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Rapid inorganic ion analysis using quantitative microchip capillary electrophoresis

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Abstract

Rapid quantitative microchip capillary electrophoresis (CE) for online monitoring of drinking water enabling inorganic ion separation in less than 15 s is presented. Comparing cationic and anionic standards at different concentrations the analysis of cationic species resulted in non-linear calibration curves. We interpret this effect as a variation in the volume of the injected sample plug caused by changes of the electroosmotic flow (EOF) due to the strong interaction of bivalent cations with the glass surface. This explanation is supported by the observation of severe peak tailing. Conducting microchip CE analysis in a glass microchannel, optimized conditions are received for the cationic species K^+, Na^+, Ca^{2+}, Mg^{2+} using a background electrolyte consisting of 30 mmol/L histidine and 2-(*N*-morpholino)ethanesulfonic acid, containing 0.5 mmol/L potassium chloride to reduce surface interaction and 4 mmol/L tartaric acid as a complexing agent resulting in a pH-value of 5.8. Applying reversed EOF co-migration for the anionic species Cl^-, $SO_4{}^{2-}$ and $HCO_3{}^-$ optimized separation occurs in a background electrolyte consisting of 10 mmol/L 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES) and 10 mmol/L HEPES sodium salt, containing 0.05 mmol/L CTAB (cetyltrimethylammonium bromide) resulting in a pH-value of 7.5. The detection limits are 20 μmol/L for the monovalent cationic and anionic species and 10 μmol/L for the divalent species. These values make the method very suitable for many applications including the analysis of abundant ions in tap water as demonstrated in this paper.

Keywords: Microchip; Capillary electrophoresis; Inorganic anions; Inorganic cations; Water analysis

1. Introduction

Rapid analysis methods are desired for industrial in-line process control. Specifically, capillary electrophoresis (CE) offers unique capabilities in miniaturized measurement systems. Here we discuss the aspects of inorganic anion and cation quantitation in drinking water. Since conventional capillary electrophoresis has already been proven as a fast and high-resolution separations technique for the determination of as many as 27 different metal species [1] as well as 30 organic and inorganic anions [2], we demonstrated that this separation method can be applied to drinking water analysis using a microchip [3]. The aim of this work is to establish the application of microchip capillary electrophoresis as a quantitative, extremely fast separation method for the control of water purification plants.

Strict regulations on the maximum allowed concentration of many potential contaminants guarantee that tap water is safe for consumption, i.e., the United States Environmental Protection Agency, for example, has listed over 80 species in the National Primary Drinking Water Regulations [4]. Similar lists have also been compiled by the European Union and the World Health Organization [5,6]. Besides the harmful substances on these lists, which need to be determined at very low concentration levels, the exact concentrations of constituents present at higher concentrations are of interest, too. These include potassium, sodium, calcium, magnesium, chloride, sulfate and bicarbonate. High concentrations of these species affect the taste of drinking water but too low amounts of sodium or calcium are considered unhealthy while the calcium and bicarbonate concentration also affect how corrosive tap water is to the plumbing system [7].

Particularly, alkali metals are used for benchmarking of the performance of microchip CE devices with conductivity detection [8–11]. Until today, however, only few publications give

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details about quantitation requirements using microchip CE [9,12–14], which indicates that quantitation is not trivial.

Next to the need for quality control, water supply companies also monitor the water softening process by the determination of water hardness, which is predominately formed by the amount of calcium and magnesium. Alternatively to separation by capillary electrophoresis, ion selective electrodes can be used for the determination of calcium and magnesium. However, ion selective electrodes are commercially available only for a limited number of species. Therefore, microchip CE is a valuable addition to the established analytical methods to determine water quality because it can be used to measure many water constituents simultaneously.

In the case of drinking water monitoring, a choice has to be made whether to determine cations and anions in separate CE runs or to analyze them in a single separation. For many inorganic ions, that typically have electrophoretic mobilities exceeding the opposing EOF it is not possible to use the EOF counter migration approach. Still a simultaneous analysis can be performed by injecting sample into both ends of the separation capillary. The cations and anions migrate to opposite ends and are detected in the middle of the capillary [15–18]. Alternatively, a chip can be designed with a channel layout that allows the sample plug to be introduced in the middle of the separation capillary, with subsequent detection at both ends [19]. A disadvantage of these two methods for simultaneous analysis is that only half the electrical field is used for the separation, which reduces the separation resolution. Lab-on-a-chip technology makes it possible to fabricate CE chips with multiple parallel separation channels on a single device and operate these simultaneously. Consequently, the separation of both anions and cations in a single separation run is not a demanding requirement.

This work establishes therefore the separation of anionic and cationic species in two independent chip analysis protocols achieving maximal performance for both types of species. The separation of calcium and magnesium from sodium in the cationic mode is optimized using complexing agents to modify the electrophoretic mobilities of the ions. The separation of anionic species is performed with EOF co-migration using CTAB to reverse the direction of the EOF [20].

2. Experimental

2.1. Chemicals

Calibration solutions for the cationic species were prepared by dissolving the chloride salts of sodium, potassium, calcium (Merck, Darmstadt, Germany) and magnesium (Baker, Deventer, The Netherlands) in deionized water (Millipore, Molsheim, France). Mixtures of the four species were prepared in the range of 0.1–2 mmol/L. The anionic calibration standards were prepared from sodium sulfate (Aldrich, Milwaukee, WI, USA), sodium bicarbonate and sodium chloride (Merck). The background electrolyte (BGE) for the cation separation was prepared from 2-(*N*-morpholino)ethanesulfonic acid (MES, Sigma, Steinheim Germany), histidine (His, Fluka, Buchs, Switzerland) using tartaric acid (Baker) and potassium chloride (Merck) as BGE modifiers for optimization of the separation performance. The anionic BGE was composed of 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES, Merck), HEPES sodium salt (Aldrich) and cetyltrimethylammonium bromide (CTAB, Fluka) as EOF modifier. Rhodamine B (Sigma) dissolved in the BGE was used as an EOF maker. The water sample was domestic tap water from the city of Enschede (Vitens, Velp, The Netherlands).

2.2. Microchip CE system

Borofloat glass chips (Fig. 1) with a double-T injector of 200 μm length were obtained from Micronit Microfluidics (Enschede, The Netherlands). All channels were etched to a depth of 8 μm and a width at the top of the channel of 56 μm using hydrofluoric acid. The effective length of the separation channel (from the double-T injector to the detection electrodes) is 2 cm. The electrodes for conductivity detection consist of thin platinum films in direct contact with the electrolyte inside of the channel. Before the chips are used for the first time they are heated in an oven for 1 h at 600 °C, which improved the separation resolution of the cations under consideration. To perform electrophoresis experiments the chips were placed in a holder made from Delrin consisting of a bottom support plate and a cover with fluid compartments. Platinum wires inserted into the compartments provided electrical contact to a high-voltage power supply (CU 411, IBIS Technologies, Hengelo, The Netherlands) with four computer controlled positive voltage outputs. Spring-loaded connection pins assembled in the

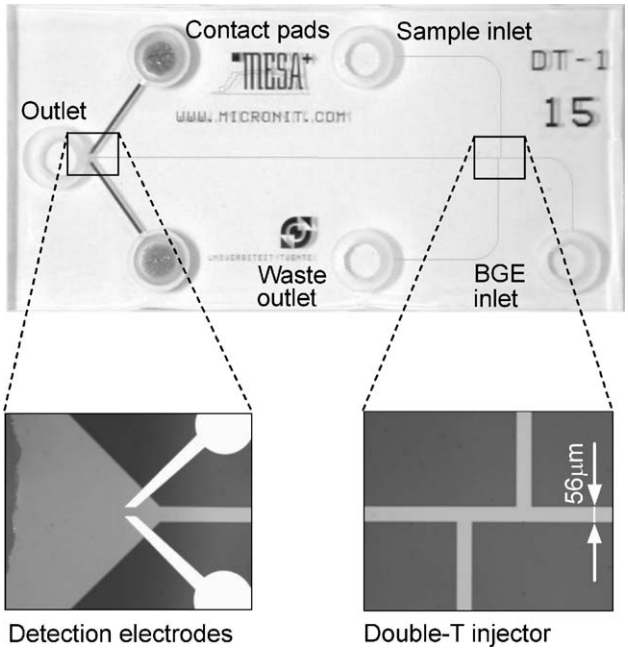

Fig. 1. Photograph of the CE microchip with dimensions of 30 mm × 15 mm. The insets show the position of the electrodes used for the conductivity detection and the channel intersection defining the sample plug.

Delrin holder were used to connect the conductivity detector electronics (Sprenkels Consultancy, Lelystad, The Netherlands) to the integrated contact pads on the microchip. The signals were recorded with a data acquisition card (DAQCard 6036E, National Instruments, Austin, TX, USA) using a personal computer. An in-house written software package combined the control of the power supply, acquisition of data from the detector and the subsequent data processing.

2.3. Separation of cationic species

The chip was filled manually with BGE and sample solution. To optimize the separation performance the BGE consisting of 30 mmol/L MES/His was modified with tartaric acid in the range of 0–5 mmol/L, resulting in a pH of 5.8–6.1. Additionally, the separation resolution was determined in the presence of 0.5 mmol/L potassium chloride and compared to the results without this BGE modifier. A pinched sample plug was formed using full plug shaping [21]. Here, sample is pumped through the double-T by applying 1000 V to the sample inlet and 0 V to the waste outlet (see Fig. 1). Simultaneously, pinching is performed by applying 800 V to the BGE inlet and 1000 V to the outlet for 60 s. The content of the double-T is injected into the separation channel and separated by switching the voltage to 1000 V at the BGE inlet, 0 V at the outlet and 600 V at the sample inlet as well as at the waste outlet. This separation protocol is continued for 60 s.

2.4. Separation of anionic species

The separation of anionic species was investigated at a pH of 7.5 using a BGE containing 10 mmol/L HEPES and 10 mmol/L sodium HEPES. The concentration of the EOF modifer, CTAB, was varied in the range of 0–0.2 mmol/L to optimize anionic EOF co-migration. The sequence of voltages used for separating cations is also used for the anions (Section 2.3) but with reversed polarity.

2.5. Determination of the electroosmotic flow velocity

To determine the EOF for various CTAB concentrations a solution with 1 mmol/L rhodamine B was dissolved in the anionic BGE and used as neutral fluorescent marker. The rhodamine solution was placed in the BGE inlet compartment (Fig. 1) while the rest of the chip was filled with BGE without the marker. A constant potential of 1000 V applied between the BGE inlet compartment and the outlet compartment was used to drive the rhodamine solution through the chip by electroosmotic pumping. The two remaining chip compartments were not connected to the voltage supply. A fluorescence microscope (Leica DM/IRM, Wetzlar, Germany) with a 100 W mercury lamp filtered through an I3 filter cube (Leica) was used for visualization of the rhodamine. The fluorescence intensity was measured at the end of the separation channel with a photosensor module (H7422-02, Hamamatsu, Japan) attached to the microscope. The EOF velocity was subsequently determined by the time at which the marker reached the detection point.

3. Results and discussion

3.1. Formation of a representative sample plug

When a sample plug on a microchip is defined by the volume of the channel intersection using full plug shaping as described in Section 2.3 the composition and the volume of the plug depends on the EOF velocity and direction, sample loading time, and mobility induced bias [14,22]. To transfer a representative sample from the reservoir to the channel intersection within a (semi)continuous monitoring system, a first requirement is to fill the intersection with sample being transported by the elctroosmotic bulk flow. Another requirement for representative plug forming is that the plug volume should be independent of the resulting EOF and the composition of the sample. However, we found that the latter requirements cannot be realized under experimental conditions on the microchip. Therefore, we investigated the use of microchip CE in quantitative water monitoring in greater detail.

It is desired to measure cationic and anionic constitutes in the water sample as described in Section 1. Since the microchip system takes the advantage of performing rapid separations we chose for both, the cationic and anionic constitutes, to operate in the co-migration mode. The CE operation, therefore, can be optimized using two independent analysis procedures which are described in Sections 3.2 and 3.3.

In order to form a representative plug for anionic sampling, the direction of the EOF needs to be reversed. Therefore, a small amount of the cationic surfactant CTAB is added to the BGE [20]. Adsorption of CTAB micelles onto the capillary surface results in the formation of a layer with positive charge causing a reduction or even a complete reversal of the EOF [23]. Fig. 2 shows this dependency of the EOF mobility on the CTAB concentration added to the BGE for our system. A CTAB concentration between 25 and 50 μmol/L already reverses the EOF in the used chip system. Further increasing the CTAB concentration to 0.1 mmol/L causes the electroosmotic mobility to stabilize at a value of approximately -3.5×10^{-4} cm^2/V s. This is almost as high as the electroosmotic mobility of $+4.2 \times 10^{-4}$ cm^2/V s

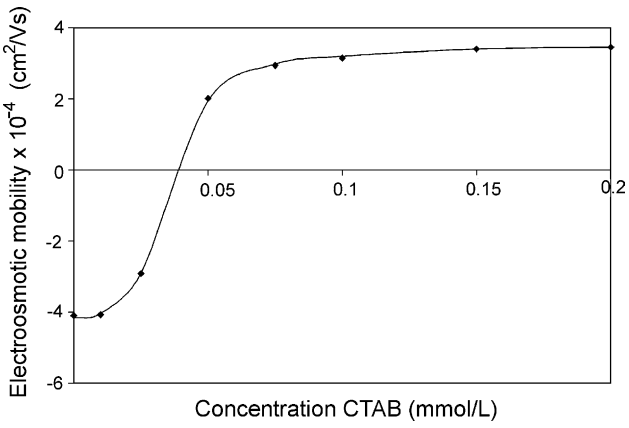

Fig. 2. Effect of the CTAB concentration on the EOF. Applying reversed EOF co-migration using a background electrolyte consisting of 10 mmol/L HEPES acid and 10 mmol/L HEPES sodium salt (pH 7.5).

Table 1
Typical concentration of selected inorganic ions in tap water, analysis results of a tap water sample and detection limits of the system

	Specified in tap water mg/L (mmol/L)[a]	Maximum allowed concentration mg/L (mmol/L)[b]	Determined in tap water (mg/L) (±2SD)	Detection limit (mg/L, mmol/L)
K^+	4.6 (0.12)	Not specified	n.d.[d]	n.d.[d]
Na^+	25 (1.1)	150 (6.52)	34.0 ± 1.3	0.46 (0.02)
Ca^{2+}	48 (1.2)	(1–2.5)[c]	59.2 ± 3.0	0.40 (0.01)
Mg^{2+}	5.7 (0.23)	(1–2.5)[c]	4.33 ± 0.32	0.24 (0.01)
Cl^-	44 (1.2)	150 (4.23)	50.8 ± 2.1	0.71 (0.02)
SO_4^{2-}	46 (0.48)	150 (1.56)	45.7 ± 2.9	0.96 (0.01)
HCO_3^-	112 (1.84)	Minimum 60 (0.98)	119 ± 4.0	1.2 (0.02)

[a] Annual average concentrations over 2003 in Enschede, The Netherlands.
[b] Values according to Dutch legislation.
[c] Combined concentration of Ca^{2+} and Mg^{2+} should be within these limits.
[d] Not determined due to overlap with the system peak.

generated by the bare glass surface, but with opposite sign. The effect of the EOF modifier on anionic separation performance is discussed in Section 3.3.

3.2. Separation of inorganic cations

Typically the most abundant cationic species in drinking water are the alkali and alkaline earth metals. Potassium, sodium, calcium and magnesium are present in the range of 0.1–1.5 mmol/L (Table 1). The first step for the determination of these species is the selection and subsequently the optimization of the BGE with respect to the resolution and the detection sensitivity of the system. Since conductivity detection is used the choice of the BGE has a large influence on the signal sensitivity. To achieve a high signal-to-noise ratio, the ionic conductivity of the BGE co-ion, which is directly related to the electrophoretic mobility, should differ from that of the analytes as much as possible [24]. A BGE formulation that is frequently used in combination with conductivity detection, also for conventional CE, is a mixture of equimolar amounts of histidine and MES. Both compounds have relatively low mobilities, which make them perfect for analysis of high mobility ions. Furthermore, their pK_a values are almost identical making the BGE an excellent buffer.

However, for the separation of calcium, sodium and magnesium this BGE is not ideal because the electrophoretic mobilities of these compounds are too close together. Various reports can be found in the literature describing organic acids as complexing agents for improving the resolution in CE separations. These include oxalic acid, lactic acid, tartaric acid and hydroxyisobutyric acid [25–27], but also neutral substances like poly(ethylene glycol) [28]. For this study tartaric acid is selected, which has been used with success for separating similar samples on conventional systems [28]. For background electrolytes with varying concentrations of tartaric acid, the effective electrophoretic mobilities and separation resolution were determined using a calibration solution with 1 mmol/L potassium, sodium, calcium and magnesium (Fig. 3A and B). The most significant change in mobility is observed for calcium, while magnesium is only slightly affected. Baseline separation (resolution higher than 1.5) is achieved with a tartaric acid concentration of 3 mmol/L. For the remaining separations 4 mmol/L is used, which makes the system more robust for small variations in the effective electrophoretic mobility.

Despite a good separation performance for calcium and magnesium the resolution between potassium and sodium is still insufficient (Fig. 4A). In particular the peak formed by potassium is characterized by extensive tailing, increasing the spatial

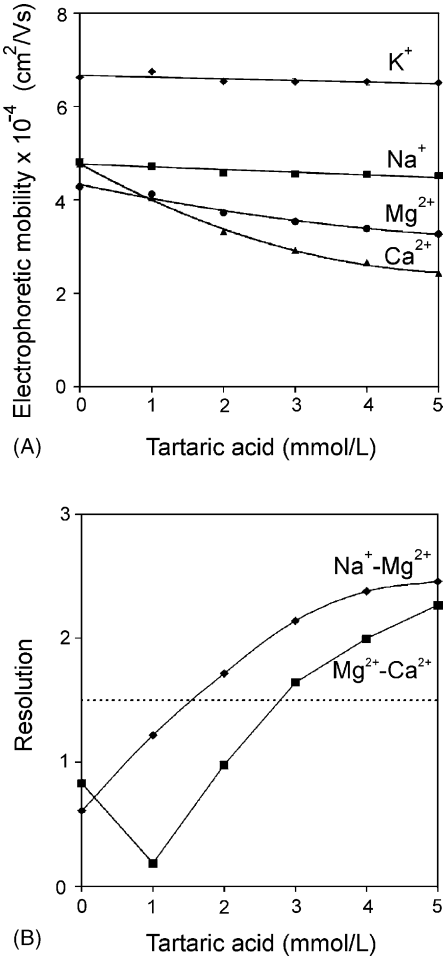

Fig. 3. Effect of the tartaric acid concentration in the 30 mmol/L MES/His, 0.5 mmol/L KCl background electrolyte (pH 5.8–6.1) on (A) the effective electrophoretic mobility of the cations and (B) the resolution between sodium and magnesium, and between magnesium and calcium. The sample consisted of a 1 mmol/L mixture of the four cations.

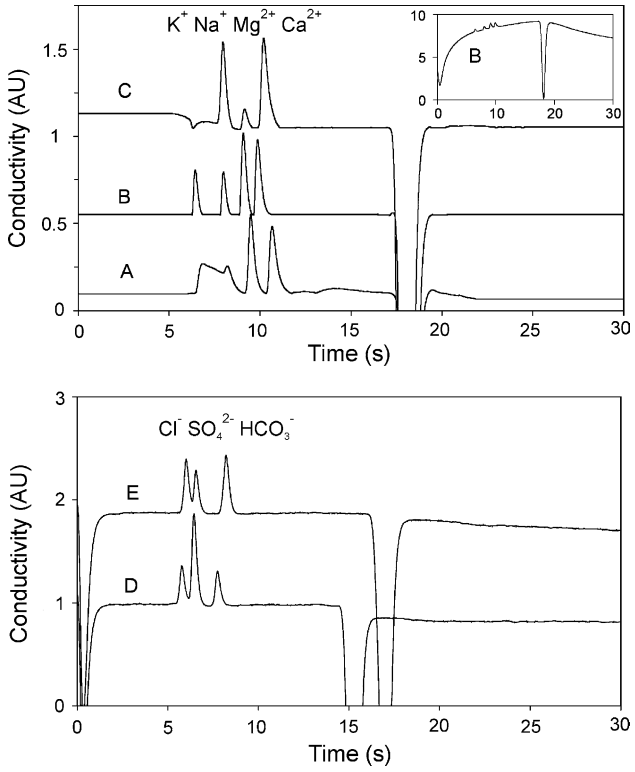

Fig. 4. Electropherogram of (A) a calibration solution consisting of 1 mmol/L K^+, Na^+, Mg^{2+} and Ca^{2+} using a BGE with 30 mmol/L MES/His and 4 mmol/L tartaric acid (pH 5.8), (B) the same calibration solution using a BGE composition as in (A) but with the addition of 0.5 mmol/L KCl and (C) a tap water sample in the same BGE as in (B). The electropherograms are corrected for baseline drift. The inset in the top figure shows the actual electropherogram for the calibration solution (B). The lower figure shows the separation of anionic species in a BGE of 10 mmol/L HEPES acid and 10 mmol/L HEPES sodium salt (pH 7.5) that contains 0.05 mmol/L CTAB. (D) Calibration solution comprised of 1 mmol/L Cl^-, SO_4^{2-} and HCO_3^- and (E) a tap water sample.

peak variance significantly. Such strong tailing behavior can be an indication that there is interaction of analytes with the glass channel surface. It is known that silica surfaces can act as an ion exchanger for inorganic cations allowing even a chromatographic separation [29]. A significant improvement of peak shapes was observed after adding a small amount of potassium (approximately 0.5 mmol/L KCl) to the BGE (Fig. 4B). We interpret the increase of performance by a saturation effect of the active sites on the glass surface, preventing further interaction of analytes with the surface. The detection sensitivity does not suffer from the small amount of potassium in the BGE as both the potassium and sodium peaks in the electropherograms became sharper and higher (Fig. 4A and B). However, the BGE system now has two co-ionic species instead of one, which can result in the occurrence of system peaks [30]. For example, a vacancy peak (i.e., a dip in the signal) can be expected near the position of potassium when there is only little potassium present in the sample affecting the ability for quantitation. Instead of KCl also the use of LiCl and CsCl as BGE additives were examined in order to shift the position of the system peak out of the time window in which the analytes migrate (electropherograms not shown here). Cesium also improved the separation resolution similar to potassium, but the electrophoretic mobility

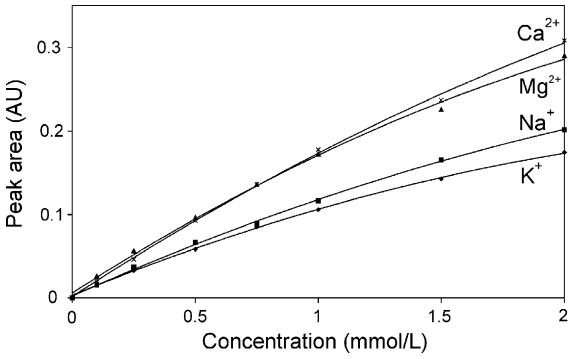

Fig. 5. Cation calibration curves. BGE 30 mmol/L MES/His, 4 mmol/L tartaric acid and 0.5 mmol/L KCl (pH 5.8).

is too close to that of potassium to prevent overlap of the system peak and potassium analyte peak. Alternatively, choosing a BGE modifier with a lower mobility than sodium, for example, lithium, is not sufficient to provide baseline separation of the analytes.

Concluding from these experiments the optimized BGE consists of 30 mmol/L MES/His, 0.5 mmol/L potassium chloride and 4 mmol/L tartaric acid. This system provides baseline separation of potassium, sodium, calcium and magnesium in less than 15 s.

After establishing the optimized conditions on the chip, the quantitative aspects for separating water samples can be examined. Calibration curves recorded for the cationic species of interest show a non-linear behavior (Fig. 5). Several possible causes can lead to this non-linearity. First of all, the detector signal itself can be non-linear with the concentration. Yet, a calibration curve measured for sodium in the absence of the other components (data not shown) was linear to at least 5 mmol/L and also the calibration curves recorded for the anions were linear. Therefore, we conclude that the injected plug is affected by the composition of the sample leading to a non-linear relation between peak area and sample concentration. To discuss this matrix effect we consider that the length of the sample plug, which is mainly determined by the size of the double-T, can vary with the EOF velocity. Additionally, the peak area can also be affected by leakage of the sample from the side channels into the separation channel due to insufficient sample pull-back. Also the pinching of the plug is influenced by the combination of electric field strengths in all four channels. And as the sample matrix varies in conductivity, some variation in the field strengths will occur. Of all these factors we believe it is most likely that the EOF in the sample channel was altered by the sample composition itself since we already observed wall interactions resulting in the tailing of the potassium peak (Fig. 4A). Alkaline earth metals in particular interact with the glass surface and can have a marked effect on the EOF. The effect of metal species on the EOF follows the trend of affinity for cation exchange materials in the order of $Ca^{2+} > Mg^{2+} \gg K^+ > Na^+$. Adding small amounts as low as 5 mmol/L of the aforementioned constitutes to an electrolyte can already cause a reduction of the EOF to half of its original value [31]. When the EOF drops in the channel containing the sample, the pinching effect becomes

stronger since EOF in the remaining channels stays constant. Consequently, this leads to a smaller volume of the sample plug in the double-T when the concentration of Ca^{2+} and Mg^{2+} in the sample increases. A surface treatment minimizing the wall interaction with the sample or a weaker pinching of the sample plug might reduce this matrix effect.

3.3. Separation of inorganic anions

Anionic species are separated on the same type of chip as used for the cations. However, as stated in Section 3.1, the electrolyte and EOF conditions have to be modified. A HEPES BGE with a pH of 7.5 is used to maintain a pH above the pK_a of 6.4 for bicarbonate. Again the buffer system is selected with the requirement of a low co-ionic mobility for sensitive conductivity detection. For the separation of bicarbonate, chloride and sulfate it was established that a moderate EOF at a concentration of 50 μmol/L CTAB offered better resolution than separation conditions using a faster EOF. However, operating in the sloped region of the EOF velocity curve can result in a less stable EOF velocity and hence less reproducible net migration time (see Fig. 2). For example, the different positions of the water peak in the electropherogram for a calibration sample compared to the one of tap water (Fig. 4D and E) visualize this effect. But with the easily identifiable water peak as reference it is possible to correct migration times of the individual ions for any variation in EOF velocity. Recording of the calibration curves with the optimized BGE show a linear behavior while repetitive runs over the course of more than 20 separations suddenly result in a decrease in the magnitude of the water peak indicating changes in the separation conditions. More importantly, the peak areas started to deviate from a linear dependence on the analyte concentration. Visual inspection of the chip indicated that the entrance of the channel in the sample compartment became blocked with a deposit. This problem appeared to be related to the use of this particular BGE system since for the cationic separations no problem with clogging was observed for more than 100 consecutive runs. Nevertheless, a series of calibration standards and samples can be run without any apparent performance shift before the chip must be cleaned.

3.4. Quantitation of inorganic ions in tap water with microchip capillary electrophoresis

Although the calibration curves of the cations depicted in Fig. 5 are not linear, quantitation is still possible. For the tap water sample shown in Fig. 4C and E the concentration of seven species was determined on the microchip (Table 1). With the exception of potassium the determined values are in good agreement with the average water composition given by the water company. Analysis of tap water showed that the sensitivity of the system is sufficient to detect sodium, calcium and magnesium, chloride, sulfate and bicarbonate.

The relative standard deviations of the determined peak areas for replicate separation runs ($n = 3$) are around 3%. Determination of potassium, which should be present at a concentration of approximately 0.1 mmol/L, was hindered by the dominating effect of the negative system peak produced by the presence of 0.5 mmol/L potassium in the BGE.

The detection limits were calculated based on three times the noise level of the baseline in the electropherograms obtained from a 100 μmol/L calibration standard (Table 1). For the alkaline earth metals calcium and magnesium, a detection limit of 10 μmol/L was reached and for the alkali metals sodium and potassium 20 μmol/L. Similarly, the detection limit was 10 μmol/L for chloride and bicarbonate and 20 μmol/L for sulfate. The stability of the system was examined during an entire day by separating a sample every 30 min. To mimic monitoring conditions at a water softening installation, the chip once filled with BGE and sample, was operated throughout an 8 h trial period. Over the course of 51 separation runs the area of the sodium peak increased with 7%, while the relative standard deviation of the peak areas is only 5%. Depending on the required accuracy only a single calibration per day can therefore suffice.

4. Conclusions

Microchip CE is a generic tool for fast ion analysis allowing separations within 15 s. A single chip design can be used for anion and cation separations after changing the BGE composition, the direction of the EOF and the polarity of the voltages. Together with the use of on-chip integrated conductivity detection a compact CE instrument is herewith feasible. At the moment the microchip system requires manual filling with BGE and sample. Since there is no defined cleaning or conditioning step before the start of each measurement there is a risk that the separating conditions change due to fouling. Especially in the anionic mode the results becomes irreproducible after 20 runs, while in the cationic mode the chip continues to operate stable.

An issue is the interaction of cationic species with the glass surface, causing extreme peak tailing and problems with EOF stability. The poor resolution between potassium and sodium can be resolved by adding a small amount of potassium to the BGE, but at the expense of producing an additional system peak. It is therefore recommended to use a surface coating for glass chips or a BGE modifier that reduces surface interaction and provides better EOF stability. The system presented in this paper offers sufficient separating performance and sensitivity for determining the concentration of abundant ions in tap water. Detection limits are 20 μmol/L for monovalent ions and 10 μmol/L for divalent ions. We therefore believe that microchip CE systems are a valuable addition to the established ion analysis techniques for water process control and related analytical fields of work.

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