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On-Line Flow Injection—Capillary Electrophoresis Instrument with Contactless Conductivity Detection for Sensitive Cation Analyses

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Abstract: A new system for on-line analyses of metal cations has been developed by combining flow injection sample introduction with on-line capillary electrophoresis. The on-line analysis instrument has a simple construction and it allows fast sample introduction from a flowing solution. The ends of the separation capillary and the electrodes were placed opposite to each other into tubings that were installed over them behaving as flow-through channels. The capillary temperature during the analyses was controlled by water cooling and the analyte monitoring was conducted with a contactless conductivity detector. The construction allowed compound detection of very low concentrations.

The instrument was used for simultaneous determination of ammonium, potassium, calcium, magnesium, and sodium as complexes in aqueous 18-crown-6 ether – acetate electrolyte solution. Flow injection analysis of sample introduction was kept apart from the ligand modified electrolyte solution. Calibration with standard mixtures of alkali metals, alkaline earth metals, and ammonium was linear in the range from 10 ng/mL to 1 μg/mL for each analyte. The intraday reproducibility for the separations was 2% (RSD). The detection limit for the cations was 10 ng/mL. The studies showed the performance of the method to be sensitive for the monitoring of inorganic ions in water treatment.

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INTRODUCTION

The determination of metal ions in various samples is important. Reliable and rapid analysis techniques are needed for their determination in medicines, environmental samples, and drinking water. Metals can be determined by a number of techniques, as based on various atomic absorption spectrometric methods, electrochemistry, and chromatography.

In capillary electrophoresis (CE), alkaline earth metal cations especially have nearly identical charge and hydrated radius and, therefore, the differences in electrophoretic mobilities are not sufficient to provide good resolution between these. Usually, the metal cation species are expected to move by electrophoresis, but not as metal ions but complexes in multicomponent solvent systems. Literature shows that metal complex formation is the most valuable approach for performing metal speciation of different oxidation states (1). The procedure to converse the metals to complexes takes place usually before the introduction of the sample into capillary or by using pre-capillary complex formation strategy. Kuban's research group separated inorganic and organic anions and cations together with metal cations by capillary electrophoresis using complex formation technique with diaminoethanetetraacetic acid (EDTA). The technique was extremely sensitive, enabling detection limits of 4-1250 ng/L (2), but their electrophoresis system was not demonstrated to work in an on-line mode.

Continuous sample flow is a main premise for on-line analyses. In previous publications we demonstrated the modification of a commercial CE machine for on-line process monitoring (3). Sampling was equipped with a sample flow cell. With this system we could determine several anions and cations out from real running process samples.

The combination of different analytical techniques, like flow injection (FI) and CE, is a common way to improve the performance of the separation method (4,5). In the cases, a flow injection technique was used to clean or pre-concentrate the samples by instrumentation of an interface for capillary and electrodes to match with a flowing liquid. A small diameter steel needle was designed as a flow-through channel that was performed as an electrode inside the capillary. Chen et al. (6) and Fang et al. (7) presented a set-up for a FI-CE-coupling, where the capillary was placed against the flow direction of the solvent. The capillary end

was in a plastic funnel that opened out into a large solvent reservoir. In their work, Tuma et al. (8) recognized a significant difference in the amount of injected analyte based on the orientation. With a perpendicular structure fewer samples were introduced towards the solvent flow. They used a polyethylene tube with a hole for the capillary to place it in two different directions. In order to achieve low dispersion of the sample and electrolyte zones, the inlet of the capillary was near the outlet of a valve that was used for solvent adjustment. A good way to avoid dispersion was to insert air segments between two liquids, like Fu et al. (9) described in their studies. They used a drop inlet as the FI to generate the air bubbles, simultaneously avoiding the premixing of sample and the electrolyte before analysis.

There are two main facts that should be considered when reproducibility and sensitivity are the issues in capillary electrophoresis studies. It is important to control the sample injection volume and the temperature during the analyses. Different designs of a perpendicular capillary inlet have been published, namely the sample introduction on either one (10,11) or both (12,13) ends of the capillary. Our group has made efforts on constructing a channel with liquid flow and an injector for sample volume control to obtain reproducibility for sample introduction. The system could be used to direct samples into flowing electrolyte solutions. In one of our designs we thermostated the on-line capillary electrophoresis system to reach good reproducibility in the determination of inorganic ions and drugs (12). As to the temperature, Petersen et al. (14) took a closer look on Joule heating and its effects for separation performance. They demonstrated that the importance of the temperature stability should not be underestimated when measuring very small ion concentrations. To obtain low detection limits sensitivity is needed. Different techniques can be used for identification of small ions. Detection was chosen according to the species and electrolyte compositions, e.g., end-column amperometric detection (9), UV detection (12) and contactless conductivity detection (C^4D) (13,15,16).

In this article we describe the main attributes for an on-line CE instrument for analyses of ammonium, potassium, calcium, magnesium, and sodium complex ions by using flow injection in sampling from a running process sample and by performing electrically aided formation of metal complexes before the analyte separation in the on-line mode. In our new instrument prototype, we chose basic features for a simple and robust apparatus construction. Furthermore, we optimized the composition of the electrolyte solution that is cheap to use, even in on-line coupling with a continuous solvent delivery units in capillary electrophoresis.

MATERIALS AND METHODS

Chemicals

Potassium, calcium, magnesium, and sodium chloride salts were obtained from Sigma–Aldrich Chemie (Steinheim, Germany). Acetic acid (98–100%) was from J.T. Baker (Deventer, Holland). 1,4,7,10,13,16-Hexaoxacyclooctadecane (18-crown-6-ether), imidazole, 2,6-pyridine dicarboxylic acid, and glycolic acid were from Fluka (Buchs, Switzerland). Ammonia (25%), pyridine, and NaOH were from Merck (Darmstadt, Germany). All reagents were of analytical purity unless otherwise stated and they were used as received. The deionized water was produced with a Milli-Q-gradient A 10 system (Millipore, Bedford, MA, USA).

Instrumentation and Analysis Conditions

Instrument in Method Development

The selections of electrolyte composition, evaluation of on-line performed continuous sampling and solvent delivery methodology for the on-line flow injection—capillary electrophoresis instrument were done by using a P/ACE MDQ capillary electrophoresis instrument (32 Carat Software, version 8.0, Beckman Coulter Instruments, Fullerton, CA, USA).

A temperature control unit (water cooling) for the capillary, a constant high voltage source (optimized to final + 16 kV), and a temperature controlled sample tray (optimized to final +20°C) led on to reproducible analyses. Two detectors were used as a sequence one after the other. The first detector was a contactless conductivity detector (TraceDec, Strasshof, Austria). The cell in the capacitive coupled conductivity detector, C^4D, was placed at the same position on the capillary as in the FI-online CE instrument in order to keep the effective separation length identical for all measurements. The data were recorded using the A/D converter available in the Beckman-Coulter MDQ CE instrument and the data acquisition software provided by TraceDec (Strasshof, Austria).

Samples were introduced for separation by + 5 kV voltage injections for 5 seconds. Analyses were performed with fused silica capillaries ($L_{tot}/L_{det}(UV)/L_{det}(C^4D)$ 60 cm/50 cm/43 cm, 50 μm i.d., 375 μm o.d., Polymicro Technologies, Phoenix, AZ, USA). Before use, the capillary was conditioned by rinsing at 20.0 psi with 0.1 M NaOH, Milli-Q water and the electrolyte solution, each for 10 min.

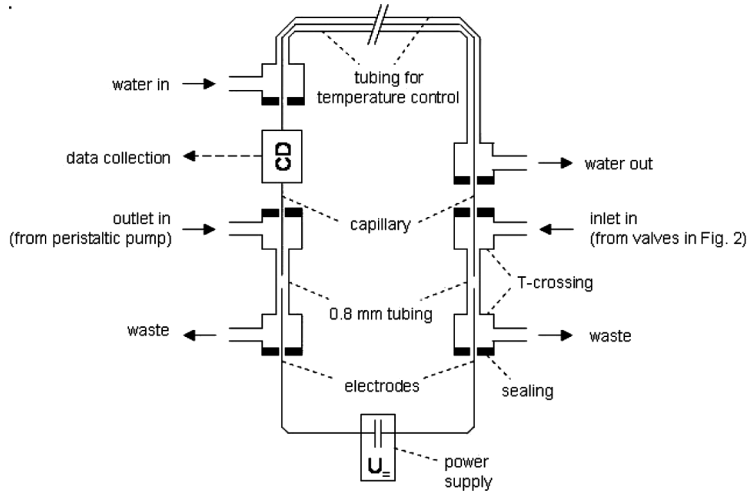


Figure 1. Schematic diagram of the online FI-CE instrument; capillary inlet and outlet are identical designed containing two T-crossings with a 0.8 mm Teflon tubing in between; in temperature control unit there is the same kind of tubing system (large diameter).

Flow Injection—On-Line Capillary Electrophoresis System

The final studies were performed with an on-line capillary electrophoresis instrument that is a combination of a flow injection (FI) module and a laboratory-made on-line CE instrument with continuous sampling and solvent delivery methodology. The construction is presented in Fig. 1 and 2. Samples are injected with FI technique from the "inlet in" (Fig. 1) by using a 2-dimensional valve system (two 4-port valves (A and B) in Fig. 2). First, the instrumental set-up is washed with the press lock closed. Secondly, the inlet part is filled with an electrolyte solution. With the valve combination (A(0) and B(1)) an

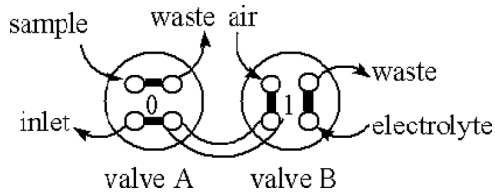


Figure 2. Scheme of valve combination for flow injection with air segments between sample and electrolyte; number 0 (off) and 1 (on) define the connection states.

air segment is generated and it pushes the electrolyte forward in the system. The air segment is short, since its sole role is to keep apart the electrolyte and the sample. With the turn of valve A(1) the sample solution is directed to enter the inlet capillary. Injection is performed when the inlet part is completely filled with the sample. According to the application a high voltage or pressure injection is possible, we performed the high voltage injection with stopped flow. After electrolyte and prior to the sample plug an air segment was made with valves A(0) and B(0). During the electrophoresis separation (high voltage switched on) the flow of the electrolyte is switched off, but the sample solution continues to flow. The valve combinations are summarized in Table 1.

The capillary is placed inside PTFE tubing, flushed with water to cool the capillary (Fig. 1). A multichannel peristaltic pump (ISMATEC, Zurich, Switzerland) was used to generate the continuous solvent flows, entrancing the capillary from the "inlet in" and exiting from the "outlet in" part. The solvent flow interfaces were made with two small PTFE tubings (0.3 mm and 0.8 mm). T-crossing connections were constructed for solvent delivery and waste. No contamination was noticed.

The capillary ends and the Pt-electrodes were adjusted opposite (Fig. 1). A high voltage power supply (Ultravolt 25A24-P15, Ronkonkoma, NY, USA) was used to adjust the separation voltage to + 16 kV across the capillary (fused silica L_{tot}/L_{det}: 50 cm/43 cm, 50 μm i.d., 375 μm o.d.). The first experiments were performed by cooling the capillary with air from a fan. However, a more efficient water cooling unit was needed to control the temperature (21–23°C) during the analyses. Its flow was generated via hydrostatic pressure. The instrumental improvements in the temperature control as well as both the capillary and the electrode positioning allowed getting a stable background in the detector. Therefore, very lower analyte concentrations could be determined.

A similar contactless conductivity detector (TraceDec, Strasshof, Austria) as used in Beckman-Coulter MDQ CE instrument was used

Table 1. Valve, press lock and flow switching for one run (0 = off; 1 = on)

Step	Wash	Air seqment	Sample	Injection	Electrolyte	Separation
Valve A	0	0	1	1	0	—
Valve B	0	1	1	1	0	—
Press lock	1	0	0	0 or 1	0	—
Flow	1	1	1	0 or 1	1	0

for the identification of the metal complexes in FI-on-line-CE instrument. The C^4D cells were placed as described in the Section, Instrument in Method Development. The data were recorded using the A/D converter (Beckman-Coulter MDQ CE). The instrument control and the data acquisition software were provided by LabView (software by National Instruments, Austin, TX, USA).

Other Instruments

Denver pH meter Model 20 (Denver Instruments, Denver, CO, USA) was used for pH measurements. The pH combination electrode was calibrated using commercial standards with pH values of 4.00, 7.00, and 10.00 (Radiometer, Copenhagen, Denmark). Pure water was made daily with a Milli-Q water purifying system (Millipore Corporation, Billerica, MA, USA).

Final Electrolyte Solutions

All electrolytes and samples were made of stock solutions at concentration of 250 mM. They were prepared by dissolving solids (18-crown-6-ether) or diluting liquids (acetic acid) of analytical grade in water. The electrolytes were made by mixing the stock solutions with water. The optimized electrolyte solution contained 20 mM of acetic acid and 1 mM of 18-crown-6-ether at pH of 3.1. In order to degas the solutions they were placed under ultrasound for 20 min.

Optimization of CE Separation

Electrophoresis conditions were optimized by changing the chemical composition of the electrolyte solutions containing imidazole, 18-crown-6-ether and organic dicarboxylic acid, its pH and ionic strength, but also by changing the instrumental conditions (capillary, injection, electric field and the C^4D detector parameters) in the on-line FI-CE instrument.

Samples and Calibration Mixtures

The samples were waters from three different water treatment apparatus, where the uses of the ion exchange cartridges were expired and needed

changing. The residue waters of the analyses were taken according to the instructions of the instrument manufacturer. Sampling volume was 100 mL. The waters were used without extra pretreatment, since they were taken through a 0.25 μm membrane in each instrument.

Stock solutions of the metal cations were prepared to 100 μg/mL by diluting their chloride salts with Milli-Q-water. The working solutions were diluted from the stock solutions with purified water to appropriate concentrations. The standard mixtures for concentration calibration were prepared from the individual stock solution at concentration levels of 0.01, 0.03, 0.1, 0.3, and 1 μg/mL and the blank sample (pure Milli-Q water). Water was tested with ICP-MS, IC-CCD, and CE-UV as routine laboratory QC tests at VTT.

The detection limit (LOD) of the cations were defined as the concentration at which the signal-to-baseline noise ratio (S/N) was 3. All the analyses were repeated 4–8 times if not otherwise stated.

Calculations

Concentration calibration was made with five concentration levels between 0.01 and 1 μg/mL. The results were obtained by the equation $y = a + b^{*}\ln(x)$, where y is the absolute peak area of the metal cation and x is the corresponding absolute migration time. The symbols a and b are the slope and the intercept, respectively. At calibration range of 0.01 mg/L−1.0 mg/L the (a;b) pairs for ammonium, potassium, calcium, magnesium, and sodium are $(5.4 \times 10^5;\ 1.2 \times 10^5)$, $(3.5 \times 10^5;\ 7.2 \times 10^4)$, $5.8 \times 10^5;\ 1.2 \times 10^5)$, $(1.1 \times 10^6;\ 2.6 \times 10^5)$, and $(7.1 \times 10^5;\ 8.1 \times 10^4)$, respectively. Electrophoretic mobilities were not used in calculations due to the acidic solution (pH 3.1).

A randomized measuring plan was used (Table 2) to observe the errors and variations during the sequences. All those experiments were

Table 2. Randomized program for calibration

Run	Concentration in μg/mL	Run	Concentration in μg/mL	Run	Concentration in μg/mL
1	water	7	1	13	0.01
2	0.03	8	water	14	1
3	water	9	0.1	15	0.1
4	0.01	10	0.01	16	0.3
5	0.3	11	0.1	17	0.03
6	0.3	12	0.3	18	0.03

carried out under +16 kV separation voltages with a 1.0 μA current for 10 minutes. Samples were introduced for separation by +5 kV injection voltages for 5 seconds.

RESULTS AND DISCUSSION

On-Line Capillary Electrophoresis

The study was conducted for two main goals: to build up a simple system for on-line complex formation of alkali metals, alkali earth metals, and ammonium by using a flow injection (FI) sample introduction with a constructed on-line capillary electrophoresis instrument (on-line CE) and a conductivity detector (C^4D), and to check the machine feasibility in on-line stability and reproducibility.

The literature mentions various CE techniques that have been used in analysis of reactions with 18-crown-6-ethers and UV-absorbing alkali metals (17) and analyses of UV-absorbing complexes concentrated by a sweeping technique by Terabe et al. (18). In addition, FI-CE was shown to be useful for some on-line monitoring applications (11,19). As far as we know, the instruments used in the experiments have not been demonstrated to work in simulated on-line process environments. To confirm the on-line potentiality, we have tested an on-line FI-CE instrument and identified the instrumental and methodological requirements needed for its utilization in a pilot scale.

The main issues for the construction of the FI-CE instrument were the liquid cooling and the sample injection. As mentioned above and shown in Fig. 1a, small PTFE tubing between two T-crossings is referred to as the inlet and the outlet part. The inner diameter of the tubing's are large enough to contain the capillary end and the electrode, but they were chosen to be as small as possible to obtain a small inlet (and outlet) volume. This is important in order to shorten the required time for electrolyte and sample replenishment. In our case, the system allowed the injection of the sample solutions (according to the procedure in the experimental section) without mixing the sample and the electrolyte inside the transfer tubing prior to the analyses. Thus, the detection limit is lower, because the sample is not diluted. However, with the use of two valves (Fig. 2) the samples were able to flow continuously. Further, there is no need for long flushing times, just the replacement of the sample and the electrolyte. With a more efficient liquid cooling system, compared to the air cooling, it was possible to obtain a stable background signal, and therefore, to determine the lower analyte concentrations.

Electrolyte Solution

A contactless conductivity detector (C^4D) allows the use of dilute electrolyte solutions. Due to the inconveniences to separate ammonia and potassium, 18-crown-6-ether (1 mM, cavity radius 1.38 Å (20)) was used to give a better resolution between them. It has been observed that crown ethers are ionophores that selectively bind alkali metal ions in solutions. The nature of the ion specificity is traditionally explained on the basis of matching the ion size with the cavity diameter of the crown ether. However, the solvent molecules play an important role in the ionophore selectivity. Vaden et al. (21) have studied 18-crown-6-ether with a few water molecules attached and noticed that the ligand is especially selective for potassium. It also effectively extracts other ions (Li^+, Na^+, K^+, Cs^+) from aqueous solutions. In the present study, 18-crown-6-ether was used as the modifier for the analytes and the electrolyte solution.

Acetic acid (20 mM) had a double-fold role, since it was supposed to act as a buffering chemical in the background electrolyte (pK_a 4.756, mobility -42.4×10^9 $m^2V^{-1}s^{-1}$) and perhaps to build the complex structures to complete their stability in acidic solution. To our knowledge, the two mentioned terms can not be separated, since it is not truly explained to exclude interactions between electrolyte chemicals and analytes. To date, three possible factors have been reported to modify the mobilities of alkali and alkaline earth metal and ammonium cations: complex formation of cations with electro-neutral cyclic polyethers, solvation/complex formation with organic compounds, and ion-pair formation with anionic ligands.

Lin et al. (22) studied the role of organic acids (e.g., acetic acid, glycolic acid, lactic acid, succinic acid, oxalic acid, and α-hydroxyisobutyric acid) added to an imidazole-based electrolyte solution in the separation of alkali and alkaline earth metal cations. They noticed that the preparation of the imidazole (pK_a 6.95 (23)) modified electrolyte made from dicarboxylic acids, gave the best resolution for the analytes. However, our studies showed that better sensitivity and selectivity was achieved not using imidazole but an acetic acid solution together with 18-crown-6-ether. We noticed in our on-line FI-CE studies that mixtures of 2,6-pyridine dicarboxylic acid together with pyridine (pK_a 5.25, (23)) or 18-crown-6-ether affected the results by making the analyses non-reproducible and by forming different metal species. As to our studies, we conclude that acetate forms cationic ion-pairs with at least calcium and magnesium, resulting in changes in separation selectivity and in electrophoretic mobilities in pyridine – glycolic acid – 18-crown-6-ether electrolyte mixtures (data not shown, but simultaneous separations have earlier been presented in refs. (1,24)).

Electrophoretic Separations

According to the assumption, in off-line mode analyzed complex formation of the metal cations with electrolyte chemicals may lead to various kinds of complexes as noticed in on-line mode during the present study. In MDQ CE instrument (off-line) different sample and electrolyte introduction ways were studied and their influence on the analyses was noticed. The electrolyte and the sample with FI were steered to move into the capillary, both in the same and in the opposite directions with variable solvent flow speeds in the capillary.

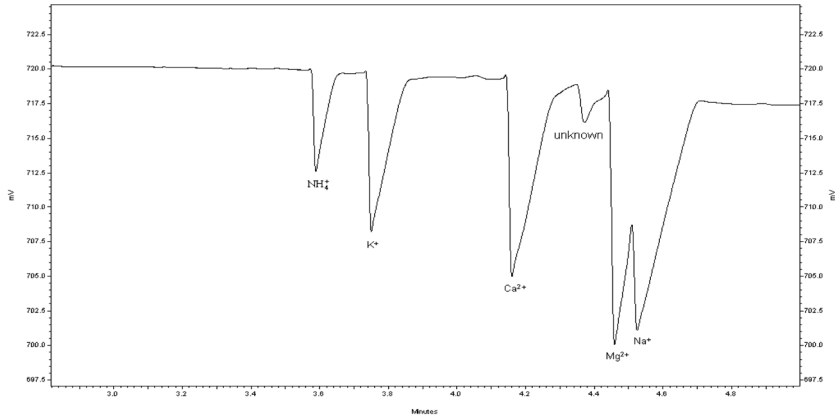
The idea of a FI-analogous flowing system solved this problem. No extra equipment was needed to perform the FI technique in the on-line capillary electrophoresis. It could be shown that the separation worked without air bubbles sticking in tubing, capillary, or electrodes. With an ideal construction of thin and short tubing between the inlet and the valves, and FI time less than one minute, the pre-treatment of the sample can be achieved before the injection. This is an advantage when the sample flows continuously or it is taken from a running process. With the optimized parameters our on-line system gave good results. As presented in Fig. 3, a stable baseline and a good resolution for the metal cation complexes in on-line mode could be obtained. Due to the on-line CE modification, the results obtained in MDQ CE (off-line) and those in on-line FI-CE instrument could be very well compared (Figs. 3a and 3b), giving simultaneous migration profiles. In the studies, the compounds were identified by a standard addition technique.

The migration order of the metal cations in optimized electrolyte solution containing 20 mM acetate and 1 mM 18-crown-6-ether was ammonium, potassium, calcium, magnesium and sodium. The migration order could not be explained by their atomic radii that are 1.51, 1.38, 1.00, 0.78, and 1.02, respectively (20).

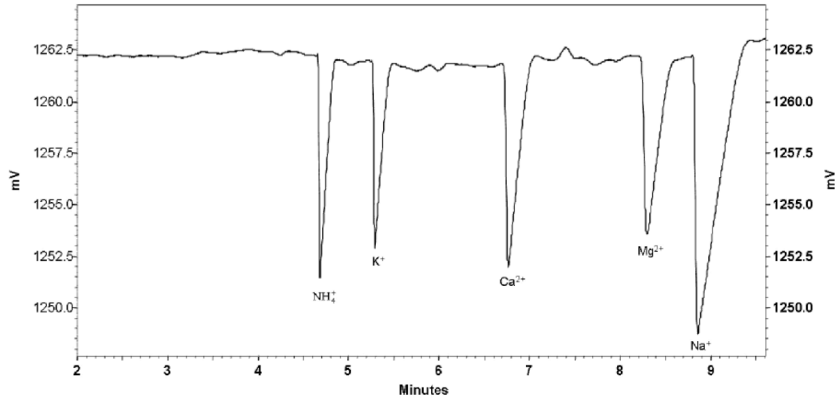
The migration orders of monovalent ions, $NH_4^+ < K^+ < Na^+$ and the divalent ions, $Ca^{2+} < Mg^{2+}$, are always the same independent of the complexing agent, but their interrelated migration order can be changed on the basis of the ligand. Linear correlation between the migration times of the metal cations in MDQ and on-line FI-CE analyses were obtained (R^2 0.9892). The method was very sensitive due to the instrumentation of sample introduction. Overloading was noticed already at 5 μg/mL metal concentration level.

Validation Data

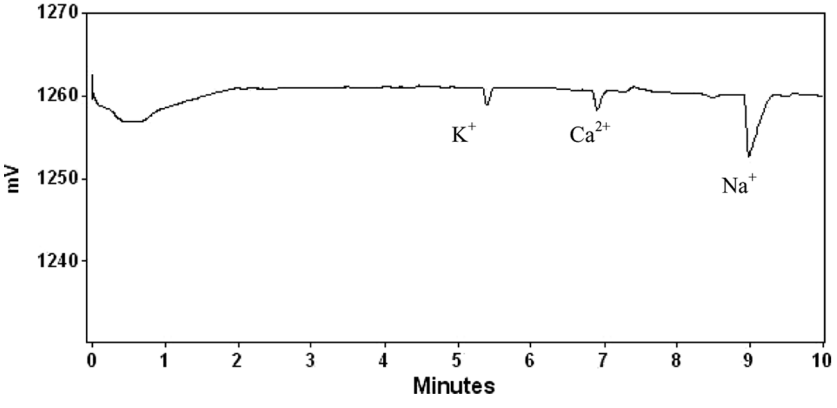
The repeatability of the analyses within a day and from day to day was examined. The final sample mixture contained 0.03 μg/mL of NH_4^+,



(a)



(b)



(c)

K^+, Ca^{2+}, Mg^{2+}, and Na^+ solution with Cl^- as the counter ion. The data was analyzed by using the migration times, peak areas and peak heights of each ion.

Table 3 shows the data of the one-day- and two-day-experiment with eight analyses. We obtained required yields for the migration times of the examined complexes. The RSD is below 1% (for one day). For peak area and peak height the resulting values varied. When comparing the two days results, the RSD of the migration times were between 1.4% and 2.2%. Fig. 4 shows the measured migration times of the ions assembled for both days.

Both Kubán et al. (13,24–27) and Chen et al. (28) have investigated the parameters that affect the performance of the hyphenated FI-CE system. Both groups found that the sample volume and the carrier flow rate of the FI system had a significant effect on the separation efficiencies and the sensitivity of CE. In our study, we observed that in the FI technique with an on-line CE instrument the most important parameters were the temperature stability during the analysis and the sample concentration. All detected data could be identified down to concentration 0.01 μg/mL. The limit of detection for the analytes was 0.01 μg/mL (S/N 3).

In the range of significant varieties, a regression was accomplished for the peak area and the migration time of every ion using logarithmic fitting ($y = a + b^*\ln(x)$). The peak area was chosen for calculations because it was noticed that peak shapes (widths and heights) differed depending on the temperature control of the capillary. Calibration curves over a concentration range of two orders of magnitude could be achieved. The correlation

Figure 3. a. MDQ-electropherogram of the separation of a 0.03 µg/mL sample (NH_4^+, K^+, Ca^{2+}, Mg^{2+}, Na^+) with 5 sec injection at + 5 kV; separation voltage + 15 kV (CZE and normal polarity), fused-silica capillary, L_{tot}/L_{det}: 60 cm/43 cm, 50 µm i.d., 375 µm o.d.; Electrolyte: 20 mM acetic acid - 1 mM 18-crown-6-ether (pH = 3.1); contactless conductivity detection is described in Experimental; b. On-line-electropherogram of the separation of a 0.03 µg/mL sample (NH_4^+, K^+, Ca^{2+}, Mg^{2+}, Na^+) with 5 sec injection at + 5 kV; separation voltage + 16 kV (CZE and normal polarity), fused-silica capillary, L_{tot}/L_{det}: 50 cm/43 cm, 50 µm i.d., 375 µm o.d.; electrolyte: 20 mM acetic acid - 1 mM 18-crown-6-ether (pH = 3.1); contactless conductivity detection is described in Experimental; c. On-line-electropherogram of the separation of a purified water sample (Milli-Q) with 5 sec injection at + 5 kV; separation voltage + 16 kV (CZE and normal polarity), fused-silica capillary, L_{tot}/L_{det}: 50 cm/43 cm, 50 µm i.d., 375 µm o.d.; electrolyte: 20 mM acetic acid - 1 mM 18-crown-6-ether (pH = 3.1); contactless conductivity detection is described in Experimental.

Table 3. Single-day (a sum of 8 runs) and between-day experiments (sum of 16 runs) with 8 runs in succession a day with the 0.03 μg/mL sample and proposed method in Fig. 4

Ion	Label	Average	SD	RSD (%)
NH_4^+	day 1	4.7	0.037	0.79
	day 2	4.8	0.045	0.94
	total	4.75	0.066	1.4
K^+	day 1	5.29	0.049	0.93
	day 2	5.41	0.064	1.2
	total	5.35	0.083	1.55
Ca^{2+}	day 1	6.77	0.056	0.83
	day 2	6.93	0.083	1.2
	total	6.85	0.108	1.57
Mg^{2+}	day 1	8.3	0.082	0.99
	day 2	8.6	0.121	1.41
	total	8.45	0.184	2.18
Na^+	day 1	8.89	0.082	0.92
	day 2	9.17	0.168	1.83
	total	9.03	0.192	2.13

coefficients for the alkali metals and alkaline earth metals as well as for ammonium, sodium, and calcium were between 0.93 and 0.99.

The instrument was used for determination of cations as their complexes in waters were taken from different water pretreatment apparatus. Very small amounts of potassium, calcium, and sodium were noticed in the samples (Fig. 3c) that indicated that the reliability and sensitivity of the on-line FI-CE instrument with a conductivity detector was very good. The results showed that the instrument can be used to monitor the need to change the ion exchange cartridges if there are no other markers

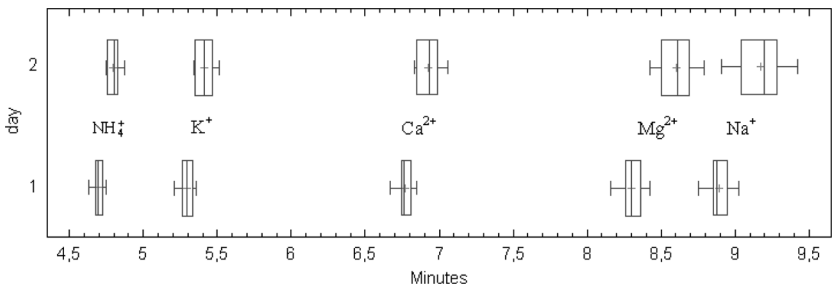


Figure 4. Box-and Whisker Plots of the inter-day-experiment. Conditions as in Fig. 3b.

available. The study showed the performance of the sensitive CE method in purity control in water treatment.

CONCLUSIONS

The study presents basic ideas for on-line CE and how to instrument a machine for using hyphenated flow injection (FI) sample introduction to an on-line performing capillary electrophoresis instrument: a conceptional prototype with a simple and robust construction. On-line performance of on-line capillary electrophoresis in analyses of metal complexes with an on-line performing flow injection sample introduction was studied. With a conductivity detector it was easy to optimize the composition of the electrolyte solution, a simple mixture of two compounds (18-crown-6-ether and acetic acid) in a low concentration and to obtain good resolution for the alkaline and alkaline earth metal complexes. Further, with the installation of a liquid cooling system the results were reproducible and well comparable with those obtained by an off-line CE. As low as 10 ng/mL concentrations could be detected from purified laboratory waters.

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