Trace Analysis of Some Bivalent Cations using Peak Focusation Technique with Microcolumn Ion Chromatography

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Dedicated to Professor W. Haerdi on the occasion of his 60th birthday

Some conditions for cation focusation on cation resin when using the microcolumn liquid chromatograph with conductometric detection are derived and verified experimentally. Separation is carried out using a complexing agent and a competitive cation in the mobile phase. Cations of transition metals, alkaline earths and lead were analysed. Sensitivity of the method ranges within tenths of p.p.b.

KEY WORDS: Ion chromatography, microcolumn liquid chromatography, bivalent cations.

INTRODUCTION

Ion chromatography has substituted a number of analytical methods used until recently. Its most important advantages consist in high selectivity and sensitivity of both cation and anion determination.

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This paper concentrates on the study of separation and determination of some bivalent cations of metals, especially metals of alkaline earths, transition metals and lead. Microcolumn chromatography was used with on-line enrichment technique on the microcolumn and with conductometric detection.

From the point of view of the column, three basic chromatographic systems used for separation of bivalent cations of metals can be distinguished: the separation of cations on the solid cation resin, the separation of complexes of the corresponding cations on columns with the reversed phase and the separation on solid sorbents prepared by chemical bonding of the complexing agent.

In the case when the cation resin is used for separation of ions of alkaline earths by ion-exchanging mechanism, the mobile phase contains a mineral acid and a competitive cation.[1] In such a case, it is also possible to add the complexing agent—mostly a hydroxy carboxylic acid—into the mobile phase.[2] Complexes (negative or neutral) being in equilibrium with cations such as transition metals appear in the mobile phase. Cation retention is determined by stability of the complexes.[2] Mobile phases contain mostly also the competitive cation, ethylenediamine in this case.

Also dynamic ion-exchangers prepared directly in the chromatographic column with the reversed stationary phase by adding an ion-pairing agent were described.[3] Separation of metal complexes is also used in reversed phase chromatography. Complexes are prepared either before injection,[4-6] or they arise in the chromatographic system by reaction with the mobile phase complexing component. In most cases, complexing agents forming with cations complexes of high molar absorption coefficient in the UV region are used. For transition metals agents such as dithiocarbamates,[4,5] EDTA,[6] β-isopropyltropolone[7] and others were used. For separation of bivalent cations of metals, also sorbents prepared by bonding of the complexing agent on silica gel[8] or alumina[9] were applied. In such systems, separation is controlled by complex formation of metals with the bonded complexing agent.

The term trace analysis is usually used with concentrations in the range from tens of p.p.m. to units of p.p.t.[10] Using conductometric detection, minimal detectable concentrations of, e.g. 50 p.p.b. Mg^{2+} and 80 p.p.b. Ca^{2+} (Reference 2) were obtained. At oxidation of dithiocarbamate complexes[4] of transition metals on the ampero-

metric detector anode, the minimal detectable concentration was from 0.01 to 1 p.p.m. Atomic absorption detection[11] reaches minimal detectable concentrations from 0.1 to 10 p.p.m. When detecting complexes of metals by spectrometric detectors in the UV or visible spectrum region, the minimal detectable concentrations are in the range from 0.01 to 1 p.p.m.[12] The most sensitive detection of transition metals was obtained using a reaction detector. Complexing agent forming coloured complexes with cations is added to the effluent after the column and detected at wavelengths of $\lambda > 500$ nm. Minimal detectable concentrations in the low range p.p.b. were reached.[13]

An enrichment technique for separation of tartrate complexes of transition metals on cation resin using the reaction detector was worked out.[14,15] Cations from the solution are enriched on the precolumn packed with cation resin. When using 2 l of the sample, the minimal detectable concentration up to 1 p.p.t. was reached.[15]

The possibility of using microcolumns in ion chromatography was mentioned even earlier.[16,17] In the present study, peak focusation[18,19] with simultaneous influence on the retention strength of the chromatographic system[20-22] was used for trace analysis of cations.

EXPERIMENTAL

Apparatus

A MHPP 20 syringe type micropump with a glass piston and a Teflon-lined cylinder (Laboratory Instruments, Prague, Czechoslovakia) was used. Glass microcolumns, 0.7 to 0.9 mm i.d. and 150 mm long, were placed in a metal jacket (CGC System, Tessek Prague, Czechoslovakia) and packed with Silasorb C cation resin (Lachema, Brno, Czechoslovakia) with the particle diameter of $d_p = 7.5\,\mu$m. The sample was injected by a four-port injection valve with an internal loop of 0.2 μl (Valco Instr., Houston, USA) and a six-port injection valve with an external loop of stainless capillary with the volume of 100 μl and 1 ml (Institute of Analytical Chemistry, Brno, Czechoslovakia). The chromatograph was equipped with a CDLC 1 conductometric detector (Laboratory Instruments, Prague, Czecho-

slovakia) with the volume of the detection cell less than 1 μl and a TZ 4100 recorder (Laboratory Instruments, Prague, Czechoslovakia).

Chemicals

The mobile phase was prepared by dissolving tartaric acid and ethylenediamine, both of analytical reagent grade (Lachema, Brno, Czechoslovakia), in redistilled water. Salts of the studied cations (Lachema, Brno, Czechoslovakia) were used to prepare stock solutions at the concentration of 0.05 M.

RESULTS AND DISCUSSION

The trace analysis of the studied cations was carried out by means of microcolumn chromatography with the column packed with cation resin and the mobile phase containing the complexing agent and the competitive cation. Cation samples were enriched by direct injection on the microcolumn. In the mentioned chromatographic system, water functions as a weak mobile phase. When characterizing the sample solvent retention strength by capacity ratio k_s and the mobile phase retention strength by capacity ratio k (both quantities refer to the given cation), the process of injection can be considered chromatography with a stepwise gradient of the mobile phase. The solute retention volume can be expressed by the relationship

$$V_R = V_M(1 + k) + V_S(k_s - k)/k_s \qquad (1)$$

where V_M is the column dead volume, V_S is the sample volume. In case that $k_s \gg k$, the relationship (1) changes into

$$V_R = V_M(1 + k) + V_S. \qquad (2)$$

The maximal volume V_S depends on capacity ratios k_s and k. The advantages of microcolumn chromatography[18] with on-column enrichment techniques were pointed out. Still the ratio of the injected volume to the dead volume $V_S/V_M = 20$ will cause no important peak broadening and the chromatograms can be well evaluated quantitatively.

For the separation of bivalent cations on the microcolumn packed with cation resin, the mobile phase containing tartaric acid as the complexing agent and ethylenediamine as the competitive cation was used. Such system proved successful when working with conventional analytical columns.[1] With an aim to optimize the designed chromatographic system, the influence of the change in tartaric acid and ethylenediamine concentrations on the retention of individual cations in the recommended[2] range of concentrations was studied. The tartaric acid concentration was changed in the range from 2 to 6 mM at the constant concentration of ethylenediamine of 3 mM. The results are given in Table 1. Retentions of cations decrease with increasing concentration of the complexing anion. The concentration of ethylenediamine was changed in the range from 3 to 7.5 mM at the constant concentration of tartaric acid of 3 mM (Figure 1). Whereas ethylenediamine is the competitive cation, the retentions of solutes decrease with its increasing concentration. In the studied range of concentrations, this decrease in retention is higher than the decrease in retentions caused by the change of the tartaric acid concentration in the mobile phase.

Retention of cations depends on the mobile phase pH; pH of 3–5 is recommended.[2] At the values of pH < 3, tartaric acid loses its capacity to form complexes; at pH > 5, the protonation of ethylenediamine is incomplete. With respect to the measurements carried out, the mobile phase containing 3 mM of tartaric acid and 4.5 mM

Table 1 Dependence of cation retention volumes, V_R (μl), on tartaric acid concentration, C, at constant ethylenediamine concentration, $C_{EDA} = 3$ mM, and pH = 4

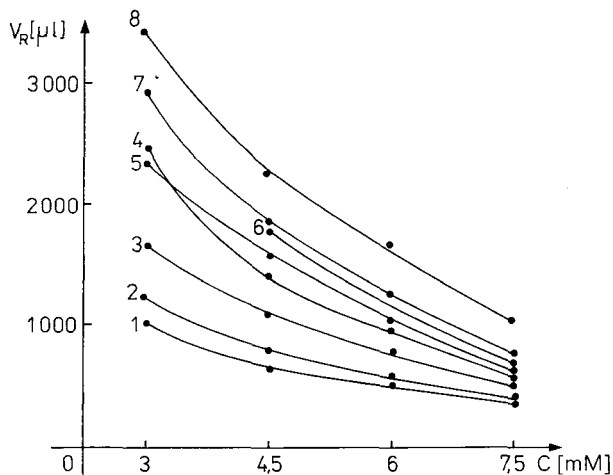| Cations	Tartaric acid concentration (mM)				
	2	2.5	3	4	5
Zn^{2+}	1220	1180	1106	1050	878
Ni^{2+}	1360	1300	1243	1186	952
Co^{2+}	1744	1652	1628	1576	1274
Cd^{2+}	2420	2367	2358	2355	2356
Mn^{2+}	2560	2509	2482	2500	2494
Mg^{2+}	—	2654	2600	2542	—
Ca^{2+}	—	2754	2715	2664	—
Sr^{2+}	—	3349	3204	3180	—

Figure 1 Dependence of cation retention volumes, $V_R(\mu l)$, on ethylenediamine concentration, C (mM), at constant tartaric acid concentration (3 mM), and pH = 4: (1), Zn^{2+}; (2), Ni^{2+}; (3), Co^{2+}; (4), Cd^{2+}; (5), Mn^{2+}; (6), Mg^{2+}; (7), Ca^{2+}; (8), Sr^{2+}; (9), Pb^{2+}.

of ethylenediamine was chosen; pH was adjusted with $HClO_4$ to pH = 4. Examples of separation of cations of transition metals, alkali earths and lead are given in Figure 2.

As follows from Eq. (1), it is necessary to know the capacity ratio of the solute in the sample matrix k_s for the estimate of enrichment on the microcolumn. The use of redistilled water acidified with perchloric acid to pH = 4 as the mobile phase results in very intensive sorption of solutes on cation resin. It was found for Zn^{2+} that $k_{sZn} > 160$. After adding 3 mM of tartaric acid to the mobile phase, the capacity ratio decreased to $k_{Zn} \doteq 50$ while other cations given in Table 2 showed higher capacity ratios in some cases even non-measurable with the given chromatographic system. It follows from the above-mentioned that $k_s \gg k$. The ratio $(k_s - k)/k_s$ for Zn^{2+} is in the interval (0.95, 1.00). Taking into account this fact, Eq. 2 was verified. Using the injected volume of 0.2 μl, the retention volumes were measured and capacity ratios for different cations were calculated. Results are given in Table 2. These values were used to calculate retention volumes for injection loops of 100 μl and 1 ml and to compare them with the quantities determined experimentally. The

dead retention volume V_M was determined experimentally for each used microcolumn. It is evident from Table 2 that the correspondence of quantities is satisfactory and, consequently, that Eq. (2) is correct.

Also separation efficiency is satisfactory under the given experimental conditions. Table 3 presents the widths of peaks for different quantities of injected volumes. Increase in peak widths in the case of injecting the samples with the volume of 1 ml is, in our opinion, due to the mixing effect in the injection loop and the stationary phase demixing effect of ethylenediamine. In consequence of that, the
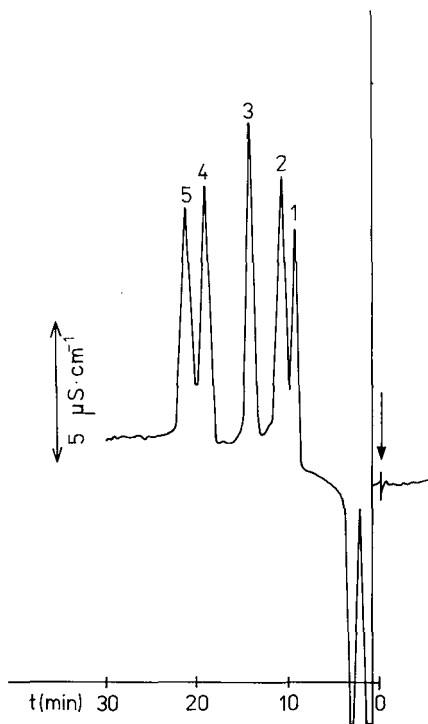

Figure 2A Separation of transition metal cations. Column: Silasorb S. Mobile phase: 3 mM tartaric acid; 4.5 mM ethylenediamine; pH = 4. Injection volume: $0.2\,\mu l$. Solutes: (1), Zn^{2+} (32 ng); (2), Ni^{2+} (59 ng); (3), Co^{2+} (59 ng); (4), Cd^{2+} (144 ng); (5), Mn^{2+} (66 ng).
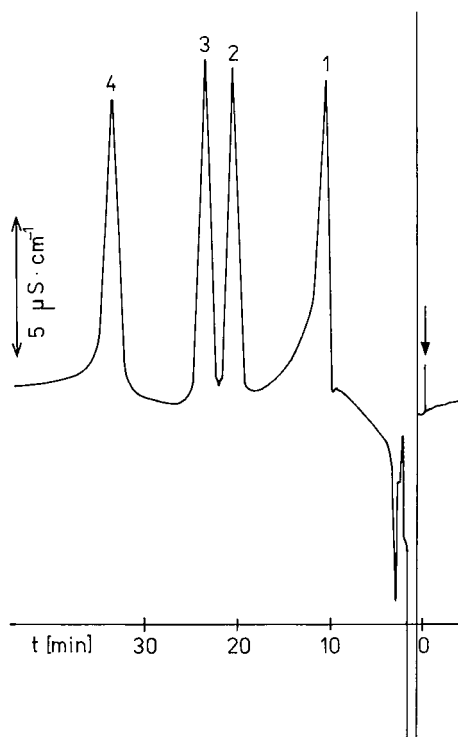
Figure 2B   Separation of alkaline earth metal cations and lead. Solutes: (1), Pb^{2+} (390 ng); (2), Mg^{2+} (48 ng); (3), Co^{2+} (80 ng); (4), Sr^{2+} (172 ng). For other conditions see Figure 2A.

sharpening effect to the stepwise gradient is suppressed by dispersion of the gradient step.

The focusing effect is shown in Figures 3 and 4. Minimal detectable concentrations, when using the injection loop of 1 ml, are given in Table 4. They range approximately from tenths to units of p.p.b. With respect to the simplicity of the conductometric detection, these limits are considered satisfactory. An example of using the microcolumn ion chromatography is given in Figure 5.

Table 2 Comparison of measured retention volumes, V_{R_E}, with volumes calculated from Eq. (2) V_{R_C}

Cation	k	$V_S = 100\ \mu l$, $V_M = 64\ \mu l$, $V_S = 1\ ml$, $V_M = 80\ \mu l$					
		$V_{R_C}\ (\mu l)$	$V_{R_E}\ (\mu l)$	V_{R_E}/V_{R_C}	$V_{R_E}\ (\mu l)$	$V_{R_C}\ (\mu l)$	V_{R_E}/V_{R_C}
Zn^{2+}	7.9	671	680	1.01	—	—	—
Ni^{2+}	10.1	812	760	0.93	2025	1888	1.07
Co^{2+}	13.3	1017	940	0.93	2175	2144	1.01
Cd^{2+}	17.8	1306	1318	1.01	2415	2504	0.96
Mn^{2+}	19.7	1427	1452	1.02	2640	2556	1.03
Mg^{2+}	19.4	1408	1482	1.05	2625	2632	1.00
Ca^{2+}	22.3	1594	1657	1.04	2850	2864	0.99
Sr^{2+}	32.0	2216	2252	1.02	3480	3640	0.99

Table 3 Peak widths in the half-height for different sample volumes

Cation	$V_S = 0.2\ \mu l$ $\sigma_V\ (\mu l)$	$V_S = 100\ \mu l$ $\sigma_V\ (\mu l)$	$V_S = 1\ ml$ $\sigma_V\ (\mu l)$
Zn^{2+}	47	44	—
Ni^{2+}	71	—	96
Co^{2+}	60	48	93
Cd^{2+}	70	60	105
Mn^{2+}	89	66	105
Mg^{2+}	80	84	90
Ca^{2+}	85	98	120
Sr^{2+}	110	119	150

Microcolumn liquid chromatography with conductometric detection and on-column enrichment technique enables us to reach minimal detectable concentrations comparable with other, mostly much more demanding, analytical techniques.
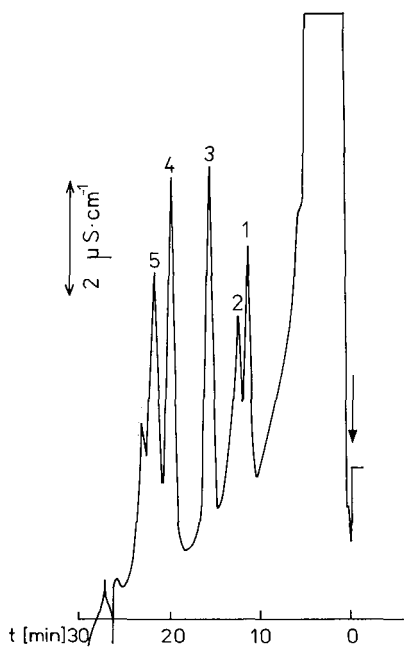
Figure 3A   Peak focusation of transition metal cations on a microbore column. Injection volume: 100 μl. Concentrations of solutes in the sample: (1), Zn^{2+} $4 \cdot 10^{-6}$ M; (2), Ni^{2+} $6 \cdot 10^{-6}$ M; (3), Co^{2+} $1 \cdot 10^{-5}$ M; (4), Cd^{2+} $1.2 \cdot 10^{-5}$ M; (5), Mn^{2+} $1.2 \cdot 10^{-5}$ M.
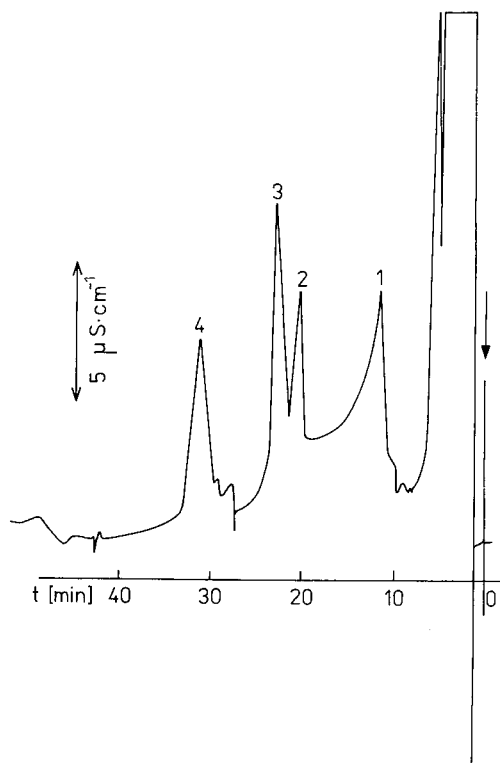
Figure 3B   Peak focusation of alkaline earth metal cations on a microbore colume. Injection volume: 100 μl. Concentration of solutes in the sample: (1), Pb^{2+} $1.6 \cdot 10^{-5}$ M; (2), Mg^{2+} $2 \cdot 10^{-5}$ M; (3) Ca^{2+} $3 \cdot 10^{-5}$ M; (4), Sr^{2+} $2 \cdot 10^{-5}$ M.
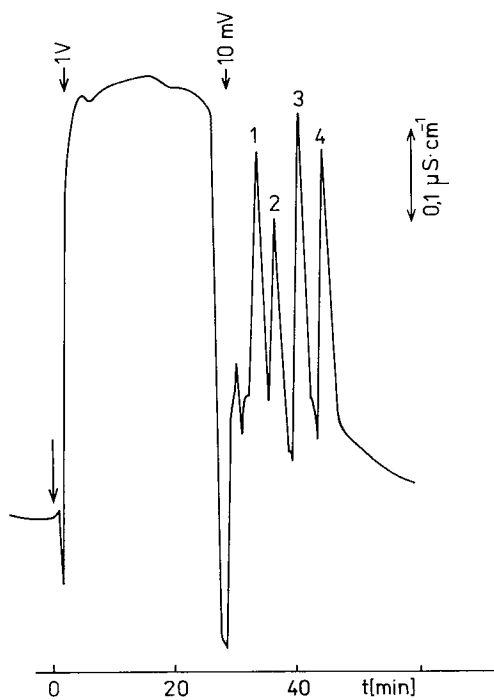
Figure 4 On column enrichment of the sample of transition metal cations. Injection volume: 1 ml. Concentration of solutes in the sample: (1), Ni^{2+} $8 \cdot 10^{-8}$ M; (2), Co^{2+} $1.2 \cdot 10^{-7}$ M; (3), Cd^{2+} $2 \cdot 10^{-7}$ M; (4), Mn^{2+} $2 \cdot 10^{-7}$ M.

Table 4 Minimal detectable concentration, C_{min}, with sample volume of 1 ml

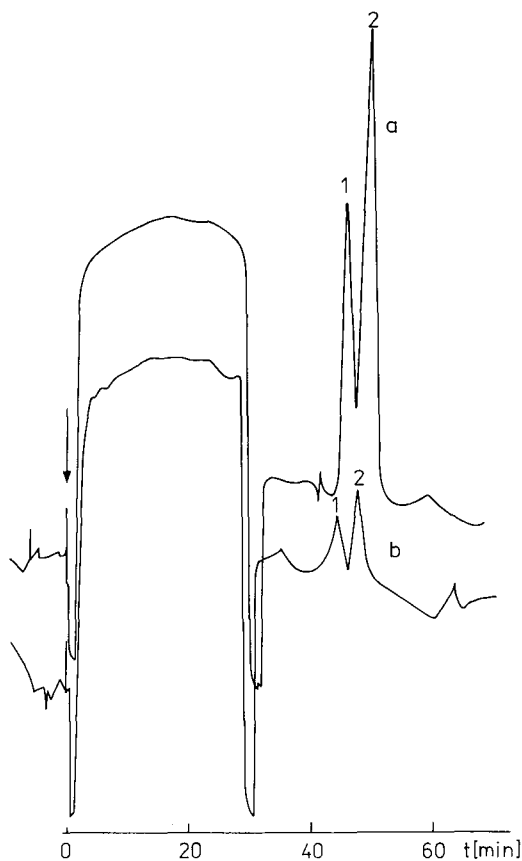| Cation	$C_{min} (mol \cdot l^{-1})$
Ni^{2+}	$6.0 \cdot 10^{-9}$
Co^{2+}	$8.7 \cdot 10^{-9}$
Cd^{2+}	$1.1 \cdot 10^{-8}$
Mn^{2+}	$1.3 \cdot 10^{-8}$
Mg^{2+}	$4.8 \cdot 10^{-8}$
Ca^{2+}	$5.0 \cdot 10^{-8}$
Sr^{2+}	$5.1 \cdot 10^{-8}$

Figure 5 Determination of Mg^{2+} and Ca^{2+} in distilled (a) and redistilled (b) water. Injection volume: 1 ml. Concentration of solutes: Mg^{2+} (a) $6 \cdot 10^{-7}$ M, (b) $1.3 \cdot 10^{-7}$ M; Ca^{2+} (a) $8.1 \cdot 10^{-7}$ M, (b) $1.6 \cdot 10^{-7}$ M.

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