Simultaneous Determination of Inorganic Anions and Equally Charged Complexes of Transition Metals with Polyaminocarboxylic Acids by Capillary Electrophoresis

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(Received August 26, 1996)

High efficiency Capillary Electrophoresis (CE) separation (440 - 760 thousand theoretical plates per meter) of metal-edta complexes and inorganic anions has been demonstrated using Kinetic Differentiation mode - Ion-Exchange Electrokinetic Chromatography (EKC). An aromatic homolog of polyaminocarboxylate (Quin 2, see Figure 1) has been used for the increase of the detection sensitivity. The detection limits of transition metals were found in the range of (0.59 -1.90) x 10^{-6} M (M = mol dm^{-3}).

The kinetic differentiation (KD) mode capillary electrophoresis demonstrates variety of metal-chelates separation in recent years.[1,2] This method provides high detection sensitivity and separation selectivity being due to thorough design of all part of the analytical system. The idea is that the combination of KD mode separation of metal-chelates and ion-exchange EKC mechanism allows us to separate simultaneously several equally charged edta and Quin 2 complexes and inorganic anions.

The determination of transition metals as complexes by CE and direct UV-VIS detection is more sensitive than cations determination with indirect UV detection.[3,4] The main problem for multi-component analysis by this manner is a choice of universal chelating agent, which combines high detection sensitivity and separation selectivity. EDTA forms stable complexes with many metal ions. However for equally charged transition metal cations the same structure of complex anions leads to the same mobility.[5] The separation selectivity of such type of complexes is very poor[6] Other method uses bidirectional injection of samples (cation separation mode) and ligand with on-column complex formation.[7] It requires the modification of standard CE equipment. The separation of equally charged metal chelates with 2,2'-dihydroxyazobenzene-5,5'-disulfonate was demonstrated using ion-association with short chain quaternary ammonium ions.[4] The method for the organic acid anions mobilities differentiation with cationic polymer addition was proposed by Terabe et al.[8] The quaternary ammonium groups of polymeric chain strongly adsorbed on silica surface and produce a stable reverse electroosmotic flow.[9] It allows to perform fast separation of organic and inorganic anions with negative polarity power supply.

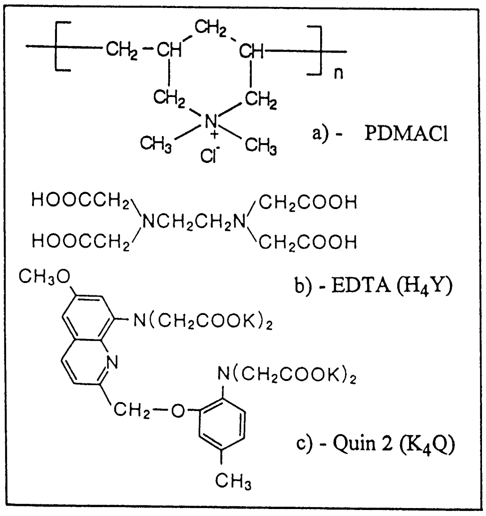

Figure 1. The structure of polymer and ligands used.

We have used this approach and the experience of Ion Chromatography (IC)[10,11] in the determination of metal-edta complexes for the improvement of CE separation selectivity. Poly(diallyldimethylammonium chloride), PDMACl was chosen as a selectivity control additive, because it has high ion-exchange affinity to inorganic anions.[12] The structures of polymer and ligands used are shown in Figure 1.

Metal-edta complexes exist as singly and doubly charged anions under neutral and slightly alkaline conditions and can be referred to medium and strongly retained type species in IC.[10,11] Commonly, IC retention of this equally charged analytes

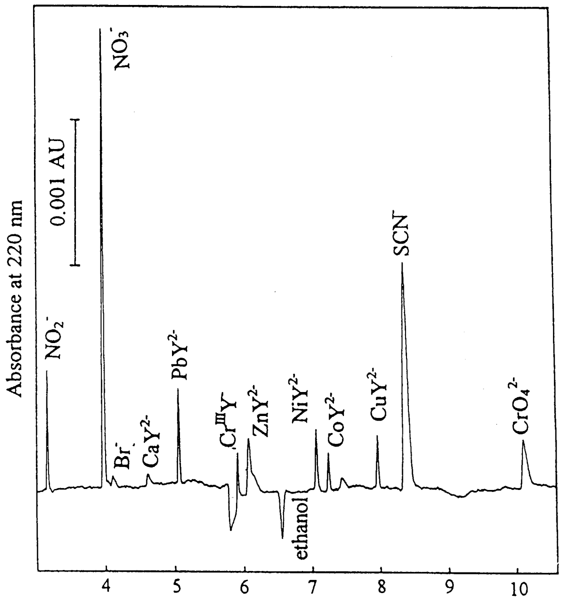

Figure 2. Simultaneous determination of several equally charged metal-edta complexes and inorganic anions.
Capillary: 45.5 cm effective length, 50 cm total length; 50 mm i.d.; buffer: 5 x 10^{-3} M Na_2SO_4, 10 x 10^{-3} M sodium acetate, pH 8.0, 53.5 x 10^{-3} M of PDMACl; sampling: pressure - 5 psi x s; conditions: -20 kV; detection: UV 220 nm; sample (10^{-3} M dm^{-3}): $[M]_T = 0.1$, $[Pb]_T = 0.2$, $[Ca]_T = 5.0$, $[Zn]_T = 0.4$, $[NO_2^-]_T = [NO_3^-]_T = 0.25$, $[SCN^-]_T = [CrO_4^{2-}]_T = 1$.

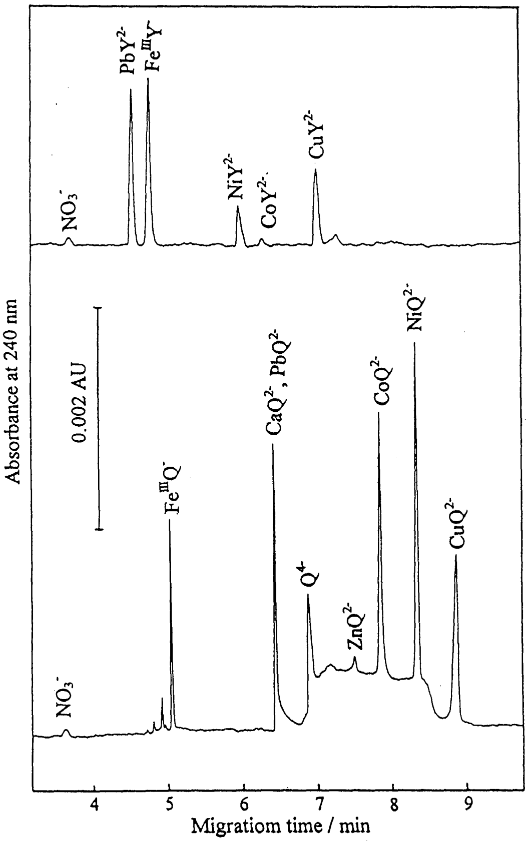

Figure 3. The comparison of selectivity and sensitivity for EDTA and Quin 2 chelates determination.
Buffer: 5 x 10^{-3} M Na_2SO_4, 30 x 10^{-3} M sodium acetate, pH 7.0, detection: UV 240 nm; sample (10^{-3} M): $[MY]_T = 0.2$, $[MQ]_T = 0.05$, other conditions see Figure 2.

increases with the increase in the stability constants of complexes (with some exceptions). The similar phenomena have been observed in KD-CE separations in the case of high polymer concentration (Figure 2).[13] Migration times of doubly charged complexes increased in the order: $CaY^{2-} < ZnY^{2-} < NiY^{2-}$, $CoY^{2-} < CuY^{2-}$. Probably, it can be explained by the differences in the size of complex anions: strong interaction in coordination polyhedron leads to its smaller size and stronger electrostatic interaction.

Table 1. Reproducibility of CE parameters, theoretical plate numbers (*N*), and detection limits (3σ basis) for some metal-edta and metal-Quin 2 chelates (n = 10).

	NO_3^-	NO_2^-	$Fe^{III}Y^-$	NiY^{2-}	$Fe^{III}Q^-$	NiQ^{2-}
r.s.d.[a]						
for migration time	0.33	0.37	0.42	0.44	0.44	0.55
for peak height	0.57	0.64	3.4	2.0	4.4	2.6
for peak area	0.87	0.84	3.1	1.5	4.6	1.4
N/1000	24	86	202	350	355	315
Detection limit/(10^{-6} M)[b]	-	-	2.5	20	0.71	0.59

[a] Relative standard deviation in %. [b] 6 nl sample injection. Other conditions see Figure 3.

In order to increase detection sensitivity 8-amino-2-[(2-aminomethylphenoxy)methyl]-6-methoxyquinoline-N,N,N',N'-tetraacetic acid (Quin 2) complexing agent with π-electronic system has been used. Stability constants of transition metal-Quin 2 complexes were found 10^6 - 10^7 times lower than for EDTA.[14] It seems reasonable that they have stronger interaction with polymeric chain owing to the large aromatic moiety in the molecular structure. Commonly metal-edta chelates are detected at 210 - 240 nm.[6,7,10] Metal-Quin 2 complexes have absorption maxima at 245 nm due to the aromatic systems, therefore, 240 nm was chosen for the comparison of the detection sensitivity. As can be seen from Figure 2 and Table 1 our assumption was confirmed and the detection sensitivity increases at least 5 times. Metal-Quin 2 chelates, even CaQ^{2-} are kinetically stable[15] and can be determined in the KD mode CE. The reproducibility of the CE system and the detection limits of the edta and Quin 2 chelates are shown in Table 1. It seems that the metal-polyaminocarboxylate complexes have some special kinetic properties and are most suitable for the separation in KD-mode.

References and Notes

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13 The CE equipment was Bio-Focus 3000 (Bio-Rad). Doubly distilled water with PYREX glass apparatus was used for the solutions preparation. All reagents used were analytical reagent grade. Disodium salt of EDTA and Quin 2 were obtained from DOJINDO (Kumamoto, Japan), PDMACl from ALDRICH (Tokyo, Japan). Metal chelates samples were prepared by addition of desired amount of metal ions to 5 x 10^{-3} M mixture of $CaCl_2$ and EDTA (pH 10, $NaHCO_3$ + NaOH) or 7.5 x 10^{-4} M of Quin 2 (pH 7.0). Cr^{III}edta-complex was synthesized separately and added to sample solution prior to the injection.
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