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# Quantification of anions and cations in environmental water samples

## Measurements with capillary electrophoresis and indirect-UV detection

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### Abstract

The aim of this study was to validate two separation methods for determination of inorganic anions and cations from natural waters with capillary electrophoresis (CE) by using indirect-UV detection. The research is related to method development for screening of groundwater samples obtained in site investigations for spent fuel of the Finnish nuclear industry. In CE analysis, anions were separated in pyromellitic acid (pH 7.7) in the order bromide, chloride, sulphate, nitrite, nitrate, fluoride and dihydrogenphosphate. Cations were separated at pH 3.6 after anions using an 18-crown-6-ether solution. In these analyses, ammonium migrated first followed by potassium, calcium, sodium and magnesium. The concentrations of the ions in the natural water samples were calculated by using two or three calibration curves made using reference solutions at concentration levels of 0.5–250 mg/l. The repeatabilities of the anion and cation methods were tested using laboratory-made reference sample mixtures with high and low salt concentrations. The limits of quantification in the analyses were between 0.02 and 0.1 mg/l, depending on the ion. Concentrations of ions tested in natural waters varied from a few milligrams to tens of grams per litre. © 1999 Elsevier Science B.V. All rights reserved.

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### 1. Introduction

Anions and cations from drinking water and environmental water samples are mainly determined by flow injection analysis (FIA), atomic absorption spectrometry (AAS), titration or ion chromatography (IC) [1]. However, capillary electrophoresis (CE) is being used more and more as a standard analytical tool for many ionic compounds, perhaps due to the possibility of sequential analysis of different kinds of

ions [2,3]. Indirect-UV methods are the most useful for screening of non-absorbing ions when commercial CE instruments are applied. Because the indirect technique is not as sensitive as the direct one, good resolution of the ion zones in the separation medium, narrow sample zones and high direct-UV absorbance of the background electrolyte (BGE) are needed to detect the low levels of the ions in real samples.

Besides the indirect-UV detection mode, fluorescence and conductivity detections have also become available [4,5]. In particular, the indirect detection method demands optimal design of the detection system by choosing ions in the background elec-

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trolyte solution on the basis of their high molar absorption. The dynamic range and linearity of calibration can be expected to increase with increasing concentration of the UV-absorbing background ion. The optimization of the system is ruined with an increase of the BGE concentration due to Joule heating problems at higher ionic strengths. Therefore, by using indirect methods the currents should be very low for repeatable analysis.

In the electropherograms the peaks are narrow if the ion in the background electrolyte (BGE) has approximately the same electrophoretic mobility as the analytes [2]. If the BGE mobility is different, optimization of the peak shapes is difficult by changing chemical parameters (pH, ionic strength) only. In such cases, the high salt concentration in the sample hampers the separation of closely migrating peaks.

The aim of the project was to validate two separation methods for determination of inorganic anions and cations from natural waters by capillary electrophoresis using UV detection. In this study, we show that two well-optimized CE methods work well for determination of bromide, chloride, sulphate, nitrate, nitrite, fluoride and dihydrogenphosphate, and the determination of ammonium, calcium, potassium, sodium and magnesium from environmental water samples. Sample pretreatment for saline waters is also discussed.

## 2. Experimental

### 2.1. Materials

Pyridine,  $\text{KNO}_3$ , NaF, KCl,  $\text{NaH}_2\text{PO}_4$ ,  $\text{CaCl}_2$  (96%) and  $\text{CH}_3\text{COONH}_4$  were obtained from Merck (Darmstadt, Germany) and glycolic acid, HPCE electrolyte (pH 7.7),  $\text{NaNO}_3$  and 18-crown-6-ether were from Fluka (Buchs, Switzerland). NaCl (99.8%) was from Riedel-deHaen (France) and NaBr,  $\text{Na}_2\text{SO}_4$  and  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  from J.T.Baker (USA). All reagents were of analytical grade.

### 2.2. Instrumentation

A Beckman P/ACE 5000 (Beckman Instruments, Fullerton, CA, USA) with UV detection at 254 nm

was used. The fused-silica capillary was 77 cm (70 cm to the detector)  $\times$  50  $\mu\text{m}$  I.D., 365  $\mu\text{m}$  O.D. and was obtained from Composite Metal Services (The Chase, Worcestershire, UK). The applied voltage was +20 kV. The samples were injected by a pressure of 0.5 p.s.i. (1 p.s.i.=6894.76 Pa) for 10 to 50 s. The temperature was maintained at 25°C with a liquid coolant system. The capillaries were rinsed with buffer for 3 min before each run.

The conductivities of the electrolyte solutions and those of the natural waters were measured at 22°C with a Denver pH/conductivity meter Model 20 (Denver Instruments, Denver, CO, USA). Dilutions of the solutions were performed using Milli-Q water (Millipore, Avondale, USA), filtered through 0.45  $\mu\text{m}$  membranes and had conductivity below 0.05  $\mu\text{S}/\text{cm}$ . The pH combination electrode was calibrated using commercial standards with pHs of 4.00, 7.00 and 10.00 (Radiometer, Copenhagen, Denmark). The conductivity meter with 1 cm cells was calibrated with 84  $\mu\text{S}/\text{cm}$  KCl standard solution (Hanna Instruments, Copenhagen, Denmark).

### 2.3. Conditioning of the capillary

Before use the capillary was conditioned by purging with 0.1 M NaOH for 10 min, with Milli-Q water for 10 min and with the background electrolyte solution used in separation 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 5 min to keep the migration time of the analytes reproducible.

### 2.4. Background electrolyte solutions

In the optimized 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). The optimized 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.

### 2.5. Standard mixtures

Pure reference materials were diluted into Milli-Q

water to obtain 1000 mg/l stock solutions. The reference sample mixtures for capillary electrophoretic studies were prepared from the stock solutions to the concentrations needed. Samples were filtered before use through 0.45  $\mu\text{m}$  membranes (Millipore, Molsheim, France).

### 2.6. Natural waters

The natural waters were groundwaters, which were sampled on-line according to standard field procedures and preserved when necessary. Some of the samples were conditioned with  $\text{HNO}_3$ . The glass bottles used for cation measurements were acid-washed to prevent oxidation. The natural waters were first screened with CE to determine the concentrations of ions. When the amount of the ion studied was high compared with the reference mixtures, the sample was diluted to 1:50, 1:100, 1:200 or 1:400. The natural water samples marked as KR9, KR11, KR41, KR42 and KR43 were taken from deep boreholes at depths of 217–225 m, 540–545 m, 883–891 m, 412–417 m and 212.5–220 m, respectively, in Southern and North-eastern Finland.

The samples were not manipulated by pH adjustment or complexation because we wanted to analyse them by simulating the natural water conditions (pH, ionic strength).

## 3. Results and discussion

### 3.1. Electropherograms

The separation of anions was good under optimized conditions. The concentrations of the compounds in the Fluka buffer as well as in the three absorbing buffer solutions with UV-chromophore (imidazole, Nitroso-R salt, benzoic acid) were tested with laboratory-made mixtures. However, the main optimization for the anion analysis was made using HPCE electrolyte buffer due to the standardized procedure of its production. The separation system was optimized by the instrumental parameters (length of the capillary, voltage and injection time). The separation, which was performed within 17 min, showed good efficiency (1–3%). The migration order of the analytes studied was: bromide, chloride,

sulphate, nitrite, nitrate, fluoride and dihydrogenphosphate (Fig. 1a).

Cations were separated in a sequential mode after anions with an electrolyte buffer containing 18-crown-6-ether (pH 3.6). In the analyses, ammonium migrated first followed by potassium, calcium, sodium and magnesium. The analysis could be performed within 10 min (Fig. 2a).

### 3.2. Linearity

Table 1 shows the reproducibility and linearity of the analysis. The concentration ranges were estimated with the screening analysis of the natural water samples, which showed that the total salt concentrations in the samples were very high. The average values of the results in linearity profiling were obtained by measuring the standard samples mixed with anions tested when anions were separated and with cations when they were in the linearity tests. There were six concentration levels for anions and five for cations in the concentration range of 0.5–10 mg/l, and nine levels for each ion in the concentration range of 1–100 mg/l. Six times at each concentration was injected and six repetitions of each concentration were carried out sequentially. Lower concentrations than 0.5 mg/l were not tested. Because of the long analysis time used in these tests, there were not enough data for within-day results.

The reproducibility of the separations was moderately good; relative standard deviations for the absolute migration times of anions were 0.11–5.8% and that of the cations varied from 0.8 to 4%. It was found that, especially, when the concentrations of the anions were low, the standard deviations were small. For CE separations, the water samples were diluted with purified water because of their high salt concentrations, especially, for chloride, sulfate, calcium and sodium ions, which were present in very high concentrations. When the amounts of the ions were low, the samples did not need to be diluted. However, increased time for injection (50 s instead of 10 s) was needed to detect some of nitrite and sulfate from real samples.

### 3.3. Quantification

The limits of detection (LODs) were calculated

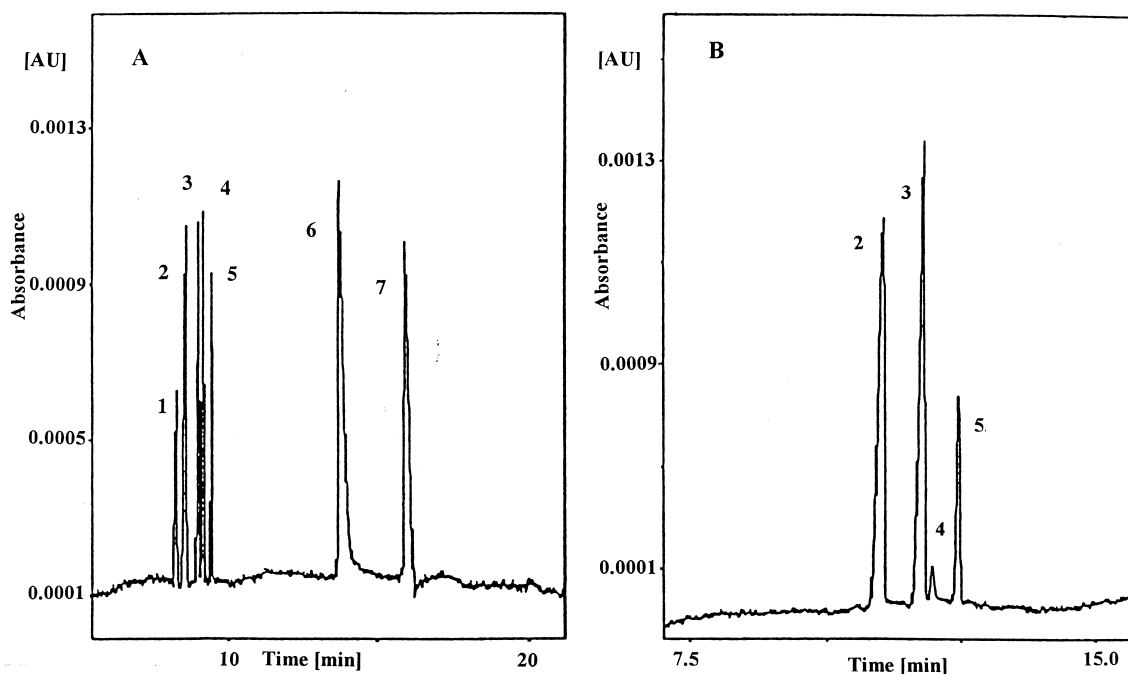


Fig. 1. Separation of anions in waters at pH 7.7. Samples: (A) standard mixture and (B) natural water (river). Peaks: (1) bromide, (2) chloride, (3) sulphate, (4) nitrite, (5) nitrate, (6) fluoride and (7) dihydrogenphosphate. Separation conditions described in Experimental.

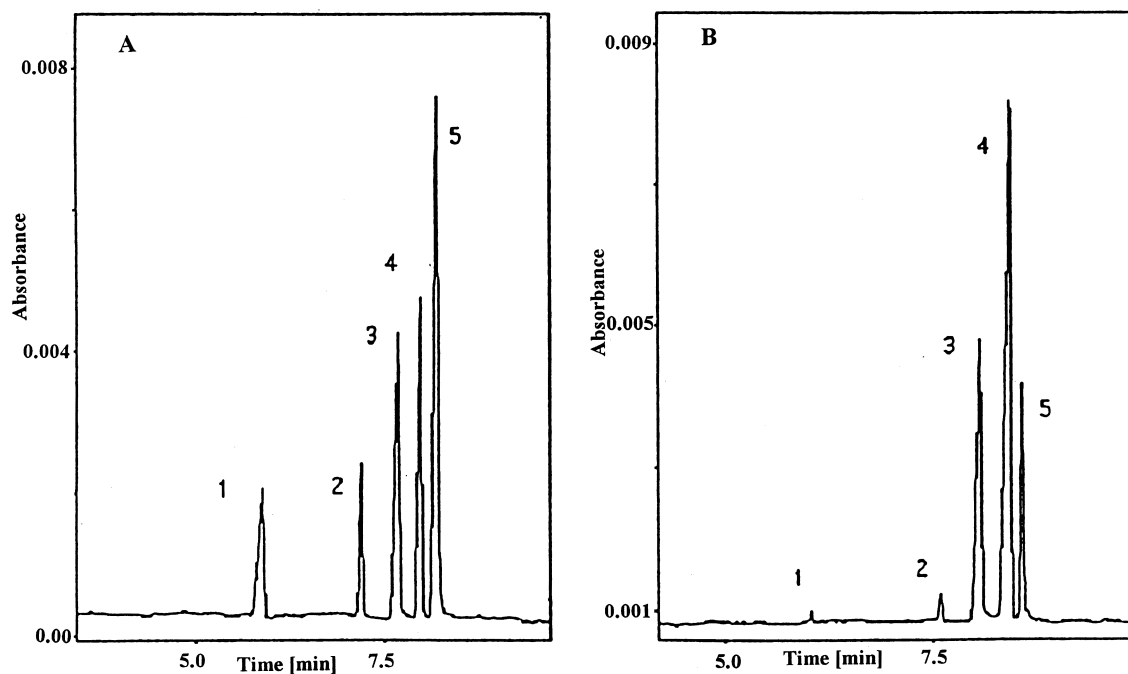


Fig. 2. Separation of cations in natural waters at pH 3.6. Samples (A) standard mixture and (B) natural water (low-saline groundwater at 540–545 m depth). Peaks: (1) ammonium, (2) potassium, (3) calcium, (4) sodium and (5) magnesium. Separation conditions described in Experimental.

Table 1  
Results of the quantitative analysis with six concentration levels and 5–10 replicates

Ion	$t_R$ (min)	SD (min)	RSD (%)	Linearity	$R^2$
Bromide	9.06	0.02	0.22	$y=268.52x-16.504$ (0.5–10 mg/l)	0.999
	8.65	0.44	5.08	$y=189.35x-165.12$ (1–100 mg/l)	0.999
Chloride	9.40	0.04	0.43	$y=636.77x-36.777$ (0.5–10 mg/l)	0.999
	8.99	0.50	5.56	$y=442.86x-401.81$ (1–100 mg/l)	0.999
Sulphate	9.93	0.03	0.30	$y=462.08x-42.501$ (0.5–10 mg/l)	0.999
	9.46	0.56	5.70	$y=388.68x-908.48$ (1–100 mg/l)	0.997
Nitrite	10.1	0.02	0.20	$y=479.14x-46.958$ (0.5–10 mg/l)	0.999
	9.62	0.56	5.82	$y=343.87x-70.904$ (1–100 mg/l)	0.997
Nitrate	10.5	0.02	0.19	$y=398.95x-43.652$ (0.5–10 mg/l)	0.999
	9.90	0.57	5.76	$y=302.86x-383.26$ (1–100 mg/l)	0.999
Ammonium	6.17	0.01	0.16	$y=613.25x+175.18$ (0.5–7 mg/l)	0.998
	6.30	0.01	0.16	$y=653.82x-848.69$ (1–100 mg/l)	0.996
Potassium	7.67	0.01	0.13	$y=409.60x+120.71$ (0.5–7 mg/l)	0.998
	7.57	0.01	0.13	$y=417.45x-111.5$ (1–100 mg/l)	0.999
Calcium	8.11	0.01	0.12	$y=612.81x+303.87$ (0.5–7 mg/l)	0.989
	8.15	0.01	0.12	$y=959.75x+1537.6$ (1–100 mg/l)	0.995
Sodium	8.50	0.01	0.11	$y=864.87x+499.7$ (0.5–7 mg/l)	0.993
	8.49	0.01	0.12	$y=930.27x+705.04$ (1–100 mg/l)	0.997
Magnesium	8.71	0.01	0.11	$y=1932.8x+256.78$ (0.5–7 mg/l)	0.998
	8.75	0.01	0.11	$y=2023.2x-2937.8$ (1–100 mg/l)	0.985

Table 2  
Limits of detection for anions: hydrodynamic injection for 50 s

Anion	LOD (mg/l)
Bromide	0.02
Chloride	0.01
Sulphate	0.01
Nitrite	0.02
Nitrate	0.02
Fluoride	0.03
Dihydrogenphosphate	0.04

Table 3  
Limits of detection for cations: hydrodynamic injection for 10 s

Cations	LOD (mg/l)
Ammonium	0.06
Potassium	0.08
Calcium	0.03
Sodium	0.02
Magnesium	0.02

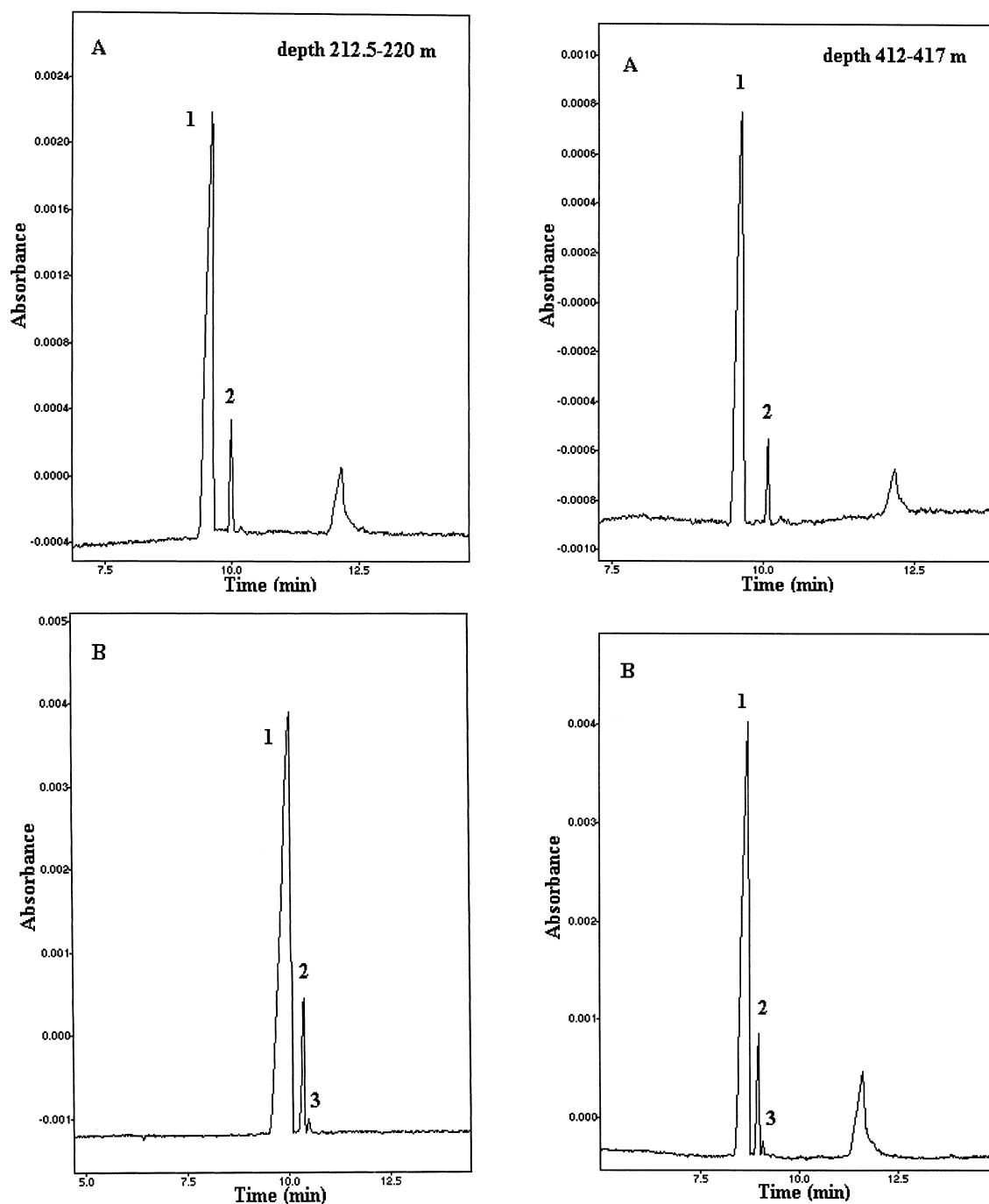


Fig. 3. Electropherograms of the anion separations of the groundwater samples (borehole) KR4 at different depths: 212.5–200 m, 412–417 m and 883–891 m. Peaks: (1) chloride, (2) sulphate and (3) nitrite. (A) Diluted with purified water (1:100), 10 s injection time and (B) diluted with purified water (1:100), 35 s injection time of sample from 212.5–220 m, 50 s injection time of sample from 421–417 m and 45 s injection time of sample from 883–891 m depth. Separation conditions described in Experimental.

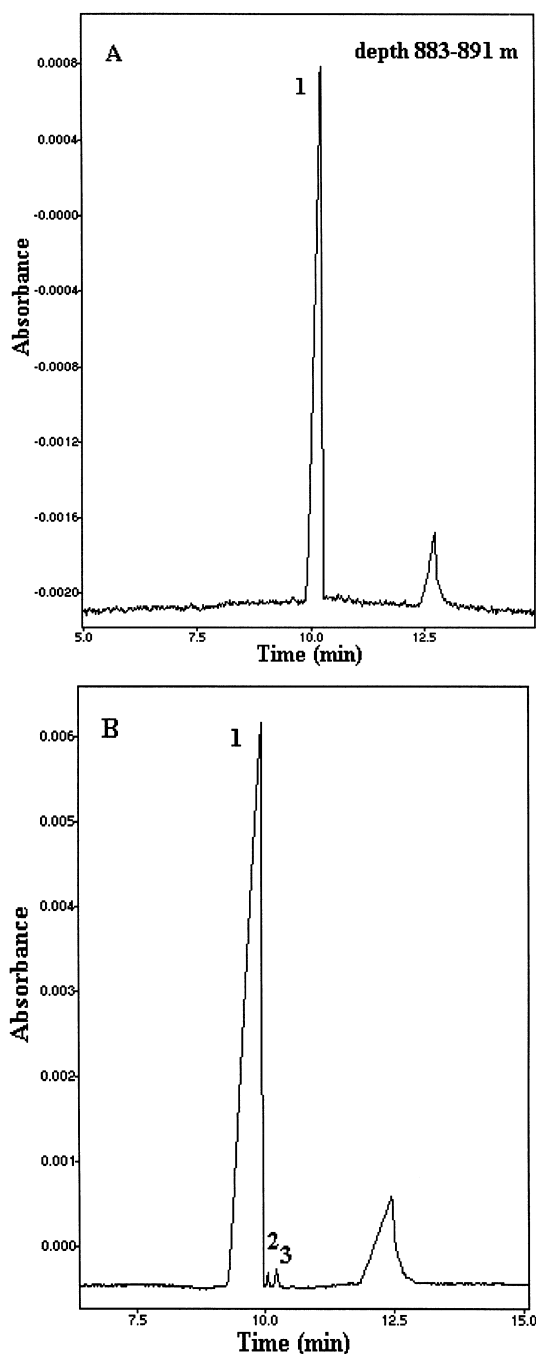


Fig. 3. (continued)

using reference samples are listed in Tables 2 and 3. The detection limits were measured by calculating the analyte concentration at a signal-to-noise ratio ( $S/N$ ) of three.

Our results showed that the concentration of bromide in natural waters was below its limit of detection. Furthermore, when the samples were analyzed off-line, no ammonium was detected. Figs. 1b and 2b show the electropherograms of undiluted water samples, which were used for quantification of the ions present at very low concentrations in natural waters.

The concentrations of the ions varied widely depending on the depth of the sampling. At 215.5–220 m, 412–417 m and 883–891 m the amounts of chloride were 5400, 2800 and 7200 mg/l, the amounts of sulphate were 800, 300 and 30 mg/l and the amounts of nitrite were 52, 20 and 55 mg/l, respectively. At the same sampling depths the concentrations of calcium were 700, 390 and 1280 mg/l, the sodium concentrations were 2500, 1400 and 2700 mg/l and the magnesium concentrations were 300, 66 and 160 mg/l, respectively. Bromide, dihydrogenphosphate, nitrate, ammonium and potassium concentrations were below their limits of detection. Figs. 3 and 4 show the separation of anions and cations in natural waters at the sampling depths. It is worthy of note, that when anions were determined the samples had to be diluted to prevent the overloading effect of the ion zones as well as the comigration of sulphate and nitrite. Due to the dilution, an increase of the injection time was necessary to detect the very low concentrations of the analytes in the saline groundwaters sampled from 215.5–220 m, 412–417 m and 883–891 m depths (Table 4).

#### 4. Conclusions

Our studies showed that two carefully optimized capillary electrophoresis methods were very suitable for the determination of bromide, chloride, sulphate, nitrite, nitrate, fluoride and dihydrogenphosphate and for the determination of ammonium, potassium, calcium, sodium and magnesium. The determination of the ions was successful in groundwaters of low ionic strength, but in saline waters potassium could not be determined. It was noticed that two ranges of concentrations were needed in the determination of all the ions from the natural water samples tested. When the concentrations were above 100 mg/l the

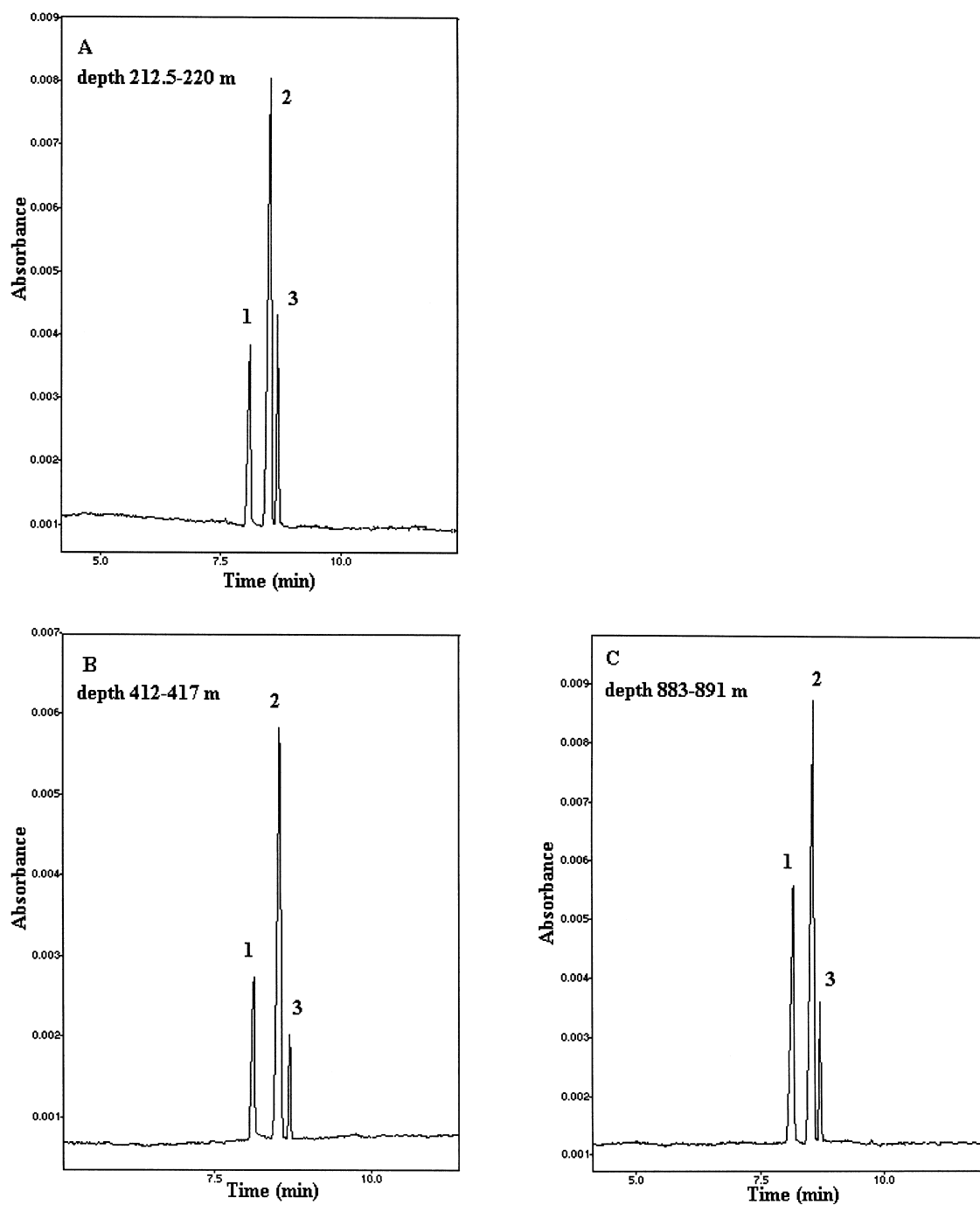


Fig. 4. Electropherograms of the cation separations of the groundwater samples (borehole KR4) at different depths: (A) 212.5–200 m, (B) 412–417 m and (C) 883–891 m. Peaks: (1) calcium, (2) sodium and (3) magnesium. Samples diluted with purified water (1:100). Separation conditions described in Experimental.



Table 4  
Selected results from the determination of the groundwater samples (eight replicates with four injections)

Sample	Cl <sup>-</sup> (mg/l)	SO <sub>4</sub> <sup>2-</sup> (mg/l)	NO <sub>2</sub> <sup>-</sup> (mg/l)	K <sup>+</sup> (mg/l)	Ca <sup>2+</sup> (mg/l)	Na <sup>+</sup> (mg/l)	Mg <sup>2+</sup> (mg/l)
KR9	5.23	4.11	0.50	0.74	12.2	18.2	0.92
217–225 m	±2%	±3%	±3%	±3%	±3%	±3%	±3%
KR11	4.10	2.27	–	1.57	11.5	19.1	1.69
540–545 m	±5%	±4%	–	±3%	±5%	±4%	±6%
KR41	7150	29.3	54.7	–	1280	2630	171
883–891 m	±4%	±3%	±6%	–	±2%	±2%	±2%
KR42	2760	331	22.6	–	390	1390	89.5
412–417 m	±3%	±4%	±5%	–	±3%	±1%	±2%
KR43	5430	795	53.4	–	706	2540	303
212.5–220 m	±3%	±3%	±3%	–	±3%	±2%	±3%

water samples were diluted to prevent the overloading effect during the capillary electrophoretic separation procedures. The relative standard deviations of the quantitative results calculated with eight replicates (four injections) were between 2 and 6% in the groundwater samples taken from the deep boreholes in Finland. The limits of quantification in the analyses were from 0.02 to 0.1 mg/l. Concentrations of the free soluble anions and the free cations in natural waters varied from a few milligrams to tens of grams per litre.

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