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# Environmental water monitoring by capillary electrophoresis and result comparison with solvent chemistry techniques

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## Abstract

The aim of this work was to determine inorganic ions from natural waters by capillary electrophoresis (CE) and to compare the results obtained with those measured with conventional solvent chemistry techniques. The project was part of a larger CE study, during which we measured inorganic ions from some lake and river systems and groundwaters in Southern Finland. Results obtained from contaminated Finnish waters were compared with samples from the River Rhine in the Düsseldorf area. Two CE methods were used for analysis: one for determination of chloride, sulfate, nitrite and nitrate at pH 7.7 and the other for ammonium, potassium, calcium, sodium and magnesium at pH 3.6, both methods using identification based on indirect UV detection. Two separation methods were used in order to prevent complex formation of metals with sulfate, hydroxide and decomposed organic matter present in the environmental samples. On the basis of the CE studies dilution was needed for those samples having more than 100 mg/l of sulfate, chloride, calcium and sodium. On average, the natural waters in the study contained ammonium, magnesium, sodium, potassium and calcium below 0.3, 20, 200, 20, and 200 mg/l, respectively. The concentrations of chloride, sulfate, nitrite and nitrate were below 20, 100, 10, and 10 mg/l, respectively. Correlation of the CE results with those acquired by titration, atomic absorption spectrometry, ion chromatography and flow injection analysis were obtained;  $R^2$  values for the comparison tests varied from 0.8816 to 0.9994 depending on the ion. The repeatabilities of the anion and cation CE methods were tested using laboratory-made reference sample mixtures with high and low salt concentration. © 2002 Elsevier Science B.V. All rights reserved.

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

## 1. Introduction

Inorganic and organic ions released to the environment may cause risks to the balance of nature. Nitrates and nitrites are involved in the eutrophication of water systems. Metals appear to contaminate the water supply systems (surface water and drinking water) and are found as concentrates in ecology systems [1–3].

Water soluble inorganic ions are mainly deter-

mined by flow injection analysis (FIA) with complexation, spectrometric techniques (atomic absorption spectrometry (AAS) or SP with complexation), titration (precipitation/acid–base titration) or ion chromatography [4]. Capillary electrophoresis (CE) has recently been used in these measurements not only because of its power of separation and detection based on the functionality of the compounds studied (e.g. molecular characteristics: acid–base properties, polarity, dissociation, solubility) [1–8], but also because of its speed, small sample and reagent volumes, resolution, selectivity and high throughput with automatization.

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The disadvantage of CE is that small ions are not detectable with UV detectors. Therefore, indirect detection methods are needed for monitoring them [5,6,9]. Because an indirect technique is not as sensitive as a direct one, good resolution of the ion zones in the separation medium and narrow sample zones are necessary for detection of the low levels of the ions in environmental samples. In particular, indirect UV identification demands optimal design of the detection system by choosing ions in the background electrolyte solution [10,11] on the basis of their high molar absorption: the dynamic range and linearity of calibration can be expected to increase with increasing concentrations of the UV-absorbing background ion.

This work was focused on the analysis of environmental water samples containing inorganic anions and cations from waters of river and lake systems, waters from pits and ions from waters sampled from contaminated areas. Also, waters from turf production areas were analysed as reference material to the contaminated water samples. The studies were part of a 4-year project to develop CE techniques for on-line monitoring of small anions and cations in process and environmental samples [6,8]. Determination of environmental waters is very challenging due to matrix interferences [6,12–14]. In our study, the results obtained with CE were compared with those analyzed by solvent chemistry instruments. However, the accuracy and repeatability of the methods are not discussed here. Contaminated waters in the River Kokemäenjoki basin in Finland were compared with those sampled in the River Rhine near Düsseldorf in Germany on the basis of the CE results.

## 2. Experimental

### 2.1. Instrumentation

A Beckman P/ACE 5000 CE instrument (Beckman Instruments, Fullerton, CA, USA) equipped with a UV detector (wave length 254 nm) was used for the analyses of the environmental water samples. The fused-silica capillaries (Composite Metal Services, The Chase, UK) were 77 cm long (separation length 70 cm × 50 μm I.D., 365 μm O.D.). The

applied voltage was 20 kV: reversed polarity for anions and normal polarity for cations. The samples were injected with a pressure of 0.5 p.s.i. (1 p.s.i. = 6894.76 Pa) for 5–20 s. The temperature was maintained at +25 °C with a liquid coolant system.

A Denver pH/conductivity meter Model 20 (Denver Instruments, Denver, CO, USA) was used for pH measurements. The pH combination electrode was calibrated using commercial standards of pH 4.00, 7.00 and 10.00 (Radiometer, Copenhagen, Denmark).

The equipments used as the reference for CE were an ion chromatograph (Dionex, USA), an atomic absorption spectrometer (Perkin-Elmer), a flow injection analysis system with a UV detector (Perkin-Elmer) and various pH meters (Radiometer) calibrated using the above mentioned standards for combination electrodes.

### 2.2. Materials

Pyridine, KNO<sub>3</sub>, KCl, CaCl<sub>2</sub> (96%), ammonia (25%) and imidazole were obtained from Merck (Darmstadt, Germany). Glycolic acid, HPCE electrolyte (pH 7.7), NaNO<sub>3</sub>, NaNO<sub>2</sub> and 18-crown-6 ether were from Fluka (Buchs, Switzerland). NaCl (99.8%) was from Riedel-de Haen (France) and Na<sub>2</sub>SO<sub>4</sub> and MgCl<sub>2</sub>·6H<sub>2</sub>O from J.T. Baker (USA). All reagents were of analytical grade.

### 2.3. Samples

The environmental waters were degassed with nitrogen and kept at +4 °C, except those obtained from Germany, which were kept frozen at –20 °C. The main samples (numbers 1–15, Table 1) were from South-western Finland (the River Kokemäenjoki basin, the centre of which was Tampere with a circular radius of ~100 km). As a reference we used surface waters from the River Rhine taken from the Düsseldorf basin in Germany (numbers D1–D6, Table 1). For CE measurements all 21 samples were first screened with CE and their concentrations were estimated (with two to three standards). When the peak resolution was not satisfactory (high ionic strength) or the ion zones were distorted, the samples were diluted 1:4, 1:10, 1:20 or 1:50 (v/v) (Table 1) with purified water (Milli-Q water, Millipore, Avon-

Table 1  
Samples and dilutions needed in the study

Environmental waters	Sample numbering	Dilution factor
Lake and river system (peat production area), Finland	1	Undiluted
	2	0
	3	Undiluted
River water (muddy area), Finland	4	Undiluted
	5	Undiluted
	6	Undiluted
	7	Undiluted
Lake water, Finland	8	1:10
Water from a well (built on a cold spring), Finland	9	Undiluted
Water of the River Kokemäenjoki, Finland	10	Undiluted
Contaminated waters from lake and river systems, Finland	11	1:20
	12	1:4
	13	1:10
	14	1:20
	15	Undiluted or 1:10 depending on the ion concentration
	River Rhine, Düsseldorf, Germany	D1
D2		1:10 or 1:50
D3		1:10 or 1:50
D4		1:10 or 1:50
D5		1:10 or 1:50
D6		1:10 or 1:50

dale, USA) and centrifuged or filtered through 0.45- $\mu$ m membranes (Millipore, Molsheim, France) to achieve better separation for quantification. The samples were not manipulated by pH adjustment or complexation, because we wanted to analyse them by simulating the natural water conditions as closely as possible.

CE quantification was performed with standard mixtures (Table 2) made of either the anions or the cations at their linear concentration levels (0.1–100

mg/l), except for ammonium which could be quantified at range 0.1–10 mg/l. The counter-ion in the standards was sodium or chloride in the anion and cation measurements, respectively. In all cases six-point calibrations were used. The samples were analyzed with at least four replicates and five injections of each sample in CE and with one or two replicates by the other methods.

#### 2.4. Background electrolyte solutions

In the optimised CE method the anions were separated in a buffer solution containing 2.25 mM pyromellitic acid, 6.50 mM NaOH, 0.75 mM hexamethonium hydroxide and 1.60 mM triethanolamine (pH  $7.7 \pm 0.2$ , Fluka, Buchs, Switzerland). The optimised CE separation of the cations was performed in 9 mM pyridine–12 mM glycolic acid–5 mM 18-crown-6 ether at pH 3.6, adjusted with 0.1 M HCl. The electrolyte solutions were ultrasonicated before use for 15 min.

#### 2.5. Conditioning of the capillary

The new capillaries were conditioned by purging

Table 2  
Concentration ranges of the standards in the measurements

Ion	Concentration range (mg/l)
Cl <sup>-</sup>	10–1000
SO <sub>4</sub> <sup>2-</sup>	5–870
NO <sub>2</sub> <sup>-</sup>	1–38
NO <sub>3</sub> <sup>-</sup>	1–85
Na <sup>+</sup>	5–1000
NH <sub>4</sub> <sup>+</sup>	0.1–10
Ca <sup>2+</sup>	1–1000
K <sup>+</sup>	0.5–100
Mg <sup>2+</sup>	0.5–100

Dilution of the sample was used if concentrations exceeded the linear range.

with 0.1 M NaOH for 10 min, with Milli-Q water for 10 min and with the background electrolyte solution in question for 10 min. Furthermore, between the analyses the capillary was washed with 0.1 M NaOH for 3 min and with the electrolyte solution for 3 min to keep the migration time of the analytes reproducible.

### 2.6. Standard mixtures

Pure chemicals were diluted in Milli-Q water to obtain 1000-mg/l stock solutions. The mixtures for capillary electrophoretic studies were prepared from the stock solutions to the concentrations needed. All mixtures were ultrasonicated daily before use. The stock solutions were kept in a refrigerator.

### 2.7. Calibration solutions

Concentrations used for quantification of the ions are listed in Table 2. The calibration curves were measured only at the ranges needed for the work. If the samples were introduced into the capillary for different time periods (5–20 s), the linear ranges of each ion were remeasured by that injection.

## 3. Results and discussion

Separation by CE of the anions studied were completed within 15 min (Fig. 1). Their migration order was: chloride, sulfate, nitrite and nitrate. Cations separated within 9 min (Fig. 2). Their migration order was: ammonium, potassium, calcium, sodium and magnesium. Limits of detection were all below 100  $\mu\text{g/l}$ , being lowest for the cations. Repeatabilities of the migration times in CE were also good (RSD 3%) and therefore natural waters could be analyzed and quantified with the methods chosen for these analyses.

The accuracy of the CE techniques used was assessed by making two reference mixtures 1 and 2 by weighing pure standard chemicals and dissolving in the two reference mixtures. Their concentrations gave models for very high (ref. 1) and low (ref. 2) salinities of the groundwaters [3]. The mixtures were analyzed with the capillary electrophoretic methods optimized for these studies. The ion concentrations

were measured with linear calibration. The results show (Table 3) that quantification with CE was possible even at 1000 mg/l, however, we used two calibration graphs so as to achieve reliable measurements.

Modifiers (diethylamine in anion analyses and 18-crown-6 ether in cation analyses) used in our study for the dynamic coating of the silanol groups on the surface of the separation capillary were used to provide advantages such as electroosmotic flow (EOF) suppression and surface shielding, in order to enhance the separation efficiency. Their main advantages in CE, obtained in high throughput screening, were long-term stability and reproducibility of the surface coating. Separation efficiency was obtained by diluting the samples containing high concentrations of chloride, sulfate, sodium and calcium. However, the background electrolyte solution was not manipulated with a constant concentration of chloride or sulfate to stabilize the separation [15].

Migration times (e.g. for sample 12, a contaminated lake water) of chloride, sulfate, nitrite and nitrate were  $11.24 \pm 0.07$  min (RSD 0.6%),  $12.14 \pm 0.09$  min (RSD 0.1%),  $12.27 \pm 0.08$  min (RSD 0.7%) and  $12.71 \pm 0.09$  min (RSD 0.7%) within a sequence, respectively. However, the repeatabilities of the peak areas used to calculate the concentrations were poorer (RSD 5–11%) due to the high ionic strengths of the many samples.

To achieve better separation between chloride and sulfate the samples were diluted for CE measurements. For example, the concentration of sulfate in sample 13 which was sampled from a contaminated lake and river system in Finland, was so high ( $801.2 \pm 22.3$  mg/l) that the sample was diluted to 1:50 (v/v) to get reliable results. All the analyses were made with five replicates and three injections of each. The uncertainty factor was  $\pm 3\%$ .

The method for cation separation was more repeatable than that used for the anions. However, only water soluble cations could be analysed. Sample 15, taken from muddy river water, was shown to contain ammonium, potassium, calcium, sodium and magnesium at migration times of  $6.33 \pm 0.01$  min (RSD 0.08%),  $7.62 \pm 0.01$  min (RSD 0.03%),  $8.16 \pm 0.05$  min (RSD 0.57%),  $8.47 \pm 0.05$  min (RSD 0.58%) and  $8.92 \pm 0.35$  min (RSD 1.87%), respectively. It was observed that the higher the ion contamination, the

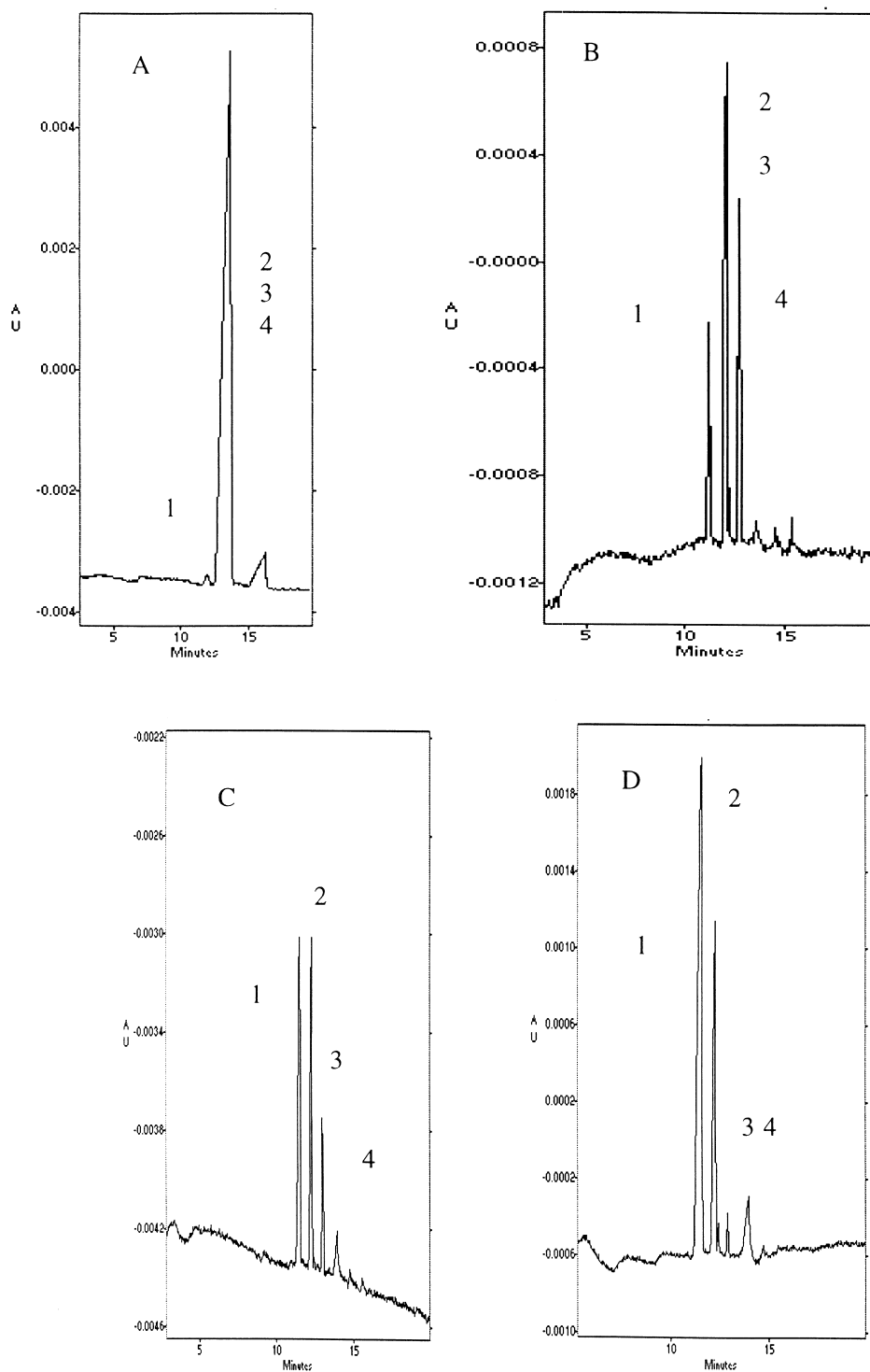


Fig. 1. Separation of anions by capillary electrophoresis at pH 7.7. Undiluted samples: (A) 14, (B) 12, (C) D4 and (D) D5. Ions in electropherograms: (1)  $\text{Cl}^-$ , (2)  $\text{SO}_4^{2-}$ , (3)  $\text{NO}_2^-$  and (4)  $\text{NO}_3^-$ .

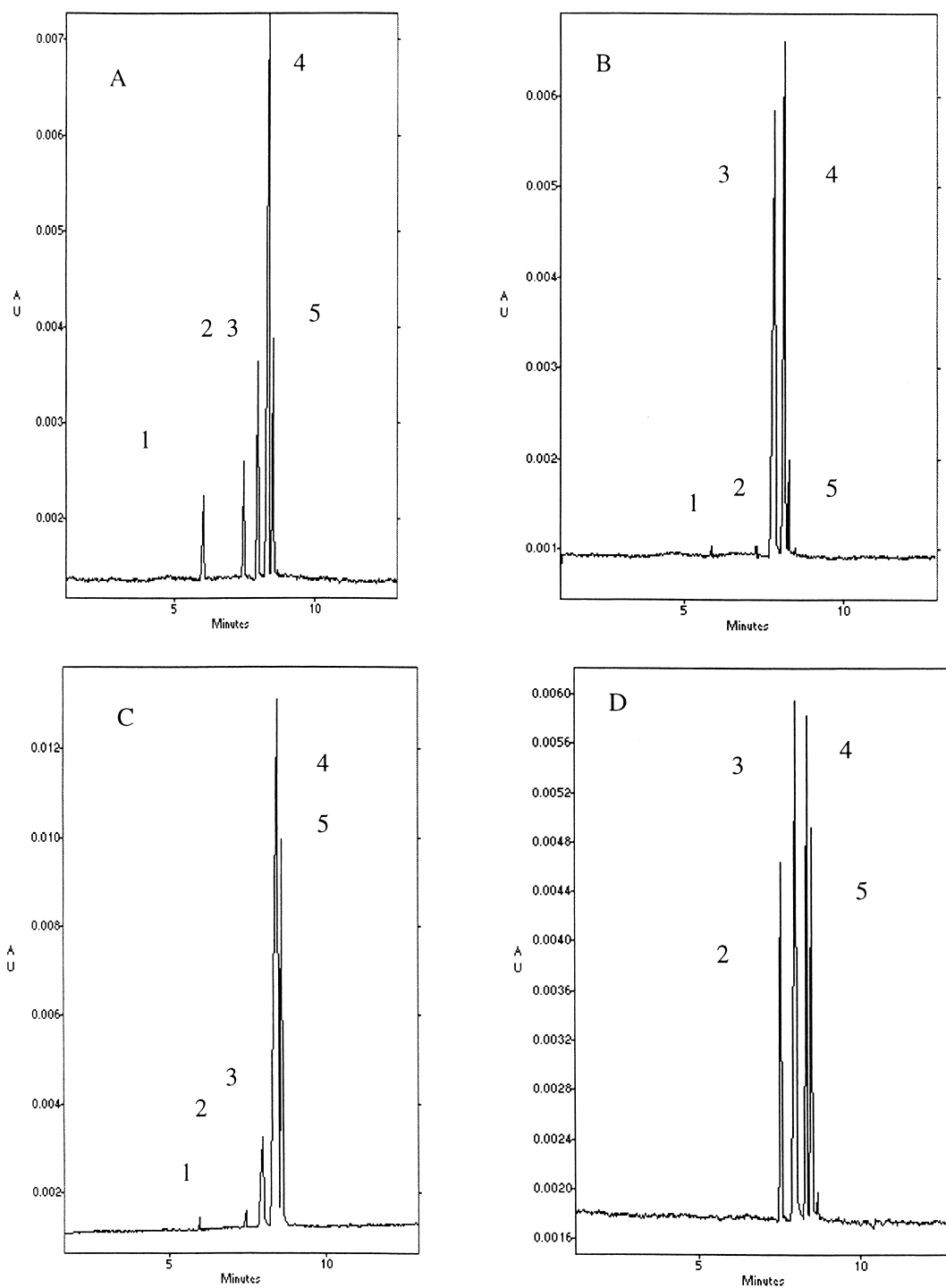


Fig. 2. Separation of cations by capillary electrophoresis at pH 3.6. Undiluted samples: (A) 12, (B) 14, (C) D5 and (D) D4. Ions in electropherograms: (1) NH<sub>4</sub><sup>+</sup>, (2) K<sup>+</sup>, (3) Ca<sup>2+</sup>, (4) Na<sup>+</sup> and (5) Mg<sup>2+</sup>.

Table 3  
Recovery tests with CE

Standard and ions	Weighed amount (mg/l)	Amounts calculated from the CE results (mg/l)
<i>Reference mixture 1 (salinity high)</i>		
Cl <sup>-</sup>	46 062	49 049 (diluted to 1:400)
Ca <sup>2+</sup>	17 343	17 807
Na <sup>+</sup>	9974	10 549
<i>Reference mixture 2 (salinity low)</i>		
Cl <sup>-</sup>	49.22	54.18
SO <sub>4</sub> <sup>2-</sup>	11.09	12.91
K <sup>+</sup>	3.78	3.66
Ca <sup>2+</sup>	17.99	17.22
Na <sup>+</sup>	51.40	56.65
Mg <sup>2+</sup>	4.78	5.15

Artificial sample: comparison of the weighed and calculated results on the basis of the CE reports.

smaller the RSD value of the peak area in the electropherogram. The reason for this was supposed to be the uncertainty factor influenced by the background, e.g. the matrix effect, which was smaller in the case of high concentrations of the ions.

The contents of the waters numbered 1–9 (normal environmental waters from a peat production area, a muddy area and a well) and especially those numbered 10–15 were compared with those of the contaminated surface waters of the River Rhine (numbered D1–D6). All the results in CE were compared with those obtained with the other techniques, namely titration, AAS and FIA, which are used in traditional solvent chemistry (Figs. 3–5). Using the traditional methods no separation of the ions can be obtained. However, in capillary electrophoresis the instrumental parameters (length of the capillary, electric field), sample amount, physico-chemical parameters inside the capillary (concentration of the electrolyte, ionic strength, co- and counter ions, pH, modifiers and viscosity) were optimized so that excellent peak resolution (Figs. 3–5), rapid migration and sensitive detection were possible.

According to our studies, concentrations of ions in Finnish river and lake waters varied from a few micrograms to nearly grams per liter (Tables 4 and 5). The results showed also that the samples from the peat production and clay areas were less rich in

calcium, chloride and sulfate than the water from a well built on a cold spring or the contaminated waters. In contaminated waters sodium, chloride and

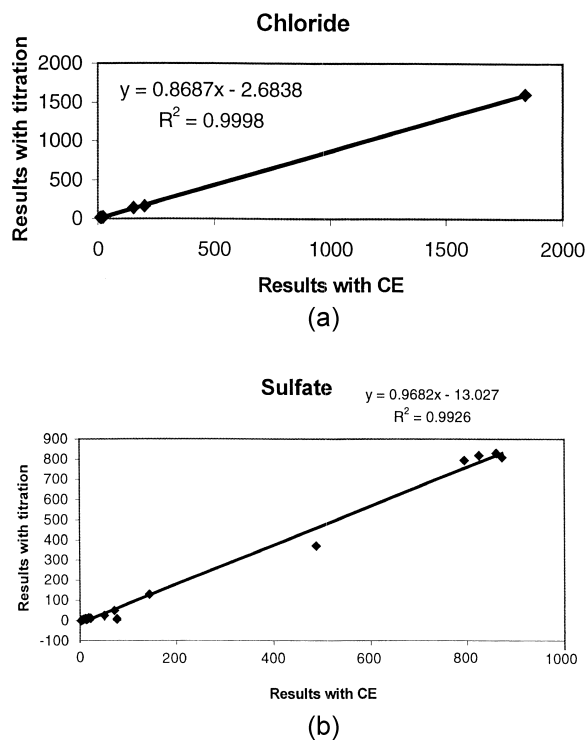


Fig. 3. Determination of (a) chloride and (b) sulfate from environmental waters. Correlation of the results with two techniques.

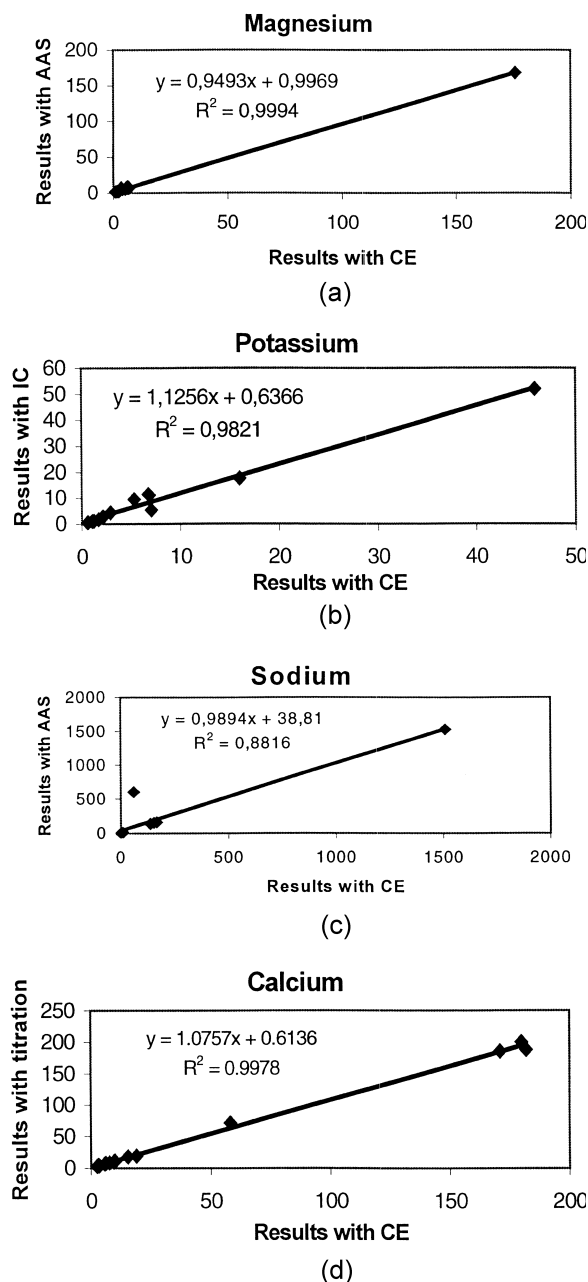


Fig. 4. Determination of (a) magnesium, (b) potassium, (c) sodium and (d) calcium from environmental waters. Correlation of the results with two techniques.

sulfate concentrations were very high independently of the sampling area. The results also showed that waters sampled from clay soils have higher amounts

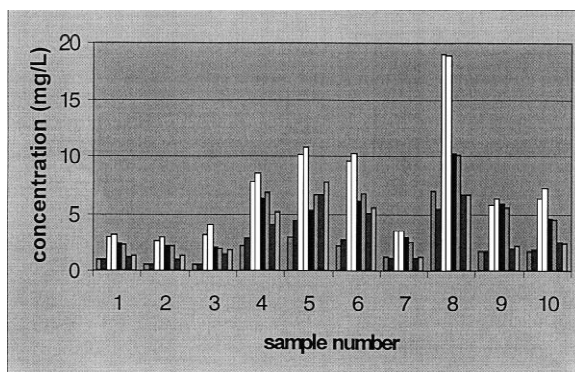


Fig. 5. Comparison of the results for potassium, calcium, sodium and magnesium obtained with different techniques. Example of number 1: first and second block, potassium measured with CE and solvent technique, respectively; continued by third and fourth, calcium with CE and solvent technique; fifth and sixth, sodium with CE and solvent technique; seventh and eight, magnesium with CE and solvent technique, respectively.

of sulfate, nitrite and nitrate than waters taken from peaty soils. Ammonium amounts were very low in all samples and only six out of 15 could be measured (Table 5).

Correlation with the results obtained by titration, AAS, ion chromatography and FIA was not obtained at very high concentrations of the ions, due to the salinity of the samples (Figs. 1 and 5). To overcome the high ionic strengths in samples they were diluted for CE measurements, which step was not needed when using the other techniques.

The  $\text{NO}_2^-$  and  $\text{NO}_3^-$  results obtained by solvent chemistry did not correlate with those calculated from the CE determinations. They were 10–100 times lower than with CE and did not correlate with the known fact that contaminated waters have high amounts of nitrogen-containing matter. Therefore, the nitrogen and nitrite results were cross-checked by another laboratory. The checked results showed that those obtained with other techniques were not true. Although the limits of quantification for  $\text{NH}_4\text{-N}$ ,  $\text{NO}_2\text{-N}$  and  $\text{NO}_3\text{-N}$  were as low as 5, 10 and 5  $\mu\text{g/l}$ , respectively, obviously there were cross reactions with nitrogen-containing analytes and therefore, only total-N could be measured to get the approximate value for the sum of  $\text{NO}_2^-$ ,  $\text{NO}_3^-$  and  $\text{NH}_4^+$ . It was noticed that good correlations ( $R^2$  values between 0.8816 and 0.9994) were obtained



Table 4  
Capillary electrophoresis results of anions in the samples listed in Table 1

Sample	Chloride, mg/l (RSD)	Sulfate, mg/l (RSD)	Nitrite, mg/l (RSD)	Nitrate, mg/l (RSD)
1	3.82 (±2%)	3.77 (±2%)	0.28 (±10%)	<LOD
2	2.65 (±3%)	2.37 (±3%)	0.11 (±8%)	0.32 (±3%)
3	2.41 (±3%)	2.59 (±2%)	0.16 (±9%)	2.00 (±3%)
4	9.87 (±1%)	13.1 (±2%)	0.74 (±4%)	3.88 (±1%)
5	7.87 (±1%)	12.4 (±1%)	0.50 (±3%)	6.26 (±1%)
6	10.1 (±1%)	14.5 (±2%)	0.64 (±4%)	3.83 (±2%)
7	3.41 (±2%)	6.60 (±2%)	0.26 (±5%)	0.50 (±2%)
8	15.4 (±3%)	71.3 (±3%)	3.08 (±4%)	28.8 (±2%)
9	6.39 (±2%)	17.8 (±2%)	0.56 (±4%)	1.03 (±5%)
10	7.93 (±3%)	10.7 (±2%)	0.57 (±3%)	4.07 (±2%)
11	2806 (±4%)	488 (±3%)	50.2 (±2%)	<LOD
12	50.8 (±4%)	143 (±5%)	8.80 (±10%)	85.5 (±5%)
13	7.29 (±1%)	825 (±3%)	46.0 (±6%)	<LOD
14	9.34 (±3%)	795 (±2%)	37.9 (±8%)	<LOD
15	10.9 (±9%)	872 (±2%)	37.0 (±4%)	<LOD
D1	153 (±1%)	50.1 (±2%)	3.65 (±6%)	3.39 (±2%)
D2	15.6 (±2%)	25.3 (±1%)	2.19 (±6%)	5.24 (±2%)
D3	21.8 (±1%)	76.6 (±1%)	2.97 (±3%)	5.85 (±2%)
D4	10.9 (±4%)	8.14 (±3%)	0.84 (±5%)	3.78 (±3%)
D5	1840 (±5%)	860 (±5%)	55.1 (±5%)	106 (±2%)
D6	201 (±2%)	830 (±2%)	52.7 (±3%)	91.1 (±2%)

Table 5  
Capillary electrophoresis results of cations in the samples listed in Table 1

Sample	Ammonium, mg/l (RSD)	Potassium, mg/l (RSD)	Calcium, mg/l (RSD)	Sodium, mg/l (RSD)	Magnesium, mg/l (RSD)
1	0.10 (±3%)	1.03 (±2%)	2.92 (±2%)	2.35 (±5%)	1.20 (±2%)
2	<LOD	0.58 (±2%)	2.60 (±1%)	2.16 (±4%)	1.00 (±2%)
3	<LOD	0.58 (±2%)	3.18 (±5%)	2.04 (±5%)	1.48 (±2%)
4	<LOD	2.12 (±1%)	7.74 (±1%)	6.27 (±2%)	4.02 (±1%)
5	0.13 (±2%)	2.89 (±1%)	10.1 (±3%)	5.28 (±2%)	6.62 (±2%)
6	<LOD	2.13 (±1%)	9.57 (±2%)	6.05 (±2%)	5.09 (±1%)
7	<LOD	1.19 (±2%)	3.46 (±2%)	2.89 (±2%)	1.07 (±3%)
8	<LOD	7.00 (±3%)	19.0 (±2%)	10.2 (±2%)	6.61 (±4%)
9	<LOD	1.68 (±2%)	5.78 (±2%)	5.81 (±3%)	1.93 (±1%)
10	0.24(±3%)	1.68 (±2%)	6.26 (±6%)	4.62 (±2%)	2.42 (±3%)
11	<LOD	45.9 (±2%)	58.2 (±3%)	1510 (±1%)	176 (±3%)
12	9.68 (±2%)	16.0 (±2%)	15.4 (±3%)	60.0 (±2%)	6.06 (±3%)
13	<LOD	6.80 (±2%)	182 (±1%)	136 (±1%)	6.09 (±2%)
14	1.84 (±2%)	5.26 (±2%)	171 (±1%)	166 (±1%)	3.44 (±1%)
15	1.23 (±4%)	6.70 (±2%)	180 (±2%)	152 (±4%)	5.51 (±2%)
D1	<LOD	3.00 (±6%)	28.0 (±4%)	82.4 (±2%)	21.3 (±3%)
D2	<LOD	8.25 (±2%)	34.6 (±3%)	7.75 (±2%)	9.10 (±2%)
D3	8.32(±2%)	11.2 (±4%)	24.8 (±7%)	12.8 (±1%)	2.10 (±3%)
D4	<LOD	12.7 (±1%)	10.0 (±3%)	7.56 (±2%)	2.05 (±2%)
D5	<LOD	30.1 (±1%)	110 (±2%)	1080 (±3%)	163 (±6%)
D6	<LOD	17.9 (±4%)	221 (±4%)	112 (±2%)	97.1 (±2%)

with all the techniques from the results of  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$  and  $\text{Mg}^{2+}$ , which had limits of quantification at mg/l level.

#### 4. Conclusions

On the basis of our experiments capillary electrophoresis is a reliable and accurate technique for the monitoring of water-soluble inorganic anions and cations from environmental waters. Especially, simultaneous quantification of chloride, sulfate, nitrite and nitrate as well as potassium, calcium, sodium and magnesium, showed that high throughput analyses are possible if automation in sampling and data processing is included. Using e.g. titration and AAS quantification of each ion was done individually. In addition, more sample was needed when conventional techniques (ion chromatography, AAS, FIA and titration methods) were used.

The concentrations of the free soluble anions and cations in the environmental waters varied from a few milligrams to tens of grams per liter. High concentrations of ammonium, sodium, calcium, chloride and sulfate and the discovery of ammonium in the sample indicated the composition of the contamination.

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