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## DETERMINATION OF MONO-, BI- AND TRIVALENT CATIONS USING NON-SUPPRESSED ION CHROMATOGRAPHY

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### SUMMARY

The ion-chromatographic separation of mono-, bi- and trivalent cations is considered both from a mechanistic point of view and with regard to the influence of the mobile phase. These methods are compared with atomic absorption spectrometry. Application to the separation of the Cs-137 and Sr-90 radionuclides is discussed.

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### INTRODUCTION

Non-suppressed ion chromatography of heavy metal cations has rapidly gained importance in recent years<sup>1,2</sup>. This method allows the separation and subsequent determination of a large number of bivalent transition metals in liquid samples in one analysis step. Even when dealing with environmental or biological samples, tedious sample clean-up procedures may be omitted in most instances<sup>3–5</sup>. Several eluent systems have been developed for use in non-suppressed cation chromatography. Owing to the large difference in affinity to the stationary phase, a clear distinction is made between eluents best suited for the determination of mono- and bivalent cations<sup>6</sup>. Monovalent cations such as alkali metals and ammonium are easily eluted with dilute solutions of nitric acid<sup>7</sup>. Separations of alkaline earth and transition metals require the use of stronger driving ions, such as ethylenediamine (EDA), and are further facilitated by the addition of complexing agents to the mobile phase<sup>8,9</sup>. The need for two eluent systems for a complete assay of mono- and bivalent cations leads to double the analysis time and expenditure. However, so far only a few studies on the simultaneous ion-chromatographic determination of metal cations of different valencies have been published<sup>10,11</sup>.

The main reactions taking place during the ion chromatography of bivalent metal ions with the eluent system ethylenediamine (EDA)–citric acid (L) at acidic pH on a stationary phase R–metal (M) are shown by the following chemical equilibria:



This shows the influence of ethylenediamine concentration and complex formation on the affinity of metal ions towards the stationary phase. In the absence of citric acid, transition metal ions are bound firmly to *e.g.* the sulphonic acid groups and elution by

the ethylenediammonium cation is governed only by the EDA concentration. Without a complexing agent, the elution of transition metals would generally be very slow. If citric acid is added to the eluent, its anionic carboxylate groups compete for the metal ion, thus favouring release from the stationary phase by ethylenediamine, eventually resulting in a decrease in retention time. The more stable the metal ion/citrate complex, the more rapidly it will be eluted. This stability depends on the nature of the metal ion and on the degree of protonation of the citrate ion<sup>12</sup>.

The aim of this study was to establish a mechanism that can be used to explain and to alter selectively the affinity of mono- and bivalent cations to the stationary phase, and to selecting eluents of appropriate ionic strength and pH to fit the conditions for the separation of bi- and trivalent cations. Also, the ethylenediamine and citric acid eluent composition that is generally used for transition metal analysis was modified and the separation mechanism was studied over a wide pH range.

## EXPERIMENTAL

### *Apparatus*

The ion-chromatographic system consisted of a Model 1330 pump (Bio-Rad Labs., Richmond, CA, U.S.A.), an Altex Model 210 injection valve with a 100- $\mu$ l loop, a conductivity detector Model HPCM (Bio-Rad Labs.) and a CR-2A integration system (Shimadzu, Kyoto, Japan). For fractionation of radioactive samples a Model 7000 Ultorac fraction collector (LKB, Bromma, Sweden) was used.

### *Atomic absorption spectrometry (AAS)*

A Perkin-Elmer (Norwalk, CT, U.S.A.) Model 2280 atomic adsorption spectrometer with an air-acetylene flame was used. The operating parameters were set according to the manufacturer's instructions. Lead was determined at 283.3 nm and chromium at 357.9 nm. A slit width of 0.7 nm was used for both elements.

### *Materials and reagents*

The stationary phase used for the separation of mono- and bivalent cations was a sulphonated porous 5- $\mu$ m silica-based ion exchanger (TSK-IC cation SW, 50  $\times$  4.6 mm I.D. column, Bio-Rad Labs.). For the separation of bi- and trivalent cations a weak cation exchanger consisting of 7- $\mu$ m non-porous polymethacrylate beads with polyethyleneimine covalently coupled to the surface and exhaustively succinylated (HRLC-MA7C, 50  $\times$  7.8 mm I.D. column, Bio-Rad Labs.) was used.

The mobile phases were prepared by dissolving analytical-reagent grade citric acid monohydrate (Merck, Darmstadt, F.R.G.) and ethylenediamine (Fluka, Buchs, Switzerland) in deionized water. The pH was adjusted to the desired value either by addition of hydrochloric acid or potassium hydroxide or by adding further amounts of citric acid or ethylenediamine<sup>13</sup>.

Metal ion solutions were prepared from analytical-reagent grade chlorides or nitrates (Sigma, St. Louis, MO, U.S.A., and Fluka). Cs-137 (185 MBq, in 1 M hydrochloric acid) and Sr-90 (37 MBq, in 1 M nitric acid), used for the separation of radioactive nuclides, were purchased from Amersham International (Amersham, U.K.).

## RESULTS AND DISCUSSION

*Separation of mono- and bivalent cations*

In order to separate mono- and bivalent cations, a silica-based porous stationary phase with sulphonic acid functional groups was investigated. Fig. 1 shows the influence of pH on the retention times of mono- and bivalent ions. The elution of monovalent cations is only slightly affected by the hydrogen ion concentration, potassium exhibiting a minor increase in retention with rising pH. Most alkaline earth and transition metal ions react in the same way, their elution becoming faster with decreasing hydrogen ion concentration.

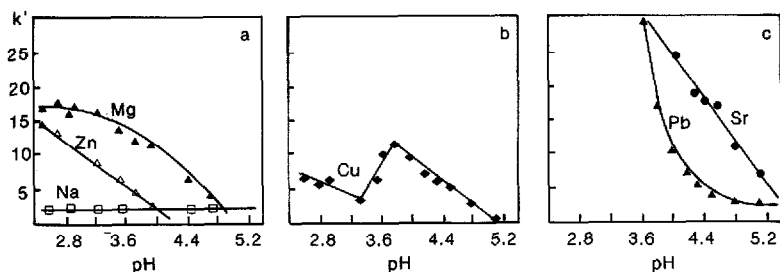


Fig. 1. Dependence of  $k'$  on the pH of the mobile phase system ethylenediamine-citric acid. Stationary phase, TSK IC cation SW; mobile phase, 3.5 mmol/l ethylenediamine-10 mmol/l citric acid; pH adjustment by addition of citric acid, ethylenediamine, HCl or KOH; flow-rate, 1 ml/min.

Some cations deviate from this behaviour and exhibit different elution patterns, which have to be considered when choosing optimum conditions for the separation of mono- and bivalent ions. Copper(II) shows a sharp decrease in retention time between pH 3.8 and 3.3, followed by an increase at lower pH (Fig. 1b). At pH 3.3, which is the pH of the mixture of 3.5 mmol/l EDA and 10.0 mmol/l citric acid, which is also the eluent proposed by the column manufacturer, copper and potassium tend to coelute. The slope of  $Pb^{2+}$  is steeper than those of the other ions and shows an exponential form, indicating that lead responds more strongly than any other ion to an increase in hydrogen ion concentration. Lead is adsorbed on the column at pH < 3.6, but may be released quickly if the pH is raised. The same applies to  $Sr^{2+}$  (Fig. 1c). This fact can be utilized for on-line preconcentration. The different elution patterns exhibited by the ions mentioned may be explained by the formation of citrate complexes of various structures. Therefore, a knowledge of both the dissociation of citric acid and of the complex stabilities of the metal ions is necessary.

Fig. 2 gives a general idea of the ion species present in an aqueous solution of citric acid, depending on pH. In the pH range covered in this study (2.50-5.20), all four species exist at varying levels. The distribution maxima for  $(citrate)^{2-}$  and  $(citrate)^{-}$  lie at pH 5.2 and 3.6, respectively. In Table I, the stability constants of complexes of certain metals with the different citrate ions are given<sup>14</sup>. In general, the stability increases with deprotonation of the ligand. The order of stability of citrate complexes of the metal ions is  $Sr^{2+} < Mg^{2+} < Zn^{2+} < Cu^{2+}$ , and the reverse order would

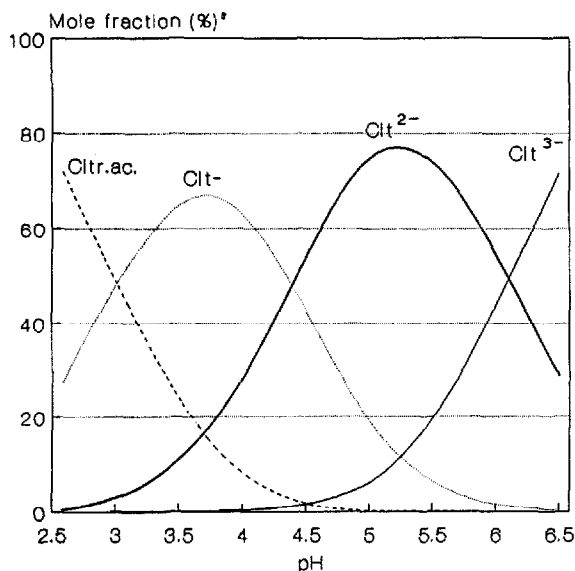


Fig. 2. Dissociation of citric acid.

correspond to their elution.  $\text{Pb}^{2+}$  forms very stable dicitrate complexes. For  $\text{Sr}^{2+}$  only complexes with the non-protonated ligand are reported.

The retention graphs of metal ions forming protonated citrate complexes ( $\text{Zn}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Cu}^{2+}$ ) appear as almost parallel lines (Fig. 1), with slopes of 4.26, 4.61 and 4.61, respectively.  $\text{Mg}^{2+}$ , however, deviates from the straight line at  $\text{pH} < 3$ , which is generally observed with ions that form low-stability complexes. This effect is attributed to the relatively high degree of protonation of the ligand, which lowers the complex stability. In this pH region, complexation reactions compete with ion-exchange mechanisms. The retention behaviour of copper may be explained by several factors attributed to unique reactions with citric acid:  $\text{Cu}^{2+}$  forms very stable complexes with  $(\text{citrate})^-$ , the species that is predominant in this pH region. Additionally, stable complexes are formed with the species  $(\text{citrate})^{2-}$ .  $\text{Pb}^{2+}$  does not fit into this scheme, as its stability constants suggest retention values close to those of the copper ion. Nevertheless, evidence can be found in Table I for the formation of very stable  $\text{Pb}^{2+}$ -dicitrate complexes. This unique feature explains the exponential decrease in the capacity factors of lead at  $\text{pH} > 3.6$ .

TABLE I

STABILITY CONSTANTS ( $\log K$ ) OF CITRIC ACID-METAL COMPLEXES<sup>14</sup>

<i>Ion</i>	$(\text{Cit}^{3-})M$	$(\text{Cit}^{2-})M$	$(\text{Cit}^-)M$	$(\text{Cit}^{3-})_2M$	$(\text{Cit}^{3-})_3M$	$(\text{Cit}^{3-})_2M_2$
$\text{Zn}^{2+}$	4.98	2.98	1.25	5.90	—	—
$\text{Mg}^{2+}$	3.37	1.60	0.84	—	—	—
$\text{Cu}^{2+}$	5.90	3.42	2.26	—	—	8.03
$\text{Sr}^{2+}$	3.05	—	—	—	—	—
$\text{Pb}^{2+}$	4.08	2.97	1.51	6.08	6.97	—

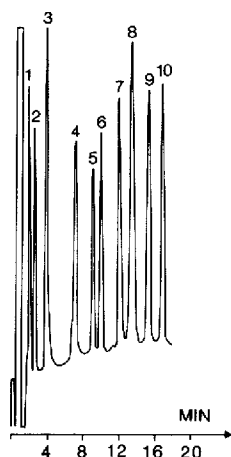


Fig. 3. Separation of alkali, alkaline earth and transition metal ions. Stationary phase, TSK IC cation SW; mobile phase, 3.5 mmol/l ethylenediamine–10.0 mmol/l citric acid (pH = 2.8, adjusted with HCl); flow-rate, 1.0 ml/min; detection, conductivity; temperature, 30°C. Peaks: 1 = Na<sup>+</sup> (5 ppm); 2 = K<sup>+</sup> (50 ppm); 3 = Cu<sup>2+</sup> (10 ppm); 4 = Ni<sup>2+</sup> (10 ppm); 5 = Co<sup>2+</sup> (10 ppm); 6 = Zn<sup>2+</sup> (10 ppm); 7 = Fe<sup>2+</sup> (10 ppm); 8 = Mn<sup>2+</sup> (20 ppm); 9 = Cd<sup>2+</sup> (10 ppm); 10 = Ca<sup>2+</sup> (15 ppm).

Sr<sup>2+</sup>, on the other hand has been shown not to form protonated citrate complexes. (Citrate)<sup>3-</sup> ions are present in solution only at a pH > 4.0. Therefore, the elution of Sr<sup>2+</sup> starts at this relatively high pH level.

Fig. 3 shows a chromatogram of alkali, alkaline earth and transition metal ions under conditions optimized for the separation of mono- and bivalent ions. At a pH of 2.80 the copper peak is well resolved from the potassium peak.

If the pH is increased to 4.2, metal ions such as Sr<sup>2+</sup> and Pb<sup>2+</sup> can be eluted and determined together with monovalent ions (Fig. 4). This fact was applied in radiochromatographic trace separations of Cs-137 and Sr-90. The eluted fractions



Fig. 4. Separation of mono- and bivalent ions. Chromatographic conditions as in Fig. 3; pH of the mobile phase, 4.2. Peaks: 1 = Na<sup>+</sup>; 2 = Cs<sup>+</sup>; 3 = Pb<sup>2+</sup>; 4 = Mg<sup>2+</sup>; 5 = Sr<sup>2+</sup>.

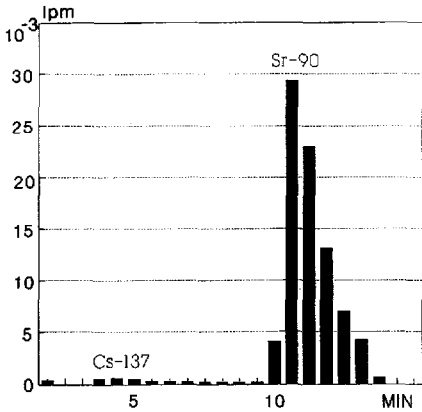


Fig. 5. Ion chromatographic trace analysis of radionuclides, impulses per minute (lpm) versus time. Sample: Cs-137 and Sr-90 in water. Stationary phase, TSK IC cation SW; mobile phase, 3.5 mmol/l ethylenediamine-10.0 mmol/l citric acid (pH 4.80, adjusted with NaOH); flow-rate, 0.7 ml/min; detection,  $\beta$ -liquid scintillation counting.

were collected and analysed using a liquid scintillation  $\beta$ -counter (Fig. 5). The peaks are well resolved from each other. This method seems promising for the simple and rapid determination of these fission products in either radioactive wastewater or biological samples, especially after on-line preconcentration.

*Separation of bi- and trivalent cations*

The stationary phase chosen for the separation of bi- and trivalent ions was a polymeric, non-porous weakly acidic cation exchanger. A nitric acid eluent was diluted step-by-step, and the elution behavior of bi- and trivalent cations was monitored and is depicted in Fig. 6. With nitric acid concentrations of 0.25 mmol/l and

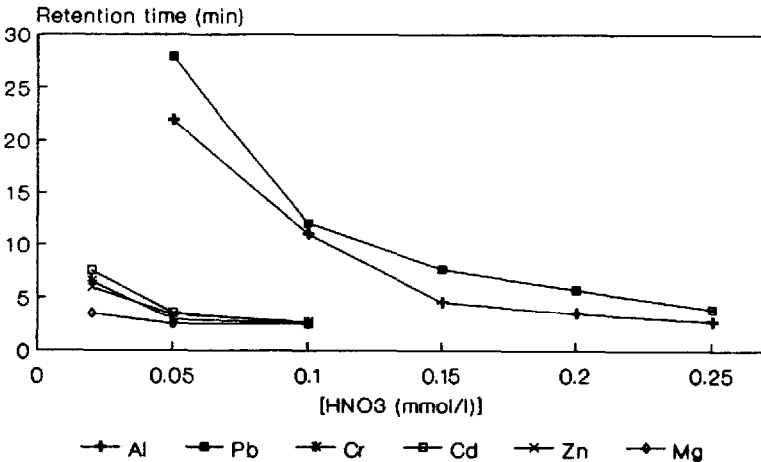


Fig. 6. Influence of nitric acid concentration on retention times of bi- and trivalent metals. Stationary phase, MA7C (50 x 7.8 mm I.D. column); mobile phase, 0.02-0.25 mmol/l nitric acid; detection, conductivity ( $R = 100$ ); temperature, 30°C; sample concentration, 1.0 ppm each.

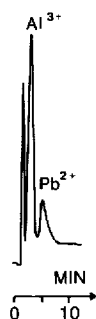


Fig. 7. Separation of bi- and trivalent cations. Sample:  $\text{Pb}^{2+}$  (0.5 ppm) and  $\text{Al}^{3+}$  (0.5 ppm). Stationary phase, MA7C (50 × 7.8 mm, I.D. column); mobile phase, 0.15 mmol/l nitric acid; flow-rate, 0.5 ml/min; detection, conductivity ( $R = 100$ ).

lower, corresponding to pH 3.53 and below,  $\text{Al}^{3+}$  and  $\text{Pb}^{2+}$  were retained and exhibited an increase in retention time when the eluent concentration was lowered, whereas other trivalent metals, such as  $\text{Cr}^{3+}$  and  $\text{Fe}^{3+}$ , eluted in the dead volume. With 0.05 mmol/l nitric acid (pH 4.24) as the mobile phase, several ions, such as  $\text{Cd}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Zn}^{2+}$  and  $\text{Mg}^{2+}$ , interacted with the stationary phase. This trend continued when the eluent concentration was decreased to 0.02 mmol/l (pH 4.47). Attempts to improve the resolution by further dilution of the mobile phase were unsuccessful owing to an unstable baseline.

In ion exchange, the degree of ionic interaction between ions and the stationary phase depends largely on their valency, trivalent ions showing the highest affinity. In this instance the elution order does not fit into this scheme, indicating that additional mechanisms contribute to the elution. The most probable reaction capable of inhibiting ionic interactions with the stationary phase is the formation of hydroxide complexes. For example,  $\text{Al}^{3+}$  is reported<sup>14</sup> to show signs of hydrolysis at pH values as low as pH 2. The order of stability of hydroxide complexes is  $\text{Mg}^{2+} < \text{Cd}^{2+} < \text{Zn}^{2+} < \text{Pb}^{2+} < \text{Cr}^{2+} < \text{Al}^{3+}$ , which explains the fact that aluminium is eluted before lead under these conditions.

Fig. 7 shows the separation of a standard solution of 0.5 ppm of  $\text{Al}^{3+}$  and  $\text{Pb}^{2+}$  using 0.15 mmol/l nitric acid as the eluent.

A comparison of this method with flame AAS for the determination of  $\text{Pb}^{2+}$  in aqueous solutions is shown in Fig. 8. The values obtained by AAS measurements were

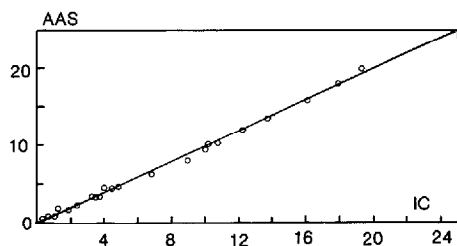


Fig. 8. Comparison of analytical data (in ppm) obtained by ion chromatography and flame AAS for  $\text{Pb}^{2+}$ . Ion chromatography: stationary phase, MA7C (50 × 7.8 mm I.D. column); mobile phase, 0.20 mmol/l nitric acid; flow-rate, 0.5 ml/min; detection, conductivity ( $R = 100$ ); temperature, 30°C. AAS: flame, air-acetylene; Wavelength, 283.3 nm; slit width, 0.7 nm.

plotted against the corresponding results obtained by the reported ion-chromatographic method. Correlation in the low concentration range shows that the ion-chromatographic method allowed the detection of  $Pb^{2+}$  concentrations as low as 0.1 ppm.

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