Determination of bromide and potassium in saline groundwaters by capillary electrophoresis without prior dilution

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Abstract

Two capillary electrophoretic analysis methods are presented; one optimized for the analysis of Br^- and the other for determination of K^+ in groundwaters of high conductivity. The water sampling was performed from the planned final disposal facility area for spent nuclear fuel at Olkiluoto in the municipality of Eurajoki, Finland. Bromide was analysed in an acidic electrolyte solution containing 5 mM formic acid and 42 mM NaCl (pH 3.5) and using direct UV detection (200 nm). Sample stacking was needed for the preconcentration. Potassium was analysed at pH 4.5 using imidazole-18-crown-6 ether solution. The accuracies of the Br^- and K^+ methods were tested using laboratory-made reference sample mixtures with high salt concentration. In the Br^- analyses, the limits of detection and determination were 0.1 and 1 mg L^{-1}, respectively. The developed CE analysis for K^+ in saline water was repeatable (RSD% 14.5–18.0) and the detection and the determination limits were 0.5 and 2.0 mg L^{-1}, respectively. The interlaboratory results showed that CE measurements of Br^- and K^+ were compatible with those made with traditional solvent chemistry techniques.
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1. Introduction

According to Finnish legislation, the responsibility for nuclear waste management lies with the waste producer (Finnish Acts, 1987). For this management, two Finnish energy companies established the company Posiva Oy, which started in January 1996. Its responsibilites are research, construction, and operation of the disposal facility. In 2001, the Finnish Parliament ratified the Decision in Principle on the final disposal facility for spent nuclear fuel at Olkiluoto in the municipality of Eurajoki from 4 alternative sites. Geological investigations at Olkiluoto were begun in 1980 (Ryhänen, 1997).

Groundwater chemistry is an important part of geological and geochemical studies concerning the performance assessment and safety analysis of final disposal of radioactive waste into bedrock. The composition of groundwater varies at different depths depending on the original source. The main sources are present in tiltrate meteoric water and Baltic Sea water (0–2500 Before Present, BP) which affects groundwater at the depth of 0–150 m, Litorina Sea water (2500–7500 BP) from 100 to 300 m, Pre-Litorina water which contains fresh glacial meltwater (7500–10,000 BP), and at the deepest level, >500 m, the Preglacial meteoric water (Pre-Quaternary). Chloride is the most abundant anion in Olkiluoto groundwater; its concentration can be as high as 43,000 mg L^{-1} (1230 mmol L^{-1}). The concentration of Br^- follows the variations of Cl^-. Levels as high as 350 mg L^{-1} of Br^- have been found in saline groundwater. The concentration of K

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also increases with increasing ECl^- content; a concentration of 22 mg L^{-1} (0.56 mmol L^{-1}) has been observed in saline groundwater (Pitkänen et al., 1998).

Capillary zone electrophoresis (CZE) is an analytical separation technique for electrically charged analytes. The separation takes place under high electric field in a narrow-bore capillary, typically made of fused silica. Sample solution is injected as a narrow plug at one end of a capillary filled with conducting background electrolyte. Upon application of an electric field, the analyte ions separate into distinct migrating zones according to their electrophoretic mobilities. The separated zones are detected by an on-column, end-column or off-column detector. Usually the detector is a UV/VIS spectrophotometer, but several other methods can be applied as well.

Capillary electrophoresis (CE) determinations of inorganic ions from different matrices have been performed for several years and reported in several reviews (Fukushi et al., 1999; Valsecchi and Polesello, 1999; Okada, 1999; Kappes and Hauser, 1999; Polesello and Valsecchi, 1999; Timerbaev and Buchberger, 1999; Pacáková et al., 1999; Sádecká and Polonský, 1999; Blatný and Kvasnička, 1999; Buchberger, 2000; Fritz, 2000; Fritz et al., 2002). The articles have handled the theme from different points of view, i.e. buffer composition, detection or matrices. Quantification of major anions and cations (Cl^-, S^{2-}, Ca^{2+}, and Na^+) and some minor ions (NO_3^-, K, and Mg) in saline groundwaters has been presented by Hiissa et al. (1999).

The most common CE techniques for both inorganic anions and cations include detection at ultraviolet (UV) wavelengths with indirect detection mode.

Bromide ion has UV absorption at 200 nm, so it can be analyzed using direct UV detection. This characteristic has been exploited when Br^- ions have been determined in raw and drinking waters (Rantakokko et al., 1999) and in seawater (Ding et al., 1998; Fukushi et al., 1998). Usually the Cl^- concentration of the electrolyte solution was adjusted according to sample salinity.

Analyses of K^+ have usually been carried out in acidic buffer solution with UV detection using indirect detection. The resolution of NH_4^+ and K^+ often requires careful attention. It can be adjusted with complexing agents, such as 18-crown-6 ether or 15-crown-5 ether (Francois et al., 1995; Oehrle, 1996; Cahours et al., 1998). Only a few articles are available concerning the determination of K^+ from environmental samples of high conductivity (Tangen et al., 1997; Salimi-Moosavi and Cassidy, 1996). The analysis of cations at lower concentrations from a matrix of high conductivity was simulated by Cahours (Cahours et al., 1998).

The aims of this study were to develop and optimize rapid methods for determination of the concentrations of Br^- and K^+ in natural groundwater samples at depths of 0–1000 m below sea level and with varying matrix conductivities.

2. Experimental

2.1. Materials

Sodium bromide (99.5%), NaCl (99.5%), and KCl (99%) were obtained from Sigma (Sigma–Aldrich Chemie, Steinheim, Germany). Formic acid (98–100%) was from J.T. Baker (Deventer Holland). Imidazole was from Merck (Darmstadt, Germany) and 18-crown-6 from Fluka (Buchs, Switzerland). All chemicals were used as received. Water was obtained from a Milli-Q purification system.

2.2. Solutions

For the method development and quantification, stock solutions of 10,000 mg L^{-1} of Br^-, Cl^-, K^+, and Na^+ were prepared. The final Br^- standard solutions were prepared by diluting the stock solution with Milli-Q water to appropriate concentration levels and adjusting Cl^- concentration in standards to 2000 mg L^{-1}.

Potassium standard solutions were prepared similarly by diluting the stock solution with 0.5% HNO_3 to the concentrations needed and adjusting the Na^+ concentration in standards to 2000 mg L^{-1}. Nitric acid was added to standard solutions, since the groundwater samples for cation analyses were conditioned with HNO_3.

The Cl^- and Na^+ concentrations used in standard solutions were chosen to simulate saline waters without excessive contamination risk of the apparatus.

Non-saline Br^- or K^+ standard solutions were prepared by diluting the stock solution with Milli-Q water to the concentrations needed without Cl^- or Na^+ addition, respectively.

2.3. Samples

The groundwater samples were obtained from Olkiluoto in the Eurajoki area in Finland, where the final repository for spent nuclear fuel is being excavated. One of the samples was surface water from the Korvensuo basin and another sample was from the percussion borehole (PR3). The others were groundwater samples from deep boreholes at various depths. Table 1 lists the information, including some physical parameters of the water samples. For cation analyses the samples were acidified with 0.5 % HNO_3. All samples were filtered before use through 0.45 μm membranes. No other sample pretreatment was used.

2.4. Carrier electrolytes

The carrier electrolyte for Br^- analyses consisted of 5 mM formic acid and 42 mM NaCl (pH 3.5) in Milli-Q water. The electrolyte solution for the K^+ analyses was 50 mM 18-crown-6 ether and 10 mM imidazole (pH 4.5)

Table 1
The groundwater samples from Olkiluoto, used in Br^- and K^+ method development and quantification

Sample, description	Physical parameters of water samples[*]	Used in analyses of
KR-11, depth 277–280 m, 29.12.1999, filtered 0.45 µm	Oxygen −0.05 ppb, pH 8.63 (mobile device 8.4), electrical conductivity 914 mS m^{-1}, Emv −504 mV	Br^-
KR-11, depth 621–629 m, 28.2.2000, filtered 0.45 µm	pH n. 8–8.1, electrical conductivity approx. 1100 mS m^{-1}, Emv approx. −200 mV	Br^-
KR-11, depth 415–423 m, 9.5.2000, filtered 0.45 µm	Oxygen approx. 0 ppb, pH approx. 8.40, electrical conductivity approx. 1120 mS m^{-1}, Emv approx. −300 mV	Br^-
KR-6, depth 98.5–100.5 m 11.7.2001, filtered 0.45 µm	pH 7.66, electrical conductivity 733 mS m^{-1}	Br^-, K^+
KR-6, depth 135–137 m 3.7.2001, filtered 0.45 µm	pH 7.78, electrical conductivity 1084 mS m^{-1}	Br^-, K^+
KR-6, depth 524–527 m 10.01.2001, filtered 0.45 µm	pH 8.8, electrical conductivity 3210 mS m^{-1}, redox −333, oxygen 0 ppb	Br^-, K^+
KR-12, depth 365–368 m 12.01.2001, filtered 0.45 µm	pH 8.0, electrical conductivity 1490 mS m^{-1}, redox −572 mV, oxygen 0 ppb	Br^-, K^+
KR-12, depth 741–751 m, filtered 0.45 µm	pH 8.2, electrical conductivity 7040 mS m^{-1}, redox −181 mV, oxygen 0 ppb	Br^-, K^+
PR3 29.8.1997	pH 8.1, electrical conductivity 96.2 mS m^{-1}	Br^-
KORVENSUO 6.6.2001, filtered 0.45 µm	pH 7.9, electrical conductivity 14.01 mS m^{-1}	Br^-
KR-13, depth 214–220 m 13.11.2001	pH 7.8, electrical conductivity 1033 mS m^{-1}, oxygen 0.01 ppb, redox, Au −473 mV, redox, Pt −474 mV	Br^-
KR-13, depth 362–365 m 8.10.2001	pH 7.61, electrical conductivity 1447 mS m^{-1}, oxygen 0 ppb, redox, Au −415 mV, redox, Pt −402 mV	Br^-, K^+

[*] Measured after sampling in the field.

in water. Buffer solutions were filtered through 0.45 µM disposable filters (GHP Acrodisc, Gelman Sciences, Ann Arbor, MI, USA) prior to analyses.

2.5. Capillary electrophoresis

The standards and samples both for Br^- and K^+ analysis were analyzed with a P/ACE MDQ capillary electrophoresis instrument with a UV detector (Beckman-Coulter, Inc., Fullerton, CA, USA). Instrumental condi-

tions for the Br^- and K^+ analyses are listed in Table 2. The capillary (obtained from Composite Metal Services, The Chase, Hallow, Worcester, UK) was conditioned by sequentially purging with 0.1 M NaOH (20 min), Milli-Q water (20 min), and buffer solution (20 min). In Br^- analyses, the capillary was rinsed first with Milli-Q water (1 min) and then with the buffer (5 min). In Br^- analyses a water plug was injected (3 s, 0.5 psi) before sample injection in order to concentrate the sample zone on-line immediately after the separation voltage was switched on.

Table 2
Instrumental parameters of the Beckman MDQ capillary electrophoresis used in the Br^- and K^+ analyses

Variable	Bromide analysis	Potassium analysis
UV		
Wavelength	200 nm	214 nm
Sampling frequency	4 Hz	4 Hz
Detection mode	Direct	Indirect
Capillary (length to detection point $= L_{det}$, total length $= L_{tot}$)	L_{det} 50 cm, L_{tot} 60 cm, internal diameter 50 µm, outer diameter 375 µm	L_{det} 100 cm, L_{tot} 110 cm, internal diameter 50 µm, outer diameter 375 µm
Temperature	30 °C	25 °C
Voltage	−11 kV	+30 kV
Run time	11 min	13 min
Injection time		
Saline samples	5 s	5 s
Non-saline samples	30 s	5 s
Injection pressure	0.5 psi (3.447 kPa)	0.5 psi (3.447 kPa)

2.6. Optimization of the quantitative measurements

Quantification of Br⁻ was performed using the external standard method. In saline sample quantification, the standard Br⁻ solutions with concentration ranges 1–35 mg L^{-1} and 1–50 mg L^{-1} were used. In both cases, the total Cl⁻ concentration was adjusted to 2000 mg L^{-1}. When non-saline waters were analyzed, Br⁻ concentration in the standard solutions was adjusted to levels between 0.05 and 3.0 mg L^{-1}, ensuring that the sample was free of Cl⁻. Six repeated analyses were performed with Br⁻ standard solutions and 3–6 repetitions with the groundwater samples in order to evaluate the repeatability of the method.

The quantification of K⁺ was made by similar a method. In saline samples, quantification of K⁺ was performed with standard concentrations of 0–35 mg L^{-1}. Six repeat runs were made with the K⁺ standards and the groundwater samples.

In this work 5 concentrations of 18-crown-6 ether were tested, namely 2.5, 5, 35, 50 and 100 mM. The co-ion in the electrolyte solution was imidazole, which had similar electrophoretic mobility to that of the analytes.

2.7. Determination of the LOD and LOQ

The detection limit (LOD) of Br⁻ was defined as the concentration at which the signal-to-baseline noise ratio (S/N) was 3. In these measurements, standards without Cl⁻ addition were used. The Br⁻ sample with chloride at 2000 mg L^{-1} was used for determination of the limit of quantification (LOQ). Bromide concentration in both the determinations was adjusted to levels between 0.05 and 5 mg L^{-1}.

Similarly, for the determination of LOQ for K⁺ in saline water, the concentration range was 0.1–5 mg L^{-1} and the concentration of Na⁺ was maintained at 2000 mg L^{-1}.

In all cases the standard samples were inroduced to the capillary with an injection pressure of 0.5 psi (3.447 kPa) using different injection times of 5–50 s (Br⁻) or 10–60 s (K⁺).

2.8. Recovery of the measurements

After quantification of the Br⁻ and K⁺ contents of the groundwater samples, the recovery was determined by adding 10 mg L^{-1} of the ion standard (anion or cation) to the groundwater samples. Both undiluted groundwater samples and spiked samples were analyzed sequentially with the Br⁻ or K⁺ standard solutions. By using the calibration curve, the concentrations of Br⁻ or K⁺ were calculated from both natural and spiked samples. Whereas the added concentration of ion was known, the differences between the original and the spiked samples were calculated and divided by the added

concentration. In the recovery tests, 6 repetitions were made with original and spiked groundwater samples, but only three repetitions with Br⁻ and K⁺ standards were needed.

3. Results and discussion

3.1. Bromide

The development of the electrolyte solution was modified from the previous studies of Rantakokko et al. (1999) and Fukushi et al. (1998). Low pH of the electrolyte solution was used to reduce the electro-osmotic flow. The Cl⁻ concentration in the electrolyte solution was optimized to obtain a low baseline and to avoid a too high current during the separation. Furthermore, the concentration of Cl⁻ in the electrolyte solution and in the sample was chosen to be 2 g L^{-1} (0.03 mol L^{-1}) in order to minimize peak broadening of Br⁻. However, according to the previous work of Hiissa et al. (2000) the Cl⁻ concentration of saline groundwaters varied in the range of 0.05–0.22 mol L^{-1}, and even the lowest concentration was too high for the requirements of capillary electrophoresis.

Bromide has a high UV absorbance in the range 190–210 nm. Direct UV detection at 200 nm was chosen to minimize the disturbance due to other inorganic anions present in the sample.

The recovery results for Br⁻ are presented in Table 3. The recoveries were satisfactory, except in the case of the sample taken from the deepest sampling section in the borehole. The reason for poor recovery in this case was that the concentrations of the major ions, Cl⁻ and SO$_4^{2-}$, interfered with the separation of the analyte, resulting in undetectable signals of Br⁻.

Table 4 lists the quantified amounts of Br⁻ in groundwater samples and the RSD values of peak areas obtained with the repetitions. In Fig. 1 the electropherograms of groundwater sample can be seen. It is evident that the Br⁻ concentration increases with the increasing depth of the sampling depth.

Table 3
Results of recovery tests of Br⁻ and K⁺

Sample	Recovery (%) of bromide	Recovery (%) of potassium
KR-6, depth 98.5–100.5 m	104	73.4
KR-6, depth 135.6–137 m	93	97.5
KR-6, depth 524–527 m	102	91.2
KR-12, depth 741–751 m	_[a]	_[a]
KR-13, depth 214–220 m	61.6	_[b]
KR-13, depth 362–365 m	80	84.4

[a] Recoveries could not be measured.
[b] No cation sample available.

Table 4
Results of the Br⁻ concentrations in groundwater samples

Sample	Bromide concentration (mg L^{-1})[*]	With interlaboratory tests (mg L^{-1})	Equation of calibration line, correlation coefficient, and relative standard deviation (RSD, %)
KR-11, depth 277–280 m	14	14	$y = 378.73x - 90.413$, $R^2 = 0.9994$, RSD 6.4
KR-11, depth 417–423 m	22	23	$y = 378.73x - 90.413$, $R^2 = 0.9994$, RSD 3.3
KR-11, depth 621–629m	15	15	$y = 378.73x - 90.413$, $R^2 = 0.9994$, RSD 3.9
KR-6, depth 98.5–100.5 m	10	7.7[b]	$y = 108.17x + 1641.5$, $R^2 = 0.9537$, RSD 6.0
KR-6, depth 135–137 m	25	11.5[b]	$y = 108.17x + 1641.5$, $R^2 = 0.9537$, RSD 6.0
KR-6, depth 524–527 m	64	88[a] 90[b]	$y = 108.17x + 1641.5$, $R^2 = 0.9537$, RSD 1.7
KR-12, depth 365–368 m	48	36[a] 37[b]	$y = 108.17x + 1641.5$, $R^2 = 0.9537$, RSD 5.0
KR-12, depth 741–751 m	208	204[a]	$y = 108.17x + 1641.5$, $R^2 = 0.9537$, RSD 3.8
KR-13, depth 214–220 m	13	11[b] 11.7[c]	$y = 388.77x - 693.62$, $R^2 = 0.9925$, RSD 8.2
KR-13, depth 362–365 m	25	23[b] 24[c]	$y = 342.32x - 143.44$, $R^2 = 0.9983$, RSD 4.9
KORVENSUO	0.05[**]	0.05[a] 0.02[b]	$y = 1755.2216x + 1.5235$, $R^2 = 0.9990$, RSD 16
PR3	0.2	0.2[a]	$y = 1755.2216x + 1.5235$, $R^2 = 0.9990$, RSD 14.1

Interlaboratory measurements using different analysis techniques.
[a] Lab 1.
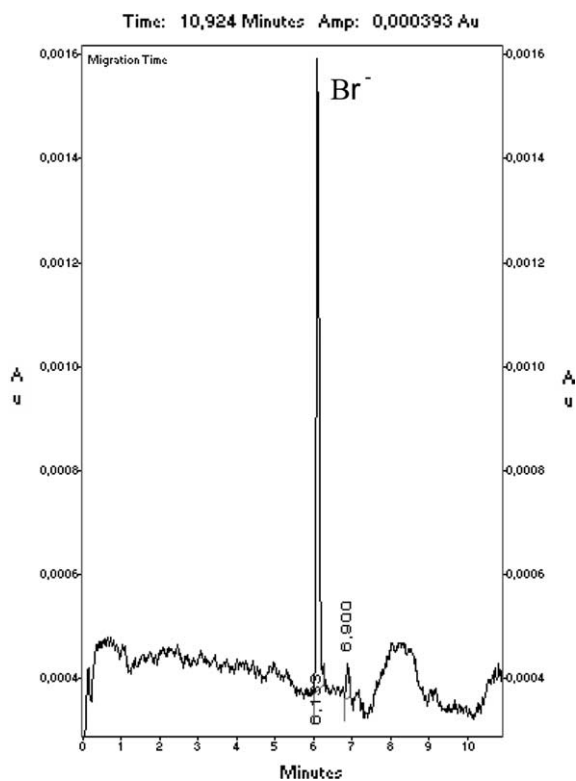[b] Lab 2.
[c] Lab 3.
[*] This study (CE)
[**] Below LOD.

Fig. 1. Electropherogram of the natural sample KR-12, taken from a depth of 365–368 m. The migration time of Br⁻ is 6.133 min. The small peak next to Br⁻ was not identified. Separation conditions: capillary 50/60 cm, +11 kV, 30 °C, 200 nm direct, injection 0.5 psi 5 s, BGE solution 5 mM HCOOH, 42 mM NaCl, pH 3.5.

The limit of quantification of Br⁻ in saline water was 1 mg L^{-1} with an injection time of 40 s and the detection limit was 0.1 mg L^{-1} with a 30 s injection time and 0.5 psi injection pressure.

3.2. Quantification of potassium ion

The concentration of K⁺ in saline groundwaters is only a fraction of those of the major cations (Ca²⁺, Na⁺, Mg²⁺) and in the CE analyses strong peak overlapping may occur. To determine the K⁺ content in saline samples without additional sample preparation steps, some enhancement of resolution between K⁺ and the major cations is needed. One possibility to solve the overlapping is to change the migration order of the analytes so that the major cations migrate first.

Changing of the migration order was effected by decreasing the migration of K⁺ by increasing the amount of 18-crown-6 ether in the electrolyte solution. In this case the ligand formed a stronger complex with K⁺ than with Na⁺ (Francois et al., 1995; Tangen et al., 1997).

With the 18-crown-6 ether concentrations of 2.5 and 5 mM K⁺ migrated before Na, whereas with the concentrations of 35–100 mM the migration order was reversed. However, the quantitation of K⁺ from groundwater samples was performed by using an electrolyte solution which contained 50 mM of the ligand. The reason was that the resolution between K⁺ and Na⁺ did not increase significantly when 100 mM 18-crown-6 ether was used.

The recovery results K⁺ are presented in Table 3. The recoveries were satisfactory, except in the case of the

Table 5
Results of the K^+ concentrations in groundwater samples received from Posiva Oy

Samples	Potassium concentration (mg L^{-1})*	Results from interlaboratory tests (mg L^{-1})	Equation of calibration line, correlation coefficient, and relative standard deviation (RSD %)
KR-6, depth 98.5–100.5 m	17	14[a]	$y = 83.277x − 95.955$, $R^2 = 0.9954$, RSD 16.0
KR-6, depth 135–137 m	16	19[a]	$y = 83.277x − 95.955$, $R^2 = 0.9954$, RSD 15.9
KR-6, depth 524–527 m	1.8**	7.2[a] 7.2[b]	$y = 83.277x − 95.955$, $R^2 = 0.9954$, RSD 14.5
KR-12, depth 365–368 m	4.4	7.3[a] 9.3[b]	$y = 83.277x − 95.955$, $R^2 = 0.9954$, RSD 15.2
KR-12, depth 741–751 m	***	17[a] 19[b]	
KR-13, depth 362–365 m	8.3	8.5[a] 8.2[c]	$y = 83.277x − 95.955$, $R^2 = 0.9954$, RSD 18.0

Interlaboratory measurements using different analysis techniques.
[a] Lab 1.
[b] Lab 2.
[c] Lab 3.
* This study.
** Below LOD.
*** Not quantified.

sample taken from the deepest sampling section of the borehole. The reason for poor recovery was that the concentrations of the major ions, Na^+ and Mg^{2+}, interfered with the separation of the analytes, resulting in undetectable signals of K^+.
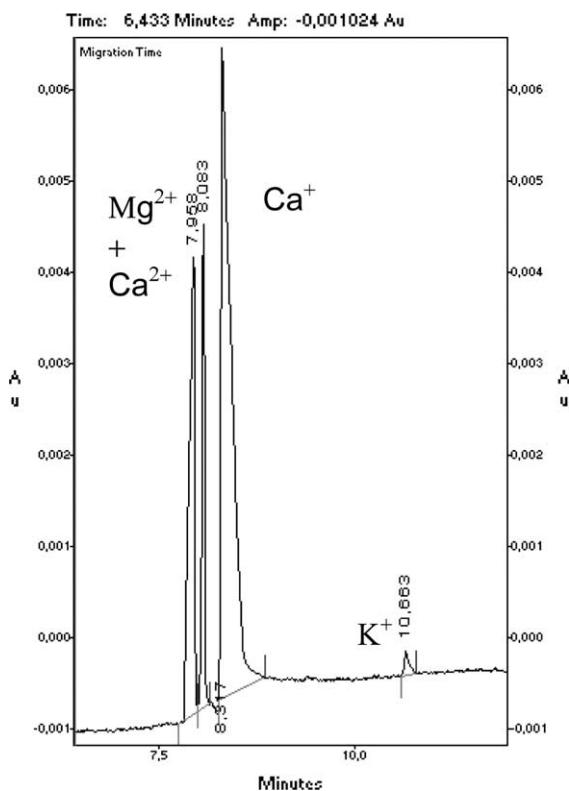

Fig. 2. Electropherogram of groundwater sample KR-6, taken from a depth 98.5 to 100.5 m. Separation conditions: capillary 100/110 cm, +30 kV, 25 °C, 214 nm indirect, injection 0.5 psi 5 s, BGE solution 10 mM imidazole, 50 mM 18-crown-6 ether, pH 4.5.

Table 5 lists the quantified amounts of K^+ in groundwater samples and the RSD values of peak areas obtained with the repetitions. As a reference, the results with solvent chemistry techniques are also presented.

The K^+ concentration in sample KR 12 at depth of 741–751 m could not be measured because Na^+ concentration was too high, which resulted in overlapping peak signals of the ions. Fig. 2 shows an example of an electropherogram of groundwater samples.

The detection and determination limits of K^+ in saline water were 0.5 mg L^{-1} and 2 mg L^{-1}, respectively, with an injection time of 50 s and 0.5 psi pressure.

4. Conclusions

Bromide and K^+ were determined from saline groundwaters pumped from borehole depths of 90–800 m below sea level. The two developed and optimized capillary electrophoretic separation methods were repeatable, selective and relatively rapid without disturbance of the high ion concentrations. Variation of Cl^- concentrations in the samples affected the peak shape of Br^-. However, the peak area of Br^- was repeatable (RSD% of the peak areas was 1.7–16). LOD and LOQ of Br^- analyses were 0.1 mg L^{-1} and 1 mg L^{-1}, respectively.

The BGE solution containing 50 mM 18-crown-6 ether was suitable for enhancing resolution between K^+ and the major cations of samples. The developed CE method was reproducible enough (area RSD% 14.5–18.0). It was also sensitivity for the real samples, since the detection and the determination limits were 0.5 mg L^{-1} and 2 mg L^{-1}, respectively.

The interlaboratory results showed that CE measurements of Br^- and K^+ were compatible with those made with traditional solvent chemistry techniques. However, CE techniques did not need extra sample

pretreatment such as derivatization and dilution. Furthermore, CE techniques are more suitable for field determinations due to the possibility of on-line sampling and the small volumes of samples needed for the experiment.

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