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Capillary electrophoresis in metal analysis Investigations of multi-elemental separation of metal chelates with aminopolycarboxylic acids

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Abstract

Capillary zone electrophoresis was applied to the separation of Co(III), Bi(III), Fe(III), Cr(III), V(IV), Pb(II), Hg(II), Co(II), Cu(II) and Ni(II) metal ions complexed with common aminopolycarboxylic acids. Ethylenediaminetetraacetic (EDTA), cyclohexane-1,2-diaminetetraacetic (CDTA) and diethylenetriaminepentaacetic (DTPA) acids were investigated and compared in order to optimize the separation resolution. The influence of carrier electrolyte parameters such as electrolyte nature, pH and concentration upon the electrophoretic behaviour of chelates was investigated and discussed. Two migration modes – counterelectroosmotic and coelectroosmotic – were compared. Better resolution was achieved using counterelectroosmotic conditions (25 kV) with 5 mmol/l DTPA electrolyte at pH 8.5 and direct UV detection at 214 nm. The separation time was less than 8 min, but the resolution of Co(II), Cu(II) and Ni(II) chelates was poor. For all metals studied the calibration graphs were linear over at least two orders of magnitude of concentration. The detection limits were in the range $2\cdot10^{-6}$–$8\cdot10^{-6}$ mol/l. A possibility of simultaneous determination of metal ions with different oxidation states such as V(IV)/V(V) and Cr(III)/Cr(VI) is demonstrated. Examples of electropherograms are presented for different samples. Application of the method to the analysis of metal ions in electroplating bath and waste water samples is also demonstrated.

Keywords: Derivatization, electrophoresis; Buffer composition; Metal complexes; Aminopolycarboxylic acids; Metals

1. Introduction

Capillary zone electrophoresis (CZE) is a relatively new separation technique which offers significant advantages: high efficiency and resolution, speed and reduced consumption of reagents. Separations by CZE are based on differences in the electrophoretic mobilities of the sample ions in an electric field. Unfortunately, the mobilities of many hydrated metal ions are very similar and mixtures of such ions cannot be separated by CZE unless an additional separation mechanism is used.

The CZE separation of metals can be grouped in two main approaches. The first one is an addition of a weak complexing agent to the electrophoretic buffer to obtain larger differences in effective mobility. This occurs by complexing the metal ions

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to differing extents. Ions that are complexed to a greater degree move more slowly through the capillary than those that have a lower fraction of the element in the complexed form. Popular ligands for these separations include α-hydroxyisobutyric acid [1–5], tartaric acid [6], phtalic acid [6] or lactic acid [6–8]. UV absorption is used widely to monitor compounds in CZE, but most metal ions do not demonstrate significant absorbance in this range. Therefore indirect detection, where the analyte ions replace a UV-absorbing organic cation (electrolyte coion), has become a commonly used technique to detect metal ions as negative peaks. Despite many advantages, poor sensitivity has limited the use of this technique for many important analysis problems.

An alternative way of adjusting selectivity of the separation is based on the complete conversion of metal ions into stable negatively charged complexes (most of all chelates) having high molar absorptivities and different mobilities [9–14]. In this technique more sensitive direct spectrophotometric detection of metal complexes can be performed.

The aim of our work is the detailed evaluation of the common aminopolycarboxylic acids as derivatizing reagents for the separation of metal ions. Attention was paid to the effect of carrier electrolyte parameters on the migration behaviour of metal complexes. Several samples were selected to demonstrate the feasibility of the method.

2. Experimental

2.1. Instrumentation

Separations were performed on a P/ACE 2100 apparatus (Beckman Instruments, Fullerton, CA, USA) equipped with a UV detector with wavelength filters (200, 214, 230 and 254 nm). Fused-silica capillaries (Polymicro Technology, Phoenix, AZ, USA) of 75 μm I.D. (375 μm O.D.) and 57 cm long (50 cm to the detector) were used. The solutes were injected in the hydrodynamic mode by overpressure (0.5 p.s.i.; 1 p.s.i.=6894.76 Pa). System Gold software was used for data acquisition. Detection was by direct UV absorbance at 214 nm. All experiments were conducted at 25°C.

2.2. Reagents and solutions

All chemicals used were of analytical-reagent grade. Deionized water was obtained by passing distilled water through a Waters Milli-Q water-purification system (Millipore, Eschborn, Germany). Stock standard solutions (0.01 mol/l) of each metal were prepared from the nitrate salts, except for V(IV) and V(V), which were prepared from vanadyl sulphate and ammonium metavanadate (Merck, Darmstadt, Germany). Metal complexes [except Cr(III) and Co(III)] were prepared by direct mixing of metal and reagent stock standard solutions before the injection. Chromium(III) and cobalt(III) complexes were prepared as described in [15,16].

Nitrilotriacetic acid (NTA), ethylenediaminetetraacetic acid disodium salt dihydrate (EDTA), cyclohexane-1,2-diaminetetraacetic acid (CDTA) and diethylenetriaminepentaacetic acid (DTPA) were obtained from Fluka (Neu-Ulm, Germany). Tetradecyltrimethylammonium hydroxide (TTAOH) was prepared from tetradecyltrimethylammonium bromide (Merck), as described in [17], using anion-exchange resin.

Electrophoretic buffer solutions were prepared from disodium hydrogenphosphate dihydrate, DTPA or sodium acetate from Merck. TTAOH solution was added to buffer solution to reverse the direction of the EOF. The pH of the electrolytes was adjusted by adding sodium hydroxide, hydrochloric acid or acetic acid solutions.

All electrolyte solutions were filtered through a 0.45 μm membrane filter and degassed by ultrasonication.

2.3. Procedures

The capillary was rinsed with 0.1 mol/l sodium hydroxide and water for 5 min, then equilibrated with carrier electrolyte for 5 or 40 min (coelectroosmotic conditions) at the beginning of each day. Between all electrophoretic separations the capillary was rinsed for 2 min with carrier electrolyte.

Electroosmotic flow velocity was evaluated from the migration time of acetone added to the sample.

3. Results and discussion

3.1. Choice of complexing agent

For complexing agents examined as reagents for precolumn derivatization of metal cations in the form of anionic complexes two distinct factors play an important role. First, to achieve a separation of multi-elemental samples the complexing agent must be able to form stable, negatively charged complexes with a great number of metal ions. Second, the complexing agent must be suitable for a sensitive detection of analyte ions. Aminopolycarboxylic acids are known for their ability to form sufficiently stable, always negatively charged chelates with many different metal ions [18]. In addition, most of these chelates show relatively high absorption at wavelengths below 230 nm. In our previous paper [19] six complexing agents were systematically investigated as derivatizing reagents for the simultaneous separation of metals and common inorganic anions by ion pair chromatography. On the basis of those results, EDTA, CDTA and DTPA were selected for CZE separations.

CZE separation is based on differences in the mobility of the ions in an electric field, which is dependent on the charge and size of the analytes. Under normal electrophoretic conditions using a fused-silica capillary (injection at anode and detection at cathode), the electroosmotic flow (EOF) is towards the cathode. Only anions having mobilities with magnitudes less than that of the EOF are detected with this configuration. The relatively small charge-to-size ratio of metal complexes with aminopolycarboxylic acids provides a possibility to separate these analytes using the configuration with positive injection side and with alkaline electrolytes, i.e., under counterelectroosmotic conditions.

Preliminary separations of ten metal complexes were performed using phosphate electrophoretic buffer at pH 8.0. Under the pH conditions used, the chelate-forming reactions with metal cations M^{n+} can be written as

$$M^{n+} + H_2Y^{2-} = MY^{n-4} + 2H^+ \quad \text{for EDTA and CDTA}$$

$$M^{n+} + H_3Y^{2-} = MY^{n-5} + 3H^+ \quad \text{for DTPA}$$

In addition, Bi^{3+}, Fe^{3+}, Cr^{3+}, Hg^{2+} and VO^{2+} ions have a stronger tendency to hydrolyse and, consequently, to form higher charged and therefore faster migrating mixed-ligand complexes

$$MY^{m-} + OH^- = M(OH)Y^{-m-1}$$

Moreover, the ability to form such complexes is stronger pronounced for less stable EDTA chelates. The effect of complexing agents on the effective electrophoretic mobilities of chelates is shown in Table 1. Comparison of the results indicates that at selected pH the effect of formation of mixed hydroxo-complexes on the migration order of chelates is hardly noticeable. The mobilities of the chelates with different complexones increase in the sequence CDTA<DTPA. The results are similar to those obtained for lanthanoid complexes [20]. EDTA has the same complexing groups as CDTA but is a smaller molecule and forms faster complexes with higher charge-to-size ratio. DTPA forms higher charged and therefore faster migrating complexes as CDTA and EDTA. This is in contrast to the results reported in [21] in which the Fe(III)–EDTA complex with a negative charge of 1 showed a higher

Table 1
Effective mobilities of metal complexes with different complexing agents

Metal	$\mu_{eff} \times 10^4$ cm^2/V s		
	CDTA	EDTA	DTPA
Co(III)	2.16	2.41	2.53
Bi(III)	2.09	2.36	3.68
Fe(III)	2.34	3.71	3.80
Cr(III)	2.41	3.88	4.36
V(IV)	4.37	4.61	4.65
Hg(II)	–[a]	–[a]	4.82
Pb(II)	4.01	4.55	4.90
Ni(II)	4.17	4.58	5.01
Cu(II)	4.21	4.61	5.08
Co(II)	4.20	4.62	5.13

[a] No peak.
Electrolyte, 10 mmol/l NaH_2PO_4, pH 8.0; applied voltage, 25 kV.

mobility than the Fe(III)–DTPA complex with a negative charge of 2. This contradiction can be explained by the fact, that in [21] the electrophoretic mobilities of Fe(III) chelates with EDTA and DTPA were compared at pH 9.3. At more basic conditions less stable Fe–EDTA chelate exists predominantly in the form of doubly charged $Fe(OH)Y^{2-}$, whereas more stable Fe–DTPA chelate is in the form of doubly charged but larger FeY^{2-}.

Preliminary experiments indicated that a DTPA system gives better resolution for both divalent and trivalent metal ions. Consequently, all further studies were carried out with the DTPA.

3.2. Optimization of separation

The pH value of the carrier electrolyte solution in CZE is the most important separation parameter for changing the selectivity of the system. The pH effect in our system could result from the following factors. First, the EOF increases with an increase in pH owing to the dissociation of capillary surface silanol groups. The effect of the EOF on the separation selectivity is given by the following equation [22]:

$$\Delta t = \frac{L_d}{E} \cdot \frac{\mu_1 - \mu_2}{(\mu_{eo} - \mu_1)(\mu_{eo} - \mu_2)} \quad (1)$$

where Δt is the difference of the migration times between two ions, μ_1 and μ_2 are the electrophoretic mobilities of these analytes, μ_{eo} is the electroosmotic mobility, L_d is the capillary length between the points of sample introduction and detection and E is the applied electric field strength. From Eq. (1) it follows that an increase of μ_{eo} with pH will decrease the value of Δt for these analytes.

Second, when phosphate buffer is neutralized with NaOH, the ionic strength of the buffer increases which results in a decreased μ_{eo} and electrophoretic mobilities of the analytes [23].

Third, the differences in the conditional formation constants of metal chelates affected by pH of the electrolyte, presumably owing to the formation of mixed- or hydroxo-complexes, can induce mobility differences between complexes.

The pH of electrolyte solutions was varied over the range from 7.0 to 9.5. A lower pH was not investigated as the separation time became longer in spite of a decrease in the EOF velocity. The concentration of phosphate in the electrolyte was kept constant at 20 mmol/l during this study. In the range of pH investigated, the pH only slightly affected the EOF velocity ($6.75 \cdot 10^{-4}$ cm^2/V s at pH 7.0 and $6.69 \cdot 10^{-4}$ cm^2/V s at pH 9.5). The most probable reason of this fact is that the pH effect and the ionic strength effect on the EOF are contrary. The effective mobilities of all metal chelates increase with increasing pH. In addition, the pH influence is more significant for M(III) and V(IV) chelates that corresponds with the stronger tendency of these analytes to form mixed hydroxo-complexes. Fig. 1 (upper panel) shows the influence of pH on the resolution of Bi(III)–Fe(III), V(IV)–Pb(II) and Ni(II)–Co(II) peak pairs. It can be seen, that in contrast to the Eq. (1), the effect of pH on R_s is contradictory and significant for the Bi(III)–Fe(III) and V(IV)–Pb(II) pairs and less pronounced for the Ni(II)–Co(II) pair. The general trends exhibited by the plots of pH versus resolution and pH versus differences between conditional formation constants for these pairs (Fig. 1, lower panel) are similar. Data for conditional formation constants were taken from [24]. For the calculations of side-reaction coefficients (α), the formation of hydroxo-complexes of the metal ion,

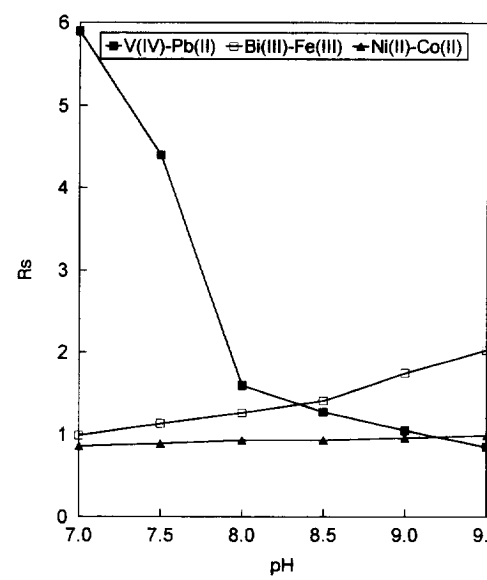

Fig. 1. Dependence of resolution (upper panel) and differences between conditional stability constants (lower panel) of chelates on the pH of carrier electrolyte.

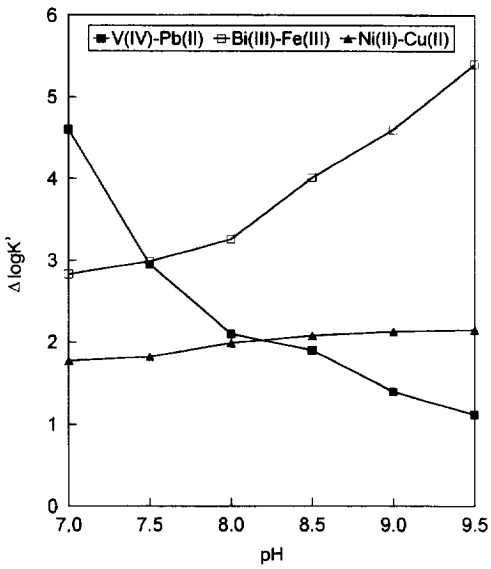

Fig. 1. (*continued*)

formation of mixed hydroxo-complexes of the type $M(OH)DTPA^{n-6}$, formation of phosphate complexes and protonation of the DTPA were taken into account. Results in Fig. 1 clearly indicate, that variation of conditional formation constants of chelates with pH was the predominant factor in separation selectivity modification. For the majority of peak pairs maximum resolution was observed at pH 8.0–8.5.

Besides the pH, the ionic strength of the electrophoretic buffer is an important parameter we can use to improve efficiency, resolution and selectivity of the separation system. Different concentrations of the phosphate buffer were tested at pH 8.0. As the electrolyte concentration was increased from 5 mmol/l to 30 mmol/l, the electrophoretic mobilities of M(III) chelates increase by approximately 5–8% while EOF mobility decreases. On the other hand, all the M(II) complexes first showed a negligible increase in μ_{eff} with phosphate concentration whereas at higher concentrations the opposite trend was observed. However, the influence of electrolyte concentration on the resolution was only negligible.

Changes in the separation selectivity can also be done by addition of alkylammonium salts to the electrophoretic buffer. This approach has been used successfully for the improvement of separation selectivity for metal complexes with 2,2′-dihydroxyazobenzene-5,5′-disulphonic acid [25]. In our system, the addition of tetrabutylammonium chloride up to the concentration of 20 mmol/l to the carrier electrolyte increases the migration times of all chelates without significant changes in the separation selectivity.

Fig. 3 shows the separation of ten metal complexes under optimum conditions. A good resolution of all solutes is obtained except for V(IV)–free DTPA and Ni(II)–Cu(II)–Co(II) pairs. Ni and Cu complexes are not separated at all and for Ni(Cu)/Co and V/DTPA no baseline resolution is obtained. In order to resolve these chelates, the separation system was investigated using DTPA solution as the carrier electrolyte.

In the solutions of M–DTPA chelates an equilibrium between free M^{n+} cations and $M\text{–}DTPA^{n-5}$ anions exists. This equilibrium depends on such factors as stability constants of the complexes, pH, DTPA concentration and others. The effective electrophoretic mobility of the metal chelate can be assumed to be a combination of the mobilities of both the species M^{n+} and $M\text{–}DTPA^{n-5}$, that move in the opposite directions when placed in the electric

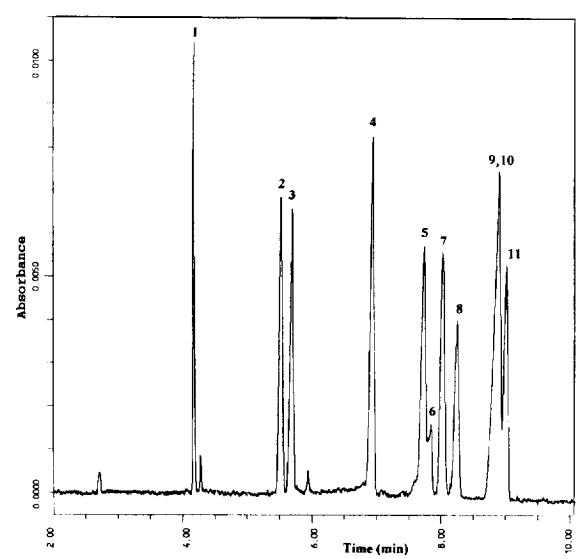

Fig. 2. Separation of 10 metal–DTPA chelates using 5 mmol/l DTPA electrolyte at pH 8.5. Other conditions as in Fig. 2. Peaks: 1 Co(III); 2 Bi(III); 3 Fe(III); 4 Cr(III); 5 V(IV); 6 Pb(II); 7 Hg(II); 8 Cu(II); 9 Ni(II); 10 Co(II).

field. This results in the peak broadening for most chelates. The more complete is the complexation of the metal ion the sharper will be the peak of the complex formed. Fig. 3 illustrates the optimized separation of ten metal–DTPA complexes using 5 mmol/l DTPA solution as the carrier electrolyte. The electropherograms of metal separations with the two different electrolytes (Figs. 2 and 3) clearly indicate that DTPA electrolyte does not improve separation efficiencies for highly stable and/or kinetically inert Bi(III), Fe(III), Co(III) and Cr(III) complexes. However, for less stable and kinetically labile M(II) chelates in the DTPA electrolyte the equilibrium is shifted towards the formation of the complex, resulting in sharper peaks. For example, the peak efficiency of Pb–DTPA and Hg–DTPA complexes increases from approximately 38 000 and 34 000 theoretical plates using phosphate to 88 000 and 96 000 theoretical plates using DTPA carrier electrolyte, respectively. In addition, in the second case the peak of the free DTPA is eliminated and a pre-capillary derivatization of metal ions forming kinetically labile complexes is not necessary. On the other hand, when using DTPA electrolyte, the detection sensitivity decreases by a factor of 1.3, because free DTPA also slightly absorbs at 214 nm. Moreover, Cu(II), Co(II) and Ni(II) chelates also are not separated at these conditions. Perhaps the separation of these species can be achieved by using longer capillary, but this way was not investigated.

The electropherogram in Fig. 4 illustrate the ability of the discussed method to determine a group of metals in the alloyed Fe–Cr–Ni electroplating bath.

Both phosphate and DTPA electrolytes were investigated also in the slightly acidic medium at pH 4.0–5.0. In this case $\mu_{M-DTPA} > |\mu_{eo}|$, so a negative power supply was used. Investigations showed that the use of slightly acidic electrolytes did not improve the separation of the complexes. The peaks for most analytes became broader and migration times were longer. For example, migration time of Cr(III)–DTPA chelate using phosphate electrolyte at pH 4.0 was found to be 26 min. But these conditions offer a possibility for the rapid and selective simultaneous separation of V(IV) and V(V) species (Fig. 5).

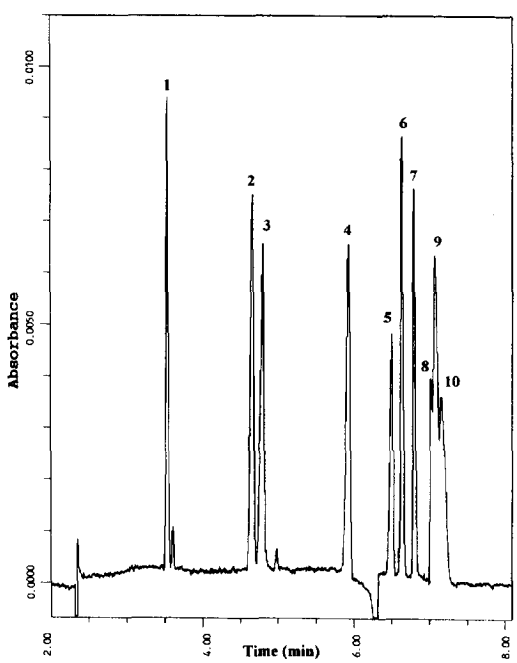

Fig. 3. Separation of 10 metal–DTPA chelates. Electrolyte, 20 mmol/l Na_2HPO_4, pH 8.0; applied voltage, 25 kV; direct UV detection at 214 nm; injection time, 4 s. Peaks: 1 Co(III); 2 Bi(III); 3 Fe(III); 4 Cr(III); 5 V(IV); 6 DTPA; 7 Pb(II); 8 Hg(II); 9 Cu(II); 10 Ni(II); 11 Co(II).

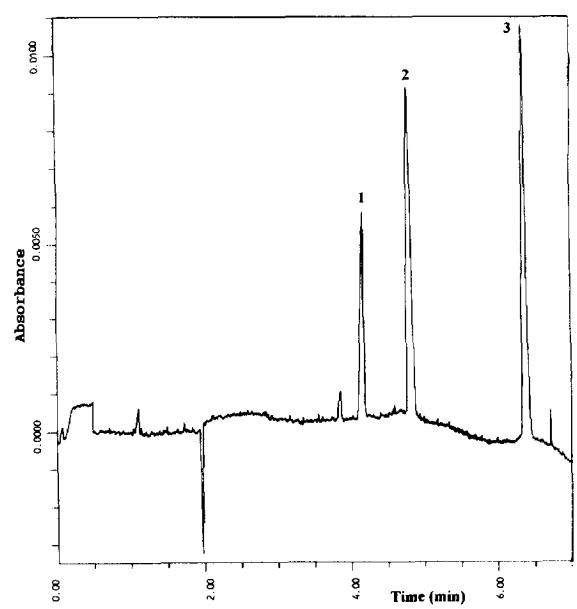

Fig. 4. Electropherogram of alloyed Fe–Cr–Ni electroplating bath (dilution 1:500). Applied voltage, 30 kV; other conditions as in Fig. 3. Peaks: 1 Fe(III); 2 Cr(III); 3 Ni(II).

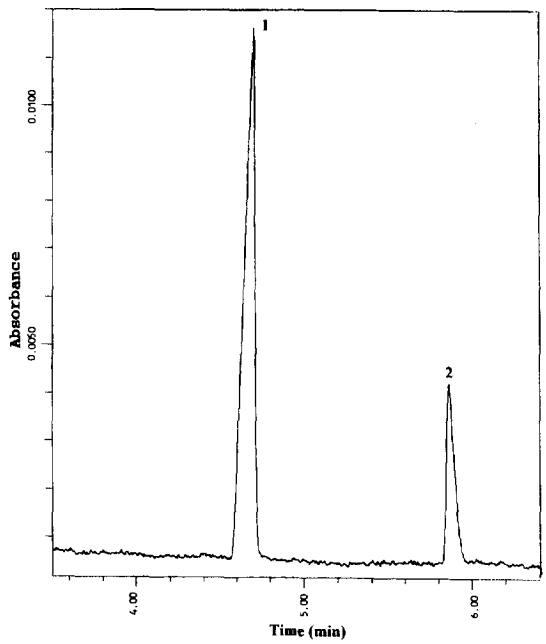

Fig. 5. Separation of V(IV) and V(V) species after complexation with DTPA. Electrolyte pH 4.0; applied voltage, −30 kV. Peaks: 1 V(V); 2 V(IV).

Common inorganic anions such as NO_2^-, NO_3^-, Br^-, CrO_4^{2-}, MoO_4^{2-} show higher mobilities, on the other hand most of metal–DTPA complexes show lower mobilities than both vanadium–DTPA species and therefore do not interfere in the determination of V(IV) and V(V). The more detailed evaluation of these investigations is in progress.

3.3. Separation under coelectroosmotic conditions

The electrophoretic behaviour of the M–DTPA chelates under coelectroosmotic conditions was also studied. This separation mode can be performed by addition to the carrier electrolyte of a cationic surfactant, such as tetraalkylammonium salt, which has the effect of reversing the direction of the EOF so that it flows from the negative electrode to the positive electrode. If the instrument is now configured with the cathode at the inlet end of the capillary and the anode at the outlet (detector) end, then the anionic solutes will migrate in the same direction as the EOF and will reach the detector. The influence of the surfactant concentration on the EOF velocity has been studied using TTAOH as cationic surfactant in 20 mmol/l phosphate electrolyte at pH 8.0. The TTAB salt was converted to the hydroxide form on the anion-exchange resin to remove bromide ion that can reduce detection sensitivity. The results obtained are summarized in Table 2. They show that at TTAOH concentration above 0.3 mmol/l the EOF is reversed. For further experiments 0.5 mmol/l concentration of TTAOH was selected, because at this concentration, the EOF is stable.

Under this configuration the migration order of chelates is completely reverse to the migration sequence of these complexes under counterelectroosmotic conditions with positive power supply. Therefore M(II) complexes with higher charge show significantly shorter migration times resulting in worse resolution than that showed above. The resolution can be improved using lower voltage and/or lower TTAOH concentration but at those conditions the migration times of M(III) complexes become very long. Slightly better but also insufficient resolution of M(II) chelates was obtained with DTPA carrier electrolyte.

The main advantages of coelectroosmotic separation mode is that both fast and slow anions can be separated in a single run. The evident illustration of this fact is the electropherogram in Fig. 6, in which a simultaneous separation of chromium(VI) and chromium(III) species in the waste water from electroplating plant within 5 min is demonstrated. It is worth noting that several simple anions, such as nitrite, nitrate, molybdate can be determined simultaneously at these conditions too. However, this

Table 2
Effect of TTAOH concentration on the EOF

Concentration, mmol/l	$\mu_{eo} \times 10^4$ cm^2/V s
0	6.37
0.1	2.21
0.2	–[a]
0.3	–[a]
0.4	−2.78
0.5	−3.56
0.7	−3.60
1.0	−3.71

[a] The EOF marker did not elute within 30 min with either electrode configuration.
Electrolyte, 20 mmol/l NaH_2PO_4, pH 8.0; applied voltage 25 kV. EOF to the anode is defined as negative.

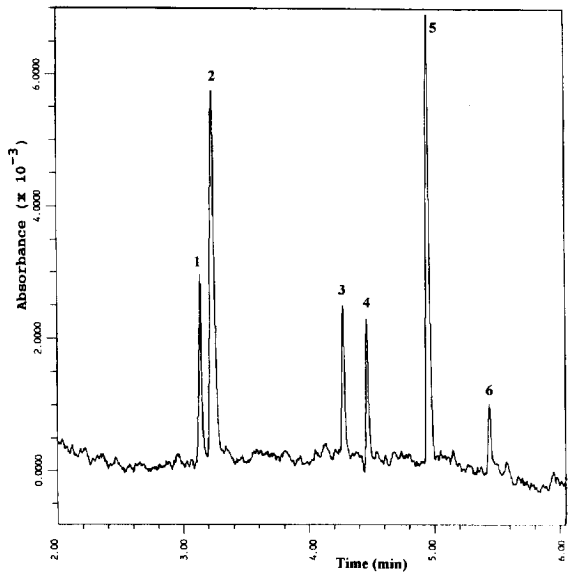

Fig. 6. Speciation of Cr(VI) and Cr(III) in waste water from electroplating plant. Electrolyte, 20 mmol/l Na_2HPO_4, 0.5 mmol/l TTAOH, pH 8.0; applied voltage, −15 kV; direct UV detection at 214 nm; injection time, 12 s. Peaks: 1 CrO_4^{2-}; 2 NO_3^-; 3 Ni(II); 4 Cr(III); 5 Fe(III); 6 unknown peak.

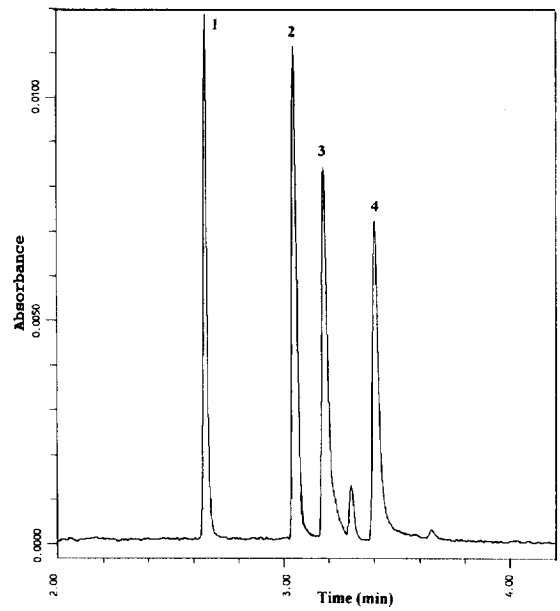

Fig. 7. Separation of aminopolycarboxylic acids after derivatization with Fe^{3+}. Electrolyte, 20 mmol/l sodium acetate, 0.5 mmol/l TTAOH, pH 4.0 with acetic acid; applied voltage, −25 kV; direct detection at 254 nm. Peaks: 1 DTPA; 2 EDTA; 3 CDTA; 4 NTA.

study was focused mainly on the separation of metals.

Another example of the capability of the proposed method is the separation of common complexones using acetate carrier electrolyte at pH 4 after pre-capillary derivatization with Fe(III) cations (Fig. 7). It can be seen that excellent resolution of all compounds was achieved within less than 4 min.

Finally, Fig. 8 demonstrates the rapid speciation of Fe–EDTA complex and free EDTA in the waste water from a photolaboratory. Free EDTA only slightly absorbs at the selected wavelength, therefore pre-capillary derivatization is necessary. The addition of Ni(II) salt solution to the sample result in a complexation of free EDTA and enables the determination of the both Fe–EDTA and free EDTA in a single run.

3.4. Analytical performance of method

Several parameters related to quantitation, including minimum detectable concentration, linearity and reproducibility, were examined under the above

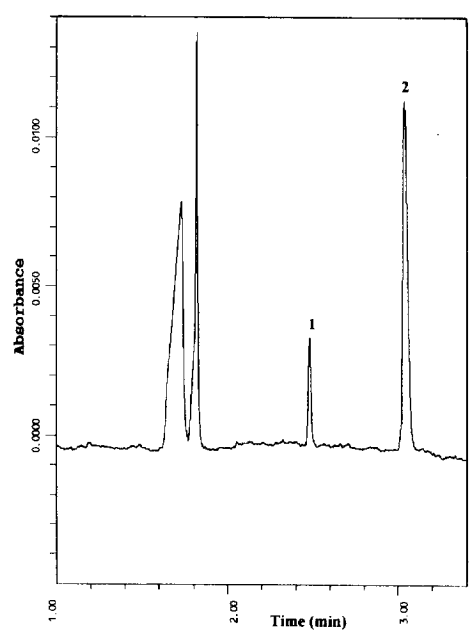

Fig. 8. Determination of Fe–EDTA and free EDTA in waste water from photolaboratory. Conditions as in Fig. 7. Peaks: 1 Ni–EDTA; 2 Fe–EDTA (see text).

optimized counterelectroosmotic conditions with DTPA electrolyte.

The detection limits for a signal-to-noise ratio of 3 and 8 s hydrodynamic injections were in the range from $2\cdot10^{-6}$ mol/l for Fe(III) to $8\cdot10^{-6}$ mol/l for Ni(II). Lower detection limits may be obtained by injecting greater volumes, but at the expense of peak efficiency. All metals studied gave a linear relationship between peak area and concentration over a range of at least two orders of magnitude. Correlation coefficients ($n=5$) were ranged from 0.996 to 0.999 for all tested metals.

The reproducibility was studied by making five consecutive runs of a mixed standard solution at a concentration of $5\cdot10^{-5}$ mol/l of each metal. The relative standard deviations of migration times and peak areas for all chelates were less than 1.0% and 5%, respectively.

In order to evaluate the quantitative performance of the method, samples of alloyed Fe–Cr–Ni electroplating bath solution and waste water from electroplating plant were analysed. Both samples investigated contain Cr(III), that forms kinetically inert chelates. Therefore, after appropriate dilution and addition of DTPA the samples were boiled for 10 min, then filtered through 0.45-μm membrane filter and injected. In order to determine both Cr(III) and Cr(VI) species the waste water was analysed under coelectroosmotic conditions (Fig. 6). Many other metal ions such as Ca^{2+}, Mg^{2+}, Zn^{2+}, Cd^{2+} often presenting in waste water samples also form stable chelates with DTPA but their absorbance is so low that direct detection at selected wavelength is not feasible.

Table 3
Comparison of CZE and AAS methods for the determination of metals ($n=5$)

Sample	Metal	Found (mg/l)	
		CZE	AAS
Fe–Cr–Ni electroplating bath	Fe(III)	3860 (1.9)[a]	3780
	Cr(III)	6620 (1.4)	6680
	Ni(II)	10 700 (1.2)	10 400
Waste water from plating plant	Cr(VI)	1.21 (4.1)	1.15[b]
	Cr(III)	0.86 (4.9)	0.92[b]
	Fe(III)	3.14 (2.6)	3.22
	Ni(II)	1.10 (4.4)	1.16

[a] The values in parentheses are the relative standard deviations (%).
[b] Spectrophotometric determination [26].

The CZE results shown in Table 3 are in a good agreement with those obtained by atomic absorption spectrometry (AAS) and spectrophotometric methods.

4. Conclusions

The results of this work demonstrate that metal complexation CE can be successfully used for the multi-elemental separations of metal ions and common complexing agents. The potential applications of the method may include the analysis of plating baths solutions, industrial waste waters, speciation of metal ions with different oxidation states in common environmental samples. In further investigations, which are still in progress, more emphasis will be paid to the quantitative aspects of metal speciation.

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