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Short communication

## Capillary electrophoretic determination of inorganic anions in the drainage and surface water samples

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### Abstract

Capillary electrophoresis was used for separation and quantitation of several inorganic anions in the drainage and surface water samples from the region with extensive use of fertilisers. Baseline separation of 13 small anions including nitrite and nitrate up to the concentrations of 100 mg/l was achieved in less than 5 min. The electrolyte consisted of 3 mM  $K_2CrO_4$ , 30  $\mu M$  cetyltrimethylammonium bromide and 3 mM boric acid at pH 8. The method yielded precisions of 1.8–7.2% (RSD,  $n=10$ ) and detection limits from 4  $\mu g/l$  ( $Cl^-$ ) up to 500  $\mu g/l$  (citrate). The results of the CE method were compared to ion chromatography using water–acetonitrile (86:14) at pH 8.6 adjusted with NaOH as the mobile phase and consistent results were obtained. © 1999 Elsevier Science B.V. All rights reserved.

**Keywords:** Environmental analysis; Water analysis; Inorganic anions

### 1. Introduction

Capillary electrophoretic separations of small ions were first established by Jandik and co-workers [1–4] under the name capillary ion electrophoresis (CIE; Waters trade name Capillary Ion Analysis, CIA). Since then rapid growth of interest in CIE (CE at present) has been noted. Several other research groups have examined the potential of capillary electrophoresis (CE) in separations of small anions, evaluated different electrolyte systems and methods for analysis of different types of samples [5–11]. Extensive comparison of CE and ion chromatography (IC) has led to the conclusion that CE usually

provides shorter analysis times, higher resolution and consumes less electrolyte and sample solutions and can be advantageously used with large number of samples [12–16]. However, the importance of IC should not be underestimated since there are still limitations in precision, day-to-day repeatability and sensitivity of CE measurements. IC should therefore be viewed not as the technique competing with CE but more often as a supplementary technique [17,18]. In some cases and/or when analysing certain kinds of samples IC should be used instead of CE. The same also applies for CE.

Several research groups have focused on development of suitable electrolyte for analysis of small, usually inorganic, anions [5–11]. The separation is usually accomplished in co-electroosmotic mode after dynamic coating of the capillary with alkyl ammonium salt containing long alkyl chain such as

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cetyltrimethylammonium bromide (CTAB) [19–21], tetradecyltrimethylammonium bromide (TTAB) [20,21], OFM Anion-BT<sup>-</sup> [3] or macrocycles [22] resulting in electroosmotic flow (EOF) reversal. Indirect UV detection is preferably used since the majority of small anions lack suitable chromophores to be detected directly, though the separations of UV-absorbing inorganic anions have been demonstrated [23,24]. Among the electrolytes used for indirect UV detection, chromate [2–4] is the most preferred one due to its convenient mobility, high molar absorptivity and absence in waste majority of the samples. Alternative electrolytes containing derivatives of aromatic acids such as trimellitic [9], pyromellitic [11,25] or naphthalenedicarboxylic acids [11] can be used.

However, even if the parameters and behaviour of the analytes in an electrolyte system are known and have been documented the electrolyte composition is not universal and must be optimised with regard to the needs of analysis, sample composition, concentration of ions in the sample etc. [26–29].

In the following paper the development of a CE electrolyte system and method for the separation and quantitation of several inorganic anions in drainage and surface waters from the region with extensive use of fertilisers and different ways of cultivation is described. The method was optimised with respect to fully resolve high concentrations of nitrite and nitrate next to the other inorganic ions present in the samples.

## 2. Experimental

### 2.1. Chemicals

All chemicals were of reagent grade. Deionised water from Aqua-dem-2 (Aqua-Osmotic, Tišnov, Czech Republic) which was further purified on a Milli-Q RG (Millipore, Bedford, MA, USA) was used throughout. Anion stock solutions, 1000 mg/l, were prepared from the corresponding sodium or potassium salts. Working solutions were prepared by mixing the stock solutions in appropriate proportions and diluted with deionised water.

The working electrolyte was prepared daily from the stock solutions containing 600 mM potassium

chromate, 30 mM CTAB (5%, v/v, ethanolic solution) and 200 mM boric acid. The pH was adjusted with 100 mM NaOH. The electrolyte was filtered through the nylon membrane filter (13 mm, 0.45 μm, Chromatography Research Supplies, Addison, USA) and degassed prior to use.

### 2.2. Instrumental

All CE separations were performed on P/ACE 5010 CE system (Beckman Instruments, Fullerton, CA, USA). Polyimide coated capillaries (Polymicro Technologies, AZ, USA) of 75 μm I.D. were used. The total length of the capillaries was 57 and 67 cm, with the detection window burned 7 cm from the capillary end. A separation potential of 25 kV was applied during all separations. Samples were introduced either by the hydrodynamic or electrokinetic injection mode. Indirect UV detection at 254 nm was used. The electropherograms were evaluated using System-Gold software system (Beckman Instruments). Ion-exchange chromatography was performed on a HP 1050 liquid chromatograph (Hewlett-Packard) with an HP-IC ion-exchange column and water–acetonitrile (86:14) adjusted to pH 8.6 with NaOH. The mobile phase contained HP mobile phase additive.

## 3. Results and discussion

### 3.1. Choice of the electrolyte and evaluation of CE system

The analysed anions do not absorb in UV therefore indirect UV detection was selected. The electrolyte consisted of 3 mM K<sub>2</sub>CrO<sub>4</sub> (6 mM for evaluation of CE system) and 3 mM boric acid at pH 8 with 30 μM CTAB as the EOF modifier.

Capillary equilibration at the beginning of each day required a series of five runs to be accomplished before the migration times stabilised. After equilibration, evaluation of the CE method with respect to different injection modes, injection times and analyte concentrations was done. The evaluation was performed with the working solution containing three inorganic anions (Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>). Two injection modes, hydrodynamic and electrokinetic were com-

Table 1  
RSD values for hydrodynamic (HD) 5 s and electrokinetic (EK) 5 kV/7.5 s injection modes ( $n=5$ )<sup>a</sup>

Anion	RSD (%)					
	Migration time		Peak area		Peak height	
	HD	EK	HD	EK	HD	EK
Cl <sup>-</sup>	0.1	0.8	1.0	1.4	1.0	1.0
SO <sub>4</sub> <sup>2-</sup>	0.1	0.8	2.6	3.0	1.1	0.8
NO <sub>3</sub> <sup>-</sup>	0.1	0.8	3.0	4.4	1.6	1.3

<sup>a</sup> The highest RSD values are given. CE conditions: 6 mM K<sub>2</sub>CrO<sub>4</sub>, 3 mM H<sub>3</sub>BO<sub>3</sub>, 30 μM CTAB at pH=8.0.

pared in terms of precision and linearity of calibration curves.

Values in Table 1 are the highest relative standard deviation (RSD) values obtained and calculated during the system optimisation. In the system optimisation, an injection time of 2–10 s was used for hydrodynamic injection mode. Injection times of 1.5–7.5 s and an injection voltage of 1.5–7.5 kV were used for electrokinetic injection mode. Most of the calculated RSD values (90–95%) ranged from 0–0.1%, 0.3–2.0% and 0.2–1.0% for migration times, peak areas and peak heights, respectively.

Calibration curves for hydrodynamic and electrokinetic injection modes were measured for the three anions in the range 0–100 mg/l and compared. The calibration curve for hydrodynamic injection resulted in a linear relationship between peak area and concentration while the relationship between peak height and concentration was non-linear. The calibration curves for electrokinetic injection for both peak area and peak height were non-linear when plotted vs. concentration of the analytes. This phenomenon has been described by Huang et al. [30] and is caused by the “bias” in electrokinetic injection.

For any further analysis hydrodynamic injection of the samples and quantitation principle based on peak area vs. analyte concentration were used.

### 3.2. Choice of the experimental conditions for separation of NO<sub>2</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup>

With the commonly used electrolyte the comigration of nitrite and sulphate was observed. The electrolyte conditions were optimised in the follow-

ing concentration ranges: chromate 3–10 mM, boric acid 3–30 mM, CTAB 10–60 μM and pH 7.5–9.0. The optimum conditions found were 3 mM chromate, 3 mM boric acid and 30 μM CTAB at pH 8.0. Complete separation of chloride, sulphate, nitrite and nitrate at concentrations as high as 100 mg/l was achieved.

### 3.3. Repeatability and limits of detection (LODs)

With the above mentioned electrolyte the separation of 13 common inorganic and organic anions could be achieved in less than 5 min (see Fig. 1). The repeatability of migration times, peak area and peak height was evaluated for a standard solution containing 50 mg/l of 13 anions. The RSDs were calculated for 10 consecutive injections of the standard solution. The values are summarised in Table 2.

LODs, defined as three-times the signal of blank solution, were determined by consecutive dilution of the standard solution of the anions and are also summarised in Table 2. The detection limit depends on many parameters, such as electrolyte composition, voltage applied and the amount of the sample injected. For instance the increase in chromate concentration can considerably improve the detection limits however the separation efficiency of nitrite and nitrate is sacrificed. Alternative preconcentration methods such as sample stacking [31] or isotachophoretic preconcentration [32] can be applied for analysis of low analyte concentrations. The detection limits achieved with proposed method and electrolyte were suitable for major part of the analysed samples and further optimisation was not necessary.

### 3.4. Quantitative analysis of the drainage and surface water samples

The suitability of calibration curve and standard addition methods was evaluated for quantitative analysis of concentrations of the analysed ions. The calibration curve method can generally be applied with hydrodynamic injection in CE provided that the sample composition is similar to the composition of the standard solutions used for the calibration. The calibration curve method was applied for the analysis of tap water sample and drainage water samples. For

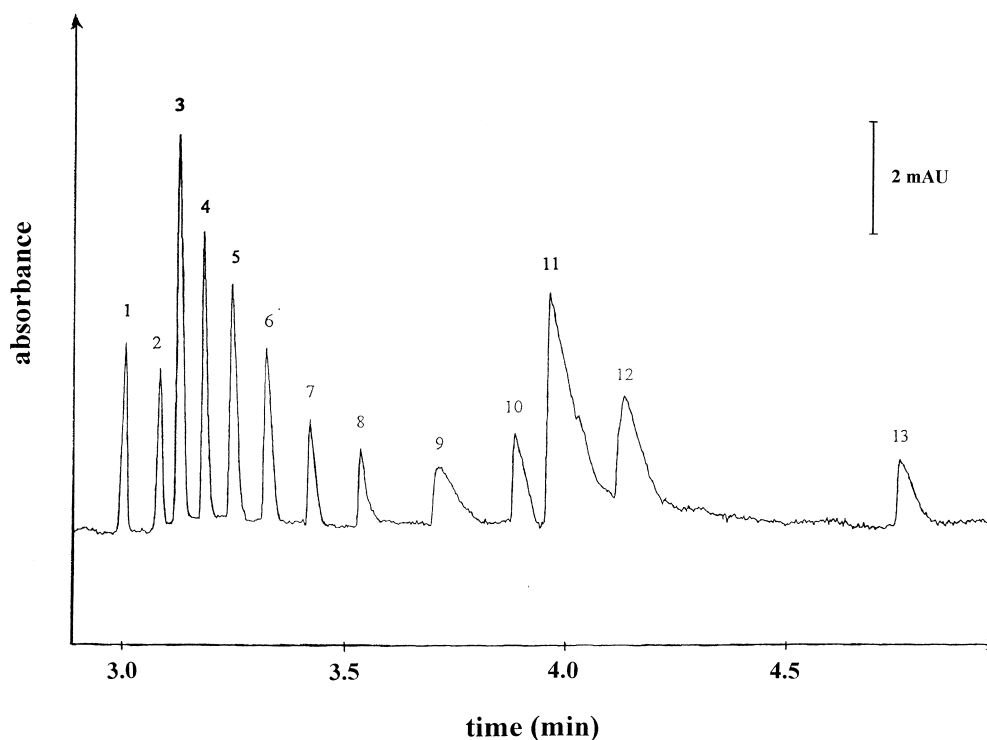


Fig. 1. Separation of 13 anions ( $c=50$  mg/l). CE conditions: 3 mM  $K_2CrO_4$ , 3 mM  $H_3BO_3$ , 30  $\mu M$  CTAB at pH 8.0. Hydrodynamic injection for 2 s, capillary length 50 cm. Peaks: 1= $S_2O_3^{2-}$ , 2= $Br^-$ , 3= $Cl^-$ , 4= $SO_4^{2-}$ , 5= $NO_2^-$ , 6= $NO_3^-$ , 7= $MoO_4^{2-}$ , 8= $WO_4^{2-}$ , 9=citrate, 10=fumarate, 11= $F^-$ , 12= $HPO_4^{2-}$ , 13= $HCO_3^-$ .

Table 2

LODs (calculated for peak heights) and RSD values for 13 anions<sup>a</sup>

Anion	LOD <sup>b</sup> ( $\mu g/l$ )	RSD (%)		
		Migration time	Peak area <sup>c</sup>	Peak height
$S_2O_3^{2-}$	250	0.1	1.8	1.2
$Br^-$	125	0.1	4.3	2.1
$Cl^-$	4	0.1	4.9	2.2
$SO_4^{2-}$	30	0.2	3.8	1.7
$NO_2^-$	125	0.1	5.0	1.9
$NO_3^-$	125	0.1	2.0	1.1
$MoO_4^{2-}$	250	0.1	4.6	0.9
$WO_4^{2-}$	500	0.0	7.2	2.1
Citrate	500	0.1	2.7	0.6
Fumarate	60	0.1	5.3	1.3
$F^-$	250	0.1	3.0	1.0
$HPO_4^{2-}$	250	0.1	3.4	1.2
$HCO_3^-$	250	0.1	7.2	0.7

<sup>a</sup> CE conditions: 3 mM  $K_2CrO_4$ , 3 mM  $H_3BO_3$ , 30  $\mu M$  CTAB at pH=8.0. Hydrodynamic injection time 7.5 s.

<sup>b</sup> LODs for IC were 0.5, 1.3 and 5.3  $\mu g/l$  for  $Cl^-$ ,  $SO_4^{2-}$  and  $NO_3^-$ .

<sup>c</sup> RSDs for IC were 2.1, 2.7 and 3.3% for  $Cl^-$ ,  $SO_4^{2-}$  and  $NO_3^-$ .

the analysis of the anions in the surface water samples the method of standard addition was used, since these samples are significantly different from the aqueous standard solutions. The results of the quantitative measurements are summarised in Table 3.

The surface water samples A–K were taken from different spots of the experimental field of the Forage Crop Institute, Vatin, Czech Republic. Different fertilisers were used for fertilising as well as different ways of land cultivation (temporary grassy land, arable land, fallow). Surface water samples A–K were collected from spots of 3 m<sup>2</sup> area. Drainage water samples DL and KL were taken in the depth of 300 mm (0.2 m<sup>2</sup> sampling area) by soil lyzimeters under the same localisation as the samples D and K. The sample of tap water P was taken in the same region. The results were compared with IC method using water–acetonitrile (86:14) adjusted to pH 8.6 with NaOH as the mobile phase. An electropherogram of the drainage water sample analysed by CE is depicted in Fig. 2. The concentrations of anions in

real samples were calculated as the mean value from 3 or 4 injections, the precision was better than 1.6% and 9.4% for CE and 0.6% and 8.3% for IC and for major and minor ions, respectively.

The use of fertilisers has minimal effect on the presence of the anions in the grassy land samples, however significant increase can be observed in the samples of the arable land (E, F). The amount of nitrate and nitrite has been found to be correlated to the use of fertilising method with particularly high concentrations of nitrate in the drainage water sample. On the other hand concentration of all anions in drainage water is significantly lower in the grassy land sample (DL). Grassy land acts as the “natural filtration media” (see D vs. DL and K vs. KL).

The analysis of tap water sample reveal rather high amounts of the nitrate (but still fulfilling the Czech State Norm CSN 75 7111) which could be attributed to the fact that the natural source of drinking water was analysed. The area where the natural source of drinking water is placed should be therefore cultivated with grass.

Table 3  
Content of anions in drainage and surface water<sup>a</sup>

Sample <sup>b</sup>	Concentration (mg/l)									
	Cl <sup>-</sup>		SO <sub>4</sub> <sup>2-</sup>		NO <sub>3</sub> <sup>-</sup>		NO <sub>2</sub> <sup>-</sup>		HPO <sub>4</sub> <sup>2-</sup>	
	CE	IC	CE	IC	CE	IC	CE	IC	CE	IC
A	0.2 <sub>5</sub>	0.3	0.2 <sub>5</sub>	0.2	0.6	0.65	0.1	0.15	1.1	1.0
B	0.5	0.5	7.2	7.0	1.2	1.1	ND	0.03	1.4	1.4
C	6.3	6.3 <sub>5</sub>	4.5	4.5	1.4	1.4	0.0 <sub>5</sub>	0.04	1.6	1.5
D	1.7 <sub>5</sub>	1.7 <sub>5</sub>	6.3	6.2	0.8 <sub>5</sub>	0.9	ND	0.01	1.8	1.9
E	4.3	4.2	3.8	3.8	7.7	7.5	ND	0.01	0.8	0.8
F	0.8	0.8	4.5	4.4	11.0	10.9	ND	0.02	0.3	0.2 <sub>5</sub>
G	3.6	3.5	4.0	3.9	1.8	1.8	ND	0.01	0.3	0.2 <sub>5</sub>
K	2.1	2.0	11.5	11.5	0.8	0.7 <sub>5</sub>	ND	0.01	2.5	2.4 <sub>5</sub>
DL <sup>+</sup>	29.2	29.7	8.4	8.3	23.5	23.4	ND	0.02	ND	0.05
KL <sup>+</sup>	23.3	23.5	38.3	38.0	145.0	143.2	ND	ND	ND	ND
P <sup>+</sup>	13.1	12.9	62.4	62.5	18.5	18.6	ND	0.03	296.0*	296.3*

<sup>a</sup> CE conditions: 3 mM K<sub>2</sub>CrO<sub>4</sub>, 3 mM H<sub>3</sub>BO<sub>3</sub>, 30 μM CTAB at pH 8.0, IC conditions: HP-IC ion-exchange column, water–acetonitrile (86:14), pH 8.6.

<sup>b</sup> A=Temporary grassy land (no fertiliser), B=temporary grassy land (dung+synthetic fertilisers), C=temporary grassy land (liquid manure+synthetic fertilisers), D=temporary grassy land (synthetic fertilisers), E=arable land (synthetic fertilisers), F=arable land (liquid manure+synthetic fertilisers), G=arable land (no fertiliser), K=fallow (no fertiliser), DL=drainage water collected in the spot D, KL=drainage water collected in the spot K, P=source of drinking water in Křižánky area, <sup>+</sup>=concentrations were determined from the linear part of calibration curves, ND=not determined (results down or equal to LODs, \*=HCO<sub>3</sub><sup>-</sup>).

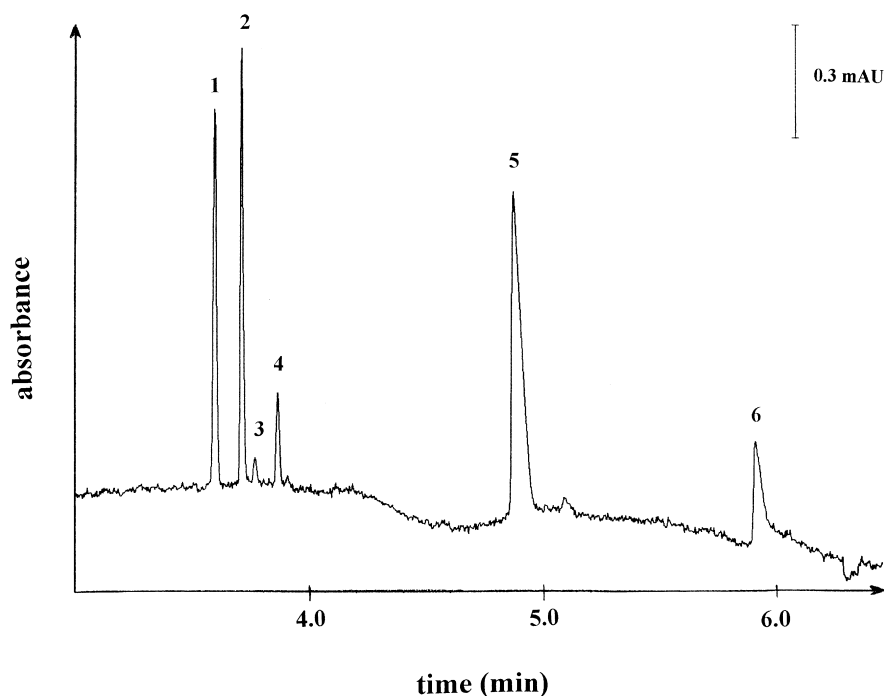


Fig. 2. Electropherogram of the drainage water sample. CE conditions: capillary length 60 cm, other conditions as in Fig. 1. Peaks: 1=Cl<sup>-</sup>, 2=SO<sub>4</sub><sup>2-</sup>, 3=NO<sub>2</sub><sup>-</sup>, 4=NO<sub>3</sub><sup>-</sup>, 5=HPO<sub>4</sub><sup>2-</sup>, 6=HCO<sub>3</sub><sup>-</sup>.

#### 4. Conclusions

The developed CE method for the analysis of small anions is fully suitable for the analysis of anions in the drainage and surface water samples. The results obtained by CE method were in excellent agreement with the IC method, which is commonly applied in the routine analysis. The CE method is two- to three-times faster than IC, provides higher separation efficiency and requires lower sample and electrolyte volumes and can be efficiently used as a rapid screening method. If high precision of the analysis and determination of extremely low quantities of some of the ions are required, IC should be preferred.

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