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Development of capillary electrophoresis for the determination of metal ions using mixed partial and complete complexation techniques

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Abstract

A new capillary electrophoretic (CE) method was developed for the selective and sensitive determination of common metal ions. The proposed method is based on conventional CE separation of metal cations followed by complete complexation of separated analytes with 1,10-phenanthroline using the zone-passing technique. This approach combines both partial and complete complexation modes and, thus, enables rapid, selective, efficient separation together with sensitive direct UV detection of metal species. The optimal conditions for the separation and derivatization reaction were established by varying type of electrolyte, electrolyte pH, introduction time and concentration of 1,10-phenanthroline. The optimized separations were carried out in 50 mmol l^{-1} glycolic acid electrolyte (pH 6.0 with imidazole) using direct UV detection at 254 nm. Five common metal cations (Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}) were separated in less than 4 min. The proposed system was applied to the determination of Fe(II) and Zn(II) in snow samples. The recovery tests established for snow samples were within the range 100±12%.

Keywords: Derivatization, electrophoresis; Snow; Metal cations; Phenanthroline

1. Introduction

During recent years, capillary electrophoresis (CE) has become established as a powerful technique for metal ion separation [1–3]. Some of the advantages of this technique are high separation efficiency, rapid separations, low sample consumption, adaptability to a variety of applications using different separation conditions to accommodate different matrices, and a wide mass range of analytes. The separation principle of CE is based on the differential electrophoretic mobility of charged compounds. The differences in the mobility of the analytes are related, in turn, to their charge densities, i.e., the charge-to-mass ratio. One of the problems in the analysis of metal ions by CE is that most of transition metal cations have almost the same mobility due to their similar size and identical charge. Obviously, the enhancement of separation selectivity is the only alternative with which to achieve a satisfactory resolution. Generally, there are two main approaches in this direction that

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imply the addition of a complexing ligand to either the carrier electrolyte or a sample solution before introduction into the capillary [1]. In the first case, the mobility of sample cations toward the cathode can be selectively moderated due to the partial complexation within the capillary, followed by the formation of metal complexes of different stability and thereby effective charge [4–7]. The second approach provides the complete pre-capillary or on-capillary conversion of metal ions into stable, charged complexes, which can move with different mobilities depending on their charge, size and stability [8–14].

Generally, partial complexation technique gives significantly better separation selectivity, higher efficiency and shorter analysis time. For instance, up to 27 metal cations have been separated in less than 6 min using lactic acid as complexing agent [7]. In most publications on CE of metal ions, absorbance detection has been used. Unfortunately, only few hydrated metal ions absorb significantly above 185 nm. For this reason the detection of metal cations separated using partial complexation mode is performed by means of indirect UV detection technique [15–17]. However, the primary limitation of this detection principle is its poor detection sensitivity.

By contrast, when complete complexation of metal ions with chromogenic reagents are used, very sensitive direct absorbance detection can be performed. Many chelating reagents such as 8-hydroxyquinoline-5-sulfonic acid [9], 4-(2-pyridylazo)resorcinol [10], several aminopolycarboxylic acids [11–14] and 1,10-phenanthroline [18–22], etc., have been already employed for the direct absorbance-based detection of alkaline earth, transition and lanthanide metal ions. Of these, 1,10-phenanthroline (phen) seems to be most advantageous with respect to detectability. For example, Xu et al. [18] were able to detect about 5×10^{-9} mol l^{-1} Fe(II) using phen as pre-capillary derivatizing reagent. However, CE separation of common analytically important metal–phen chelates such as $Fe(phen)_3^{2+}$, $Ni(phen)_3^{2+}$ and $Co(phen)_3^{2+}$ is difficult because in this case only small differences in the ratio of charge to radius are observed, that result in nearly identical electrophoretic mobilities of these chelates [20–22]. For this reason it is useful to develop a technique which combines both partial and complete complexation modes and, thus, enables rapid, selective, efficient separation together with sensitive direct UV detection of metal species.

The aim of this study was to evaluate the zone-passing derivatization technique for a selective and sensitive CE determination of selected metal ions. The proposed system is based on CE separation of metal cations using partial complexation mode followed by complete in-capillary complexation of separated analytes with phen and sensitive direct UV detection of metal–phen chelates formed.

2. Experimental

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 capillary (Polymicro Technology, Phoenix, AZ, USA) of 57 cm total length (50 cm to the detector)× 75 μm I.D.×375 μm O.D. was used. Samples were injected in the hydrodynamic mode by overpressure (3.43×10^3 Pa). System Gold software was used for data acquisition. UV detection was employed at 254 nm. All experiments were conducted at 25 °C.

Deionized water was obtained by passing distilled water through a Waters Milli-Q water-purification system (Millipore, Eschborn, Germany). Imidazole was purchased from Sigma (Sigma, St. Louis, MO, USA). All other reagents were of analytical-reagent grade obtained from Merck (Darmstadt, Germany). Stock solutions (0.01 mol l^{-1}) of analyte cations and phen were prepared from appropriate salts. Working solutions were prepared daily before use by suitable dilution.

Unless otherwise stated, all carrier electrolyte solutions were prepared from stock solution of 0.5 mol l^{-1} glycolic acid and adjusted to pH 6.0 with imidazole. All electrolyte solutions were filtered through a 0.45-μm membrane filter and degassed by ultrasonication before use. The capillary was rinsed with 1.0 mol l^{-1} sodium hydroxide and water for 5 min, then equilibrated with carrier electrolyte for 20 min at the beginning of each day. Between all electrophoretic separations the capillary was automatically rinsed with 0.1 mol l^{-1} NaOH (1 min) and with carrier electrolyte (2 min).

Freshly collected snow samples were filtered through a membrane filter. Then 5.00 ml of the sample solution was transferred to the polyethylene vessel and 1.00 ml of internal standard (2×10^{-5} mol l^{-1} benzidine diluted in 1 mmol l^{-1} glycolic acid) and 4.00 ml of water and/or appropriate cation standard solution were added and analyzed.

3. Results and discussion

3.1. Separation and derivatization principle

As stated in Section 1, the proposed system is based on CE separation of metal cations using partial complexation mode followed by complete in-capillary complexation of separated analytes with phen and sensitive direct UV detection of metal–phen chelates formed. Such zone-passing derivatization can be achieved by successive introduction of the reagent solution, the carrier electrolyte and the sample solution from the anodic capillary end [23–25]. The position of the reagent zone in the capillary can be varied by changing the injection time of the electrolyte. After the high voltage has been applied, the separation of the sample cations starts and the analytes migrates towards the detector (cathode). The reagent zone also migrates into the same direction but with lower velocity than the analyte cations. During this step the analyte cations are separated. After specified periods of time for each analyte, its zones passes through the reagent zone. During the passing step the analyte reacts with the reagent forming $Me(phen)_3^{2+}$ chelate, which further migrates at its own velocity faster than the reagent. This derivatization principle can be performed automatically using commercially available CE instrumentation.

3.2. Choice of the complexing agent

In order to achieve an electrophoretic separation of Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} metal cations, their mobilities should be additionally modified by introduction of the complex-forming equilibrium. In such cases addition of the complexing reagent to the carrier electrolyte is used to obtain larger differences in effective mobility. This occurs by complexing the metal cations to different extents. The following four complexing agents were investigated initially: acetic acid, glycolic acid, oxalic acid and tartaric acid. Preliminary experiments were performed in electrolyte containing 20 mmol l^{-1} of appropriate acid neutralized with NH_3 to pH 5.0. Hydrodynamic introduction of 2×10^{-3} mol l^{-1} phen, of the carrier electrolyte and of 1×10^{-4} mol l^{-1} of each analyte was performed sequentially for 6, 40 and 6 s, respectively. Using oxalic acid as the complexing agent, the mobilities of the cations significantly decreased, so the analytes moved slower than the phen zone. As a result, the derivatization reaction does not occur and the cations are not detected. A similar picture was also observed using reversed introduction order (sample–electrolyte–phen). These results indicate that using oxalic acid the mobilities of the analytes and the reagent became close. With acetic acid it was possible to detect all five analytes, but the Fe^{2+}, Co^{2+} and Ni^{2+} cations comigrate. Tartaric acid and glycolic acid showed the best overall separation performance. However, copper(II) is more strongly complexed with tartaric acid and does not reaches the phen zone under conditions used. In the glycolic acid system all the analytes were completely or partially resolved and detected. Based on these results, glycolic acid was chosen for further optimization.

3.3. Separation optimization

The net electrophoretic mobility of metal ions is dependent on the degree of complex formation, and thus the separation of the ions can be influenced by the concentration of complexing agent. Therefore, the concentration of glycolic acid was studied over the range 10–100 mmol l^{-1} at pH 5.0. Higher concentrations than 100 mmol l^{-1} of glycolic acid were not investigated because an extremely high current was observed. As the glycolic acid concentration increases, the electroosmotic flow (EOF) decreases resulting in a slight increase in the migration times for all the cations and phen. In addition, an increase in the glycolic acid concentration up to 50 mmol l^{-1} causes significant increase in separation efficiency and in analyte peak response. At higher concentrations, the peaks of the analytes begin to

broaden and tail, possibly due to additional Joule heating. Carrier electrolyte containing 50 mmol l^{-1} glycolic acid provides the best compromise between separation selectivity, efficiency and detection sensitivity.

The effect of electrolyte pH on the migration times of the analytes and phen is demonstrated in Fig. 1. At higher pH values the increased EOF causes decrease in the migration times of the cations. In addition, due to the deprotonation the net charge and, consequently, the mobility of phen cation decreases with pH resulting in better resolution between Zn(II) and phen peaks. The best overall separation was obtained in the pH range 5.5–6.0. All further separations were performed in 50 mmol l^{-1} glycolic acid electrolyte at pH 6.0. To avoid any adverse effect due to electrolytic degradation of non-buffered electrolyte, imidazole (pK_a=6.9) was chosen instead of NH_3 for the electrolyte preparation.

Another important parameter affecting the separation selectivity in the proposed in-capillary derivatization technique is the position of the reagent zone in the capillary at the moment when the voltage is applied. In this experiment the introduction times of the sample solution and the reagent solution were maintained constant but the introduction time of the carrier electrolyte was varied from 20 to 100 s. Fig. 2 compares the migration times obtained for five analytes and phen at different electrolyte introduction times. As can be observed, the analytes show different migration behaviour when electrolyte introduction time increases: migration times of Zn(II), Cu(II) and Ni(II) increase, whereas the migration times of Co(II) and Fe(II) slightly decrease. Since the EOF mobility does not depend on position of phen zone in the capillary, completely reversed trend was observed for effective mobilities of the analytes (results not shown). Such behaviour can be explained by the fact that a part of the migration way analytes migrate as partially complexed cations and, after derivatization reaction, they migrate as cationic chelates, i.e., their mobilities change during the separation. At longer electrolyte introduction time the length of migration way of partially complexed cations increases, whereas that of metal–phen chelates becomes shorter. Consequently, if the mobility of partially complexed cation is higher than that of its chelate, the migration time of this analyte decreases (average effective mobility increases) with longer electrolyte introduction time and vice versa. However, due to the high electrolyte concentration it is difficult to measure the effective mobilities of non-absorbing metal cations under conditions used

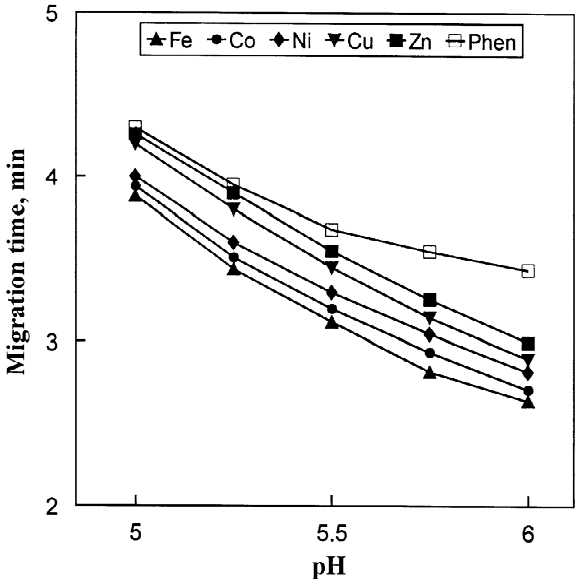

Fig. 1. Effect of electrolyte pH on the migration times of the analytes and phen. Electrolyte, 0.05 mol l^{-1} glycolic acid; injection, 6 s 2×10^{-3} mol l^{-1} phen, 40 s electrolyte, and 6 s 1×10^{-4} mol l^{-1} analyte solution; voltage, 30 kV; direct UV detection at 254 nm.

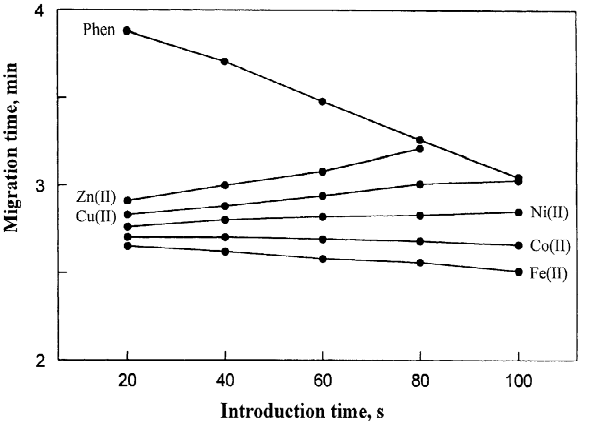

Fig. 2. Effect of electrolyte introduction time on the migration times of the analytes and phen. Electrolyte, 0.05 mol l^{-1} glycolic acid, pH 6.0 with imidazole; other conditions as in Fig. 1.

and to compare them with those obtained for metal–phen chelates. Since after derivatization reaction metal–phen chelates migrate with almost equal velocities (the effective mobilities of metal–phen chelates ranged from 2.42×10^{-4} cm^2 V^{-1} s^{-1} for Fe(II), Co(II) and Ni(II) to 2.26×10^{-4} cm^2 V^{-1} s^{-1} for Zn(II)), the separation of the analytes occurs in the capillary length from the injection end to the phen zone. This length and, consequently, the separation selectivity increase with longer electrolyte introduction time. The results showed that electrolyte injection time of 60 s gave complete resolution of the analytes. At electrolyte introduction times longer than 80 s, Zn^{2+} cations do not reach the phen zone and are not detected.

3.4. Derivatization reaction

The derivatization technique described here requires rapid, quantitative or at least reproducible reaction between metal cations and phen. Therefore, the effect of phen concentration on the derivatization reaction was investigated. The phen concentration was increased, whereas the concentration of the metal cations was kept constant. Fig. 3 shows the effect of phen concentration on the peak areas of the chelates formed. As can be seen, the peak areas of the Fe(II), Co(II), Ni(II) and Zn(II) chelates reach maximum for c(phen)–c(Me) ratios higher than 3.0–3.5. The further increasing of the phen concentration up to 5×10^{-3} mol l^{-1} did not show any statistically significant changes in the peak areas of the chelates. This indicates that the derivatives of these analytes are 1:3 metal–ligand complexes. Similar results were also obtained for other concentrations of the analytes. However, the peak area of Cu(II) chelate does not increase in the studied concentration range indicating that most likely the derivatization of this analyte is not complete. For this reason the completeness of the derivatization reaction was additionally investigated. In this experiment peak areas of the in-capillary derivatized analytes were compared with those measured for the same concentrations (2×10^{-5}–5×10^{-4} mol l^{-1}) of the analytes derivatized using conventional pre-capillary derivatization technique. No statistically significant differences (=10%) in the peak areas of Fe(II), Co(II), Ni(II) and Zn(II) chelates were obtained by both procedures. For copper(II), however, the peak areas obtained using proposed derivatization technique were about 2–2.5 times lower than those measured using conventional technique.

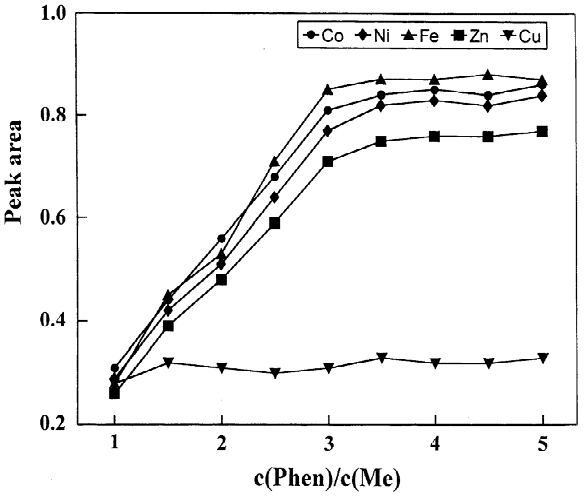

Fig. 3. Effect of phen concentration on the peak areas of the chelates formed. Conditions as in Fig. 2.

Finally, the influence of the phen zone introduction time (from 2 to 15 s) on the derivatization performance of Cu(II) ions was briefly studied. At longer phen introduction time, its zone became longer, thus causing an increase of the contact time between analyte and reagent. No improvement in the derivatization performance for Cu(II) was observed during this experiment. The possible explanation of these results may be the formation of mixed Cu(II)–phen–glycolate complexes. Such a behaviour of the Cu(II) ions was recently reported by Yokoyama et al. [21,26]. They showed that Cu(II) pre-capillary complexed with phen or its derivatives migrated in the electrolyte containing some carboxylate ions (formate, acetate, propionate, etc.) as mixed-ligand $[Cu(Phen)_2(RCOO)]^+$ complex. Since the complexing ability of the glycolate is similar to that of above mentioned ligands [27] the formation of mixed Cu(II)–phen–glycolate complex may also occur during the derivatization. Moreover, in our system Cu^{2+} at first reacts with glycolate and only then reaches the phen zone. Consequently, in this case the derivatization reaction should be much more complicated. It should be noted, that when a non-complex-

ing imidazole–chloride electrolyte was used the peak areas of in-capillary derivatized Cu(II) were only about 15–20% lower than those obtained under the same conditions by pre-capillary derivatization technique. This suggests that glycolate anions play an appropriate role in the derivatization reaction of Cu(II). However, it is difficult to prove experimentally the stoichiometry of the complex formed.

3.5. Sample analysis

Based on the obtained results and taking the separation efficiency, resolution, detection sensitivity and running time into consideration, the best separation of tested metals was obtained using carrier electrolyte consisting of 50 mmol l^{-1} glycolic acid (pH 6.0 with imidazole) at a running voltage of 30 kV (Fig. 4). As can be observed, an excellent separation of five metal ions was obtained in less than 4 min. In comparison, using conventional pre-capillary complexation technique, Fe(II), Co(II) and Ni(II) chelates with phen were not resolved [21].

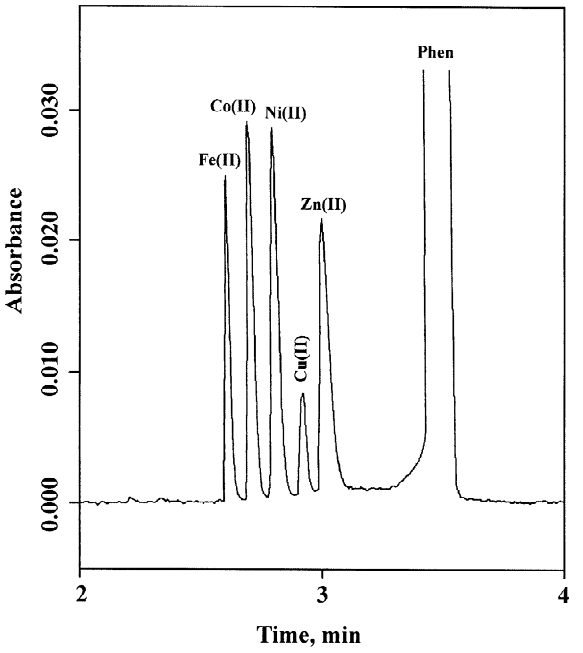

Fig. 4. Electropherogram obtained for a standard solution of the metal cations. Injection, 2 s 5×10^{-3} mol l^{-1} phen, 70 s electrolyte, and 5 s 1×10^{-4} mol l^{-1} analyte solution; other conditions as in Fig. 2.

The little tailing of the Zn(II) peak most probably takes place due to the on-capillary dissociation of less stable Zn(II)-phen chelate.

The major problem in the analysis of oxidizable metal species is their protection from oxidation by dissolved oxygen prior and during the analysis. This is especially important for Fe(II), which is known to be prone to oxidation. For this reason the stability of Fe(II) solutions was briefly investigated at room temperature. The peaks obtained for Fe(II) standards freshly prepared in oxygen-free (a) 1 mmol l^{-1} HCl, (b) 1 mmol l^{-1} HCl containing 1 mmol l^{-1} hydroxylamine hydrochloride, (c) electrolyte solution, and (d) electrolyte solution containing 1 mmol l^{-1} hydroxylamine hydrochloride, were measured using imidazole–glycolate electrolyte and the same electrolyte containing 1 mmol l^{-1} hydroxylamine hydrochloride. No statistically significant differences in the peak areas were observed in all four cases using both electrolytes during 30 min after preparation. After 1 h, however, the peak areas of Fe(II) standards prepared in both water and electrolyte without hydroxylamine hydrochloride and measured using electrolyte without reducing agent decreased about 18–24% indicating that Fe(II) was partly oxidized to Fe(III). These results indicate, that for the speciation of Fe(II), samples should be prepared in scrupulously degassed medium and analyzed immediately after sampling, whereas for the determination of total Fe they should be additionally pre-treated with hydroxylamine hydrochloride.

The repeatabilities (run-to-run precision) for migration time and peak areas were calculated as the relative standard deviation (RSD) of six consecutive injections of a standard solution of 5×10^{-5} mol l^{-1} each cation. The run-to run precision of the Fe(II), Co(II), Ni(II) and Zn(II) cations ranged from 0.3 to 0.5% for migration time and from 2.3 to 4.5 for peak area. Copper(II), however, showed significantly lower precision (3.9% for migration time and 18.2% for peak area) likely due to more complicated derivatization reaction. For this reason Cu(II) was not quantified.

Calibration curves of the Fe(II), Co(II), Ni(II) and Zn(II) ions were linear in the range 1×10^{-5}–5×10^{-4} mol l^{-1} with an average correlation coefficient of 0.998. With the 12-s pressure injection, detection limits (signal-to-noise ratio of 3) were from 1.5×

10^{-6} mol l^{-1} for Fe(II) to 5.4×10^{-6} mol l^{-1} for Zn(II). Due to the sample preconcentration occurred by electrostacking, the detection limits obtained using electromigrative sample introduction (10 kV for 5 s) were about 100 times lower. Because the proposed derivatization principle does not require pre-capillary sample treatment with the reagent, it is very useful for the speciation of metal ions in low ionic-strength matrices such as atmospheric precipitation. This effect is demonstrated in Fig. 5 in which two electropherograms obtained for a snow sample (a) and the same sample spiked with small amount (1×10^{-6} mol l^{-1}) for each metal ion (b) are compared. Benzidine was used as an internal standard. Two snow samples were analyzed by the proposed CE method using a standard addition procedure and the results are presented in Table 1. As can be observed, the recoveries in all the cases were within the range 100±12%.

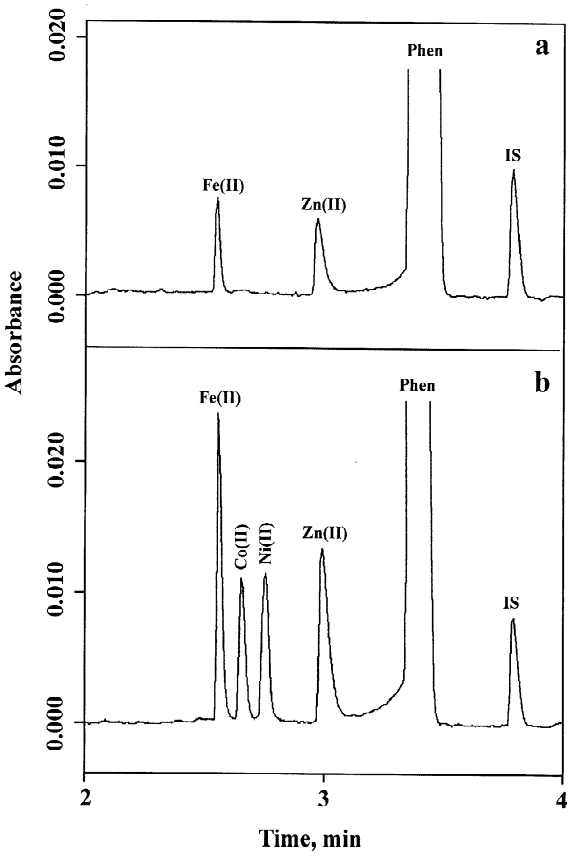

Fig. 5. Electropherograms of 1:1 diluted snow sample (a) and the same sample spiked with 1×10^{-6} mol l^{-1} of each cation (b). Injection, hydrodynamic, 2 s 5×10^{-3} mol l^{-1} phen, 70 s electrolyte, and electromigration, 10 kV for 5 s sample; I.S., benzidine.

Table 1
Results of the determination of metal cations in snow samples ($n=3$)

Sample no.	Analyte	Found (μmol l^{-1})	Added (μmol l^{-1})	Found total (μmol l^{-1})	Recovery (%)
1	Fe(II)	0.84	0.25	1.07	92
	Co(II)	NF[a]	0.25	0.24	96
	Ni(II)	NF	0.25	0.23	92
	Zn(II)	0.98	0.25	1.20	88
2	Fe(II)	1.16	1.00	2.09	93
	Co(II)	NF	1.00	1.05	105
	Ni(II)	NF	1.00	0.95	95
	Zn(II)	0.65	1.00	1.55	90

[a] Not found.

A major limitation of the proposed system is that it can be applied only to the metal ions that forms sufficiently stable and kinetically labile chelates. Less stable Fe(III)–phen, Mn(II)–phen, Cd(II)–phen complexes completely decomposes during the separation process and, consequently, cannot be determined. However, the addition of free ligand to the electrolyte to suppress dissociation of the chelates is impossible in the described derivatization technique.

On the other hand, in comparison with conventional pre-capillary derivatization technique, described system exhibits significantly higher overall separation selectivity. In addition, since the proposed technique does not require any manipulation with the sample prior to injection, it could be potentially applicable to the speciation analysis. For example, after addition of phen to sample solution containing Co(II) and Fe(III) ions the oxidation of $[Co(phen)_3]^{2+}$ with $[Fe(phen)_3]^{3+}$ takes place due to a change in the standard redox potentials of $[Co(phen)_3]^{3+}/[Co(phen)_3]^{2+}$ and $[Fe(phen)_3]^{3+}/[Fe(phen)_3]^{2+}$ pairs [21]. No decrease in the peak area of Co(II)–phen chelate was observed and no peak of Fe(II)–phen chelate was detected when standard solutions containing Co^{2+} and Fe^{3+} ions were analyzed by in-capillary derivatization technique. An example on speciation analysis is the separation of Co(II) and Co(III) species in electro-

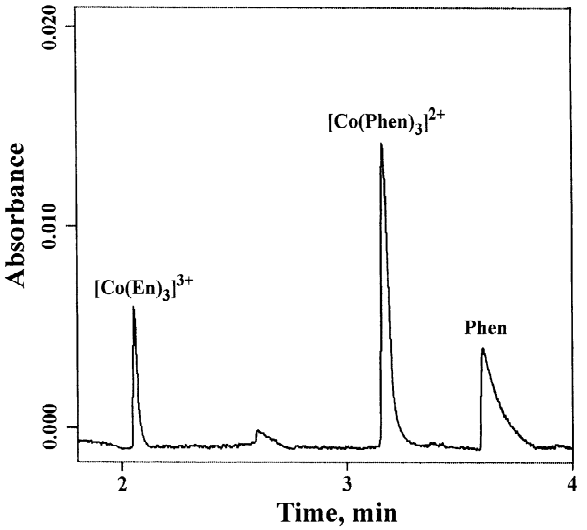

Fig. 6. Electropherogram of 1:250 diluted electroless copper plating bath sample. Electrolyte, 0.05 mol l^{-1} glycolic acid, pH 6.0, with LiOH; direct UV detection at 214 nm; injection conditions as in Fig. 4.

less copper plating bath (Fig. 6). The initial plating bath usually contains $CuSO_4$, $CoSO_4$ and ethylenediamine (En). During the plating process the $[Co(En)_3]^{2+}$ complex is oxidized to $[Co(En)_3]^{3+}$. The stabilities of both complexes differ significantly ($\log \beta_3 = 12.0$ for $[Co(En)_3]^{2+}$ and $\log \beta_3 = 48.7$ for $[Co(En)_3]^{3+}$) [27]. Using conventional CE technique less stable $[Co(En)_3]^{2+}$ completely decomposes during the separation [28]. The in-capillary derivatization of Co(II) with phen enables the determination of both Co species in a single analysis. Very stable and kinetically inert $[Co(En)_3]^{3+}$ chelate does not react with phen. It should be noted, that because in such solutions the oxidation of Co(II) with ambient oxygen takes place, both plating and separation should be performed in Ar atmosphere. More detailed investigations on this are in progress.

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