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Determination of Na^+ , K^+ , Mg^{2+} and Ca^{2+} in mixtures of seawater and formation water by capillary electrophoresis

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Abstract

A method has been developed for the determination of Na^+ , K^+ , Mg^{2+} and Ca^{2+} in mixtures of seawater and formation water from oil wells in the North Sea by capillary electrophoresis with indirect UV detection. The carrier electrolyte contained 5.0 mM 4-methylbenzylamine (UVCAT-1), 6.5 mM α -hydroxyisobutyric acid (HIBA), 6.2 mM 18-crown-6 and 25% (v/v) methanol. Baseline separation was achieved for concentrations below 70 ppm Na^+ , 20 ppm K^+ , 50 ppm Mg^{2+} , 30 ppm Ca^{2+} , 10 ppm Sr^{2+} and 10 ppm Ba^{2+} . The limits of detection were 0.14 ppm Na^+ , 0.15 ppm K^+ , 0.08 ppm Mg^{2+} , 0.08 ppm Ca^{2+} , 0.18 ppm Sr^{2+} and 0.15 ppm Ba^{2+} . The accuracy was checked by analysis of a reference water sample. The precision was better than 3.0%.

Keywords: Seawater; Formation water; Sodium; Potassium; Magnesium; Calcium; Cations

1. Introduction

The first application of capillary electrophoresis (CE) to the determination of metal cations was published by Hjerten in 1967 [1]. For many years, this approach received little attention [2–4], but in the last few years a number of papers have appeared in this field [5–27]. Applications to the analysis of real samples like serum, fermentation broth, etching baths and apple vinegar have been described [3,8,11,13,14], but most reports deal with the analysis of synthetic samples that consist of a number of elements added in similar concentrations. Baseline separation of the peaks is quite easily achieved in such systems and detection limits are low (ppb levels). However, these conditions are rarely found

in real samples, and certainly not in mixtures of seawater and formation water from oil wells.

The composition of mixtures of seawater and formation water varies a lot: Typical ranges for the samples studied in this work were 8–70 g/l Na^+ , 0.2–6 g/l K^+ , 0.1–3 g/l Mg^{2+} and 0.3–30 g/l Ca^{2+} . In addition, the samples contained small amounts of Sr^{2+} and Ba^{2+} . Na^+ and Ca^{2+} were often greatly in excess of K^+ and Mg^{2+} . The diversity of concentrations makes baseline separation of these elements a challenging task for CE. Although the analytical problem may be solved by using e.g. ICP-AES, there is a need for a method that is suitable for analysis offshore. The method should be based on simple and rugged instrumentation, which preferably does not require safety measures. All demands are met, within reason, by CE instruments. An oil reservoir in the North Sea contains oil

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and formation water. In order to increase the recovery of oil, seawater is introduced into the oil reservoir to maintain a high pressure inside the reservoir. The composition of seawater is different from the composition of the formation water. After some time, "production water" will come up with the oil and cause precipitations ("scale") in the pipelines. Various chemicals are added to avoid expensive interruptions in oil production due to scaling, but it is not desirable to use more of these chemicals than is necessary. Thus, it is important to monitor the composition of the production water by chemical analysis. In this work, a CE method is developed for the analysis of mixtures of seawater and formation water.

2. Experimental

2.1. Apparatus

A Waters Quanta 4000 capillary electrophoresis system, equipped with a positive power supply and a fused-silica capillary (60 cm total length, 75 μm I.D.; Waters, AccuSep), was used. The distance from the point of sample introduction to the detector window was 52 cm. Indirect UV detection was achieved at 185 and 254 nm with a mercury lamp and optical filters. A Digital Venturis data station with Millennium Chromatography Manager Software (Waters) and Microcal Origin 3.5 software was used to record and evaluate the electropherograms. Polyethylene sample vials were used as containers for the carrier electrolyte and for all of the standards and samples.

2.2. Reagents and samples

All solutions, electrolytes and standards were prepared using distilled, deionized water. The water was purged with He to remove air. Electrolytes and samples were filtered through 0.45 μm mixed cellulose esters-PVC filters (Millex SLHA 025 BS, Millipore). The following reagents were used: α -Hydroxyisobutyric acid (HIBA, Fluka, puriss), 4-methylbenzylamine (UVCAT-1, Waters), 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6, Merck, for synthesis), NaCl (Fluka, p.a), $\text{Sr}(\text{NO}_3)_2$

Table 1

Concentration range of method: Limit of detection (LOD) and upper limit for baseline separation, compared with expected concentrations for diluted samples

Element	Lower (LOD) and upper limit (ppm)	Expected concentration in samples after 1:1000 dilution (ppm)
Na	0.14–70	8–70
K	0.15–20	0.2–6
Mg	0.08–50	0.1–3
Ca	0.08–30	0.3–30
Sr	0.18–10 ^a	0.01–1
Ba	0.15–10 ^a	0–2

^aConcentrations used for Sr and Ba; the upper concentration limit for baseline separation was not investigated.

(J.T. Baker, p.a), methanol, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, KCl, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (all Merck, p.a).

The seawater was collected at Drøbak at a depth of 40 m and the formation water was obtained from an oil company. The certified reference material BCR CRM 399 Major elements in freshwater (high contents) was obtained from Community Bureau of Reference (Brussels, Belgium).

2.3. Procedure

The carrier electrolyte and samples were filtered (0.45 μm) prior to analysis. The samples of mixtures of seawater and formation water were diluted prior to analysis, so that the final concentrations came within the optimum range of the method, as shown in Table 1. The recommended electrolyte contained 6.5 mM HIBA, 5.0 mM UVCAT-1 (UV background-providing agent), 6.2 mM 18-crown-6 and 25.00% (v/v) methanol. The apparent pH was 4.8 (aqueous buffers were used for calibration).

The samples were introduced into the capillary using 20 s hydrostatic injections, from a height of 9.8 cm. The separation voltage was set at 20.00 kV and the temperature was set at 13.0°C. The capillary was purged for 2.0 min between runs. Indirect UV detection was used at 185 nm. Area- and time-corrected area were used for quantitation, which was done by means of a calibration curve. The migration times were measured at peak maximum.

3. Results and discussion

An electrolyte with 5.0 mM UVCAT-1 and 6.5 mM HIBA was used by Weston et al. [11] for the determination of alkali and alkaline earth metals. In this electrolyte, the elements migrate in the following order: K^+ , Ba^{2+} , Sr^{2+} , Ca^{2+} , Na^+ and Mg^{2+} . The electropherogram shown in Fig. 1A was obtained with this electrolyte, for a mixture of 1 ppm of each of these elements. As can be seen from the figure, baseline separation is achieved for all elements. However, when the same electrolyte is used for the

analysis of diluted mixtures of seawater and formation water, the large excess of Na^+ and Ca^{2+} will cause strong peak overlaps, as illustrated in Fig. 1B for a sample containing 70 ppm Na^+ , 30 ppm Ca^{2+} and 1 ppm of the other elements. One way of solving this problem is to use a carrier electrolyte that changes the migration order of the elements. The elements that are present in the highest concentrations, i.e. Na^+ and Ca^{2+} , should preferably come first in the migration order. This can be achieved by adding 18-crown-6 and methanol to the electrolyte [21]. An electropherogram of the same solution as in

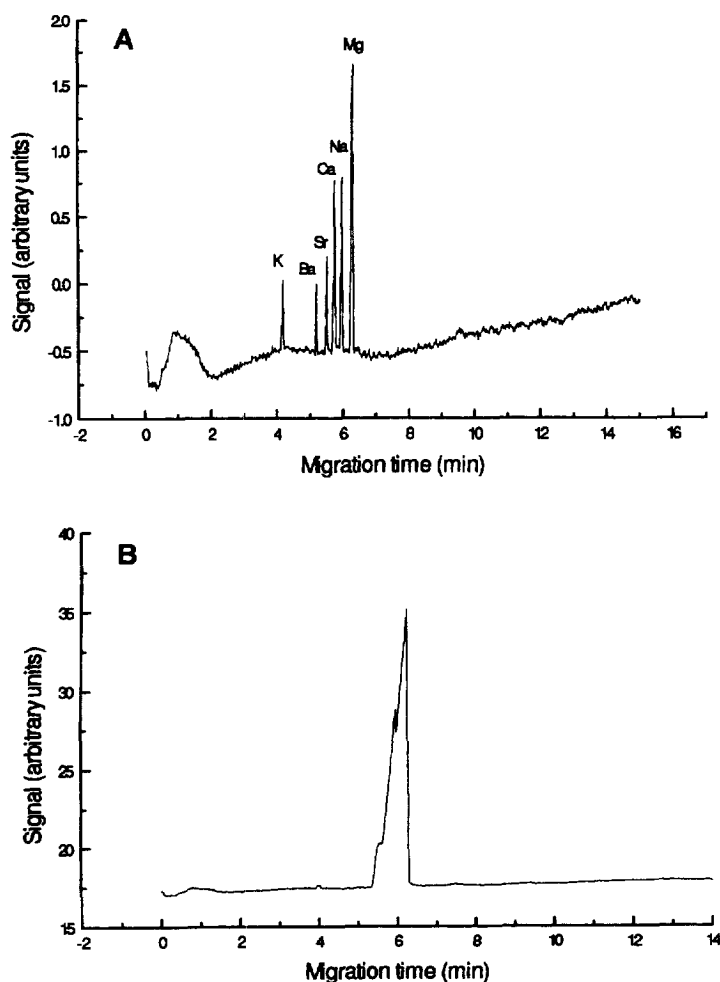


Fig. 1. (A) Electropherogram of 1 ppm of K^+ , Ba^{2+} , Sr^{2+} , Ca^{2+} , Na^+ and Mg^{2+} . (B) Electropherogram of 70 ppm Na^+ , 30 ppm Ca^{2+} , 1 ppm Mg^{2+} , Sr^{2+} , Ba^{2+} and K^+ . Electrolyte: 6.5 mM HIBA and 5.0 mM UVCAT-1.

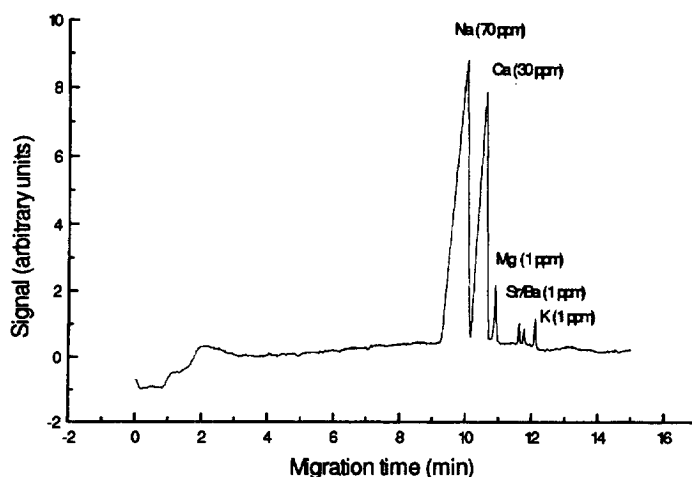


Fig. 2. Electropherogram of 70 ppm Na^+ , 30 ppm Ca^{2+} , 1 ppm Mg^{2+} , Sr^{2+} , Ba^{2+} and K^+ . Electrolyte: 6.5 mM HIBA, 5.0 mM UVCAT-1, 6.2 mM 18-crown-6 and 25.00% (v/v) methanol.

Fig. 1B, but with 18-crown-6 and methanol also added to the carrier electrolyte, is shown in Fig. 2.

The effect of methanol and 18-crown-6 on the migration times is further illustrated in Fig. 3. For Na^+ , K^+ and Ba^{2+} , the addition of methanol [25.00% (v/v)] increased the migration times by about 50%. In the case of Ca^{2+} , Mg^{2+} and Sr^{2+} , the migration times increased even more. Increased migration time with increasing concentration of methanol was also reported by Shi and Fritz [21].

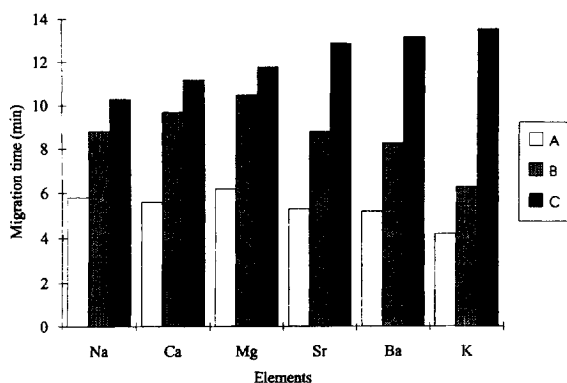


Fig. 3. The effect of methanol and 18-crown-6 in the electrolyte on the migration time, at 13°C. Sample: 1 ppm of K^+ , Ba^{2+} , Sr^{2+} , Ca^{2+} , Na^+ and Mg^{2+} . (A) 5.0 mM UVCAT-1 and 6.5 mM HIBA. (B) Addition of methanol (25.00%, v/v). (C) Addition of methanol (25.00%, v/v) and 18-crown-6 (6.2 mM).

According to Lee et al. [28] and Kenndler [29], the electroosmotic flow decreases with the addition of an organic solvent to the electrolyte. The pK_a value for orthosilic acid increases with the addition of methanol to the electrolyte [29]. Accordingly, the electroosmotic flow decreases. Thus, increased migration times are expected.

The addition of 18-crown-6 also raises the migration times; the increase is as follows (in decreasing order): K^+ (110%), Ba^{2+} (60%), Sr^{2+} (40%), Na^+ (17%), Ca^{2+} and Mg^{2+} (13%). This result is in good agreement with the complexation properties of 18-crown-6; the log K -values of the formation constants of the respective complexes are 0.8 (Na^+), 0.5 (Ca^{2+}), 2.1 (K^+), 2.8 (Sr^{2+}) and 3.8 (Ba^{2+}) [30]. Other authors also describe the use of 18-crown-6 to improve the separation of alkali and alkaline earth metals [12,18,20,21,27]. Fifteen concentrations of 18-crown-6 were tested within the range 0–14.0 mM. The optimal resolution was obtained with 6.2 mM 18-crown-6.

The presence of HIBA also has an influence on the mobility of the cations [10,11,16,17,19]; the formation constants of the HIBA complexes are larger for Ca^{2+} and Mg^{2+} than for Sr^{2+} and Ba^{2+} [11,31].

The migration time increased with decreasing temperature; the effect was most marked for K^+ . The low temperature (13.0°C) also served to minimize methanol evaporation; the electrolyte should not be

used for more than 4 h. Careful temperature control was needed to assure reproducible (R.S.D. $\leq 2.3\%$, $n=6$) migration times. A separation voltage of 20 kV was found to be the best choice. Higher voltages caused baseline noise spikes, probably due to capillary boiling.

Because the elements do not absorb UV radiation, UVCAT-1 is used as a UV background-providing agent. Thus, indirect UV detection is achieved. UVCAT-1 is also the co-ion of the carrier electrolyte. It was found that detection at 185 nm gave better sensitivity than detection at 254 nm.

The lower and upper concentration limits for each element are given in Table 1. The upper limit in the table corresponds to the maximum concentrations that could be handled without sacrificing baseline separation. For Sr^{2+} and Ba^{2+} , the upper concentration limit for baseline separation was not investigated, because Sr^{2+} and Ba^{2+} were below the limit of detection (LOD) in most real samples. The lower concentration limit in Table 1 corresponds to the limit of detection, defined as three times the standard deviation obtained for a solution containing 1 ppm of each element ($n=6$). (The use of a "blank" solution will give a less realistic estimate of the LOD). Similar LOD estimates were obtained for an electrolyte containing only 6.5 mM HIBA and 5.0 mM UVCAT-1.

The use of peak area as well as time-corrected peak area provided a linear response for all the elements in the following ranges: 10–50 ppm Na^+ ($n=6$), 2–10 ppm K^+ ($n=5$), 1–10 ppm Mg^{2+} ($n=6$), 1–25 ppm Ca^{2+} ($n=6$), 3–5 ppm Sr^{2+} ($n=3$) and 1–5 ppm Ba^{2+} ($n=5$). The precision was found to be 3.0% or better based on the analysis of the same solutions. The accuracy was determined by analysing the certified reference material BCR CRM 399 Major elements in freshwater (high contents). This reference sample was chosen because the concentration of alkali and alkaline earth metals was similar to that found in the samples analyzed in this work. The results for the reference sample are given in Table 2; the results obtained are not significantly different from the certified values (t -test, $p=0.05$).

The method was used for the analysis of real samples of mixtures of seawater and formation water; an electropherogram of such a sample is shown in Fig. 4. The quantitative results for four samples are given in Table 3. For comparison, the results obtained by an oil company using an ICP-AES method are also given in Table 3. The values obtained by the two methods agree very well for K^+ , Mg^{2+} and Ca^{2+} , but less so for Na^+ . Although the four samples are from two different locations in the North Sea, the concentrations are quite similar. As can be seen from the table, the concentration of Na^+

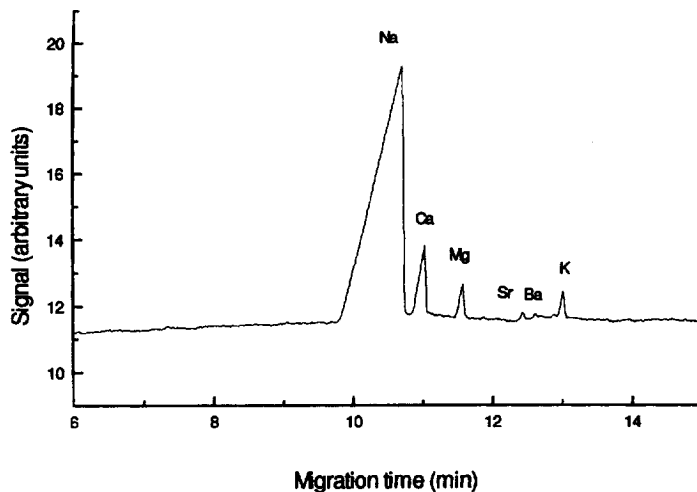


Fig. 4. Electropherogram of a mixture of seawater and formation water diluted by a factor of 125. Electrolyte: 6.5 mM HIBA, 5.0 mM UVCAT-1, 6.2 mM 18-crown-6 and 25.00% (v/v) methanol.

Table 2
Results for the freshwater reference sample BCR CRM 399

Element	Capillary electrophoresis ^a		BCR CRM 399 certified values	
	Mean (ppm)	S.D. ^b (ppm)	Mean (ppm)	Uncertainty ^c (ppm)
Na	29.4	0.080	30.4	0.7
K	2.98	0.076	2.99	0.12
Mg	15.4	0.27	15.1	0.2
Ca	77.7	1.1	79.2	0.9

^a*n* = 6, except for the determination of K (*n* = 4).

^bStandard deviation.

^cHalf width of the 95% confidence interval of the mean.

Table 3
Results (g/l) obtained for the analysis of mixtures of seawater and formation water using CE^a and ICP-AES^b

Element	Sample 1		Sample 2		Sample 3		Sample 4	
	CE	ICP-AES	CE	ICP-AES	CE	ICP-AES	CE	ICP-AES
Na	12.5 ± 0.3	11.1	12.5 ± 0.3	13.1	11.9 ± 0.2	12.0	12.3 ± 0.2	11.3
K	0.33 ± 0.04	0.37	0.40 ± 0.06	0.42	0.32 ± 0.04	0.36	0.27 ± 0.02	0.25
Mg	1.07 ± 0.05	1.03	0.99 ± 0.04	0.97	1.00 ± 0.08	1.00	0.90 ± 0.02	0.89
Ca	0.84 ± 0.07	0.78	0.74 ± 0.02	0.76	0.63 ± 0.3	0.60	0.99 ± 0.1	0.99

^aCapillary electrophoresis. Result ± standard deviation (*n* = 3).

^bAnalysis performed by an oil company.

is more than ten times higher than the concentration of the other elements for all samples.

The concentration of alkali and alkaline earth metals is very high in mixtures of sea water and formation water, up to 7 and 3% of Na⁺ and Ca²⁺, respectively. Therefore, the samples were diluted by a factor of 100–1000, so that the final concentration of the major ions Na⁺ and Ca²⁺ were below 70 and 30 ppm, respectively. From Table 1 it can be seen that for a 1:1000 dilution, the expected levels of Na⁺, K⁺, Mg²⁺ and Ca²⁺ in mixtures of seawater and formation water will be within the recommended concentration range of the method. However, when this degree of dilution was used, the concentrations of Sr²⁺ and Ba²⁺ were normally below the LOD of the method.

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