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Metal ion capillary zone electrophoresis with direct UV detection: determination of transition metals using an 8-hydroxyquinoline-5-sulphonic acid chelating system

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ABSTRACT

The application of capillary zone electrophoresis to the separation and determination of metal ions after the precolumn formation of negatively charged chelates is described. Multi-component mixtures of transition metal complexes with 8-hydroxyquinoline-5-sulphonic acid (HQS) were separated in about 10 min in a fused-silica capillary column with a borate buffer of pH 9.2 at an applied voltage of 15 kV followed by direct UV detection. The capillary pretreatment with an electroosmotic flow modifier, namely a tetraalkylammonium salt, is necessary to achieve resonable migration times of these metal complexes. Incorporating the chelating reagent in the electrophoretic buffer markedly improves the detectability of relatively unstable chelates, such as those of Co(II), Zn(II) and Cd(II), and allows the separation of metal ions that form unstable HQS chelates, such as Mn(II) and alkaline earth metals. The effects of electrophoretic buffer parameters affecting the complexation reaction and migration behaviour are discussed. Linearity of calibration graphs is observed for about three orders of magnitude with sub-ppm detection limits. The applicability of the method to the analysis of real samples is demonstrated.

INTRODUCTION

High-performance capillary zone elctrophoresis (CE) is a highly efficient separation method capable of yielding excellent resolution of ionized compounds based on the combined effects of electrophoresis and electroosmosis. Although a multitude of CE applications have been reported in the past decade, this method has been introduced into inorganic analysis only in the last 3 years [1–4]. The determination of metal ions by CE, particularly transition metal ions as ionic species of nearly identical charge and dimensions, and hence very similar electrophoretic mobilities, is still a complicated problem because the efficiency of CE might often be inadequate for the separation. Obviously, the enhancement of separation selectivity would be the only alternative to achieve a satisfactory resolution.

A fairly promising approach in this direction is based on the addition of complexing components to the electrophoretic buffer. These complexing agents can selectively moderate the mobility of metal cations owing to the formation of metal complexes of different stability within the capillary. This CE separation mode was first proposed by Foret *et al.* [5] in combination with indirect UV detection for the separation of lanthanides (using hydroxyisobutyric acid as a complexing counter ion) and then intensively developed by Weston *et al.* [6]. Swaile and Sepaniak [7] employed the formation of fluorescent complexes of 8-hydroxyquinoline-5-sulphonic acid (HQS) for the sensitive detection of metal ions separated by CE using laser-based fluorimetry.

Another promising possibility of complexation

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CE is the complete conversion of metal ions into negatively charged chelates (instead of establishing only an equilibrium between free and complexed metal ions), which can move with different mobilities in the opposite cathode-to-anode direction. In addition, direct spectrophotometric detection of metal chelates can be performed, as has been used in ion chromatography [8,9].

This paper presents a detailed evaluation of HQS for the CE of transition and alkaline earth metals as precolumn-formed chelates. The migration behaviour and the optimization of the separation conditions for metal-HQS complexes by controlling the electrophoretic buffer parameters are discussed. Special attention is paid to consideration of the effects of the precolumn and on-column complexation conditions on mobility, separation efficiency and detectability.

EXPERIMENTAL

Reagents

8-Hydroxyquinoline-5-sulphonic acid was obtained from Aldrich Chemie (Steinheim, Germany). The reagent was dissolved in 0.01 A4 sodium tetraborate to give a $5 \cdot 10^{-3}$ A4 stock solution. Standard solutions of metal ions were prepared from the nitrates (Merck, Darmstadt, Germany) at a concentration $2 \cdot 10^{-3}$ A4 in 0.01 *M* nitric acid. Borate buffers prepared by dissolving appropriate amounts of sodium tetraborate (Merck) in doubly distilled water and containing $1 \cdot 10^{-4}$ A4 HQS were used as the main electrophoretic buffers. The pH of the electrophoretic buffer was adjusted with 0.1 *M* HCl or NaOH. All chemicals were of analytical-reagent grade.

Apparatus

A Waters Quanta 4000 CE system with a negative and a positive high-voltage power supply was used. Separations were carried out in a fused-silica capillary of 35 cm in effective length and 75 μm I.D. obtained from Waters (AccuSep). The voltage applied was adjusted to 15 kV. Detection was performed by on-column UV measurements at 254 nm. Electropherograms were recorded and processed with a Hewlett-Packard Model 3359 data acquisition system.

Procedure

For conditioning of the capillary, it was flushed once a week with 5 m*M* tetradecyltrimethylammonium bromide (TTMAB) (Fluka, Buchs, Switzerland) for 15 min followed by water and the electrophoretic buffer for the same duration. All electrophoretic buffers were filtered through 0.45-μm membrane filters before use. The sample solutions were injected with a siphonic injection technique for a specified time and were separated using the negative power supply. Electroosmotic flow velocity was determined from the migration time of acetophenone (Merck), which served as a neutral marker, using the positive power supply.

Sample preparation

Samples of tap water were acidified to $pH \approx 2$ with concentrated nitric acid and stored in a refrigerator in polyethylene bottles at 4°C prior to analysis.

RESULTS AND DISCUSSION

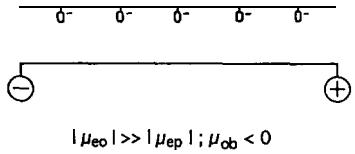
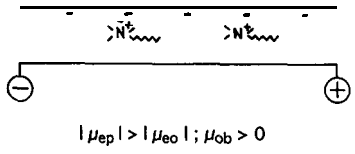
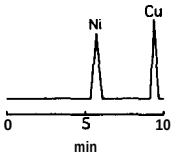
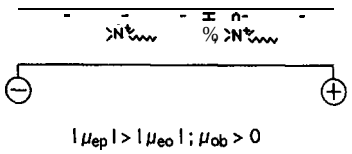
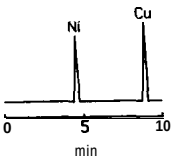
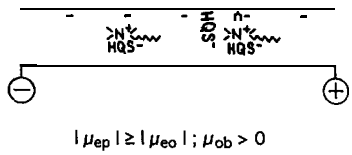
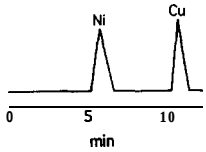
Capillary electrophoretic behaviour of metal-HQS complexes

In CE, separation is based on the differences in electrophoretic mobility (EPM) of solutes in the presence of an electric field, which is dependent on the charge and size of the solutes. In this investigation, the electroosmotic flow (EOF) was towards the cathode whereas the electrophoretic flow (EPF) was in the opposite direction, in contrast to ref. 7, where both EPF and EOF were towards the detector (the negative end of the capillary). Another distinguishing feature of the CE system studied by Swaile and Sepaniak [7] is that the metal analytes (zinc, magnesium and calcium) were separated in the HQS-complexes form, but of different composition and charge (due to the stepwise complexation equilibrium under CE conditions). Thus, for metal–HQS complexes as for the negatively charged solutes, the migration direction and velocity must be strongly influenced by the electrophoretic ***versus*** electroosmotic flow ratio and, consequently, by CE system parameters affecting the vectorial combination of EPM and electroosmotic mobility (EOM).

According to the above, we observed the following migration behaviour of the complexes depicted schematically in Table 1. Using an untreated fused-

TABLE I

MIGRATION BEHAVIOUR OF METAL-HQS COMPLEXES IN CAPILLARY ZONE ELECTROPHORESIS

CE conditions	Electrophoresis versus electroosmosis and modification effects in the capillary	CE behaviour
(A) Untreated capillary-borate buffer		No peaks
(B) Capillary pretreated with TTMAB -borate buffer		
(C) Pretreated capillary-borate buffer + 0.1–0.2 m*M* HQS		
(D) Pretreated capillary-borate buffer + 0.4 m*M* HQS		

silica capillary and alkaline buffers, no peaks could be recorded in the electropherograms, because under these conditions the EOM ($-71.7 \cdot 10^{-5}$ $cm^{-2}/V \cdot s$ in 10 m*M* borate buffer) is much higher than the EPM (Table I, A) and metal complexes move to the cathode (reversed movement), their velocity decreasing with increasing EPM. A further reason for the non-appearance of peaks might be that the complexes undergo decomposition as a result of ligand-exchange reactions with surface silanol groups. This experimental fact is well described in reversed-phase chromatography [10].

The treatment of the capillary with a hydrophobic tetraalkylammonium salt, namely TTMAB, resulted in a marked decrease in EOF ($\mu_{eo} = -19.8 \cdot 10^{-5} cm^2/V \cdot s$). As a result, the EPM becomes large enough to counteract the EOF (Table I, B) and the complexes migrate in the opposite direction (decelerated movement). With the treated capillary, the apparent mobilities correspond to the EPM.

It should be noted that the migration order of metal-HQS complexes is completely the reverse of the elution sequence of these chelates in ion-pair reversed-phase chromatography [11]. The CE separation may be explained (i) by some "chromatographic" effects (see below) and (ii) by the effective charge of the solute, which can be a factor controlling the migration ability (divalent metal 1:2 complexes are of approximately the same size). In confirmation, the overall stability constants, β_n, as a parameter closely connected with the electron-acceptor strength of metal ion, were found to be well correlated with normalized observed mobilities, $\mu'_{ob}(M) = \mu_{ob}(M) / \mu_{ob}(Fe)$, where M = metal (Fig. 1; to obtain more reproducible results, the iron complex was used as an internal standard).

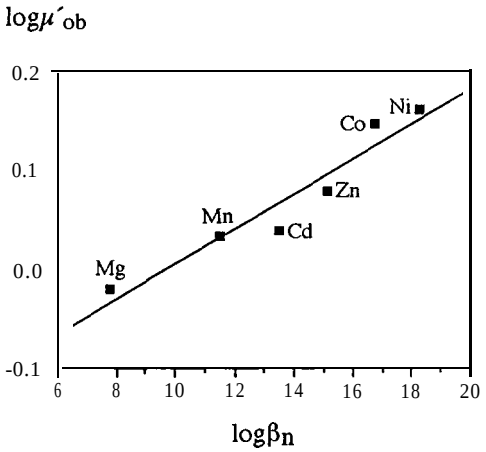


Fig. 1. Plot of log μ'_{ob} *vs.* log β_n values for metal-HQS chelates.

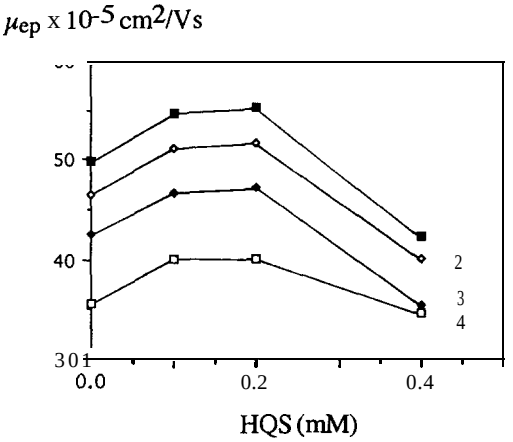


Fig. 2. Dependence of the electrophoretic mobilities of metal complexes on the HQS concentration in the electrophoretic buffer. 1 = Ni; 2 = Zn; 3 = Fe; 4 = Cu. Electrophoretic buffer: 10 m*M* borate buffer (pH 9.2).

When the free ligand is added to the electrophoretic buffer (see below), a decrease in the EOF occurs (μ_{eo} = − 16.6. 10^{-5} cm^2/V . s at $1 \cdot 10^{-4}$ A4 HQS in 10 m*M* borate buffer), resulting in an increase in the observed mobility of metal complexes. Obviously, HQS molecules can partially adsorb at the capillary walls, mainly by a hydrophobic mechanism (but electrostatic interaction are also probable), giving a decrease in the electroosmotic velocity (it will be shown below that the adsorption of HQS has an experimental manifestation). It is also possible that the EOF-modifying effect is not the only reason for reduced migration times. The long alkyl chains may also act as a pseudo-stationary phase, interacting by hydrophobic association with chelate molecules carried along with EPF. If this is so, HQS can prevent this "chromatographic" effect owing to its highly hydrophobic nature [12] and, as a consequence, increase the EPM. This effect of the free ligand in the buffer can be seen in Fig. 2.

However, if higher HQS concentrations are used (which are desirable to complete the complexation reaction for metals of low complex stability), a decrease in the mobilities followed by a decrease in efficiency will be observed (Table I, D). One of the presumable explanations for this effect is the formation of the next adsorption layer at the capillary–buffer interface via dynamic coating of the hydrophobically treated wall with an excess of HQS molecules. This secondary negatively charged layer can re-establish the initial charge separation between the capillary walls and electrophoretic medium and hence increase the EOF velocity (μ_{eo} = -20.2 · 10^{-5} $cm^2/V \cdot s$ at $4 \cdot 10^{-4}$ A4 HQS).

Optimization of metal complexation conditions

The applicability of the proposed metal ion CE mode presupposes the completeness of the complex formation under the electrophoretic conditions, otherwise constancy of the complex composition cannot be ensured so that the observed mobility of the resulting peak will be determined by the equilibrium between the different possible forms of the metal ion (complexed and non-complexed). This observed mobility would be a combination of the individual mobilities of those forms. In addition, this problem could become complicated by the creation of multiple peaks. Finally, determination of metals becomes difficult and the separation is less efficient.

To overcome these problems, two approaches commonly adopted in the high-performance liquid chromatographic determination of metal ions may be used, namely the application of higher concentrations of chelating reagent in the injected samples or its incorporation in the electrophoretic buffer. We studied both of these complexation techniques.

Precolumn complexation. When using a stroichiometric HQS concentration. the complex formation

is complete only for metals of high complex stability, such as copper(H) and iron(III), and to a lesser extent nickel(II). Following the addition of an excess of HQS (up to a threefold excess) with resultant more complete complexation, the detectability is substantially improved, especially for metals such as Zn(II), Co(II), Cd(II) and Mn(II) (even less stable complexes of alkaline earth metals can be detected). However, beginning from a 3: 1 molar ratio, an increase in HQS concentration is followed by increasing interference with the metal detectability. Large reagent excesses impair the signal-to-noise ratio (due to the increased background signal) and also cause overlapping peaks (HQS migrates with a mobility between those of the zinc and the iron chelate).

Further, the pH of the electrophoretic buffer must be controlled during complexation optimization, as it affects the conditional formation constant of the complexes, Increasing the pH above 9.5 or decreasing it below 7.5 decreases the complex formation (as is generally the case for metal complexes in solutions), resulting in smaller peak areas and zone spreading. Moreover, on further decreasing the pH (below 6.5), the peaks become very broad and even split (divalent metals can react with HQS to form both 1:1 and 1:2 complexes). Therefore, we considered that moderately alkaline buffers should be studied for optimum detectability of metal ions.

Electrophoretic buffer complexation. Incorporating the chelating reagent into the electrophoretic buffer will favour the complexation reaction and facilitate the establishment of the equilibrium after sample injection. Therefore, when the effect of HQS concentration in the buffer is considered, a general increase in detectability will be expected with increasing concentration. The corresponding electropherograms for precolumn-formed metal chelates at different concentrations of HQS are shown in Fig. 3. As can be seen, increased peak intensities can be observed only with sufficiently low concentrations of HQS (*cf.*, electropherograms a and b). At 0.2 m*M* and especially 0.4 m*M* HQS an increase in the absorbance background, a reduction in the observed mobilities and band broadening take place, all of which reduce detectability. As stated above, the last two effects are connected with the impact of HQS on the EOF velocity.

Complexation without addition of HQS to the injected samples is far from completion, even with 0.4 m*M* HQS (the largest concentration investigated) and for the most stable complexes. This is probably a result of both comparatively small migration times ***(i.e.,*** insufficient reaction times) and a low flow mixing in the narrow-bore capillary. Because of slow kinetic effects one could not use simply the on-column complexation alone to maintain the equilibrium conditions in the capillary.

Therefore, the complete on-column formation of complexes requires a certain amount of HQS in the sample. The electropherograms shown in Fig. 4 will be used to illustrate the influence of varying HQS concentration on detectability.

As for the precolumn complexation, lower HQS to metal ion ratios (even if the most favourable 0.1 m*M* concentration of HQS in the buffer is used) resulted in peaks with small heights and poor efficiency for Ni, Co and Zn complexes (less stable manganese, magnesium and calcium chelates were detected as very broad and asymmetric zones). Further, a lack of chelating reagent in the sample not only led to incomplete complex formation, but also additional unfavourable detection effects (a slow positive baseline drift, a small rapidly migrating peak and a matrix dippeak) were observed. The main reason of these effects, which are typical of metal ion chromatography with HQS-containing eluents [12,13] (we came across them specifically in ion-pair reversed-phase chromatography [11]), is the large adsorption of HQS and the perturbation of the adsorption equilibrium between HQS and the stationary phase (here the hydrophobically treated capillary).

Increasing the HQS concentration will improve the complex-forming conditions and thereby increase detectability; the aforementioned "chromatographic" effects also disappear. The most probable reason for the latter improvements is that the sample matrix closely matches the electrophoretic buffer. On reaching an optimum concentration ratio, corresponding to a *ca.* threefold molar excess of reagent, a further increase in the HQS concentration has little effect on peak heights, but interferes with the detection of the iron(III) complex (Fig. 4c).

Summarizing, it should be stressed that the achievement of optimum metal detectability with this method requires the reasonable combination of pre- and on-column complexation techniques.

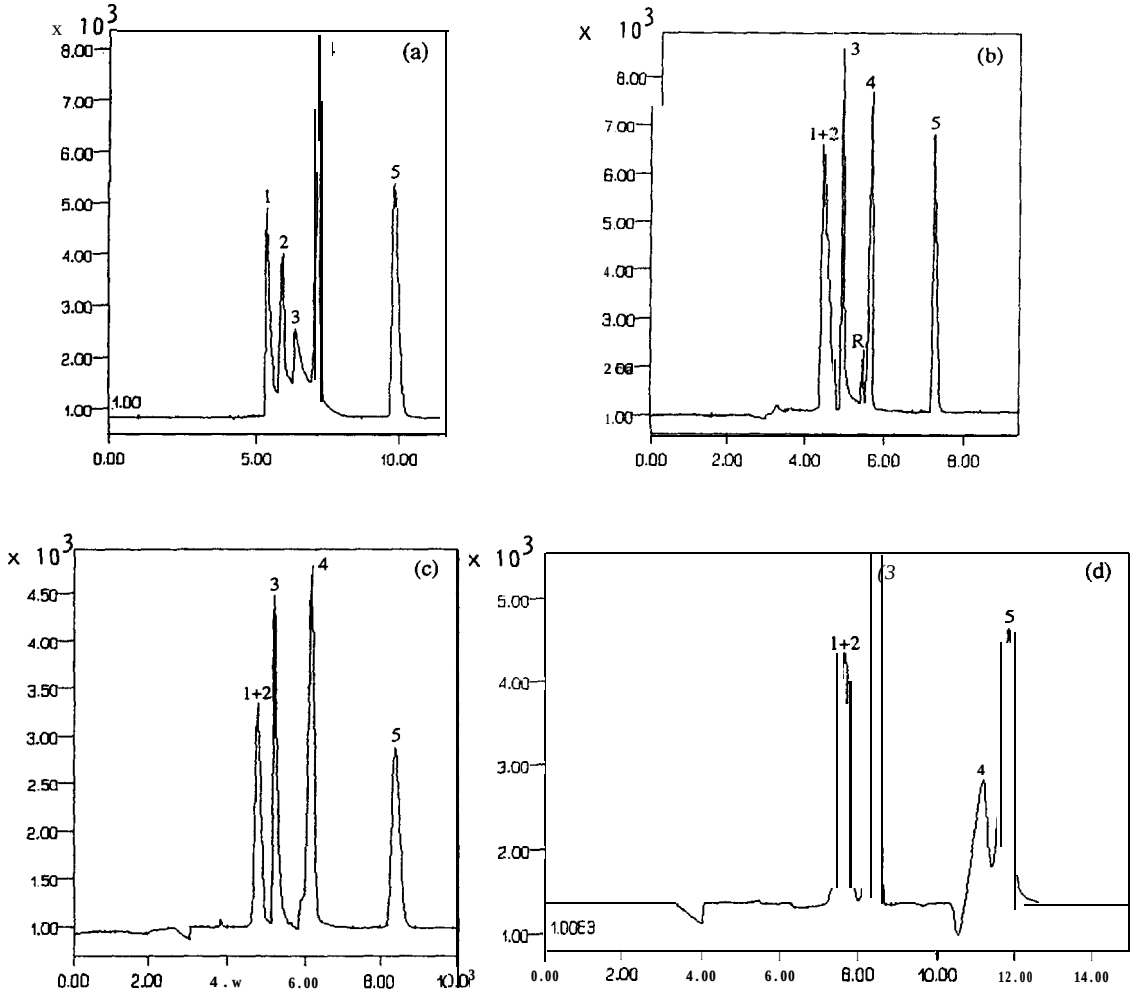


Fig. 3. CE of metal-HQS chelates at various concentrations of HQS in electrophoretic buffer. Peaks: 1 = Ni; 2 = Co; 3 = Zn; 4 = Fe; 5 = Cu; R = HQS. Electrophoretic buffer: 10 m*M* borate buffer containing HQS at (a) 0, (b) 0.1, (c) 0.2 and (d) 0.4 m*M*. Applied voltage: 15 kV. Complexation conditions: [metal ion] = 1.8 10^{-4} *M*; [HQS] = 2.8 10^{-3} M. Y-axis represents absorbance units.

Optimization of separation

Among the factors that affect the observed velocity of metal complexes and thereby the separations, we considered the nature, concentration, pH and content of HQS in electrophoretic buffer and the applied voltage.

Applied voltage. Increasing the applied voltage only slightly improves the resolution. Although a higher efficiency is obtained by applying higher voltages, the smaller differences in migration time observed tend to level out this effect. Hence this CE parameter is insufficiently effective for the increase in resolution. In this work we used an applied voltage of 15 kV, which was chosen mainly with respect to decreasing the analysis time.

Nature of buffer. Borate buffers are more preferable for the separation owing to the more complete complexation, better detectability and resolution.

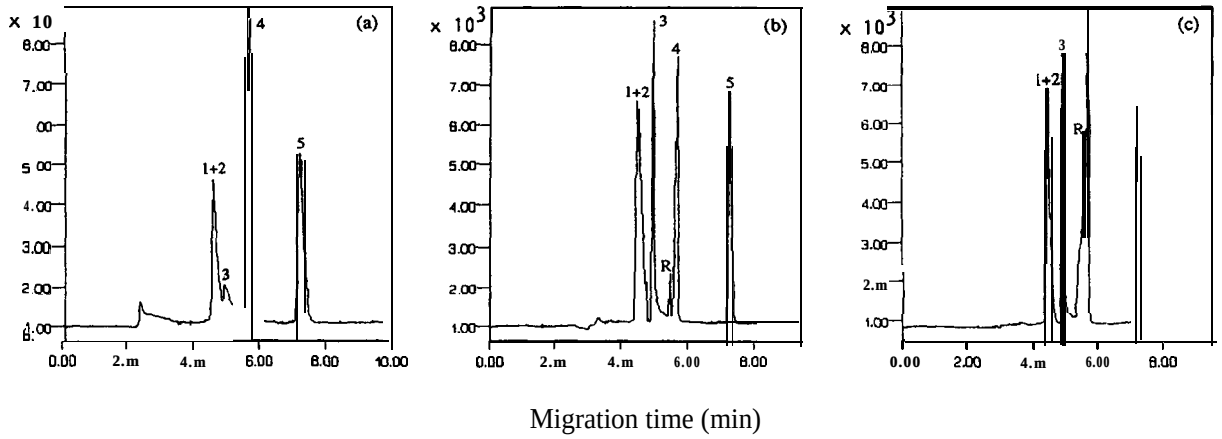


Fig. 4. Effect of HQS concentration in the samples on detectability. Electrophoretic buffer: 0.1 m*M* HQS. Complexation conditions: [HQS] = (a) 2.5, (b) 2.8 and (c) 3.0 m*M*. Other conditions as in Fig. 2. Y-axis represents absorbance units.

Using phosphate buffers with the same pH, larger peak broadening (especially for the less stable complexes) and lower mobility were observed. The poorer efficiency is probably a result of the counteraction from the phosphate ions (as a stronger complexing agent than the borate ions). Carbonate buffers provide very good selectivity, but with the drawback of a lower average mobility and a longer analysis time (migration times reach more than 20 min).

pH. The pH dependence of the resolution can be complicated by cooperative and counteractive effects of EPM and EOM changes [14]. For instance, when using pH adjustment to optimize mobility differences, one should take into account that the changes in the buffer composition also affect the EOF (Fig. 5). We observed an unexpected decrease in the EOF with increasing the pH, although the deviations in ionic strength were negligitably small ($\pm$ 0.003 *M*). This disagreement with literature data for fused-silica capillaries [15] can be assumed to be related to the partially hydrophobic nature of the capillary walls. Nevertheless, the "bell-shaped" Δt_M *vs.* pH plots shown in Fig. 6 indicate a certain optimum pH range, in which the highest resolution is obtained. However, this range is narrow, because at higher and lower pH values negative pH effects on the efficiency are strongly pronounced (see above).

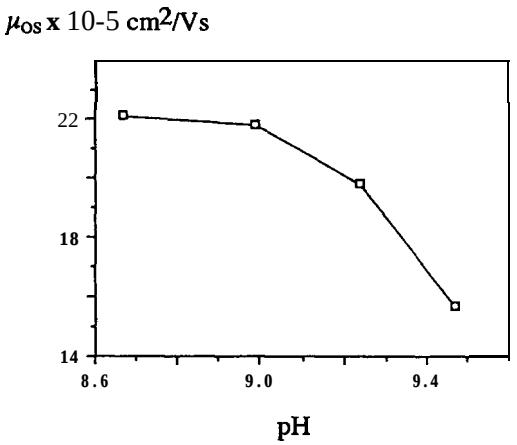


Fig. 5. Effect of borate buffer pH on electroosmotic flow.

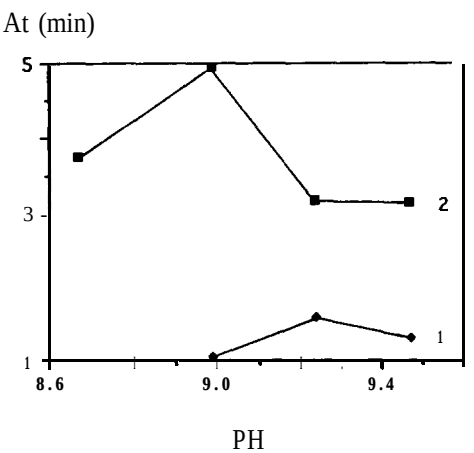


Fig. 6. Dependence of mobility differences of metal complexes on pH. 1 = Ni-Fe; 2 = Fe–Cu.

TABLE II

DEPENDENCE OF ELECTROOSMOTIC AND ELECTROPHORETIC MOBILITIES OF METAL COMPLEXES ON BORATE BUFFER CONCENTRATION

Concentration (m*M*)	$-\mu_{os}$ (10^{-5} cm^2/V s)	μ_{ep} (10^{-5} cm^2/V s)			
		Cu	Fe	Zn	Ni
5	23.6	40.8	48.2	52.1	55.7
10	19.8	37.1	43.8	46.8	50.8
15	16.5	37.5	44.8	48.5	51.2
20	16.7	38.0	45.3	48.8	52.2

The use of a pH scale with a fixed ionic strength (by adding a 0.1 *M* solution of different salts to 10 m*M* sodium tetraborate) revealed that the effect of ionic strength on migration times is much stronger than the "pure" pH effect. An increase in ionic strength of 15 m*M* reduces the migration time by 4–7 min, depending on the metal complex, whereas decreasing the pH by 1.5 units is accompanied by a decrease of only cu. 0.6 min. These results correspond well with the double-layer theory [14], according to which EOMs are influenced by changes in pH and ionic strength in the opposite way, the pH being less important than ionic strength.

Concentration. Table II shows the EPM of metal complexes at different borate buffer concentrations together with the corresponding EOM values. As the buffer concentration was increased, the EPM gradually decreased, reaching some constant level at a concentration of 10 m*M*. The EOM related to buffer concentration displays approximately the same dependence. Thus, varying the buffer concentration within the range 5-20 m*M* influenced the migration to only a minor extent.

The improvement in resolution that might be observed at higher borate concentrations as a result of the increase in efficiency with increasing current cannot be obtained, as shown in Fig. 7. Based on these data, a borate concentration of 10 m*M* was chosen because its use allowed not only the selectivity but also the detectability to be enhanced.

Content of HQS. As the effect of HQS in the electrophoretic buffer on the EOF is strongly pronounced (Table I), mobilities can also be manipulated by changing this buffer parameter. However, much shorter migration times observed with some

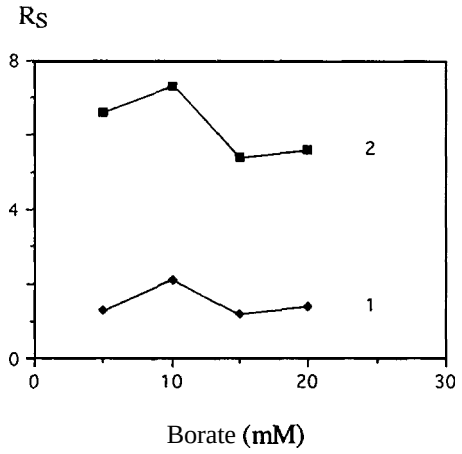


Fig. 7. Effect of borate concentration on resolution of metal complexes. 1 = Ni-Zn; 2 = Fe–Cu.

HQS-bearing buffers (*cf.*, electropherograms a and b in Fig. 2) can result in a decreased selectivity for metal complexes. Therefore, when choosing the electrophoretic buffers for metal determination, one should try to attain a good compromise between resolution and detectability.

An electropherogram showing the representative separation of a six-component metal ion mixture under optimum conditions is presented in Fig. 8

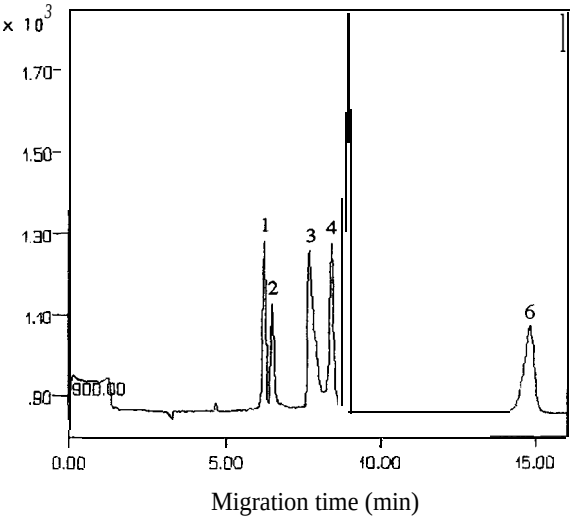


Fig. 8. CE separation of metal chelates of HQS. Electrophoretic buffer: 10 m*M* borate buffer containing 0.1 m*M* HQS. Applied voltage: 15 kV. Injection: 2 s. Peaks: 1 = Ni; 2 = Co: 3 = Zn; 4 = Cd; 5 = Fe; 6 = Cu. Metal ion concentration: $1 10^{-4}$ *M* Ni, Zn, Fe, Cu and $2 10^{-4}$ *M* Co, Cd. Y-axis represents absorbance units.

TABLE III

PARAMETERS OF CALIBRATION GRAPHS

CE conditions as in Fig. 3b. Injection: 25 s. n = 4–6.

Metal ion	Concentration range (M)	Intercept	Slope $\times 10^6$	Correlation coefficient
Ca(II)	$2 \cdot 10^{-6}$–$9\ 10^{-4}$	-43.6	47.1	0.9997
Cd(II)	$1\ 10\text{-}s\text{-}4.5\ 10^{-4}$	11.5	8.5	0.9914
Co(II)	$5\ 10^{-6}$–$4.5\ 10^{-4}$	3.6	11.9	0.9928
Cu(II)	$4\ 10^{-7}$–$1\ 10^{-4}$	37.1	77.0	0.9991
Fe(III)	$4\ 10\text{-}7\text{-}2\ 10^{-4}$	7.6	50.4	0.9997
Mg(II)	$4\ 10^{-6}$–$9 \cdot 10^{-4}$	− 26.8	44.1	0.9998
Mn(II)	$1\ 10^{-6}$–$9\ 10^{-4}$	60.9	24.5	0.9999
Ni(II)	$4 \cdot 10\text{-}7\text{-}2\ 10^{-4}$	7.0	44.2	0.9997
Zn(II)	$4\ 10\text{-}7\text{-}2\ 10^{-4}$	27.5	59.2	0.9973

[a] The upper limit corresponds to the maximum concentration studied,

(manganese, magnesium and calcium complexes migrate with close mobilities between those of the cadmium and iron chelates, whereas the aluminiurn-HQS complex co-migrates with the iron chelate).

Calibration and detection limits

The calibration graphs of peak area against metal concentration are given in Table III with the respective regression coefficients. The linear dynamic range was at least two orders of magnitude and reached about three orders of magnitude for metals that form more stable complexes and/or complexes with a higher absorptivity, such as copper@), zinc (II), iron(III), nickel(II) and cobalt(II). In the absence of HQS in the electrophoretic buffer, peak area gave a comparatively narrow dynamic range.

Table IV gives the detection limits of injected concentration and amount for metal ions as HQS chelates, defined as three times the signal-to-baseline noise ratio, for an electrophoretic buffer containing 0.1 mM HQS. Injected volumes were determined as described in ref. 14 for an elevation of 10 cm of the injection vial. It should be pointed out that the detection wavelength of 254 nm is an instrumental constraint, but not the optimal wavelength for the detection of HQS complexes. Also, a background signal detected for some metals, mainly zinc(II) and iron(III), originating from metal impurities in the electrophoretic buffer and water used, limits the detectability of these metals.

The relative standard deviations of the peak areas were found to be 1.5, 0.8, 0.6, 0.6 and 1.1% for Cu(II), Fe(III), Ni(II), Co(II) and Zn(II), respectively, for six replicate runs with $4 \cdot 10^{-5}$ M of each metal ion. As these values indicate reasonable reproducibility, there was no necessity to use an internal standard.

TABLE IV

DETECTION LIMITS

Metal ion	Minimum detectable concentration[a]		Minimum detectable amount (pg)
	M	ppb	
Ca(II)	$2 \cdot 10^{-6}$	80	1.5
Cd(II)	$2\ 10^{-6}$	225	26.0
Co(II)	$1 \cdot 10^{-6}$	58.9	1.6
Cu(II)	$5\ 10^{-8}$	3.2	0.06
Fe(III)	$3\ 10^{-7}$	16.7	1.0
Mg(II)	$4\ 10^{-6}$	97	1.7
Mn(II)	$1\ 10^{-6}$	55	2.5
Ni(II)	$4\ 10^{-7}$	23.5	1.1
Zn(II)	$1\ 10^{-7}$	6.5	0.6

[a] Injection time 5 s.

Analytical data

In order to evaluate the quantitative performance of the method, a sample of tap water was analysed. Fig. 9 gives a typical electropherogram in comparison with an electropherogram of the same sample spiked with a small amount of zinc. The second

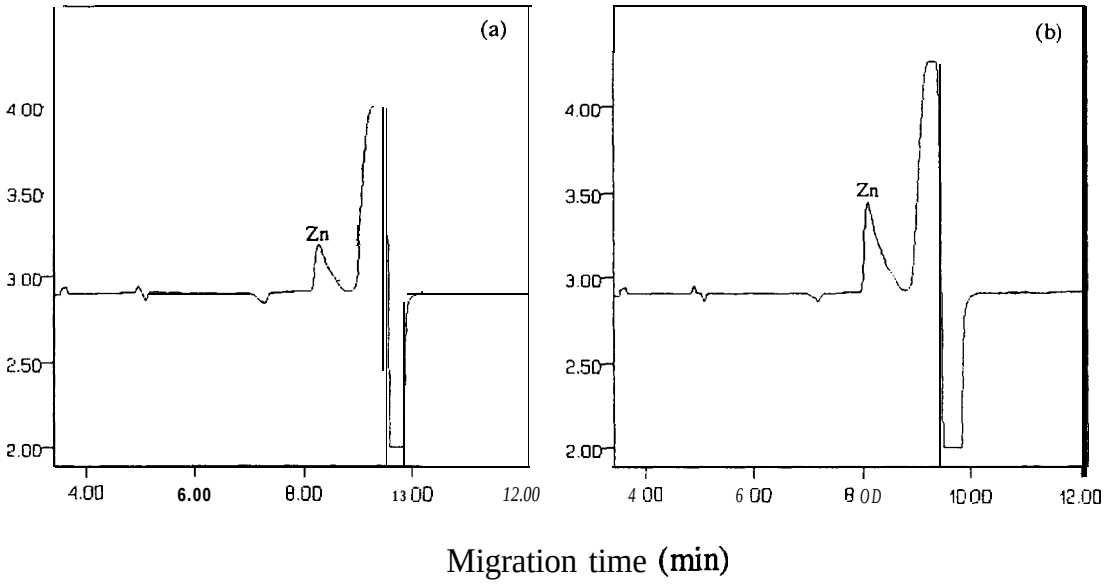


Fig. 9. Electropherograms of (a) a tap water sample and (b) the same sample spiked with 14.5 ppb of zinc. Injections: 25 s. Other conditions as in Fig. 8. Y-axis represents absorbance units.

peak migrating just after the Zn-HQS complex is attributed to iron-and alkaline earth metal-HQS complexes. Owing to the sufficiently high sensitivity, this method can be recommended for environmental samples without preconcentration techniques. However, the following relatively minor problem should be taken into account. The comparatively high background signal of metal impurities mentioned previously, mainly because of inadequate purity of the reagent, necessitates a "blank" analysis and subtraction of the "blank" electropherogram from the sample electropherogram (the dip peak observed in Fig. 9 is caused by this operation).

CONCLUSIONS

HQS is a promising reagent in metal ion CE. The application of this reagent to the CE separation and determination of transition metal ions after precolumn formation of negatively charged chelates appears to be a good alternative to traditional capillary methods for ion analysis. Complete chelation before the separation not only allows the direct spectrophotometric detection of metal ions in the mid-ppb range, but also imparts a negative charge to the metal ion which makes its adsorption interactions with capillary walls negligible. In addition, as only one metal-containing species exists within each zone when using a sufficiently strong chelating reagent, small band broadening and small competing complexing effects of buffer components should be expected. Further, incorporating HQS in the electrophoretic buffer markedly improves the detectability and makes it possible additionally to regulate the separation.

Useful developments of the method, which are worthy of further investigation, might be connected with extending greatly the range of metals that can be determined (involving aluminium group metals, molybdenum, tungsten and vanadium or platinum metals), introducing new chelating agents (e.g., dithiocarbamic acids containing ionized groups) and the extension of practical applications.

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