

# Separation of some metals as their anionic oxalate complexes by reversed-phase ion-interaction chromatography

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## ABSTRACT

The separation of some metal cations in the form of their oxalate complexes was investigated in a reversed-phase system with tetrabutylammonium cation ( $TBA^+$ ) as an ion-interaction agent. The analyte retention is governed by the ion-interaction mechanism and is predominantly affected by the oxalate concentration and by the other eluting anion (perchlorate) concentration and also by the  $TBA^+$  concentration. Further, the analyte retention and separation can be influenced by the mobile phase pH and by the addition of an organic modifier to the mobile phase. The dependences of the analyte capacity factors on the above-mentioned mobile phase parameters have a similar character, which were observed in common anion separations by ion-interaction chromatography.

## INTRODUCTION

At present, high-performance liquid chromatographic (HPLC) methods have a major role in metal determinations [1]. Metal cations are usually separated on special low-capacity cation exchangers by ion-exchange chromatography (IEC) [2-4]. The separation may also occur on non-polar stationary phases with the addition of the ionogenic, ion-interaction agents to the mobile phase [5] (reversed-phase ion-interaction chromatography, RP-IIC).

Some metals may be separated and determined in the form of anionic complexes by either IEC or BP-IIC. For example, platinum group metals and other noble metals have been determined in the form of the cyano [6,7]plexes

[12].

[11]ability method of Jones et al. to the separation of other metal cations, especially divalent metal cations. Factors that affect analyte retention (eluting ion concentration in the mobile phase, pH, addition of organic modifiers) were studied.

## EXPERIMENTAL

### Apparatus

The liquid chromatograph consisted of an HPP 5001 high-pressure pump, an LCI 30 injection valve, a 20- $\mu$ l sampling loop, a chart recorder (all from Laboratorní Přístroje, Prague, Czechoslovakia) and a Model 732 870 UV-Vis spectrophotometric detector (Knauer, Berlin, Germany) operating at 254 nm. In some instances postcolumn derivatization was used for

[11] Jones et al. [

detection, in which event the apparatus was supplemented with another HPP 5001 pump and an RE-2M postcolumn reactor (Laboratorní Přístroje). Detection was carried out at 520 nm. A glass column (150 × 3 mm I.D.) packed with an octadecyl-bonded silica gel, Separon SGX RPS (5 μm), was used for the separation. A saturation column (30 × 3 mm I.D.) packed with silica gel Separon SGX (7 μm) (all columns from Tessek, Prague, Czechoslovakia) was connected between the pump and the injection valve to presaturate the mobile phase with dissolved silica and to prolong the lifetime of the analytical column. Before measurements the columns were washed with methanol and water and then with the mobile phase at a flow-rate of 0.1 ml min<sup>-1</sup> overnight.

The mobile phase was deaerated in an ultrasonic bath before measurement. Measurements were carried out at laboratory temperature (22 ± 2°C).

### Chemicals

1<sup>-1</sup>ck solutions of 0.1 mol tetrabutylammonium hydroxide (TBA-OH) (Fluka, Buchs, Switzerland), oxalic acid and sodium perchlorate were prepared. Mobile phases were prepared by mixing these stock solutions in the required proportions, with additions of organic modifier (methanol, propanol, butanol) and with pH adjustment using dilute NaOH solution. In addition, stock solutions of 0.1 mol l<sup>-1</sup> MnCl<sub>2</sub>, CuCl<sub>2</sub>, NiCl<sub>2</sub>, CoCl<sub>2</sub> and Ce(NO<sub>3</sub>)<sub>3</sub> were prepared; these solutions were subsequently diluted to concentrations of 1 mmol l<sup>-1</sup> (MnCl<sub>2</sub>, NiCl<sub>2</sub> and CoCl<sub>2</sub>), 0.2 mmol l<sup>-1</sup> [Ce(NO<sub>3</sub>)<sub>3</sub>] or 0.02 mmol l<sup>-1</sup> (CuCl<sub>2</sub>) before measurement. A solution of 0.2 mmol l<sup>-1</sup> 4-(2-pyridylazo)resorcinol (PAR) in 1 mol l<sup>-1</sup> acetic acid-3 mol l<sup>-1</sup> ammonia solution was used as the postcolumn derivatization agent [5,13].

All chemicals were of analytical-reagent grade from Lachema (Brno, Czechoslovakia), except TBA-OH. The solutions were prepared in redistilled water.

### RESULTS AND DISCUSSION

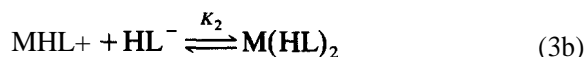
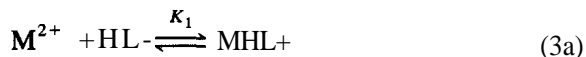
Metal cations are separated on a C<sub>18</sub> column using a mobile phase containing the quaternary

ammonium cation (Q<sup>+</sup>), oxalate ions and, as the case may be, another eluting cation (perchlorate, E<sup>-</sup>). It is assumed that metal ions are retained on the stationary phase surface by an ion-interaction mechanism in the form of anionic complexes. Such a system, however, is comparatively complex and, depending on the conditions of the respective measurement (concentration, pH, metal-to-ligand ratio), a number of side-reactions may take place:

dissociation of oxalic acid:



complex-forming equilibria of metal cations with oxalate anions (HL<sup>-</sup> or L<sup>2-</sup>, depending on the degree of dissociation):



etc., or



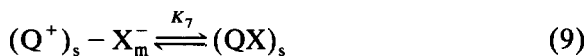
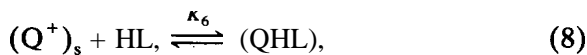
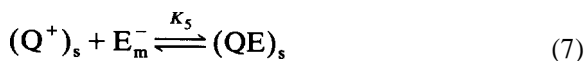
etc. For the total concentrations of the metal (c<sub>M</sub>) and oxalate (c<sub>L</sub>) in the mobile phase, we have

$$\begin{aligned} c_M = & [\text{M}^{2+}] + [\text{MHL}^+] + [\text{M}(\text{HL})_2] + \dots \\ & + [\text{M}(\text{HL})_n^{2-n}] + [\text{ML}] + [\text{ML};-] + \dots \\ & + [\text{ML}_n^{2-2n}] \end{aligned} \quad (4)$$

$$\begin{aligned} c_L = & [\text{L}^{2-}] + [\text{HL}^-] + [\text{H}_2\text{L}] + [\text{MHL}^+] \\ & + 2[\text{M}(\text{HL})_2] + \dots + n[\text{M}(\text{HL})_n^{2-n}] \\ & + [\text{ML}] + 2[\text{ML}_2^{2-}] + \dots + n[\text{ML}_n^{2-2n}] \end{aligned} \quad (5)$$

In the presence of the quaternary ammonium cation, negative charge-bearing complexes can be retained by the mechanism under consideration. A purely general solution of the retention model is difficult. For simplicity, we shall assume that, under certain conditions (at constant pH), only one type of ligand and of the anionic

complex prevail in the mobile phase. Let us assume first that in an acidic medium, where oxalic acid is not fully dissociated,  $\text{HL}^-$  is the prevailing oxalate anion, and the metal ions are retained in the form of an anionic complex  $\text{M}(\text{HL})_3^-$  (hereafter referred to as  $\text{X}^-$ ). In the course of the retention of analytes by an ion-interaction mechanism, particularly two types of equilibria [14–16] are effective: sorption of the ion-interaction agent on the stationary phase surface and ion exchange among ions of the analyte and eluting ions. The processes that occur can be expressed by the following equations (the dynamic ion-exchange model):



where the subscripts *m* and *s* refer to the mobile and stationary phases, respectively, and A, represents the free adsorption sites on the stationary phase.

The capacity  $K_0$  of the column is given by the sum

$$K_0 = [\text{A}_s] + [(\text{QE})_s] + [(\text{QX})_s] \quad (10)$$

Further, it holds for the capacity factor that

$$k' = q \cdot \frac{[(\text{QX})_s]}{c_M} \quad (11)$$

where *q* is the phase ratio.

After the above simplification and using eqn. 4 as a basis, the total concentration of a metal can be expressed by means of the respective stability constants:

$$c_M = \left[ \frac{[\text{X}^-]}{K_1 K_2 K_3 [\text{HL}^-]^3} + \frac{1}{K_2 K_3 [\text{HL}^-]^2} + \frac{1}{K_3 [\text{HL}^-]} + 1 \right] \quad (12)$$

Combining eqns. 10–12 and rearranging, we obtain a relationship describing the dependence of the reciprocal of the capacity factor on the mobile phase composition:

$$\frac{1}{k'} = \frac{\frac{1}{K_1 K_2 K_3 [\text{HL}^-]^3} + \frac{1}{K_2 K_3 [\text{HL}^-]^2} + \frac{1}{K_3 [\text{HL}^-]} + 1}{q K_0} \times \left( \frac{1}{K_4 K_7 [\text{Q}^+]} + \frac{K_5 [\text{E}^-]}{K_7} + \frac{K_6 [\text{HL}^-]}{K_7} + [\text{X}^-] \right) \quad (13)$$

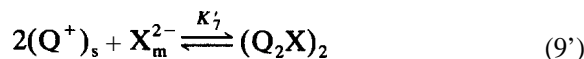
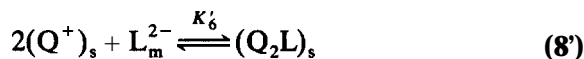
Eqn. 13 expresses a comparatively complex dependence of the capacity factor on the concentration of oxalate ion that acts simultaneously as both a **complexing** agent and eluting ion. Fortunately, under normal conditions where the oxalate concentration is markedly higher than that of the metal ions, lower complexes may be neglected and eqn. 13 acquires the following form:

$$\frac{1}{k'} = \frac{1}{q K_0} \left( \frac{1}{K_4 K_7 [\text{Q}^+]} + \frac{K_5 [\text{E}^-]}{K_7} + \frac{K_6 [\text{HL}^-]}{K_7} + [\text{X}^-] \right) \quad (14)$$

According to eqn. 14, the reciprocal of the capacity factor is directly proportional to the concentration of the eluting ions  $\text{E}^-$  and  $\text{HL}^-$  and to the reciprocal of the concentration of the quaternary ammonium cation  $\text{Q}^+$  in the mobile phase. Eqns. 13 and 14 express also the dependence of the capacity factor on the analyte concentration. This dependence applies, however, only in those cases when the analyte concentration is very high. This dependence may be neglected under the common conditions of HPLC analysis, which is obvious directly from eqn. 10 if the last term on the right-hand side is neglected. Eqn. 14 is analogous to a relationship derived by Xianren and Baeyens [16] for the separation of monovalent anions.

When the measurement is carried out at higher pH, it is necessary to assume that the oxalic acid is fully dissociated and the formation of complexes proceeds in accordance with eqns. (3a'), (3b'), etc. Now, let us assume that the prevailing anionic complex is  $\text{ML}_2^{2-}$  (henceforth denoted  $\text{X}^{2-}$ ). Equations describing the processes taking

place on the column have to be modified as follows:



In this case eqns. 6 and 7 also hold true. Solving the system of equations yields

$$k' = \frac{4}{4 \left( \frac{1}{K'_1 K'_2 [L^{2-}]^2} + \frac{1}{K'_2 [L^{2-}]} + 1 \right)} \times \left\{ \left[ \frac{K'_7 (1 + K_4 K_5 [Q^+][E^-])^2}{4 K_4^2 [Q^+]^2 (K'_6 [L^{2-}] + K'_7 [X^{2-}])^2} + \frac{2 K_0 K'_7}{K'_6 [L^{2-}] + K'_7 [X^{2-}]} \right]^{0.5} - \frac{(K'_7)^{0.5} (1 + K_5 K'_7 [Q^+][E^-])}{2 K_4 [Q^+] (K'_6 [L^{2-}] + K'_7 [X^{2-}])} \right\}^2 \quad (15)$$

indicating that if polyvalent ions participate in processes taking place on a column, the **dependences** of analyte retention on the composition of the mobile phase may be complicated.

The dependences of the capacity factor on mobile phase parameters were studied experimentally with the **divalent** cations  $Mn^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$  and  $Cu^{2+}$  and, for comparison, also with the  $Ce^{3+}$  cation.

In Fig. 1 are shown the dependences of  $1/k'$  on the concentration of perchlorate in the mobile phase at **constant** concentrations of oxalate,  $TBA^+$  and **pH**. The dependences are linear, consistent with observations acquired with **analogous** systems when separating monovalent inorganic anions [16,17]. Fig. 2 illustrates the dependences of  $1/k'$  on oxalate concentration at constant **pH** and  $TBA^+$  concentration; perchlorate ions were not present. These dependences are also linear over a fairly wide range. Hence the dependences in Figs. 1 and 2 satisfy the eqn. 14 well in spite of the fact that the conditions on which the derivation of this equation was based (e.g., degree of dissociation as given by the **pH** value) were not fully satisfied during the measurements. It is also worth noting that no significant difference was observed between the

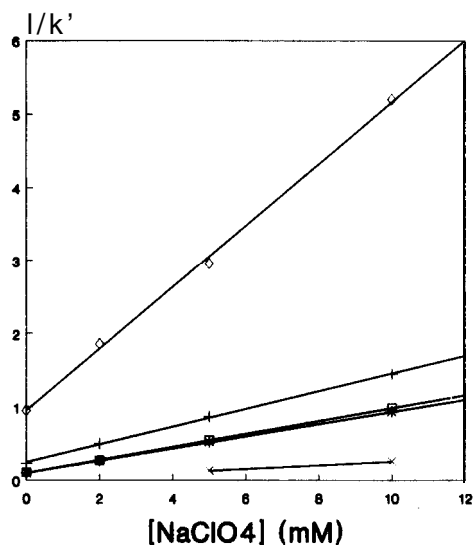


Fig. 1. Effect of perchlorate concentration on analyte retention. Mobile phase:  $2 \text{ mmol l}^{-1} TBA-OH-2 \text{ mmol l}^{-1}$  oxalic acid- $NaClO_4$  (pH 4.5). 0 =  $Mn^{2+}$ ; + =  $Co^{2+}$ ; \* =  $Ni^{2+}$ ; x =  $Cu^{2+}$ ; □ =  $Ce^{3+}$ .

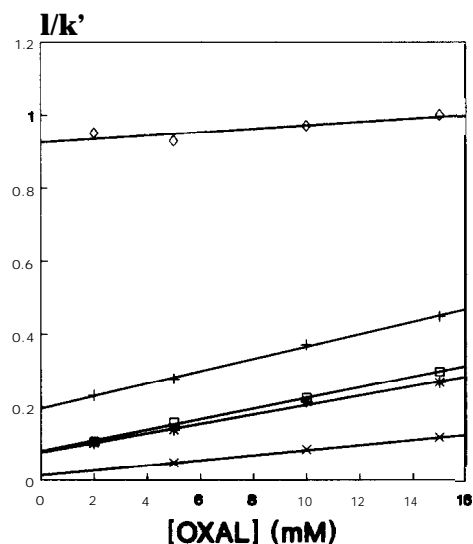


Fig. 2. Effect of oxalate concentration on analyte retention. Mobile phase:  $2 \text{ mmol l}^{-1} TBA-OH-oxalic$  acid (pH 4.5). Symbols as in Fig. 1.

behaviour of di- and trivalent cations (see also ref. 12).

The  $1/k'$  vs.  $1/[TBA^+]$  dependences at constant **pH** and eluting ion concentration are demonstrated in Fig. 3. It can be seen that the

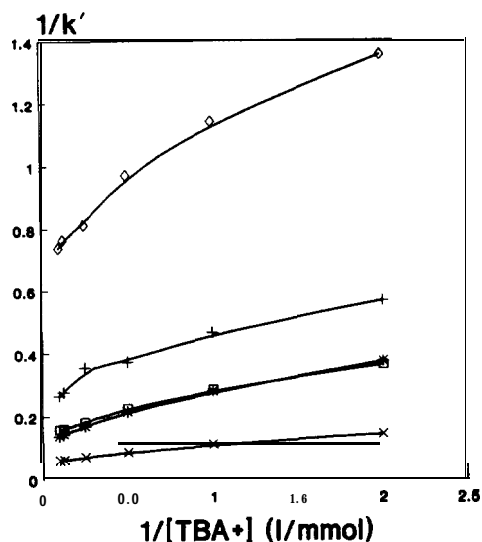


Fig. 3. Effect of ion-interaction agent ( $\text{TBA}^+$ ) on analyte retention. Mobile phase:  $\text{TBA-OH-2 mmol l}^{-1}$  oxalic acid ( $\text{pH } 4.5$ ). Symbols as in Fig. 1.

experimental dependences deviate from the linearity predicted by eqn. 14 at higher concentrations of the ion-interaction agent. Similar deviations were observed in the separation of inorganic anions and are connected with the limited capacity of the stationary phase (for a more detailed discussion, see ref. 16).

The  $\text{pH}$  of the mobile phase significantly affects the retention of analytes in the systems examined. The effect of  $\text{pH}$  can manifest itself particularly in two ways: the degree of dissociation of the mobile phase (oxalic acid) and hence also its eluting capacity increase with increase in  $\text{pH}$ ; and the  $\text{pH}$  influences the course of complex-forming reactions, the composition of complexes and thus also the capability of the complexes to be retained on the column.

The first of the above effects can be interpreted best with the aid of the dual species approach [18–20]. A mathematical description, however, is complicated in this instance. The experimental dependences shown in Fig. 4 are at least in qualitative agreement with this model.

Analyte retention in the RP-IIC may be affected by the addition of an organic modifier to the mobile phase. Organic modifiers influence especially the sorption of the ion-interaction agent on

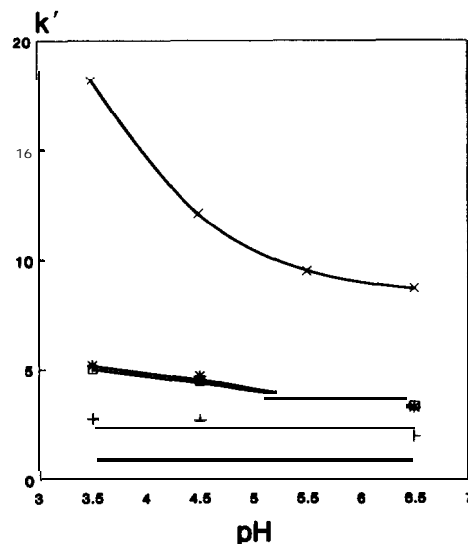


Fig. 4. Effect of mobile phase  $\text{pH}$  on analyte retention. Mobile phase:  $2 \text{ mmol l}^{-1} \text{ TBA-OH-10 mmol l}^{-1}$  oxalic acid,  $\text{pH}$  adjusted with  $\text{NaOH}$ . Symbols as in Fig. 1.

the non-polar stationary phase. Jandera et al. [21] expressed the relationship between the capacity factor and the organic modifier concentration  $c$  as

$$\log k' = A - Bc \quad (16)$$

Both the constants  $A$  and  $B$  were discussed by Zou et al. [22] and the equation was verified for separations of various phenylamine- and naphthylaminesulphonic acids on a  $\text{C}_{18}$  column in the presence of the  $\text{TBA}^+$  cation.

It can be seen from Fig. 5 that the dependences of the capacity factor on methanol concentration satisfy eqn. 16 comparatively well. An addition of higher alcohols affects the retention of analytes more strongly than the addition of methanol. Whereas adding 10% of methanol permits a very good separation within a reasonable time, addition of 5% of propanol or butanol renders the separation almost impossible. An example of separation is shown in Fig. 6; negative peaks belong to anions injected with the sample and separated by the conventional IIC mechanism.

Direct spectrophotometric detection as adopted in the present study is hardly universal. It can be used advantageously for the detection

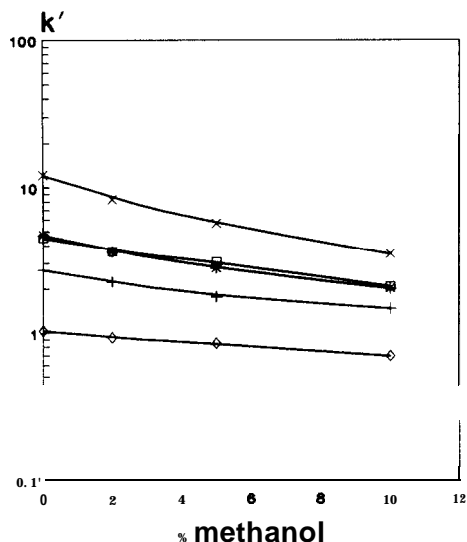


Fig. 5. Effect of methanol concentration on analyte retention. Mobile phase:  $2 \text{ mmol l}^{-1}$  TBA-OH- $10 \text{ mmol l}^{-1}$  oxalic acid-methanol (pH 4.5). Symbols as in Fig. 1.

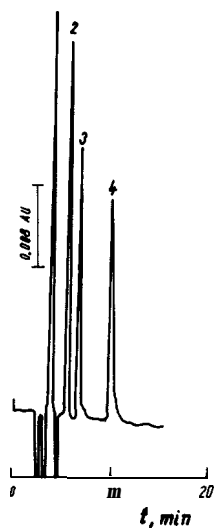


Fig. 6. Separation of the ions (1)  $\text{Mn}^{2+}$ , (2)  $\text{Co}^{2+}$ , (3)  $\text{Ni}^{2+}$  and (4)  $\text{Cu}^{2+}$ . Mobile phase:  $2 \text{ mmol l}^{-1}$  TBA-OH- $2 \text{ mmol l}^{-1}$  oxalic acid- $10\%$  (v/v) methanol (pH 4.5). Detection at 254 nm.

of  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ , and particularly for  $\text{Cu}^{2+}$  (the detection limits are 3-5 ng for the former three ions and about 0.1 ng for  $\text{Cu}^{2+}$ ). When a more universal method of detection, postcolumn

TABLE I

CAPACITY FACTORS ( $k'$ ) OF SOME METAL CATIONS WITH MOBILE PHASE CONTAINING  $2 \text{ mmol l}^{-1}$  TBA-OH,  $2 \text{ mmol l}^{-1}$  OXALIC ACID AND 5% (v/v) METHANOL (pH 4.5)

Cation	$k'$	Cation	$k'$
$\text{Mn}^{2+}$	0.86	$\text{Cd}^{2+}$	0.87
$\text{Co}^{2+}$	3.14	$\text{Pb}^{2+}$	2.00
$\text{Ni}^{2+}$	6.57	$\text{Zn}^{2+}$	4.86
$\text{Cu}^{2+}$	28.00		

derivatization with PAR, is used, other metal cations can also be determined in the given system. In this instance the sensitivity of detection (slope of the calibration line) is higher, but at the same time the noise of the baseline becomes greater, so that the detection limits are at the ng level. The retention characteristics of some cations are presented in Table I. Of the elements detectable with PAR,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Hg}^{2+}$  and  $\text{Bi}^{3+}$  ions do not form any peaks within a reasonable time. The alkaline earth elements and some other cations ( $\text{Al}^{3+}$ ,  $\text{Cr}^{3+}$ ) cannot be detected using PAR [23], so they do not interfere with the determination. An example of the separation is given in Fig. 7.

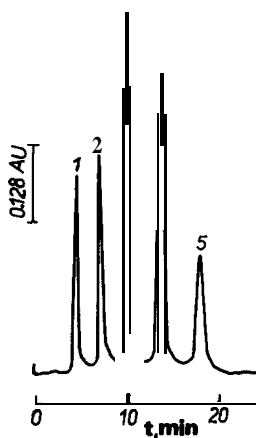


Fig. 7. Separation of the ions (1)  $\text{Cd}^{2+}$ , (2)  $\text{Pb}^{2+}$ , (3)  $\text{Co}^{2+}$ , (4)  $\text{Zn}^{2+}$  and (5)  $\text{Ni}^{2+}$ . Mobile phase:  $2 \text{ mmol l}^{-1}$  TBA-OH- $2 \text{ mmol l}^{-1}$  oxalic acid-5% (v/v) methanol (pH 4.5). Detection at 520 nm following postcolumn derivatization with PAR.

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