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Simultaneous determination of inorganic anions and cations by capillary electrophoresis with indirect UV detection

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Abstract

The development of a separation system for the simultaneous determination of inorganic anions and cations, low-molecular-mass organic acids and aliphatic amines by capillary electrophoresis with indirect UV detection using new electrolyte systems is described. Different principles of the experimental enforcement are compared. The principle of both-side injection was investigated using two different electrolyte systems. In order to avoid system peaks caused by the presence of different electrolyte co-ions, the selection of useful electrolyte components is more difficult than the choice of electrolytes for separate anion or cation analysis and special preparation procedures are necessary. The applicability of the method is shown by investigations of reproducibility, linearity of the calibration and by the analysis of drinking water including a comparison with results of measurements carried out with atomic absorption spectrometry for the cation determination, and ion chromatography for the anion determination.

Keywords: Background electrolyte composition; Inorganic anions; Inorganic cations; Organic acids; Amines

1. Introduction

Over the past decade, there have been several investigations into the separation of low-molecular-mass anions and cations by capillary electrophoresis (CE) [1–9]. In most cases the systems utilize indirect UV detection and are optimized either for the analysis of anions or cations. Due to the individual electrophoretic migration behaviour of positively and negatively charged species, CE is suitable for their simultaneous determination [10,11]. Therefore some general requirements must be fulfilled by the electrolyte system. Firstly the differences of the electrophoretic mobilities must be sufficient for the separation of the anionic analytes as well as for the separation of the cationic analytes. For that purpose several additives, e.g. complexing agents like 18-crown-6 [12] or hydroxyisobutyric acid (HIBA) [7,13–15], have been proved in CE. The second requirement is that both negatively and positively charged analytes have to migrate towards the detector. Furthermore, it is necessary that all analyte ions are recorded by the detector. Due to the lack of absorption of the most low-molecular-mass ions in a suitable UV range, the indirect detection mode is required to measure these species. The use of indirect UV detection for simultaneous anion and cation determination demands the presence of anionic and cationic UV absorbents in the background electrolyte (BGE). This paper compares three different principles for the simultaneous determination of small cations and anions. Furthermore, the

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development, optimization and application of the new electrolyte systems is described.

2. Experimental

2.1. Chemicals

Dimethyldiphenylphosphonium iodide (DIPP) and trimesic acid (TMA) were obtained from Fluka (Buchs, Switzerland) all other chemicals from Merck (Darmstadt, Germany). All chemicals were of analytical reagent-grade purity. All solutions, electrolytes and standards were prepared using water purified with a Milli-Q system (Millipore, Eschborn, Germany).

2.2. Instrumentation

The experiments were carried out using two different CE devices. First approaches were carried out using a modular composed device combining a high-voltage power supply (F.u.G., Rosenheim, Germany), a UV detector (Dionex, Sunnyvale, CA, USA) and a separation unit consisting of capillary and vials. Furthermore a commercially available CE device (HP 3D, Hewlett-Packard, Waldbronn, Germany) was employed.

The fused-silica capillary (75 μm I.D.) was rinsed for 5 min with 0.1 *M* sodium hydroxide solution, water and electrolyte at the beginning of each day and for 2 min with electrolyte between all electrophoretic separations.

3. Results and discussion

3.1. Principles of the simultaneous determination of anions and cations

Fig. 1 shows three different possibilities to realize the detection of cationic and anionic species during one electrophoretic run.

3.1.1. Utilization of the electroosmotic flow

The principle of this procedure is given in Fig. 1a. It requires an EOF which is so strong that species migrating against the EOF are transported in direction of the detector. The sample injection is done in the usual way at the side of the capillary opposite to the detector. Under the electrophoretic conditions and in case of an uncoated capillary the cations reach the detector first. Then the EOF follows which transports all neutral species inside the original sample zone. Thereafter the ions with opposite charge (anions in this case) follow but only those who have a smaller velocity than the EOF. Usually the magnitude of the EOF is not sufficient to reverse the migration direction of small ions having high mobilities. For that reason it is necessary to increase the velocity of the EOF to analyse inorganic cations and anions simultaneously. Due to the pH dependence the most effective way to speed up the EOF is to increase the pH value of the electrolyte solution. In the matter of inorganic ion analysis this possibility is limited by the formation of alkaline earth metal hydroxides and by the requirement that the cationic component of the BGE is still protonated.

3.1.2. Electrolyte flow generation by external pressure

Fig. 2a shows an electropherogram obtained with an electrolyte system specially developed for the simultaneous determination of cations and anions with indirect UV detection. The separation is carried out under conditions (pH 6.0) that still allow the determination of alkaline earth metal ions. The EOF is not strong enough to transport small anions toward the detector. Due to the above mentioned conditions for the analysis of cations it is not possible to accelerate the EOF by increasing the pH value of the electrolyte solution. For that reason the principle utilizing only the EOF to reverse the migration direction of the anions can be used for analysis of cations and slow migrating anions but it is not practicable for the simultaneous determination of cations and inorganic anions.

Alternatively to the EOF an additional flow in the system can be generated using pressure at one side of the capillary or using a vacuum at the other side of the capillary. This procedure is described in Fig. 1b. In this way it is possible to chose any flow velocity with high precision. Therefore optimum conditions concerning the velocities of the analytes can be adjusted. As can be seen in Fig. 2b the principle of applying pressure at the inlet side of the capillary

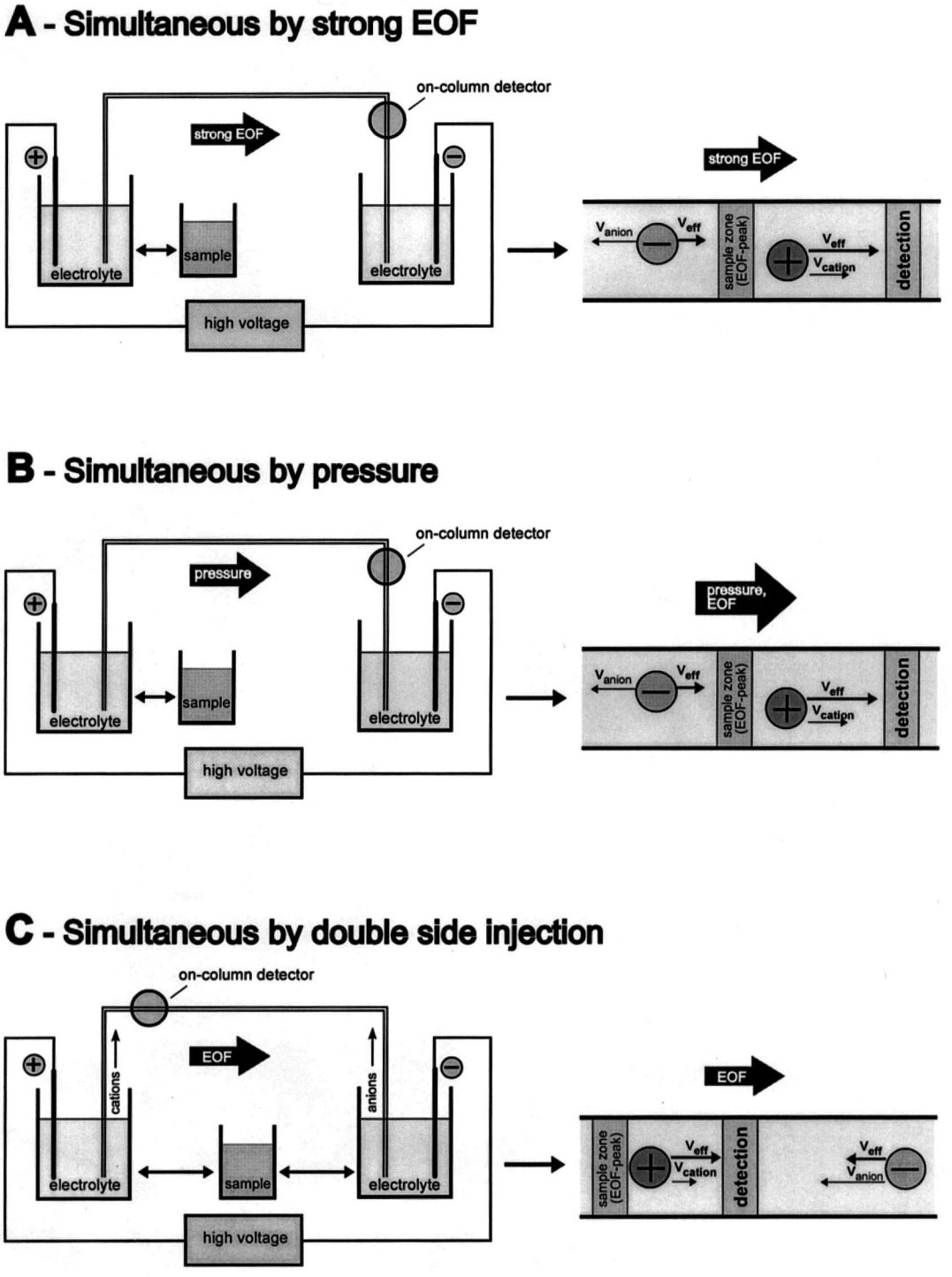

Fig. 1. Principles of the simultaneous determination of cations and anions.

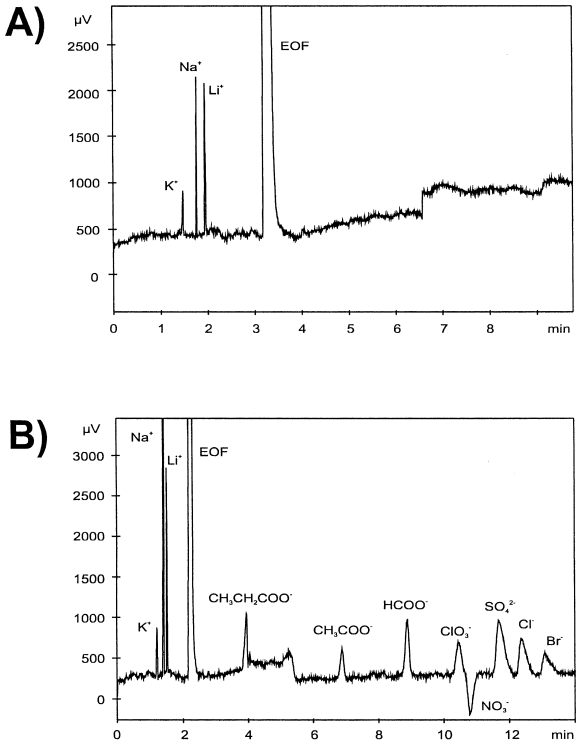

Fig. 2. Electropherograms of simultaneous cation and anion separation. (a) Separation by utilization of the EOF (b) Separation with electrolyte flow generation by external pressure (pressure application of 200 mbar at the anodic end of the capillary) Conditions: electrolyte: 5 m*M* imidazole, 5 m*M* thiocyanate; capillary: fused-silica 60 cm total length×75 μm I.D.; detection: indirect UV detection (220 nm); separation: 30 kV; injection: 50 mbar, 10 s.

permits the simultaneous determination of inorganic cations and anions. The sample solution is the same as that used to obtain the electropherogram shown in Fig. 2a.

On account of the counter-flow migration of the anions the signals of the highly mobile anions appear after the signals of the less mobile anions. Another effect of this procedure on the separation is the increase in pressure which increases zone broadening due to the parabolic flow profile of the hydrodynamic flow. In particular, peak broadening occurs (see Fig. 2b) for anions with high mobilities like sulfate and chloride. Furthermore the resolution of the cations decreases in comparison to the system without pressure (see Fig. 2a and b). Therefore, the application of pressure is disadvantageous for the simultaneous determination of inorganic ions.

3.1.3. Sample injection on both sides of the capillary [10,11]

In Fig. 1c the principle of the simultaneous determination due to the injection on both sides of the capillary is schematically shown. After sample injection on both sides the electric field is applied. The cations and anions migrate to the detector from opposite sides.

The position of the detector has been determined in advance. A restriction is sometimes given by the capillary position in the CE instrument. The optimum position of the detector is chosen with regard to the migration velocity of the fastest and slowest cations and anions as well as the direction and velocity of the EOF. To avoid an overlapping of the signals of anions and cations, or of the analytes and the EOF in the detection window it is important to match the appearance of the species exactly.

For correct quantification hydrodynamic injection is preferred over electrokinetical injection. For hydrodynamic injection the sample is introduced successively on both sides of the capillary. The sample volume of the first injection must be larger than that of the second injection since at the second injection the injected volume is put out of the capillary at the other side. To avoid this partially loss of the first injection volume it is possible to inject a small electrolyte zone between the two sample injections. An electropherogram obtained by using this procedure is given in Fig. 3. In comparison with the above-mentioned principles the advantages of this method are that no extremely strong EOF is necessary and that there is no additional zone broadening caused by applying an external pressure. Therefore the following investigations were carried out using the principle of sample injection on both sides of the capillary.

3.2. Selection and optimization of the electrolyte systems

In order to apply indirect UV detection the electrolyte system must contain UV active cations as well as UV active anions.

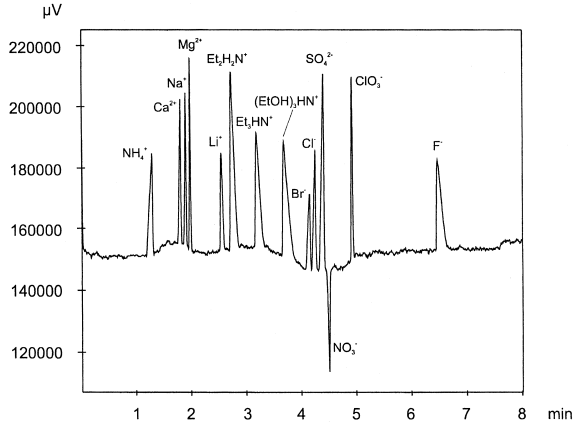

Fig. 3. Electropherogram of a simultaneous cation and anion separation using the imidazole–thiocyanate system. Electrolyte: 5 m*M* imidazole, 5 m*M* thiocyanate, 2 m*M* citric acid, 1 m*M* 18-crown-6; capillary: fused-silica, 16 cm from the anodic and 50 cm from the cathodic end of the capillary to the detector, 50 µm I.D.; detection: indirect UV detection (220 nm); separation: 30 kV; injection: electrokinetic 3 kV, 10 s.

3.2.1. Imidazole–thiocyanate system

The first system described in this paper consists of imidazole as cationic component and thiocyanate as anionic component. Thiocyanate is not commercially available as free acid but as potassium salt. In order to avoid the appearance of a system peak caused by the presence of a second cationic co-ion, potassium is replaced by protons using an ion-exchange procedure before preparing the electrolyte solution [10]. Additionally this has the effect that imidazole is protonated and useful as cationic co-ion to supply the indirect UV detection of the positively charged analyte ions. To resolve ammonium and potassium 18-crown-6 was added to the electrolyte. Citric acid was used for better separation of the alkali earth ions. It was found that the addition of citric acid inhibits the electroosmotic flow. The effective length of the capillary which is available for the separation of the anions and cations is given by the position of the detector. To avoid an overlapping of the signals it is important that the slowest cation has left the point of detection before the first anion arrives at the detector. As demonstrated in Fig. 3 the length of the capillary sections can be chosen in a way that the signals of the inorganic cations appear first in the electropherogram and then the signals of less mobile cations (e.g. aliphatic amines), immediately followed by the signals of the inorganic anions. (For nitrate a negative peak is received because the stronger UV absorption in comparison to the co-ion thiocyanate at the wavelength 220 nm.) Nevertheless if real samples contain cations with low electrophoretic mobilities a disturbance of the anion determination is possible. But samples containing only highly mobile cations can be analyzed without problems. Fig. 4 shows the determination of inorganic ions in a sample of drinking water. The comparison with results of atomic absorption spectrometry (AAS) and ion chromatography (IC) measurements is given in Table 1.

Further applications of the imidazole–thiocyanate system are shown in Fig. 5. The analysis of an alcoholic beverage and a special mineral water containing lithium is possible using the described system.

3.2.2. DIPP–TMA system

A possibility to avoid overlapping of cation and anion signals is given by the use of an electrolyte system which creates a stronger EOF than the electrolyte system described above. Since the EOF moves toward the cathode it is guaranteed that no overlapping of anion signals by cationic species occurs if the EOF signal appears in front of the anion peaks. This can be realized using an electrolyte

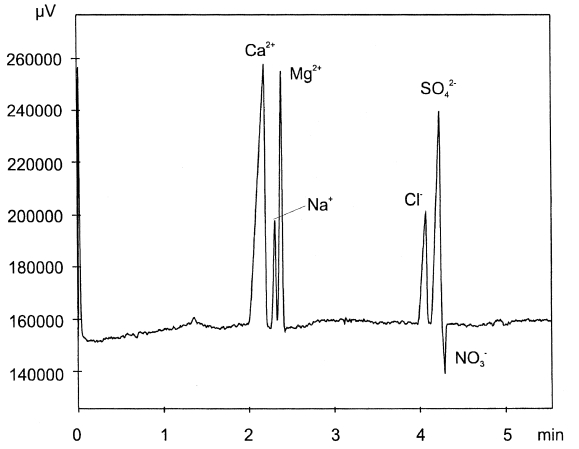

Fig. 4. Simultaneous determination of cations and anions in drinking water (dilution 1:20). Injection: hydrodynamic (10 cm for 10 s at the anodic end and 10 cm for 5 s at the cathodic end; other conditions see Fig. 3.

Table 1
Analysis of drinking water

	Levels (mg/l)					
	Sodium	Magnesium	Calcium	Chloride	Sulfate	Nitrate
Simultaneous capillary zone electrophoresis	10.1	17.5	101.2	25.3	40.3	15.1
Ion chromatography				24.1	39.9	13.7
Atomic adsorption spectrometry	10.3	18.6	98.0			

system consisting of DIPP ions as cationic UV absorbent, TMA as anionic UV absorbent and HIBA as additive for the optimization of the cation separation.

For the optimization of the system all analytes must be sufficiently separated from each other and there must be enough space between the EOF signal and the first anion peak. The separation was developed by optimization of three parameters: pH, temperature and capillary length. The first aspect for the optimization is the choice of the pH value of the electrolyte system. Several parameters like the migration time of the EOF, the charge of the analytes and of the electrolyte components depend on the pH value.

For pH<4.5 it was observed that anionic analytes show peak broadening and smaller peaks. The reason for that effect is the lower effective charge of the electrolyte anion TMA resulting in lower mobility. Therefore, the fronting of the anionic analyte peaks becomes stronger.

For pH>5.5 the velocity of EOF becomes higher. Therefore, the resolution of the cations at this pH was lower. Furthermore, longer migration times result for the anions due to the stronger counter movement of EOF.

For this system it was found that the most advantageous pH is 4.8.

A further point for the optimization is the choice of the most suitable length of the capillary sections for the cation separation as well as for the anion separation. The difference between the migration

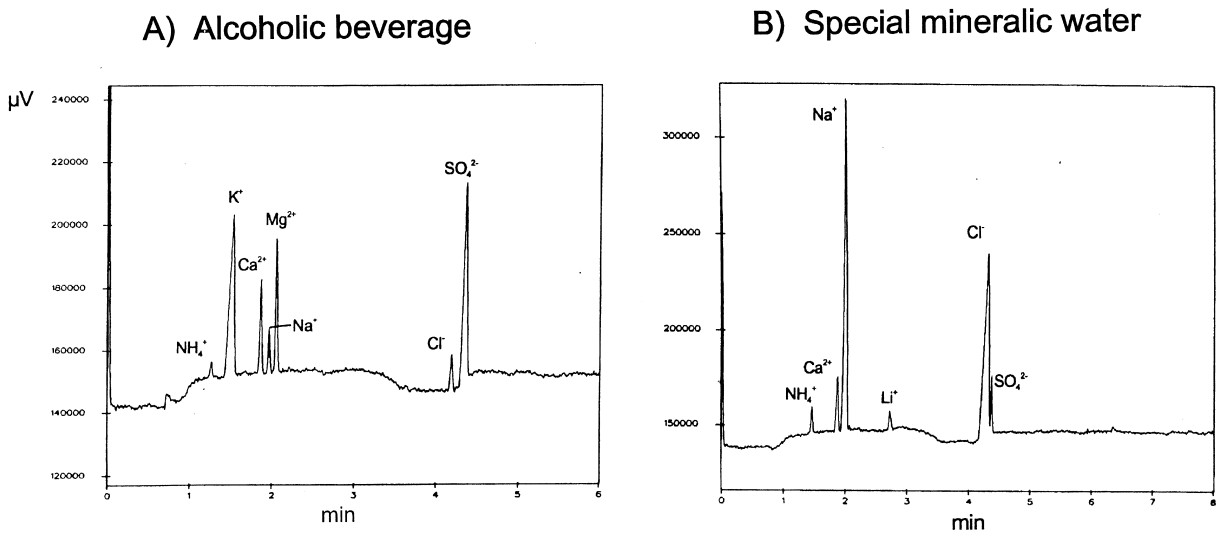

Fig. 5. Applications (dilution each 1:20); conditions see Fig. 3.

time of the EOF signal and the first anion should be at least 30 s to guarantee that the quality of the separation is not effected by small shifts of the migration times due to small changes of outer conditions (e.g. changes of the capillary surface or small alternation of the electrolyte pH). The distance from the EOF signal to the anion peaks can be influenced by changing the capillary length between the cathodic end of the capillary and the detector (Fig. 6).

More comfortable to handle in practice is the optimization by the regulation of the temperature. This affects the velocity of the EOF, mainly owing to the temperature dependence of the electrolyte

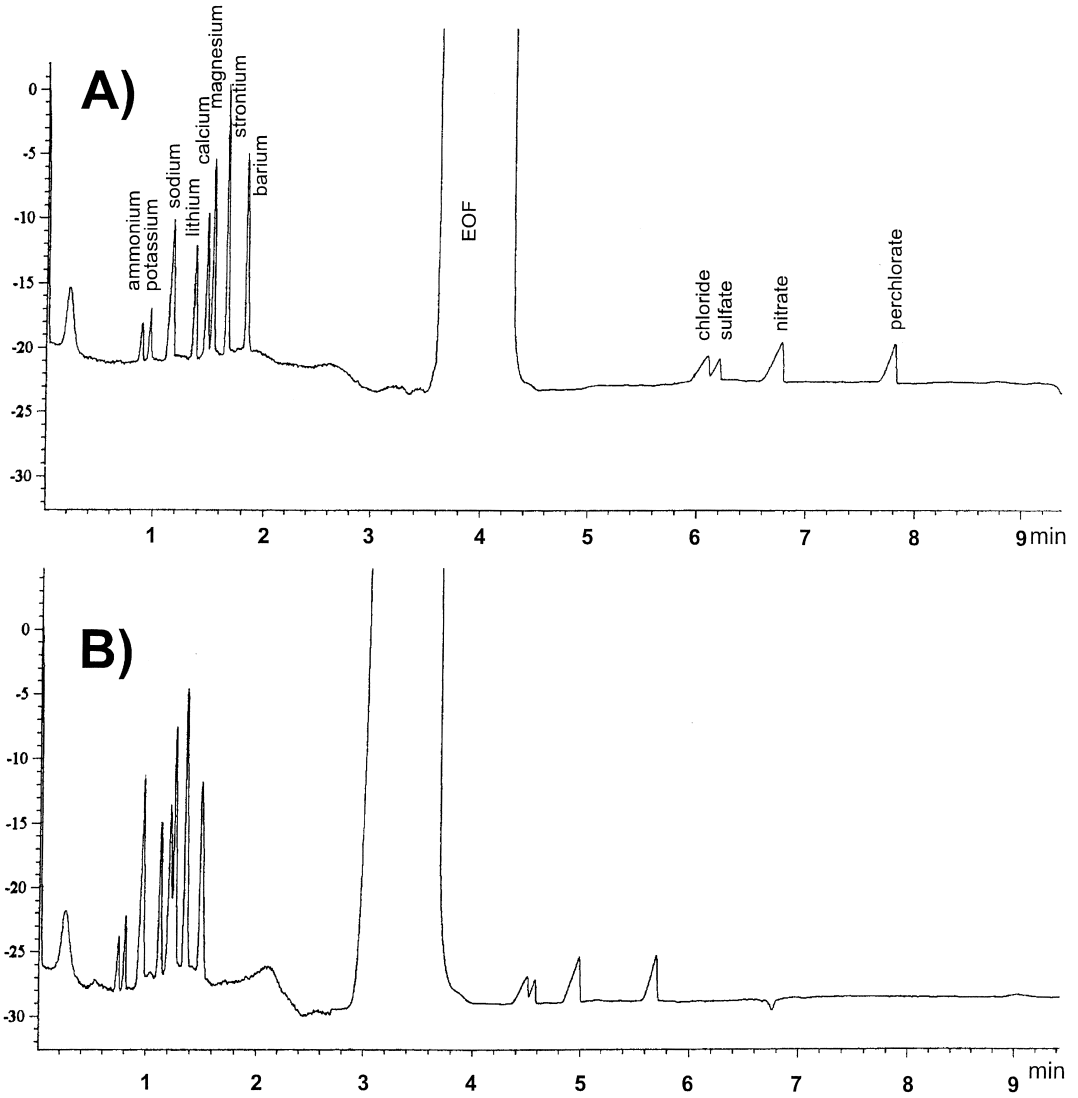

Fig. 6. Optimization of the separation by changing the capillary length. Electrolyte: 12 m*M* DIPP, 4 m*M* TMA, 1.5 m*M* HIBA, 2.3 m*M* 18-crown-6, pH 4.8. Capillary: (A) fused-silica, 16 cm from the anodic and 70 cm from the cathodic end of the capillary to the detector, 75 μm I.D.; (B) fused-silica 16 cm from the anodic and 60 cm from the cathodic end of the capillary to the detector, 75 μm I.D.; detection: indirect UV detection (220 nm); separation: −30 kV, 23°C; injection: 50 mbar for 30 s at the cathodic and −50 mbar for 15 s at the anodic inlet of the capillary.

viscosity. It was found that at 20°C the distance between the EOF signal and the anion peaks is too small, which can lead to overlapping. For a temperature of 25°C the velocity of EOF increases and the distance between EOF and the anions also increases. At higher temperatures the increasing migration times for low mobile anions are disadvantageous. A temperature of 23°C was chosen for further separations. Selecting the temperature of the electrolyte system is a fast and easy method to choose the best conditions for different analytical tasks.

A simultaneous separation of cations and anions using the optimized conditions described above is shown in Fig. 7. Thiosulfate as the most mobile anion is well separated from the EOF signal and appears later in the electropherogram. Therefore it is not possible that any cationic component of the sample disturbs the determination of the anions.

To demonstrate the applicability of this system some quantitative data are given in Table 2. The calibration function is linear up to about three orders of magnitude above the limit of detection (LOD), which is placed in the low μM range depending on the analyte ions. The precision of the migration times calculated as relative standard deviation from six measurements is always below 1.5%. The precision of the peak area is up to 2% except the values for chloride and sulfate because the data were collected at different concentrations and the resolution of chloride and sulfate is worse at higher amounts.

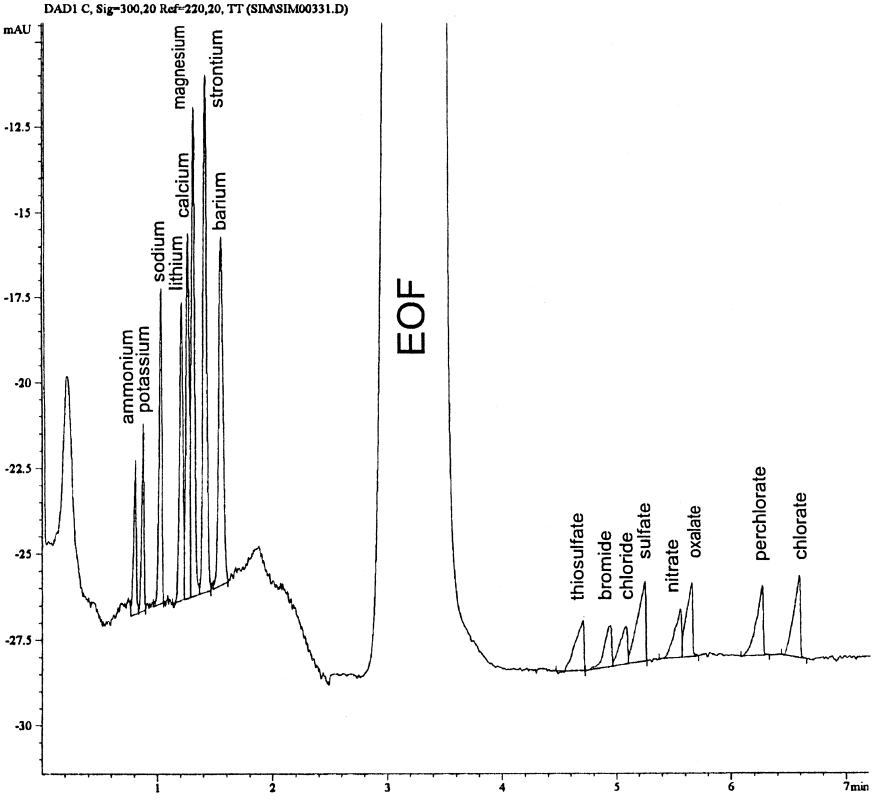

Fig. 7. Simultaneous determination of cations and anions using the DIPP–TMA system. Capillary: fused-silica, 15.5 cm from the anodic and 60 cm from the cathodic end of the capillary to the detector, 75 μm I.D.; other conditions see Fig. 6.

Table 2
Characterization of the optimized system

	Potassium	Sodium	Magnesium	Chloride	Sulfate	Nitrate
LOD (μM)	5.0	5.0	2.0	5.0	5.0	5.0
Correlation coefficient (R)	0.99940	0.99955	0.99951	0.99465	0.99615	0.99996
Precision of migration time (%)	0.81	0.81	0.50	1.20	1.32	1.12
Precision of peak area (%)	2.1	0.8	1.1	3.7	2.2	0.8

4. Conclusion

The simultaneous determination of low-molecular-mass cations and anions by CE using indirect UV detection can be carried out with different separation techniques. The most advantageous method utilizes the sample injection at both sides of the capillary and opposite migration directions of anions and cations. The electrolyte system has to be selected with respect to the special requirements for the separation and the indirect UV detection of both cationic and anionic analytes. The development and the optimization of these systems is more extensive compared with electrolyte systems for separate cation or anion analysis.

However, in comparison to the single systems no rearrangement of equipment like changing of capillary and electrolyte system is necessary. The optimized system allows the simultaneous determination of cations and anions in less than 10 min. More information about the sample can be received in one run. No loss in LOD or precision occurs in comparison to the single systems. The method is especially useful for fast routine analysis of samples with similar composition.

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