The Simultaneous Analysis of Metal–EDTA Complexes and Inorganic Anions by Suppressed Ion Chromatography

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Abstract

This work extends a multiple species retention model to the retention behavior of EDTA complexes of Cu, Zn, and Pb together with inorganic anions (Cl^-, NO_2^-, Br^-, NO_3^-). The study incorporates an ion-exchange system with a carbonate eluent at various concentrations and pH levels. A theoretical framework is developed when complexation effects are present in the sample. The unknown values for the ion-exchange equilibrium constants, which are required in the model, are determined by repetitive minimization using a nonlinear regression algorithm and are then used to compare observed and predicted retention data. The results are in good agreement for all metal–EDTA complexes and simple anions studied. Practical application of the retention model to the determination of the elution behavior of the species proves successful and demonstrates the reliability of the model. Furthermore, the new method for simultaneous analysis is successfully applied in a quantitative manner using a mixed carbonate eluent and EDTA as a complexing agent in the sample. The detection limit with this method is about 1 order of magnitude better than in a nonsuppressed system that uses EDTA as the eluent.

Introduction

Since its introduction in 1975 by Small and co-workers (1), ion chromatography has increased in importance for the determination of microgram-per-liter concentration levels of ionic species in water samples.

One of the most effective developments in ion chromatography in the last several years is the introduction of a procedure that allows the simultaneous separation of metal cations and simple anions. The interest in techniques that yield complete anion and cation sample characterization has grown in the past years (2). Methods developed for this purpose involve the

use of single and dual detection systems (3); dual anion and cation columns with a single conductivity detector and synchronal sample injection (4); anion and cation separators in series with two detectors (5); and mixed bed ion-exchange columns (6) that contain alumina and silica. Yamamoto and co-workers (7) demonstrated that simultaneous analysis could be successfully achieved by separating the metal ions as anionic EDTA complexes using an anion-exchange column and EDTA as the eluent in a nonsuppressed system. One noteworthy consideration is that the chromatographic separation and the analytical parameters of the procedure are strongly influenced by ion charge, ion size, type of eluent, eluent concentration, mobile phase pH, conductivity background, and stability of the complex (8). In addition, detection of metal complexes is complicated by the large excess of EDTA in the mobile phase. Also, the water used to prepare the eluent may contain metal contaminants that would bind the excess unreacted EDTA in the mobile phase, producing spurious peaks.

Optimization of the conditions for effective use of ion chromatography has been of particular interest. Computer optimization has proved advantageous over conventional methods in the determination of optimum conditions, such as eluent concentration and pH, before the separation process (9,10). Three main retention models have been described (11): single species eluent, multiple species eluent, and single interaction sites. The model involving a single species eluent is considered to be the simplest. Retention models that involve multiple species eluent (e.g., phosphate [12] and carbonate) are more complex because of the presence of additional equilibrium opportunities. Our previous papers (13,14) and that of Jenke (15) were the earliest studies to consider not only multiple species in the eluent, but also multiple species of the analyte. They were successfully used to determine the retention behavior of multiprotic anions including selenite, phosphate, citrate, malonate, and tartarate.

The aim of this work was to extend the application of our model by predicting the retention behavior of EDTA complexes

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of Cu, Pb, and Zn in the presence of inorganic anions and to demonstrate the reliability of the model when complexing effects are present in the sample. The study takes into consideration all possible analyte species, and simultaneous determination is achieved in a quantitative manner using carbonate buffer, the most widely used eluent system for the determination of anions in a suppressed IC system. In our work, an addi-

tional complexing agent, EDTA, is added to the sample rather than to the eluent to increase the selectivity and sensitivity of the separations and to decrease the limit of detection of the analysis. The eluents contain carbonate buffer in a suppressed conductivity system. This significant decrease in conductance of the mobile phase can be used to enhance detection of metal–EDTA complexes and additional inorganic anions.

Table I. Eluent Compositions Used in the Experimental Procedure

Eluent conc. (mM)	pH	$Na_2CO_3/NaHCO_3$ (mM)	OH^- conc. (mM)	Na_2CO_3 conc. (mM)	$NaHCO_3$ conc. (mM)
2.5	9.69	0.50:2.00	0.049	0.70	1.80
2.5	10.26	1.25:1.25	0.182	1.48	1.02
2.5	10.40	1.50:1.00	0.251	1.67	0.83
2.5	10.66	2.00:0.50	0.457	1.96	0.54
2.5	10.86	2.50:0.00	0.724	2.13	0.37
5.0	9.68	1.00:4.00	0.048	1.38	3.62
5.0	9.82	2.00:3.00	0.066	1.72	3.28
5.0	10.14	3.00:2.00	0.138	2.61	2.38
5.0	10.24	2.50:2.50	0.174	2.90	2.10
5.0	10.68	4.00:1.00	0.479	3.96	1.04
5.0	11.03	5.00:0.00	1.070	4.47	0.53
6.5	9.69	1.50:5.00	0.049	1.82	4.68
6.5	10.34	3.25:3.25	0.219	4.13	2.37
6.5	10.44	4.00:2.50	0.275	4.46	2.04
6.5	10.60	2.50:4.00	0.251	4.33	2.17
6.5	10.62	5.00:1.50	0.417	4.99	1.51
8.0	9.44	1.00:7.00	0.028	1.44	6.56
8.0	9.82	2.00:6.00	0.066	2.75	5.25
8.0	10.27	4.00:4.00	0.186	4.77	3.23
8.0	10.63	6.00:2.00	0.427	6.18	1.82
8.0	10.86	7.00:1.00	0.724	6.82	1.18

Table II. Ion-Specific and Intereluent Chromatographic Ion-Exchange Selectivity Constants for Complex Forms of Cu^{2+}, Pb^{2+}, and Zn^{2+}

Ion-exchange constant	Eluent concentration (CO_3^{2-} + HCO_3^-) (mM)				Mean ± σ_{n-1}*
	2.5	5.0	6.5	8.0	
$K_{CuHEDTA/HCO3}$	0.765	0.854	0.792	0.732	0.786 ± 0.05
$K_{CuEDTA/HCO3}$	8.796	8.161	7.812	7.591	8.090 ± 0.53
$K_{OH/HCO3}$	1.228	1.098	1.391	1.357	1.269 ± 0.13
$K_{CO3/HCO3}$	13.559	13.857	13.503	13.659	13.645 ± 0.16
$K_{PbHEDTA/HCO3}$	0.743	0.762	0.808	0.757	0.768 ± 0.03
$K_{PbEDTA/HCO3}$	3.206	3.187	3.174	3.293	3.215 ± 0.05
$K_{OH/HCO3}$	1.499	1.496	1.496	1.409	1.475 ± 0.04
$K_{CO3/HCO3}$	13.567	13.728	13.614	13.993	13.726 ± 0.19
$K_{Pb(OH)3/HCO3}$	10.985	10.925	10.483	10.231	10.656 ± 0.36
$K_{ZnHEDTA/HCO3}$	0.799	0.820	0.942	0.727	0.822 ± 0.09
$K_{ZnEDTA/HCO3}$	6.776	6.480	6.390	6.337	6.496 ± 0.20
$K_{OH/HCO3}$	1.379	1.379	1.386	1.441	1.396 ± 0.03
$K_{CO3/HCO3}$	13.743	13.902	13.721	13.867	13.808 ± 0.09
$K_{Zn(OH)3/HCO3}$	3.746	3.676	3.726	3.963	3.778 ± 0.13
$K_{Zn(OH)4/HCO3}$	8.388	8.358	8.376	8.776	8.475 ± 0.20

*Mean plus or minus the standard deviation.

Theory

The model involves strict consideration of all equilibrium opportunities within and between the eluent and analyte. We shall consider the equilibrium distribution and separation of anionic metal–EDTA complexes of Pb, Zn, and Cu in the presence of inorganic anions (Cl^-, NO_2^-, Br^-, and NO_3^-). The sep-

aration is performed using carbonate, a multiple species eluent. The theory is based on extension of the ion-exchange equilibrium by the use of protonation and complex formation equilibria.

In general, the ion-exchange equilibrium in which a solute anion (A^{y-}) competes with a prebound eluent anion (E) for a

Table III. Ion-Specific ($K_{A/HCO3}$) and Intereluent ($K_{CO3/HCO3}$) Chromatographic Ion-Exchange Selectivity Constants for Bromide, Chloride, Nitrite, and Nitrate Anions, Determined at Different Eluent Concentrations

Selectivity constant	Eluent concentration (CO_3^{2-} + HCO_3^-) (mM)				Mean ± σ_{n-1}*
	2.5	5.0	6.5	8.0	
$K_{Br/HCO3}$	1.733	1.774	1.808	1.822	1.784 ± 0.04
$K_{CO3/HCO3}$	13.769	13.953	13.895	13.814	13.858 ± 0.08
$K_{OH/HCO3}$	2.000	1.660	1.635	1.713	1.752 ± 0.17
$K_{Cl/HCO3}$	0.687	0.665	0.623	0.604	0.645 ± 0.04
$K_{CO3/HCO3}$	13.988	14.006	13.850	13.994	13.960 ± 0.07
$K_{OH/HCO3}$	1.647	1.616	1.461	1.505	1.557 ± 0.09
$K_{NO2/HCO3}$	1.043	0.983	0.966	0.943	0.984 ± 0.04
$K_{CO3/HCO3}$	13.773	13.998	13.710	13.776	13.814 ± 0.13
$K_{OH/HCO3}$	2.000	1.675	1.682	1.592	1.737 ± 0.18
$K_{NO3/HCO3}$	2.226	2.137	2.098	2.040	2.125 ± 0.08
$K_{CO3/HCO3}$	13.998	13.998	13.784	13.994	13.944 ± 0.11
$K_{OH/HCO3}$	1.596	1.657	1.566	1.565	1.596 ± 0.04

*Mean plus or minus standard deviation.

Table IV. Comparison of Predicted and Observed Retention Volumes for CuEDTA, PbEDTA and ZnEDTA

| Eluent conc. (mM) (CO_3^{2-}+HCO_3^-)	pH	Retention volume (mL)					
		CuEDTA		PbEDTA		ZnEDTA	
		Measured	Calculated	Measured	Calculated	Measured	Calculated
2.5	9.69	26.30	25.06	11.47	10.88	21.29	20.42
2.5	10.26	14.54	13.18	6.24	6.15	11.35	10.88
2.5	10.40	13.66	11.91	5.54	5.65	10.38	9.87
2.5	10.66	11.67	10.38	4.47	5.04	8.57	8.63
2.5	10.86	11.93	9.64	3.98	4.75	8.17	8.04
5.0	9.68	13.71	13.08	6.74	6.12	11.55	10.81
5.0	9.82	10.23	10.97	5.09	5.28	8.52	9.11
5.0	10.14	7.13	7.97	3.59	4.08	5.92	6.70
5.0	10.24	7.32	7.39	3.69	3.85	5.99	6.23
5.0	10.68	6.30	5.90	3.01	3.26	4.93	5.04
5.0	11.03	6.31	5.38	2.71	3.06	4.67	4.62
6.5	9.69	9.37	10.15	4.91	4.95	8.07	8.45
6.5	10.34	5.75	5.65	3.19	3.16	4.87	4.84
6.5	10.40	6.59	5.47	3.51	3.09	5.55	4.69
6.5	10.44	5.24	5.37	2.87	3.05	4.34	4.61
6.5	10.62	4.96	4.98	2.60	2.90	4.00	4.30
8.0	9.44	10.94	11.68	5.74	5.56	9.46	9.68
8.0	9.82	7.08	7.29	3.90	3.81	6.08	6.15
8.0	10.27	4.90	5.05	2.82	2.93	4.19	4.36
8.0	10.63	4.18	4.32	2.40	2.63	3.46	3.76
8.0	10.86	4.15	4.07	2.15	2.53	3.41	3.56

*Mean of errors: CuEDTA, 7.77%; PbEDTA, 7.08%; ZnEDTA, 4.96%.

Table V. Comparison of Predicted and Observed Retention Volumes for Bromide, Chloride, Nitrite, and Nitrate*

| Eluent conc. (mM) (CO_3^{2-}+HCO_3^-) | pH | Retention volume (mL) | | | | | | | |
| | | Bromide | | Chloride | | Nitrite | | Nitrate | |
		Measured	Calculated	Measured	Calculated	Measured	Calculated	Measured	Calculated
2.5	9.69	–	–	3.51	3.38	–	–	–	–
2.5	10.26	5.14	5.22	2.94	2.86	3.69	3.56	6.12	5.92
2.5	10.40	4.94	5.03	2.92	2.79	3.64	3.46	6.06	5.70
2.5	10.66	4.21	4.78	2.60	2.70	3.27	3.32	5.20	5.26
2.5	10.86	4.14	4.66	2.59	2.66	3.01	3.25	4.94	5.26
5.0	9.68	5.78	5.25	2.93	2.87	3.84	3.58	6.45	5.97
5.0	9.82	–	–	2.80	2.75	3.39	3.40	5.59	5.58
5.0	10.14	4.24	4.38	2.47	2.56	2.97	3.10	4.70	4.93
5.0	10.24	4.34	4.27	2.54	2.51	3.04	3.03	4.80	4.79
5.0	10.68	3.92	3.94	2.41	2.40	2.78	2.85	4.37	4.40
5.0	11.03	3.63	3.81	2.25	2.35	2.62	2.78	4.02	4.25
6.5	9.69	4.85	4.81	2.67	2.71	3.31	3.33	5.40	5.43
6.5	10.34	–	–	2.36	2.38	2.83	2.83	4.39	4.34
6.5	10.40	4.18	3.84	2.53	2.36	2.93	2.80	4.62	4.29
6.5	10.44	3.71	3.82	2.28	2.35	2.67	2.79	4.10	4.25
6.5	10.62	3.50	3.72	2.24	2.31	2.57	2.73	3.87	4.14
8.0	9.44	–	–	2.69	2.81	3.41	3.48	5.58	5.76
8.0	9.82	4.34	4.27	2.50	2.51	3.04	3.04	4.91	4.80
8.0	10.27	3.73	3.74	2.30	2.32	2.70	2.75	4.11	4.17
8.0	10.63	3.62	3.53	2.20	2.25	2.59	2.63	3.81	3.92
8.0	10.86	3.17	3.46	2.04	2.22	2.35	2.59	3.36	3.83

*Mean of errors: Br , 4.77%; Cl⁻, 3.03%; NO_2^-, 3.55%; NO_3^-, 4.18%.

position on the stationary phase (R), may be defined by the following equation:

$$yR_x - E + xA^{y-} \xrightarrow{K_{A/E}} x R_y - A + yE^{x-} \qquad \text{Eq 1}$$
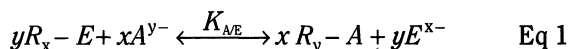
The ion-exchange equilibrium constant ($K_{A/E}$) can also be expressed in terms of the molar concentration of species present in each phase:

$$K_{A/E} = \frac{(A^{y-})^x \; [E^{x-}]^y}{[A^{y-}]^x \; (E^{x-})^y} \qquad \text{Eq 2}$$

where the square brackets and parentheses represent the molar concentration of the species in the mobile and stationary phases, respectively. At any point in which an equilibrium is established, the ratio of the analyte concentration in the stationary phase to that in the mobile phase may be expressed as the distribution coefficient, which in turn may be defined in terms of $K_{A/E}$.

$$D_A = \frac{(A^{y-})}{[A^{y-}]} = K_{A/E}^{1/x} \; ((E^{x-})/[E^{x-}])^{y/x} \qquad \text{Eq 3}$$

The total ion-exchange capacity is expressed as the number of eluent anions able to take a position on the stationary phase.
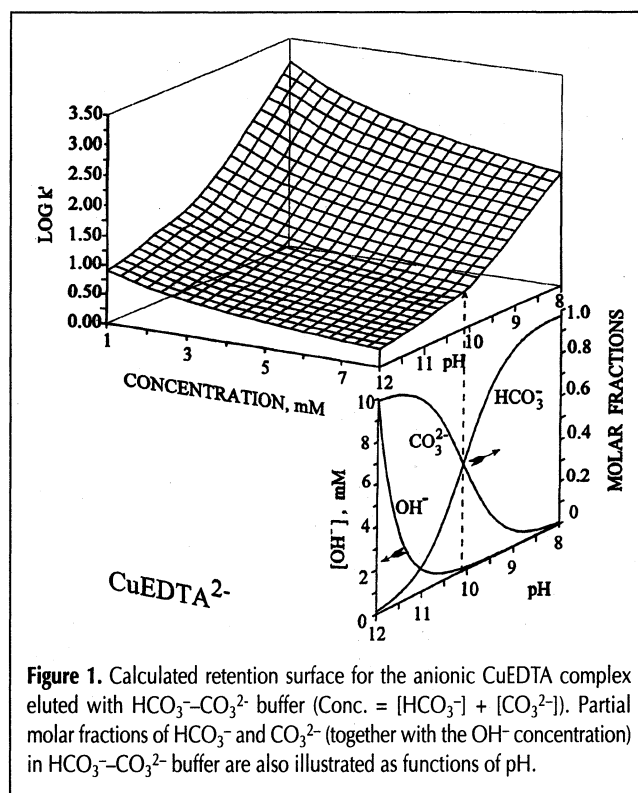

Figure 1. Calculated retention surface for the anionic CuEDTA complex eluted with HCO_3^-–CO_3^{2-} buffer (Conc. = [HCO_3^-] + [CO_3^{2-}]). Partial molar fractions of HCO_3^- and CO_3^{2-} (together with the OH⁻ concentration) in HCO_3^-–CO_3^{2-} buffer are also illustrated as functions of pH.

At any one point in the separation process, it is assumed that the eluent anion (E^{x-}) occupies x number of sites, out of a total of Q, on the stationary phase.

$$(E^{x-}) = \frac{Q}{x} \qquad \text{Eq 4}$$

By substituting this formula into the second part of Equation 3, we can express the distribution coefficient in the following way:

$$D_A = K_{A/E}{}^{1/x} \ (Q/x)^{y/x} \ [E^{x-}]^{-y/x} \qquad \text{Eq 5}$$
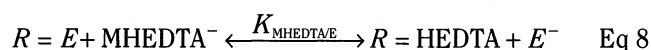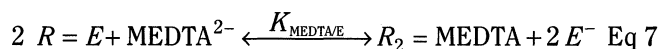
Then, by taking the logarithm, we will obtain the following:

$$\log D_A = 1/x \ \log K_{A/E} + y/x \ \log Q/x - y/x \ [E^{x-}] \qquad \text{Eq 6}$$

Complexation and ion-exchange equilibria of metal ions

To enable simultaneous separation of inorganic anions, the metal cations are complexed with EDTA to form anionic EDTA–metal complexes. The nature of the complexes formed is dependent on the pH of the mobile phase. In the pH range of 8–12, the formation of protonated EDTA complexes and hydroxo complexes can occur. Thus, in the systems studied, the following species were taken into account: $PbEDTA^{2-}$, $PbHEDTA^-$, $Pb(OH)_3^-$, $ZnEDTA^{2-}$, $ZnHEDTA^-$, $Zn(OH)_3^-$, $Zn(OH)_4^-$, $CuEDTA^{2-}$, and $CuHEDTA^{2-}$. The metal ions studied in this work do not form stable carbonate or hydrocarbonate complexes.

The ion-exchange equilibrium for the anionic metal–EDTA

$$2\,R = E + MEDTA^{2-} \xleftrightarrow{\ K_{MEDTA/E}\ } R_2 = MEDTA + 2\,E^- \quad \text{Eq 7}$$

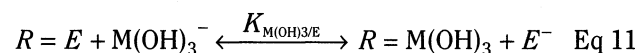$$R = E + MHEDTA^- \xleftrightarrow{\ K_{MHEDTA/E}\ } R = HEDTA + E^- \quad \text{Eq 8}$$

complexes may be expressed by the following equations: where E^- represents the eluent species HCO_3^-. The equilibrium constants for Equations 7 and 8, respectively, may be

$$K_{MEDTA/E} = \frac{(MEDTA^{2-})\ [E^-]^2}{[MEDTA^{2-}]\ (E^-)^2} \qquad \text{Eq 9}$$

$$K_{MHEDTA/E} = \frac{(MHEDTA^-)\ [E^-]}{[MHEDTA^-]\ (E^-)} \qquad \text{Eq 10}$$
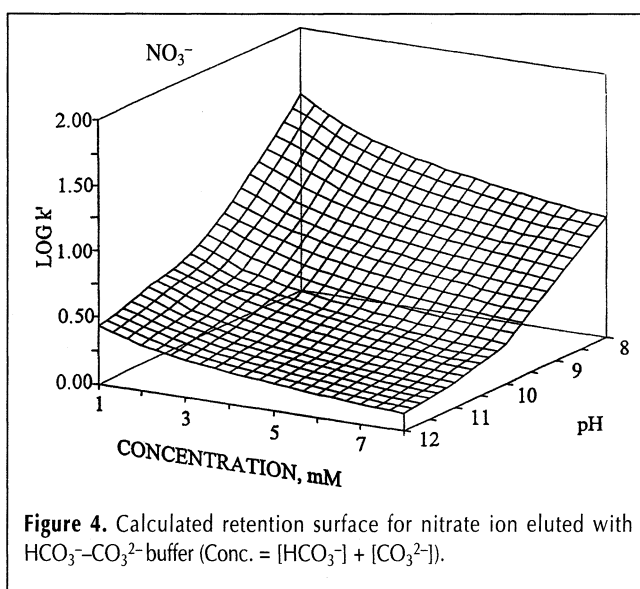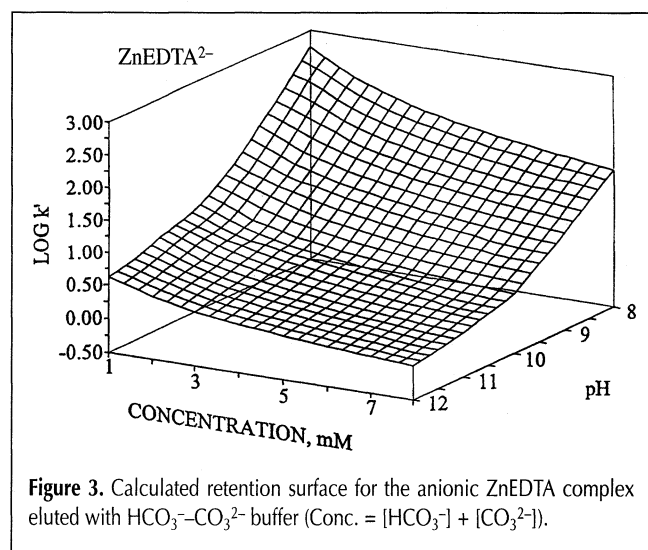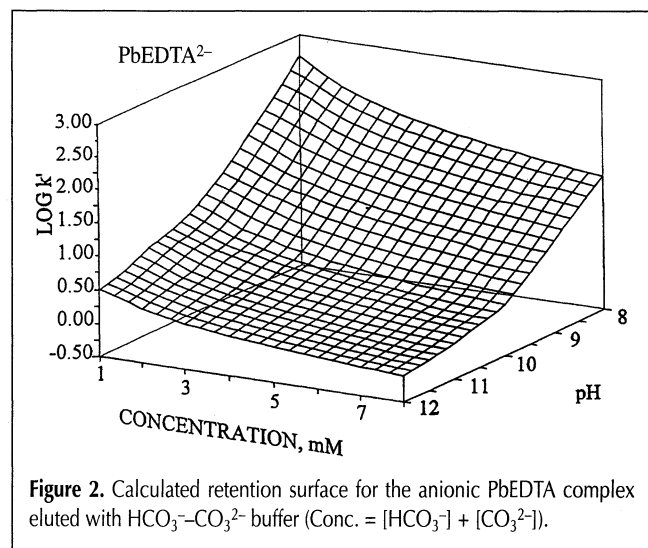
given by the following:

In the case of the species considered in this study, the formation of hydroxo complexes must also be taken into consideration. The ion-exchange equilibrium is given by the following:

$$R = E + M(OH)_3^- \xleftrightarrow{\ K_{M(OH)3/E}\ } R = M(OH)_3 + E^- \quad \text{Eq 11}$$

where

$$K_{M(OH)3/E} = \frac{(M(OH)_3^-)[E^-]}{[M(OH)_3](E^-)} \qquad \text{Eq 12}$$

Figure 2. Calculated retention surface for the anionic PbEDTA complex eluted with HCO_3^-–CO_3^{2-} buffer (Conc. = $[HCO_3^-]$ + $[CO_3^{2-}]$).

Figure 3. Calculated retention surface for the anionic ZnEDTA complex eluted with HCO_3^-–CO_3^{2-} buffer (Conc. = $[HCO_3^-]$ + $[CO_3^{2-}]$).

Figure 4. Calculated retention surface for nitrate ion eluted with HCO_3^-–CO_3^{2-} buffer (Conc. = $[HCO_3^-]$ + $[CO_3^{2-}]$).

The distribution coefficient (D_M) in this instance is considered to be the sum of the distribution coefficients of the individual species containing M. This may be expressed by using Equations 9, 10, and 12:

$$D_M = \frac{K_{MEDTA/E}(E)^2}{[E]^2}\phi_{MEDTA} + \frac{K_{MHEDTA/E}(E)}{[E]}\phi_{MHEDTA}$$

$$+ \frac{K_{M(OH)3/E}(E)}{[E]}\Phi_{M(OH)3} \qquad \text{Eq 13}$$

where Φ_{MEDTA} and Φ_{MHEDTA} may be expressed as the following:
The actual values for the molar fractions may be calculated

$$\phi_{MEDTA} =$$

$$\frac{[MEDTA^{2-}]}{[M^{2+}]+[MHEDTA^-]+[MEDTA^{2-}]+\overset{n}{\underset{i=1}{x}}[M(OH)_i^{2-i}]}$$

$$\text{Eq 14}$$

$$\phi_{MHEDTA} =$$

$$\frac{[MHEDTA^-]}{[M^{2+}]+[MHEDTA^-]+[MEDTA^{2-}]+\overset{n}{\underset{i=1}{\sum}}[M(OH)_i^{2-i}]}$$

$$\text{Eq 15}$$

from the protonation constants of MEDTA^{2-} (16) as it is given for $\Phi_{M(OH)3}$:

where β is the complex formation constant of the metal hy-

$$\phi_{M(OH)3} =$$

$$\frac{\beta_3[OH]^3}{1 + K_{MEDTA}[EDTA] + K_{MHEDTA}K_{EDTA(H)1}[H][EDTA]^+ \overset{3}{\underset{i=1}{\sum}}\beta_i[OH]^i}$$

$$\text{Eq 16}$$

droxo complexes. This expression compensates for the first hydroxo complexes of Pb and Zn, which have three hydroxo ligands. In the case of Zn, there is a complex with four hydroxo ligands. The molar fraction may be derived using a similar derivation. The molar concentrations may be calculated using the protonation constants for the hydroxo complexes.

Ion-Exchange Equilibria of Eluent Ions

The carbonate eluent is a multiple species eluent that contains three competing anions (CO_3^{2-}, HCO_3^-, OH^-). In simultaneous ion exchange, with the presence of competing anions, the ion-exchange capacity of the column is best described by the following equation:

The series of ion-exchange equilibrium processes for the eluent species may be given by the following:

$$Q = 2(CO_3^{2-}) + (HCO_3^-) + (OH^-) \qquad \text{Eq 17}$$
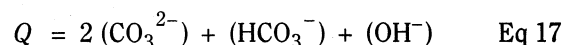
where each equilibrium constant may be expressed as
By rearrangement of Equations 20 and 21, the concentration

$$CO_3^{2-} + 2R = HCO_3 \xleftarrow{\quad K_{CO3/HCO3} \quad}$$
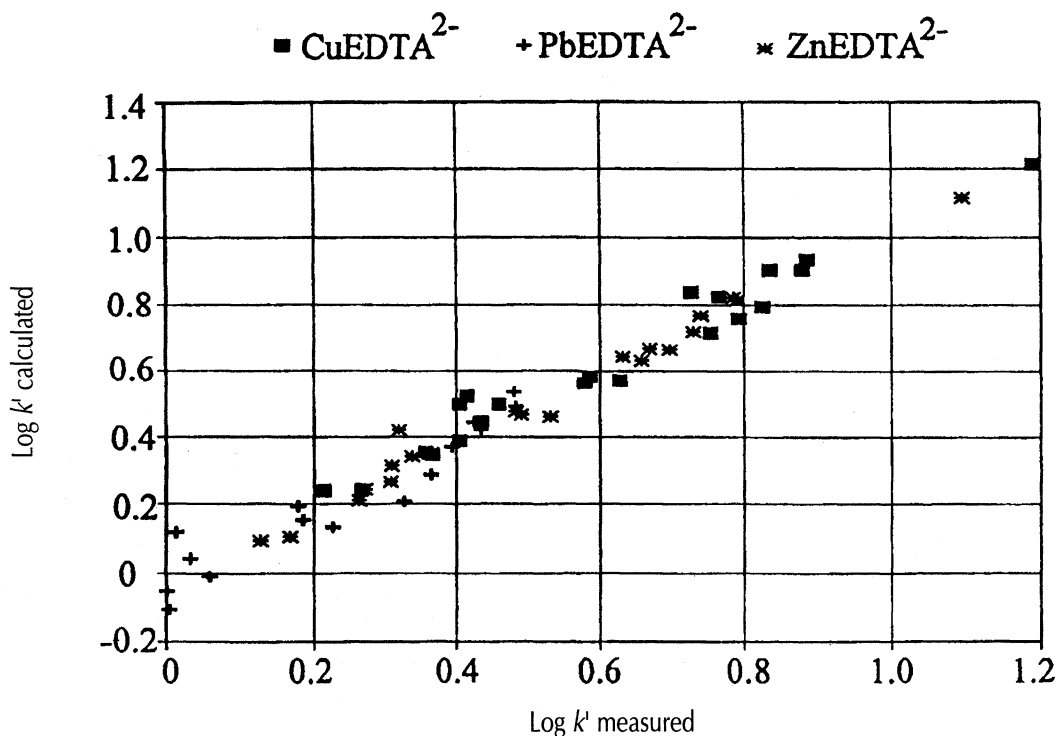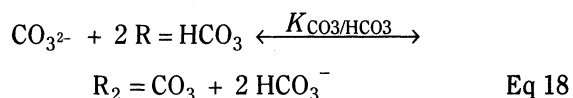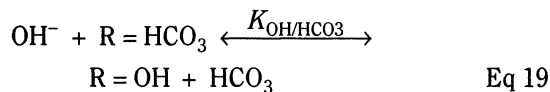
$$R_2 = CO_3 + 2HCO_3^- \qquad \text{Eq 18}$$

Figure 5. Relationship of measured and calculated capacity factors for anionic metal–EDTA complexes eluted with carbonate buffer (slope: 1.085 ± 0.022; correlation coefficient: 0.987 for 63 data pairs).

$$OH^- + R = HCO_3 \xrightarrow{\quad K_{OH/HCO3} \quad}$$
$$R = OH + HCO_3 \qquad\qquad\qquad \text{Eq 19}$$

$$K_{CO3/HCO3} = \frac{(CO_3^{2-})\,[HCO_3^-]^2}{[CO_3^{2-}]\,(HCO_3^-)^2} \qquad \text{Eq 20}$$

$$K_{OH/HCO3} = \frac{(OH^-)\,[HCO_3^-]}{[OH^-]\,(HCO_3^-)} \qquad \text{Eq 21}$$

Figure 6. Chromatogram of anionic metal-EDTA complexes and simple anions obtained by using carbonate eluent ((conc. $[HCO_3^-]$ + $[CO_3^{2-}]$ = 3.5mM, $CO_3^{2-} - HCO_3^-$ = 2.0/1.5). The pH was 10.4, the sample volume was 50 µL, and a conductivity detector was used.

of CO_3^{2-} and OH^- in the stationary phase may be expressed in terms of HCO_3^-. If these expressions are substituted for CO_3^{2-} and OH^- into Equation 17, the quadratic form of the ion-exchange capacity (Q) results.

A value for HCO_3^- can be substituted into Equation 13 in place of (E) by solving Equation 22 for HCO_3^-. After the calculation of the molar fractions for the complex anions, one of the final forms of the model may be obtained.

$$Q = \frac{2\,K_{CO3/HCO3}[CO_3^{2-}]}{[HCO_3^-]^2}(HCO_3^-)^2 +$$
$$\left(1 + \frac{K_{OH/HCO3}[OH^-]}{[HCO_3^-]}\right)(HCO_3^-) \qquad \text{Eq 22}$$

Ion-exchange equilibria of inorganic anions

The ion-exchange behavior of mono- or divalent simple anions of strong acids can be described by Equation 5 (including the solution of Equations 20–22). Thus, the treatment of their elution data does not need any further theory.

Finally, in order to eliminate the instrument-specific void volume (V_0), the distribution coefficient (D_A), can be expressed in terms of the capacity factor (k'),

$$D_A = \frac{V_0\,k'}{V_S} \qquad \text{Eq 23}$$

where V_S is the volume of the stationary phase, which can also be easily determined.

Experimental

Reagents and solutions

Eluents were prepared by using analytical grade Na_2CO_3, $NaHCO_3$, and carbonate-free NaOH (Fluka; Switzerland). High purity water was obtained using a Milli-Q system (Millipore; Bedford, MA). All eluents were treated with an ultrasonic bath and ultrafiltration to remove air and particles. Standard solutions of metals, simple anions, and the chelating agent (EDTA) were prepared by dilution of a concentrated stock solution of analytical-grade salts (Fluka). Unless otherwise stated, all sample injections (50-µL volume) contained the following concentrations: [Pb] = 0.124 mmol, [Zn] = 0.055 mmol, [Cu] = 0.085 mmol, and [EDTA] = 0.532 mmol. The sample pH was adjusted to the appropriate value using NaOH.

Instrumentation

A Dionex series 2010i ion chromatograph was used with a conductivity detector equipped with an AMMS anionic membrane suppressor (Dionex; Sunnyvale, CA). The separation column was a 16-µm polystyrene divinylbenzene substrate, agglomerated with an anion-exchange latex that had been completely aminated (250 × 4-mm i.d.) (AS9, Dionex). The latex had a polyacrylate backbone that contains the actual ion-exchange
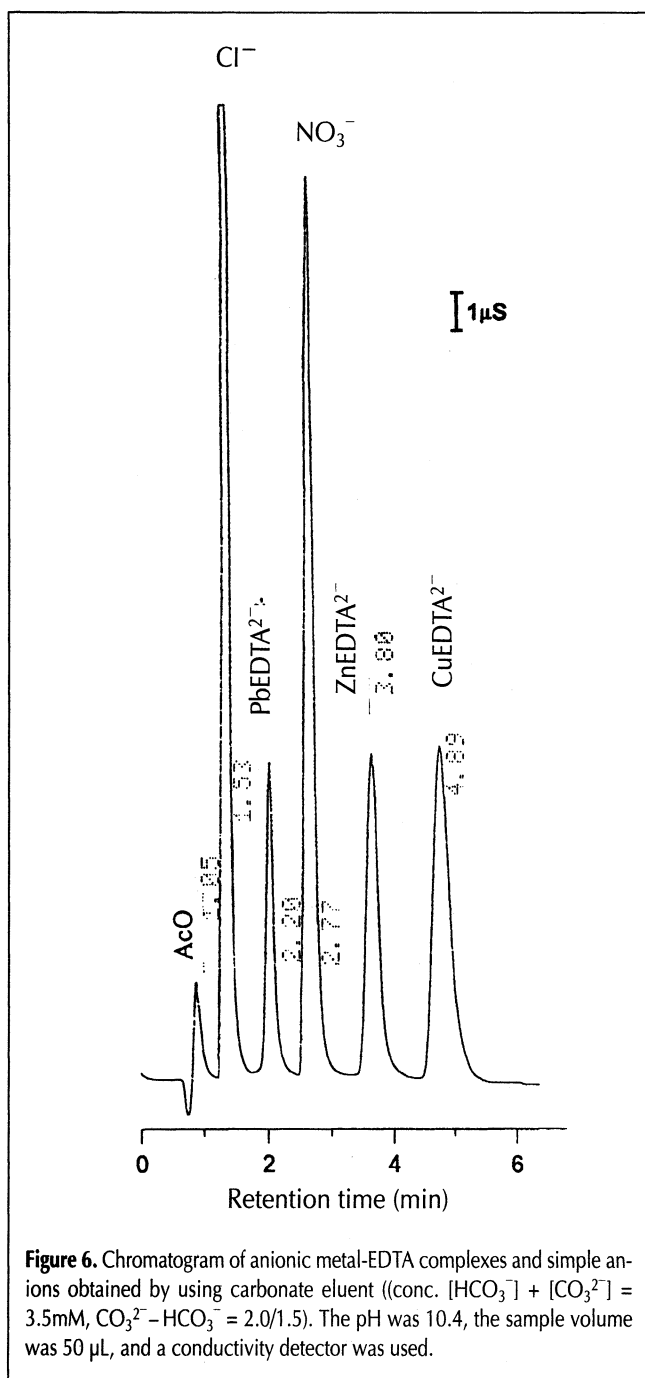
sites. The ion-exchange capacity was determined empirically (20 µequiv per column) (17). All chromatograms were obtained at room temperature at a flow rate of 1.6 mL/min. All retention times obtained were the result of triplicate injections of a sample containing all the analytes.

Results and Discussion

The retention behavior of three anionic metal–EDTA complexes (Cu, Pb, Zn) and four inorganic anions were considered. All experimental retention data, obtained from various eluent compositions and pH levels (Table I) were evaluated. The data was used to determine the unknown values for the analyte–eluent and intereluent ion-exchange equilibrium constants required in the model. The nonlinear regression algorithm (Nelder and Mead simplex method) used in repetitive minimization was then used successfully to compare the observed and predicted retention data. The behavior of each ana-

lyte was compared at varying eluent compositions and pH levels. The protonation and complex formation constants required in the calculations were taken from the literature (16,18). The activity coefficients were calculated using the Davies extension of the Debye–Hückel equation.

The calculated values of the ion-exchange equilibrium constants are summarized in Tables II and III. From these tables, it can be seen that the intereluent ion-exchange equilibrium constant is independent of the analyte present and the eluent concentration. The analyte eluent ion-exchange equilibrium constants are also independent of the eluent concentration. These values are of particular importance when considering simultaneous separation. The comparison of observed and predicted retention volumes are shown in Tables IV and V. These results unambiguously show that good correlation between the observed and predicted retention volume was obtained for all analytes. The errors are given as absolute differences and are calculated by the expression $(|V_{calc} - V_{meas}|)/V_{meas}$. The mean of errors at the bottom of the tables is a clear indication that the model demonstrates reliability and is indeed suitable for this study.

The calculated ion-exchange equilibrium constants were used in the preparation of a retention surface diagram for the metal complexes studied (Figures 1–3). The retention surface diagram for nitrate is also shown (Figure 4) as an example of the typical diagram obtained for the simple anions. These retention surfaces give a clear picture of the relationship between the value of $\log k'$, the eluent concentration, and pH. Since the selectivity constant of CO_3^{2-} is significantly higher than that of HCO_3^-, increasing the pH results in decreasing values of $\log k'$, which was observed with decreasing retention time. All the retention surfaces show a slight break at about pH 10.1. This phenomenon can be attributed to the inflexion point on the molar fraction plot of CO_3^{2-}, which is the determining eluent ion (Figure 1). The reliability and applicability of the proposed model is confirmed by the good agreement between the measured and calculated capacity factors, as demonstrated in Figure 5 for the EDTA complexes in this study.

The retention model was used successfully in predicting the retention of the analytes prior to their simultaneous separation using new eluent compositions. A typical chromatogram is shown in Figure 6.

In order to confirm that the simultaneous separation process could lead to a quantitative analytical method, a series of calibration graphs were obtained for Cu, Pb, and Zn (Figure 7). The chosen eluent was one in which good resolution was achieved for the metal complexes and simple anions. The concentration range for the sample ions was
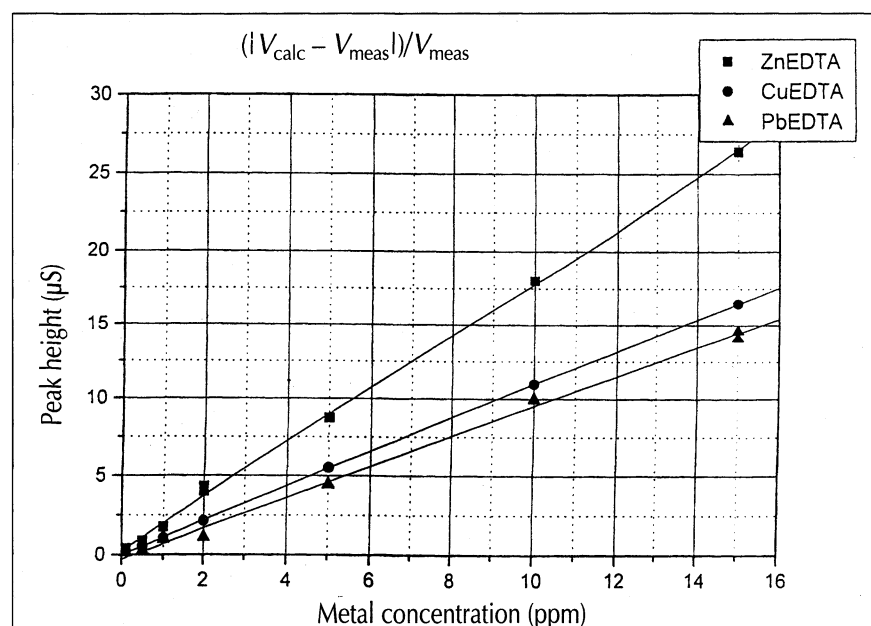

Figure 7. Calibration curves for quantitative determination of anionic metal-EDTA complexes in suppressed ion chromatography (eluent: 3.5mM $Na_2CO_3/NaHCO_3$=2.5/1, pH =9.98).

Table VI. Sensitivity and Detection Limits* for Quantitative Determination of Anionic Metal-EDTA Complexes by Ion Chromatography

| Ions | Sensitivity (µs·L/mg) | Regression coefficient | Detection limit | | |
			Conc. (ng/µL)	Mass (ng)[†] (suppressed)	Mass (ng)[‡] (nonsuppressed)
CuEDTA	1.10	0.9999	0.12	6.0	250.0
PbEDTA	0.98	0.9970	0.81	40.5	225.0
ZnEDTA	1.75	0.9995	0.34	17.0	150.0

* Based upon a 50-µL injection. Eluent: 3.5mM Na_2CO_3 –$NaHCO_3$ (2.5:1, pH 9.98).
[†] EDTA used as the complexing agent.
[‡] EDTA used as the eluent (20).

0.1–15 ppm (a common analytical detection range). The linear regression lines for the experimental results showed reliably good linear relationships (Figure 7). This demonstrates that the simultaneous separation of metal–EDTA complexes and anions could be used as a quantitative analytical method. The sensitivities (defined as the slope of the calibration graph) and the detection limits, expressed as absolute mass units and concentration units, are shown in Table VI.

The limit of detection is commonly defined in the literature as the analyte concentration giving a signal equal to the blank signal plus twice the standard deviation of the blank (19). In the last two columns of Table VI, the detection limit using suppressed and nonsuppressed methods for the separation of metal complexes are shown. The detection limits attained for metal chelate anions by using 2.5mM Na_2CO_3–1mM $NaHCO_3$ (pH 9.98) as the eluent are 0.34 mg/L, 0.12 mg/L, and 0.81 mg/L for ZnEDTA, CuEDTA, and PbEDTA, respectively. No preconcentration step was necessary under these conditions. This method has a detection limit that is about 40 times lower for Cu, 5 times lower for Pb, and 10 times lower for Zn than the method that uses EDTA as an eluent (20).

Conclusion

Low detection limits were attained for all of the anions investigated despite the low conductivity of the metal-chelate complexes. A relatively good detection sensitivity and low detection limit was obtained for PbEDTA despite the fact that the lead complex slightly coelutes with EDTA anions in some cases. Six replicate injections of different samples produce coefficients of variation that are within expected limits of error for this type of analysis (1.0% or less). This method offers a theoretical and practical treatment of a simple and sensitive technique for the simultaneous analysis of complex and inorganic anions.

Acknowledgments

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