

Studies on the retention behaviour of metal–EDTA complexes in cation chromatography

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Abstract

Separation of metal–EDTA complexes (e.g. with Cu^{2+} , Ni^{2+} and Pb^{2+}) has been carried out with a cation-exchange polymer based column. Two mobile-phase systems, containing either nitric or perchloric acid, have been studied and the metal complexes with EDTA have been detected by UV spectrophotometry. A retention model has been developed. It takes into account both ion-exchange and adsorption phenomena of all positive, neutral and, as an attempt, negative metal–EDTA species. The ion-exchange behaviour of the metal–EDTA complexes and the adsorption effects due to neutral species have been applied for an on-line preconcentration procedure.

1. Introduction

The ion chromatographic determination of metal–EDTA complexes (MY) can be performed with anion-exchange columns [1–8]; in this way anions and metals can be separated as anionic complexes in the same run. Alternatively the separation of MY can be carried out with a cation-exchange column [9]. The retention mechanism of analytes involves the cation exchange of free metal ions (e.g. Cu, Fe, Zn, Ni, Pb, Mn, alkali metals and alkali-earth metals) which are present at low pH values.

Theoretical approaches to the retention behaviour of anionic metal complexes, taking into account only negatively charged species, have been developed for anion exchange [8,10], for cation exchange [11–15] and for dynamic ion

exchange [15,16]. In fact at slightly basic or acid pH values, the negatively charged species generally represent the total molar fraction. Nevertheless, if cation exchange is selected as separation method, not only the free metal but also the neutral, positive and negative species must be considered.

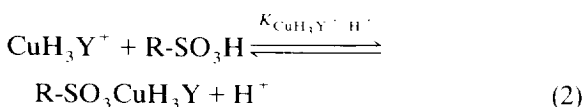
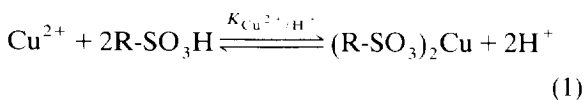
In this work the cation-exchange behaviour of some MY complexes has been investigated. Factors affecting retention have been examined and the trends observed have been related to the nature of the complexes which exist under the chromatographic conditions used. The use of a cationic system for the separation of metal complexes broadens the scope of cation chromatography. In this system elution may be effected by progressively varying the mobile phase in an acid pH range. Negatively and positively charged species have been considered in a retention theory and some adsorption effects have been discussed. The behaviour of neutral species has

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been utilized to develop an on-line preconcentration procedure.

2. Theory

The theory for ion-exchange of metal cations (M^{n+}) in the presence of complexing ligands has been investigated by Haddad and Foley [15] and Sevenich and Fritz [12]. But, if cationic complexes are present, e.g. in the case of copper-EDTA chelates, more than one positively charged species exists. The chromatographic system contains several ionic species, such as Na^+ , H^+ , EDTA in the eluent and different complex forms in the sample. Furthermore, the eluted metal ions are partly complexed and partly exist in solution as free metal cations. In order to have a reliable retention model all forms of cationic species in the system must be considered in the same run:



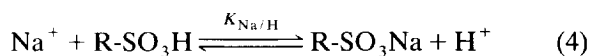
where $R-SO_3H$ represents the resin exchange site.

By considering the related ion-exchange selectivity coefficients $K_{Cu/H}$ and $K_{CuH_3Y/H}$ the distribution ratio is:

$$\begin{aligned} D_{Cu} &= \frac{(Cu^{2+}) + (CuH_3Y^+)}{C_{Cu}} \\ &= \frac{K_{Cu/H}[Cu^{2+}](H^+)^2}{C_{Cu}[H^+]^2} + \frac{K_{CuH_3Y/H}[CuH_3Y^+](H^+)}{C_{Cu}[H^+]} \\ &= \frac{K_{Cu/H}[Cu^{2+}](H^+)^2 + K_{CuH_3Y/H}[CuH_3Y^+]H^+}{C_{Cu}[H^+]^2} \quad (3) \end{aligned}$$

where round and square brackets refer to stationary and mobile-phase concentrations, respectively.

As there may be more than one eluent ion, e.g. H^+ and Na^+ , an intereluent ion-exchange equilibrium must be considered:



The column capacity Q (expressed as mol/l) is:

$$Q = (Na^+) + (H^+) \quad (5)$$

and by substituting (Na^+) obtained from the equilibrium constant

$$(Na^+) = \frac{K_{Na/H}[Na^+](H^+)}{[H^+]} \quad (6)$$

Eq. 5 results in:

$$\begin{aligned} Q &= \frac{K_{Na/H}[Na^+](H^+)}{[H^+]} + (H^+) \\ &= \frac{K_{Na/H}[Na^+] + [H^+]}{[H^+]}(H^+) \quad (7) \end{aligned}$$

From Eq. 7 one can obtain:

$$(H^+) = \frac{Q[H^+]}{K_{Na/H}[Na^+] + [H^+]} \quad (8)$$

and by substituting Eq. 8 into Eq. 3, Eq. 9 derives:

$$\begin{aligned} D_{Cu} &= K_{Cu/H}Q^2(K_{Na/H}[Na^+] + [H^+])^{-2}\Phi_{Cu^{2+}} \\ &\quad + K_{CuH_3Y/H}Q(K_{Na/H}[Na^+] \\ &\quad + [H^+])^{-1}\Phi_{CuH_3Y^+} \quad (9) \end{aligned}$$

where Φ is the molar fraction of the cationic species with respect to the total metal concentration C_{Cu} . Values of Φ were calculated according to our previous work [8], which was developed for elution of anionic metal complexes when a carbonate buffer was present in the eluent.

$$\Phi_{Cu^{2+}} = \frac{[Cu^{2+}]}{C_{Cu}} \quad (10)$$

$$\Phi_{CuH_3Y^+} = \frac{[CuH_3Y^+]}{C_{Cu}} \quad (11)$$

On a cation-exchange column the general expression for the capacity factor, k' , of a metal ion in the presence of ligands and considering all the interacting species is:

$$k' = \frac{V_s}{V_m} \sum_i K_i Q^{n_i} [E^+]^{-n_i} \Phi_i \quad (12)$$

where V_s and V_m are the stationary and mobile-phase volumes, K_i are the ion-exchange constants for the different species, n_i are the absolute values of their charge and E^+ represents the eluent ions (e.g., if Na^+ and H^+ are the eluent ions, $[E^+] = K_{\text{Na}^+/\text{H}^+}[\text{Na}^+] + [\text{H}^+]$ as described in Eq. 9).

The adsorption effects due to the neutral species are defined for $n = 0$ and therefore $Q^{n_i} [E^+]^{-n_i} = 1$. If at a selected pH only the neutral species exists, its molar fraction is 1 and Eq. 12 becomes:

$$k' = \frac{V_s}{V_m} K$$

where K is the partition constant of the neutral species considered.

The negatively charged species are involved in a way similar to that of the positive ones (see Section 4).

3. Experimental

3.1. Reagents and solutions

The eluents were prepared by dissolving analytical reagent grade chemicals in high-purity water obtained using a Milli-Q system (Millipore, Bedford, MA, USA) and filtering through a 0.45- μm filter. The reagents were perchloric acid (65%) and EDTA (Carlo Erba, Milan, Italy), nitric acid (65%) and sodium hydroxide (Merck, Darmstadt, Germany). Working solutions of metal ions, namely Cu(II), Ni(II) and Pb(II), were prepared by dilution of concentrated standard stock solutions (Merck).

3.2. Instrumentation

A Dionex Series 4000i ion chromatograph was used with an UV-Vis variable-wavelength detector (Dionex, Sunnyvale, CA, USA). The chromatograms were recorded with an SP 4270 data module integrator (Carlo Erba). Curve fittings

and regressions, based on the Marquand-Levenberg algorithm, and graphic elaborations have been performed by Sigma Plot software (Jandel Scientific) on a PS/2 56 486SLC2 IBM personal computer. The sample loading for the preconcentration procedure has been performed with a Model DQP-1 pump (Dionex).

The separation column (Dionex CS 10, 250 \times 4 mm I.D.) and the preconcentration column (Dionex CG 10, 50 \times 4 mm I.D.) were cation-exchange polymer based, functionalized with sulphonic groups and having a medium hydrophobicity. The void volume V_m has been obtained experimentally as the water dead volume, therefore stationary-phase volume V_s was defined by $V_{\text{column}} - V_m$, where V_{column} is the geometric volume of the column (computed). The column capacity Q has been given by the producer.

All chromatograms were obtained at room temperature. The flow-rate was 1.0 ml/min unless otherwise stated. Retention times were the mean of triplicate injections of single samples containing a single metal at $1.0 \cdot 10^{-5}$ M prepared using the eluent solution.

4. Results and discussion

Studies were performed in order to verify the effectiveness of the cation-exchange column, Dionex CS10, for metal-EDTA complex separation. Not only the sample but also the mobile phase was $5.00 \cdot 10^{-4}$ M EDTA (ligand to metal ratio 50:1) in order to avoid complex dissociation owing to inadequate ligand concentration. To evaluate the influence of pH and ionic strength (i.s.), two different procedures were adopted. In the first case eluents were prepared by dissolving Na_2EDTA salt ($5.00 \cdot 10^{-4}$ M) which gives a solution of pH 5.0. Then the pH was adjusted to the proper value by adding either concentrated acid or sodium hydroxide. In the second case HClO_4 was added to $5.00 \cdot 10^{-4}$ M EDTA solution to obtain pH 0.80; this eluent was used as such or by varying the pH in the range 0.80–6.00 by addition of concentrated NaOH. The first eluent enabled us to study the influence of pH on k' by working at the lowest i.s. consistent with

ligand concentration, the second furnished an i.s. value constant for all experiments, $[H^+] + [Na^+]$ being constant at all pH values. During the preliminary studies HNO_3 was used to modify the eluent pH values; in this case Cu(II)–EDTA and Pb(II)–EDTA complexes were detected at 242 nm, but the detection of other complexes, e.g. those with Ni(II), which have a lower molar absorptivity with a behaviour similar to nitrate, required the use of eluents with a higher transmittance. For this reason perchloric acid has been adopted.

Figs. 1–3 compare the k' behaviour obtained for MY at the different eluent compositions investigated, the k' computed by Eq. 12 for the above systems and the molar fractions of MY species as a function of pH for copper, lead and nickel. The molar fractions of the MY species have been computed on the basis of the formation constants reported in the literature for these metals [17,18]; the eluents were obtained according to the first procedure and the terms of Eq. 12, referring to the MHY^- and MY^{2-} species, have been calculated by considering the modulus of the charge values. Taking copper as an exam-

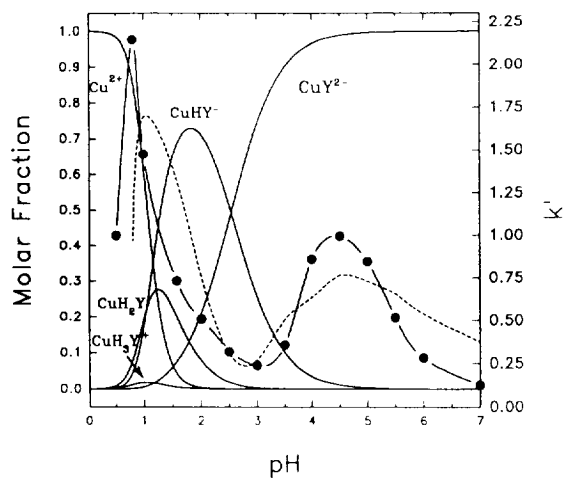


Fig. 1. Molar fractions of Cu–EDTA species, experimental k' (dots) and the respective calculated curve (dashed line) as a function of pH. Experimental conditions: eluent $5.00 \cdot 10^{-4} M Na_2EDTA$, pH adjusted with either $HClO_4$ or $NaOH$, flow-rate 1.0 ml/min; 100- μ l samples prepared in eluent and containing $1.0 \cdot 10^{-3} M Cu^{2+}$; UV detection at 242 nm.

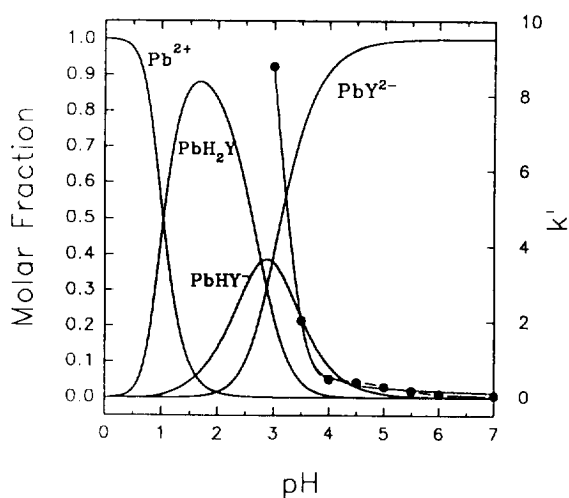


Fig. 2. Molar fraction of Pb–EDTA species, experimental k' (dots) and the respective calculated curve (dashed line overlapping the experimental curve) as a function of pH. Experimental conditions as Fig. 1.

ple for the computation, the equation results in a summation of 5 terms: 2 terms due to the cationic species, 1 term due to the neutral species and 2 terms due to the anionic species.

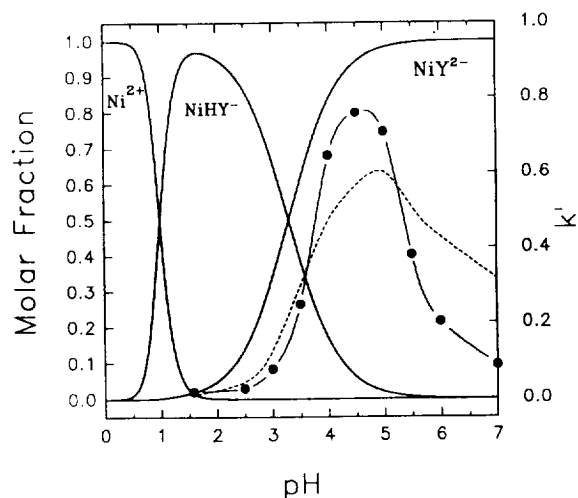


Fig. 3. Molar fraction of Ni–EDTA species, experimental k' (dots) and the respective calculated curve (dashed line) as a function of pH. Experimental conditions: eluent $5.00 \cdot 10^{-4} M Na_2EDTA$, pH adjusted with either $HClO_4$ or $NaOH$, flow-rate 1.0 ml/min; 100- μ l samples prepared in eluent and containing $1.0 \cdot 10^{-3} M Ni^{2+}$; UV detection at 240 nm.

The molar fraction, Φ , of each species and the eluent ion concentrations have been calculated for each pH value. At this point Φ_i and E^+ are known and theoretical plots are obtained by regression of this equation with the experimental data.

The k' values for copper (Fig. 1) show a maximum due to the high molar fraction value of Cu^{2+} species at pH 0.8. Nevertheless, for $\text{pH} < 0.8$ the very high ionic strength results in a k' decrease. At pH values greater than 1.00, one and two negatively charged Cu–EDTA species appear and, in agreement with the nature of the stationary phase, are repelled, lowering the k' values. An anomalous behaviour is evidenced around pH 4–5 where a relative maximum of k' occurs. This fact, as regards the ion-exchange mechanism, disagrees with the molar fraction distribution of copper and nickel (see below), because only negative species are predicted for $\text{pH} > 4$. Since small variations of ionic strength, obtained by increasing or reducing the pH 5.0 value, have a strong effect on k' , one may assume that retention and interaction with the stationary phase are caused by the anionic secondary layer. Two opposite effects are predicted from the ionization model at a pH range 3–7. Increasing the pH of the eluent ($3 < \text{pH} < 4.5$) will increase the capacity factors, because the analyte is converted from the MHY^- to the MY^{2-} form. Increasing the pH of the eluent to $4.5 < \text{pH} < 7$, the capacity factors decrease progressively because the predominant form of the eluent becomes HY^{3-} ($\log K_{\text{H}_2\text{Y}^{2-} \rightarrow \text{HY}^{3-}} = 6.18$) and the molar fraction of the analyte is constant. The modelling, by introducing the anionic species, shows a good agreement between the experimental and computed behaviour of the k' values for Cu and Ni; however, it does not explain the absence of the same peak for Pb. A second consideration regarding the similar behaviour of Ni and Cu could be based on the similar structure of the complexes PbY^{2-} and CuY^{2-} , and their ability to be protonated at the pH values considered. In this case neutral species should be formed and retained; on the other hand a comparison of the k' values of the Cu species at pH 4.5 and at pH 1.25, where the

Table 1
Ion-exchange selectivity coefficients calculated according to Eq. 12 for metal–EDTA species

Species	$K_{\text{species}/\text{H}^+}$ low i.s. (see Fig. 3)	$K_{\text{species}/\text{H}^+}$ high i.s. (see Fig. 4)
Cu^{2+}	16	28
CuH_3Y^+	$4.6 \cdot 10^{-5}$	$8.0 \cdot 10^{-6}$
CuH_2Y	$2.8 \cdot 10^{-6}$	$1.6 \cdot 10^{-7}$
Pb^{2+}	$2.4 \cdot 10^{-8}$	700
PbH_2Y	32	$5.0 \cdot 10^{-9}$

Experimental conditions as for Fig. 1.

neutral species CuH_2Y is active, agrees with this supposition.

Table 1 shows the values of ion-exchange selectivity coefficients for metal ions and their species calculated from the experimental data. The values have been obtained as the result of the regression mentioned above. The intereluent Na^+/H^+ ion-exchange equilibrium constant, $K_s = 1.5$, has been selected according to the literature values [19]. By comparing the behaviour of k' (Figs. 1–3), species distribution and computed ion-exchange selectivity coefficients, the relative contribution to the retention mechanisms (ion exchange and adsorption) are evidenced. While in the case of copper the free metal cation exchange and the double-charged species interactions prove to be the main active retention mechanisms, in the case of lead neutral species adsorption is dominant (see Fig. 2). Lead (PbH_2Y) proves to be totally retained between pH 0.5 and 3.0; on the other hand below pH 0.5 i.s. competition hinders the cation-exchange mechanism. The behaviour of nickel is similar to that of copper for $\text{pH} > 2.5$ but due to detection problems the nickel peak was not visible at low pH and high i.s.

The experiments performed with eluents at high i.s. (0.16 M HClO_4) are compared in terms of k' as a function of pH for copper and lead (see Fig. 4). For pH values lower than 2.0 the free cation (Pb^{2+}) and neutral species (PbH_2Y) are totally retained. At increasing pH values, according to the previous experiments, k' values decrease both for copper and lead; however, for

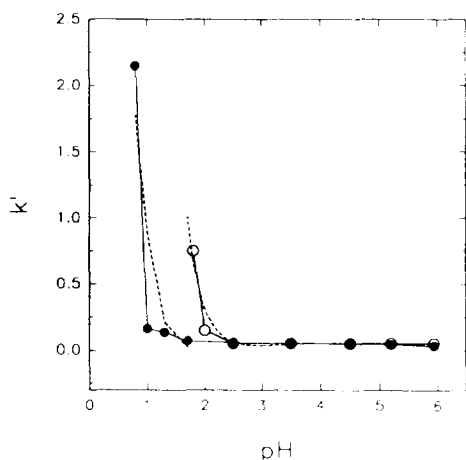


Fig. 4. k' Behaviour of copper (dots) and lead (circles) as a function of pH and for high ionic strength (dashed line = calculated curve). Experimental conditions: eluent, $5.00 \cdot 10^{-4} M$ Na_2EDTA , $0.158 M$ HClO_4 , pH adjusted with NaOH , 1.0 ml/min flow-rate; $100\text{-}\mu\text{l}$ samples prepared in eluent and containing $1.0 \cdot 10^{-5} M$ of every metal; UV detection at 225 nm.

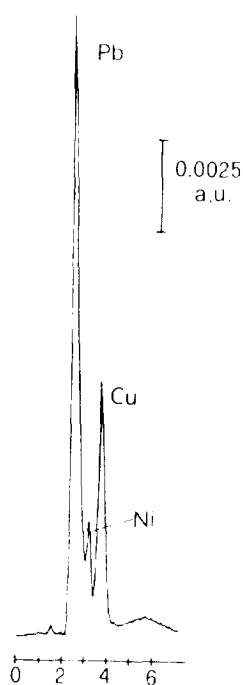


Fig. 5. Chromatogram of Pb(II)- , Ni(II)- and Cu(II)- EDTA complexes. Experimental conditions: eluent, $5.0 \cdot 10^{-4} M$ Na_2EDTA , HClO_4 up to pH 4.30 , 1.0 ml/min flow-rate; $100\text{-}\mu\text{l}$ sample, metals $1.0 \cdot 10^{-5} M$ each in eluent; UV detection at 240 nm.

the latter at pH 2.0 , owing to the maximum value for the molar fraction of the neutral species, the k' value is still consistent. The two different behaviours give further information on the retention mechanisms involved.

Fig. 5 shows a chromatogram of the metals investigated, obtained after eluent and procedure optimization.

Furthermore, from an experimental point of view, the behaviour of Pb-EDTA complexes as a function of pH and ionic strength provides data that can be used to develop a selective method for preconcentrating and determining Pb at trace levels. The above results suggested the possibility to retain and preconcentrate lead species on a cation microcolumn (CG 10) by working at pH values between 1.0 and 2.0 . Measurements of preconcentration recoveries at pH 1.5 (optimal value), performed by loading 100.0-ml samples at $5.0 \mu\text{g/l}$ Pb onto the CG 10 which replaced the injection valve loop, gave 70%

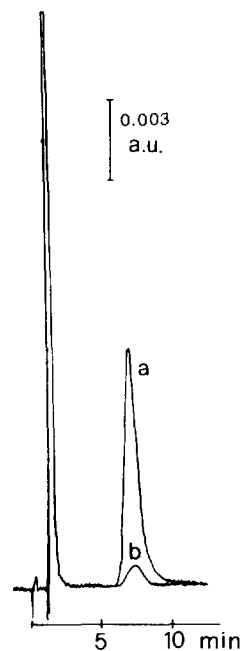


Fig. 6. Preconcentration of lead: $5.0 \mu\text{g/l}$ standard solution (a) and blank (b). Experimental conditions: eluent $5.0 \cdot 10^{-4} M$ Na_2EDTA , $0.100 M$ HClO_4 ; NaOH up to pH 1.7 , flow-rate 1.5 ml/min; 100-ml sample containing $5.0 \cdot 10^{-4} M$ Na_2EDTA and HClO_4 up to pH 1.5 , flow-rate of preconcentration 4.0 ml/min; UV detection at 242 nm.

recovery and 0.5 $\mu\text{g/l}$ as the Pb detection limit. One has to consider that this pH does not allow retention of the ionic species and only the neutral complex (about 80% of total species) contributes to the retention mechanism.

A chromatogram showing the preconcentration of lead in comparison with the blank is shown in Fig. 6.

Acknowledgement

We acknowledge financial support from Consiglio Nazionale delle Ricerche (CNR, Italy) and OTKA-2562 (Hungary).

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