Application of multi-dimensional liquid chromatography to the separation of some transition and heavy metals

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Abstract

Multi-dimensional liquid chromatography was applied to the separation of the toxic metals Cd^{2+} and Pd^{2+} and other transition and heavy metals in sea, natural and waste waters to enhance the selectivity and determination sensitivity. The separation and determination of Cu^{2+}, Ni^{2+}, Co^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+} and Fe^{2+} were achieved on a dynamically coated sorbent column with conductimetric detection. After passing through the conductimetric cell, the eluate zones containing insufficiently separated components were withdrawn from the eluate flow and injected into a second ion chromatographic system. Complete separation of Pb^{2+}, Zn^{2+}, Mn^{2+} and Cd^{2+} was achieved on this second column filled with a chelate sorbent containing iminodiacetate groups. UV detection with postcolumn reaction with 4-(2-pyridylazo)resorcinol was used in the second system.

1. Introduction

The development of new ion chromatographic (IC) techniques for the separation and determination of metals in natural, waste and industrial waste waters is an important task. Transition and heavy metals are toxic when their concentrations in water exceed certain values. The most toxic heavy and transition metals are Hg^{2+}, Cu^{2+}, Pb^{2+}, Cd^{2+}, Cr^{3+}, Zn^{2+} and Ni^{2+} and the most toxic alkaline earth metals are Be^{2+}, Ba^{2+} and Sr^{2+}.

In some instances, isocratic IC separation is not achieved for multi-component mixtures of these metals. In order to increase the selectivity of separation of metals with a similar sorption properties and to eliminate interferences by macro-components (*e.g.*, Mg^{2+} and Ca^{2+} in sea

water), we used the method of multi-dimensional chromatography.

2. Experimental

A Hewlett-Packard Model 1084A liquid chromatograph with two high-pressure pumps and a spectrophotometric detector was used. A Rheodyne (Berkeley, CA, USA) sample injector, a high-pressure switching valve equipped with a 100-μl loop, combined with iminodiacetate (IDA)-containing sorbent-packed cartridge (3 × 3 mm I.D.); and a conductimetric detector were included in the multi-dimensional chromatographic scheme. Postcolumn reaction with 4-(2-pyridylazo)resorcinol (PAR) [1] was performed with an additional low-pressure pump. The analytical columns used were 100 × 3 mm I.D. filled with 7.5-μm Silasorb C_{18} (Tessek,

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Prague, Czech Republic), 150×3 mm I.D. filled with a chelating sorbent with IDA groups (El-siko, Russian Federation) and 50×3 mm I.D. packed with chelating Amidoxim sorbent containing amidoxime groups (Elsiko). All chemicals were of analytical-reagent grade and purified water obtained using a Milli-Q apparatus (Millipore) was used throughout.

3. Basis of multi-dimensional chromatography

This method was applied previously in IC for the determination of organic and inorganic anions [2–5]. Multi-dimensional chromatography is named by analogy with planar chromatography, where the components of the mixture are separated in consecutive order by two different eluents in different dimensions to increase the selectivity.

Fig. 1 shows a scheme of the multi-dimensional IC device and Fig. 2 shows an example of its application. As can be seen from Fig. 2, neither

Fig. 2. Example of application of the multi-dimensional IC scheme. (a) Metal separation on column 1 in isocratic regime; (b) metal separation on column 2 in isocratic regime; (c) metal separation according to the multi-dimensional IC scheme. T_1 = Time of separation on column 1; T_2 = time of separation on column 2.
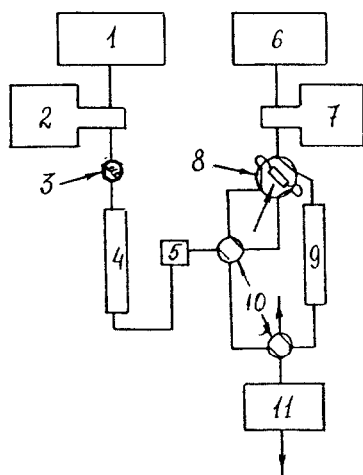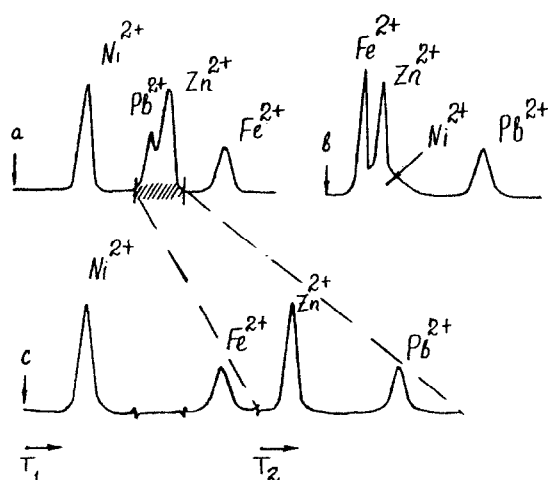

Fig. 1. Schematic diagram of multi-dimensional ion chromatographic system. 1 = Eluent 1; 2 = pump 1; 3 = injector 1; 4 = separation column 1; 5 = conductimetric detector; 6 = eluent 2; 7 = pump 2; 8 = injector 2 with precolumn; 9 = separation column 2; 10 = switching valves; 11 = UV–Vis detection system including postcolumn reaction with PAR.

of the two IC systems separates selectively all four components of a mixture of metals with isocratic elution. Pb^{2+} and Zn^{2+} ions are not selectively separated by the first system and Fe^{2+} and Zn^{2+} ions are not selectively separated from Ni^{2+} by the second system. However, the combination of these two chromatographic systems in the multi-dimensional method permits this problem to be solved. After separation on the first column and detection of the sufficiently separated components, the eluate zone containing poorly separated Pb^{2+} and Zn^{2+} is withdrawn from the eluate flow by the additional switching valve (Fig. 1). The withdrawn zone of the eluate passes to the preconcentration column via the injector of the second separation system. The second system selectively separates Pb^{2+} and Zn^{2+} ions. Thus all the components are selectively separated and determined by the combination of two chromatographic systems.

Our preliminary task was to devise isocratic IC systems for the selective separation of metals. The combination of such systems in the multi-

dimensional scheme was then applied to the analysis of metal mixtures

4. Results and discussion

There are two main approaches to IC separation of transition and heavy metals: in the form of their anionic complexes and in their cationic form. We performed the determination of heavy and transition metal anionic complexes with oxalate ion. The separation was carried out on the complexing sorbent Amidoxim, which has a silica gel-based matrix with amidoxime functional groups [6].

The metal–oxalate complexes were separated by ion-exchange and complexing mechanisms on this sorbent. The factors that influence the selectivity of metal separation were studied and the optimum conditions for the determination of transition and heavy metals were established. Fig. 3 illustrates the separation of metal mixtures under different conditions and shows that the Amidoxim sorbent can be used successfully for the determination of Cd^{2+}, Pb^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+} and Cu^{2+}. The very strong retention of Fe^{2+} on this sorbent should be mentioned, as this eliminates the interference of iron on the determination of other metals.

The determination of metals in their cationic form on dynamically coated and chelating sorbents was studied. We used Silasorb C_{18} sorbent treated with dodecylbenzenesulphonic acid under static conditions as the dynamically coated sorbent, and chelating silica gel-based sorbent with IDA groups. For each sorbent the optimum conditions for the separation of the metals were found.

Fig. 4 shows the most rapid and selective separation of metals using the dynamically coated sorbent and ethylenediamine–citric acid–tartaric acid solution (pH 3.2) as the eluent. A high separation selectivity was achieved for most of the metals with the exception of the Pb^{2+}–Zn^{2+} and Mn^{2+}–Cd^{2+} pairs (for these pairs the cations have the same retention time).
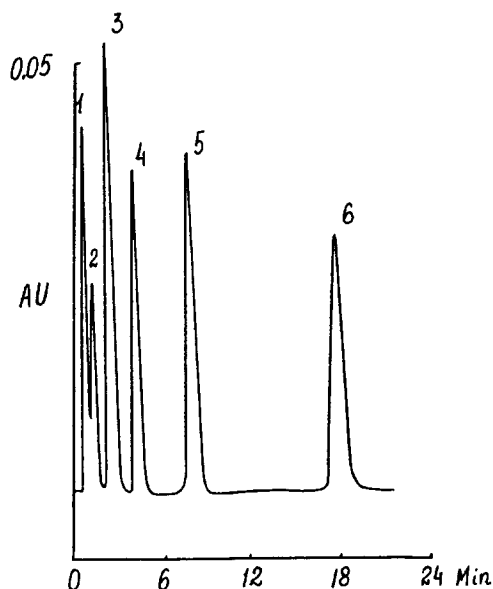
The separation of metal cations using the

Fig. 3. Separation of transition metals on Amidoxim column. Column, 50 × 3 mm I.D., packed with Amidoxim sorbent; eluent, 5 mM oxalic acid; flow-rate, 1 ml/min (pH 2.2); detection, UV–Vis at 540 nm; postcolumn PAR reaction. Peaks: $1 = Cd^{2+}$; $2 = Pb^{2+}$; $3 = Co^{2+}$; $4 = Zn^{2+}$; $5 = Ni^{2+}$; $6 = Cu^{2+}$.
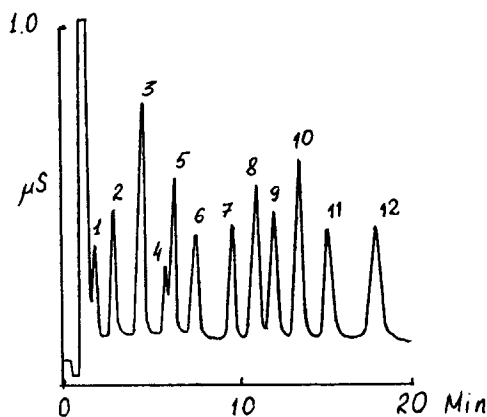

Fig. 4. Separation of transition and alkaline earth metals on dynamically coated column. Column, 100 × 3 mm I.D., packed with Silasorb C_{18}, coated with dodecylbenzenesulphonic acid; eluent, 2.5 mM ethylenediamine–2.5 mM citric acid–2.5 mM tartaric acid (pH 3.2); flow-rate, 1 ml/min; detection, conductimetric. Peaks: $1 = Fe^{3+}$; $2 = Cu^{2+}$; $3 = Ni^{2+}$; $4 = Pb^{2+}$; $5 = Zn^{2+}$; $6 = Co^{2+}$; $7 = Fe^{2+}$; $8 = Mg^{2+}$; $9 = Cd^{2+}$; $10 = Ca^{2+}$; $11 = Sr^{2+}$; $12 = Ba^{2+}$. Metal concentrations, 1–10 mg/l.
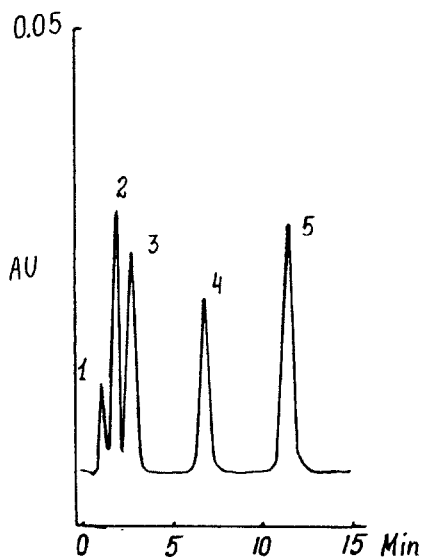
Fig. 5. Separation of transition metals on IDA-containing sorbent. Column, 150×3 mm I.D., packed with IDA sorbent; eluent, 15 mM oxalic acid–3 mM ethylenediamine (pH 2.8); flow-rate, 1 ml/min. Peaks: 1 = Fe^{2+}; 2 = Co^{2+}; 3 = Zn^{2+}; 4 = Cd^{2+}; 5 = Pb^{2+}.
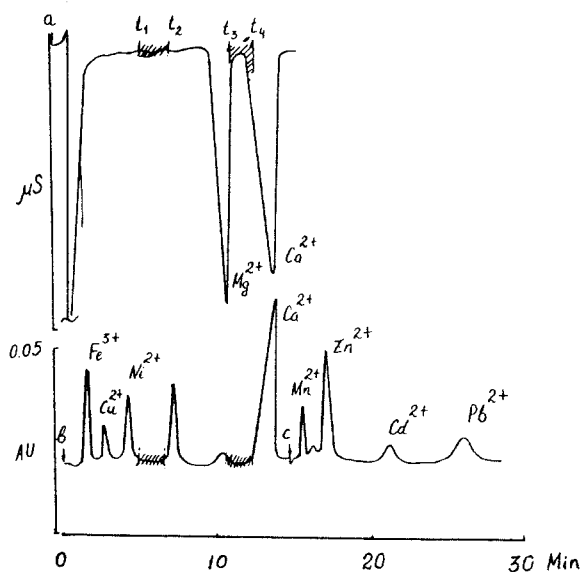

Fig. 6. Separation of metal mixtures using the multi-dimensional IC scheme. (a) Separation of metals on dynamically coated column. Conditions as in Fig. 4. t_1, t_2, t_3, t_4 = Times of valve switching; withdrawn zones of insufficiently separated metals are stained. (b) Separation of metals on dynamically coated column. Conditions as in Fig. 4. (c) Separation of metals on IDA column. Conditions as in Fig. 5.

IDA-based chelating sorbent [7] is shown in Fig. 5. This sorbent is well known for its high selectivity for the separation of heavy and transition metal cations. As Fig. 5 shows, the selective separation of Co^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} was achieved, and macro amounts of Mg^{2+}, Ca^{2+} and Fe^{3+} did not interfere. Cu^{2+} and Fe^{3+} cations are very strongly retained on this sorbent.

The selectivity of the metal separations was evaluated for each chromatographic system studied. It was found that metals with similar sorption properties are present in each system, but for each system these metals are different. For this reason it was possible to arrange the multi-dimensional IC system for the simultaneous determination of heavy and transition metals according to the scheme is Fig. 1. The switching mechanism is interactive with the conductimetric detector (5 in Fig. 1) and the switching is done manually by the analyst.

Separations of multi-component metal mixtures are shown in Fig. 6. In this instance the separation selectivity was increased by combining the sample separation on the dynamically coated sorbent using an eluent consisting of ethylenediamine–citric acid–tartaric acid with a second separation of the selected eluate zone on the chelating IDA sorbent with an oxalic acid-containing eluent.

The analysis of an Azov sea water sample taken near a metallurgical plant using the multi-
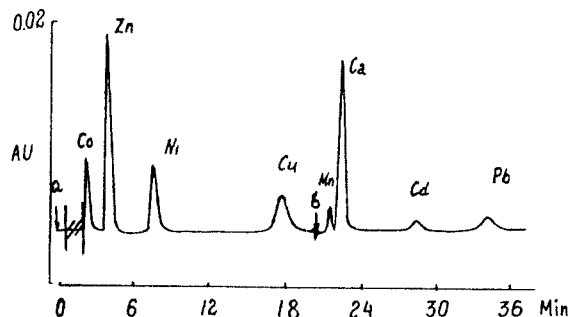

Fig. 7. Determination of transition metals in Azov sea water using multi-dimensional IC. (a) Separation on Amidoxim column, Conditions as in Fig. 3. (b) Separation on IDA column. Conditions as in Fig. 5. Withdrawn zones of insufficiently separated metals are shaded.

dimensional scheme is shown in Fig. 7. The metal concentrations in the sample were 0.005–0.05 mg/l.

The technique described has been demonstrated to be suitable for the determination of heavy, transition and some alkaline earth metals, and for the investigation of unknown samples by isocratic and multi-dimensional ion chromatography.

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