 1 mM Ce(NO<sub>3</sub>)<sub>3</sub> solution was used as the eluent and UV detection at 254 nm was applied. The analysis time for a mixture of Mg<sup>2+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup> and Ba<sup>2+</sup> under these conditions did not exceed 5 min. This technique for the determination of

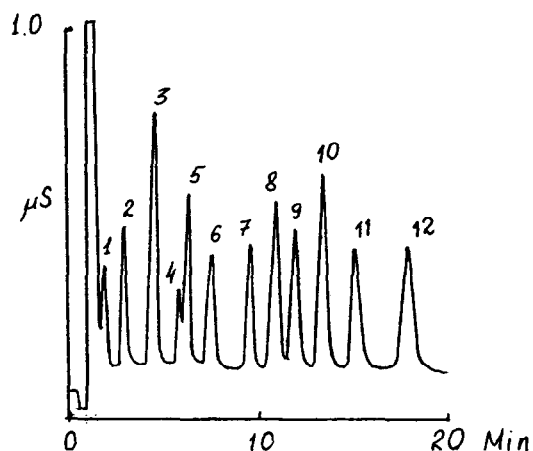


Fig. 1. Separation of transition metal ions on a dynamically coated column. Column,  $100 \times 3$  mm I.D., packed with Silasorb  $C_{18}$ , coated with dodecylbenzenesulphonic acid; eluent, 2.5 mM ethylenediamine–2.5 mM citric acid–2.5 mM tartaric acid (pH 3.2); flow-rate, 1 ml/min; detection, conductimetric. Peaks: 1 =  $Fe^{3+}$ ; 2 =  $Cu^{2+}$ ; 3 =  $Ni^{2+}$ ; 4 =  $Pb^{2+}$ ; 5 =  $Zn^{2+}$ ; 6 =  $Co^{2+}$ ; 7 =  $Fe^{2+}$ ; 8 =  $Mg^{2+}$ ; 9 =  $Cd^{2+}$ ; 10 =  $Ca^{2+}$ ; 11 =  $Sr^{2+}$ ; 12 =  $Ba^{2+}$ . Metals concentrations, 1–10 mg/l.

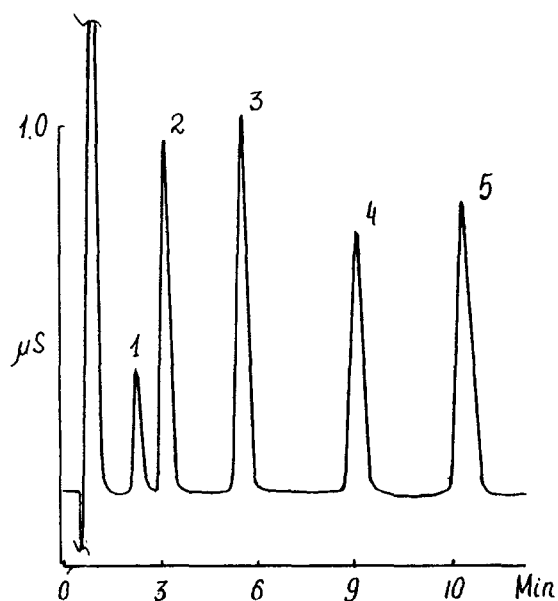


Fig. 2. Separation of alkaline earth metal ions on a dynamically coated column. Eluent, 2.5 mM ethylenediamine–3.5 mM oxalic acid (pH 3.4); other conditions as in Fig. 1. Peaks: 1 =  $Be^{2+}$ ; 2 =  $Mg^{2+}$ ; 3 =  $Ca^{2+}$ ; 4 =  $Sr^{2+}$ ; 5 =  $Ba^{2+}$ .

alkaline earth metals is more sensitive than that with conductimetric detection. The determination limit of alkaline earth metal cations is 0.01 mg/l. Unfortunately, the determination of transition metals by this technique is not possible, as the selectivity of the separation of these cations is low when a  $Ce(NO_3)_3$ -containing eluent is used.

A technique for determining transition metals in the form of their anionic complexes was worked out. The separation is carried out on the standard reversed-phase Silasorb  $C_{18}$  column. The eluent used permits the production of the anionic metal complexes in the analytical column and these complexes can be detected by direct UV methods. An analogous technique has been proposed for the determination of metals in the form of their cyanide complexes with UV detection at 214 nm [6]. We used an eluent consisting

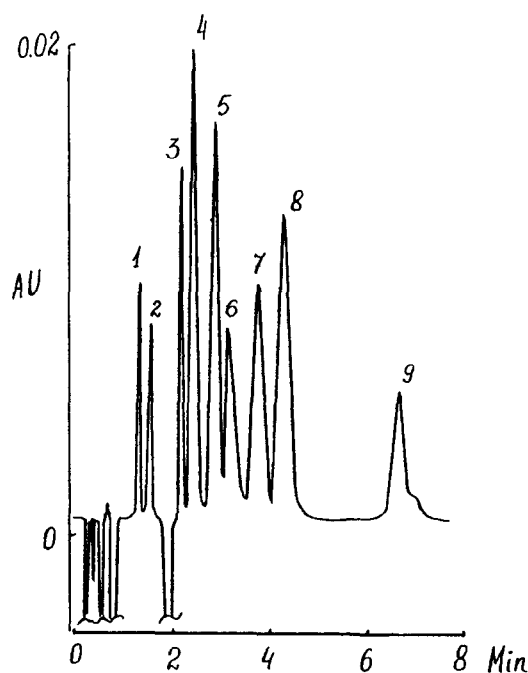


Fig. 3. Separation of transition metals by ion-pair chromatography. Column,  $100 \times 3$  mm I.D., packed with Silasorb  $C_{18}$ ; eluent, 5 mM sodium oxalate–0.3 mM pyridinedicarboxylic acid–1 mM tetrabutylammonium hydroxide (pH 5.5); flow-rate, 0.5 ml/min; detection, UV at 254 nm. Peaks: 1 =  $Pb^{2+}$ ; 2 =  $Fe^{3+}$ ; 3 =  $Cu^{2+}$ ; 4 =  $Ni^{2+}$ ; 5 =  $Zn^{2+}$ ; 6 =  $Co^{2+}$ ; 7 =  $Mn^{2+}$ ; 8 =  $Cd^{2+}$ ; 9 =  $Hg^{2+}$ .

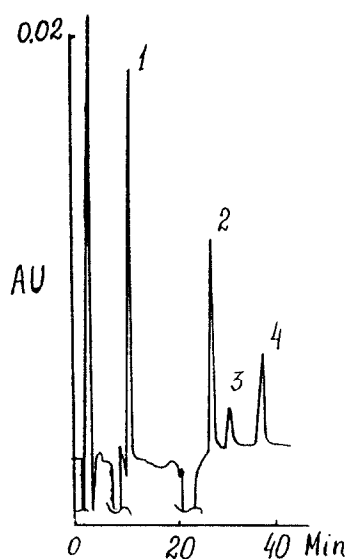


Fig. 4. Chromatogram of Moscow drinking water obtained by direct sample injection. Column,  $100 \times 3$  mm I.D., packed with Silasorb  $C_{18}$ , dynamically coated with cetyltrimethylammonium iodide; eluent, 2 mM sodium oxalate–0.2 mM pyridinedicarboxylic acid–1 mM tetrabutylammonium iodide (pH 5.2); flow-rate, 0.5 ml/min; detection, UV at 254 nm. Peaks: 1 =  $Fe^{3+}$  (0.2 mg/l); 2 =  $Cu^{2+}$  (0.04 mg/l); 3 =  $Ni^{2+}$  (0.02 mg/l); 4 =  $Zn^{2+}$  (0.1 mg/l).

of 2 mM sodium oxalate–0.2 mM dipicolinic acid–1 mM tetrabutylammonium hydroxide. Dipicolinic acid has been shown to be a convenient eluent for the separation of heavy and transition metals with postcolumn PAR reaction detection [7]. The eluent used in this technique permits direct UV detection at 254 nm. The limit of determination of the transition metals is 0.005 mg/l.

Fig. 3 shows the separation of a mixture of transition metal cations obtained by ion-pair chromatography. The selective separation of  $Pb^{2+}$ ,  $Fe^{3+}$ ,  $Mn^{2+}$ ,  $Cu^{2+}$ ,  $Ni^{2+}$ ,  $Zn^{2+}$ ,  $Co^{2+}$ ,

$Cd^{2+}$  and  $Hg^{2+}$  was achieved. All the inorganic ions were eluted before the system peak caused by the sorption of dipicolinic acid. The high sensitivity of the technique makes it possible to perform the determination of some transition metals in natural water samples without pre-concentration. Fig. 4 shows a chromatogram for Moscow drinking water obtained by direct sample injection. This separation was carried out on the Silasorb  $C_{18}$  column treated with cetyltrimethylammonium bromide.

Ion-pair and ion-interaction chromatography are practical methods for determining cations of metals and their anionic complexes. The technique described can be successfully used in routine analyses for heavy, transition and alkaline earth metal cations and also for investigations of unknown samples. The developed techniques utilize direct and indirect conductimetric and UV detection. The ability to use all of these detection modes enhances the usefulness of LC for the determination of cations in environmental samples.

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