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Analysis of highly saline samples by capillary zone electrophoresis: enhanced direct UV detection of inorganic anions using on-capillary preconcentration and clean-up techniques

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Abstract

The ability to analyze samples with disparate levels of analyte and matrix ions is among the important benefits defining the practical utility of modern capillary electrophoresis. To compensate for the sensitivity limitations regarding trace-level inorganic anions, a number of on-line approaches that should offer an improved S/N ratio in direct UV detection were examined. The novel use of reversed pre-electrophoresis (at the applied voltage opposite to the separation voltage) made it possible to efficiently remove the most part of high chloride levels from the sample and hence to lower the background signal and to inject increased quantities of fast analyte anions. Specifically, by taking these advantages the sensitivity response of iodide was improved by a factor of 5 over normal CE mode. Using isotachophoretic sample stacking, a two-fold increase in detectability was obtained for moderately mobile anions, nitrate and nitrite, that corresponds to the minimum detectable concentrations close to their natural occurrences in seawater. Furthermore, field-amplified sample injection at increased electrolyte-to-sample matrix concentration ratios enabled the maximum S/N enhancement, with detection limits at the level of 10^{-6} M and lower in the presence of $\geq 5 \cdot 10^4$-fold molar excess of chloride.

Keywords: Sample preparation; Detection, electrophoresis; Buffer composition; Inorganic anions

1. Introduction

Capillary zone electrophoresis (CE) is a powerful and practical method for high-resolution separation of inorganic anions within complex matrices [1–4]. However, a major problem has always existed, that is, separation performance is usually degraded by the presence of salts in samples, such as seawater, geothermal brine, groundwater, some biological fluids, etc. Such samples normally would require removal of ionic matrix components by an off-line sample clean-up technique, e.g., membrane-based solid-phase extraction [5] or precipitation [6], prior to analyte separation by CE. In both cases the

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formation of insoluble salts is the chemistry involved in removing high concentration of ionic contaminants. As a more straightforward approach for eliminating matrix interference from the major ionic components of high-salt samples, anion separations may be performed in electrolytes containing high salt concentrations. Such an approach looks especially promising in combination with direct UV detection of anions having sufficient absorbance in the UV region. For instance, several reported CE procedures related to separation of seawater anions benefit an increased resolution due to the use of chloride ion added to the electrolyte solution in the range 100–1500 m*M* [7–9]. Likewise artificial seawater, undiluted [10] or a ten-fold diluted [11], can be adopted as the carrier electrolyte. Electrolytes loaded with a high chloride were found suitable for anionic analyses of saline biofluids such as urine and serum [12] or blood plasma [13–15].

It is far more challenging, however, to develop a CE methodology that works well for the determination of trace-level anions in samples with an uneven distribution of concentrations. For example, though chloride is known as a UV-transparent anion, it can produce an interfering peak when injecting undiluted seawater [9] or other samples with quite a high matrix concentration of NaCl [16,17]. Even with a high ionic concentration in the carrier electrolyte detection and quantification of anions continue to be difficult. The problem is mainly due to the fact that the high concentrations of sample salts cause alterations in peak heights and peak distortion associated with an enhanced dispersion during sample introduction, laminar flow broadening and, to a certain extent, Joule heating [8,18,19]. Along with this salts added to the electrolyte solution would itself generate an elevated baseline signal [9,11]. As follows from the above-mentioned citations, only a limited number of seawater anionic constituents with moderate natural occurrences (bromide [8,11], nitrate [7,10,11] and nitrite [7,10]) could for this set of complications be subject to reliable quantification. Similarly only modest detection limits were attained during anion analyses of subterranean water samples despite 100 m*M* NaCl incorporated into the carrier electrolyte [19].

Application of a selective sample enrichment procedure compatible with the following CE stage would be a solution to the problem, and according to a decade of literature [1,20–22], the on-line combination of isotachophoresis (ITP) prior to CE appears to be a promising alternative for the desired analyses. An impressive practical use of ITP–CE in terms of concentration factors achieved and permissible matrix-to-analyte ion molar ratios has been demonstrated by Kaniansky et al. [23]. However, when performed in a coupled-capillary arrangement, ITP–CE requires additional hardware modifications that sets a limit for its adaptation in most commercially available systems. Also it can be difficult to find a suitable isotachophoretic leading electrolyte for separating the fast-migrating anions of a high disparity in concentration. Moreover, if the mobilities of the matrix and analyte anions are similar (what is the case), the separation and thus the sample clean-up can be slow or incomplete.

Therefore, the main objective of the present study was to evaluate on-capillary approaches for improvement of the detection sensitivity for UV-active anions in the samples of high salt content. The test analytes encompassed in this study were a series of inorganic anions relevant to trace seawater analysis, the subject of the authors' particular interest. The approaches tested involved on-capillary preconcentration techniques common in the practice of CE, such as field-amplification and isotachophoretic sample stacking. Special attention was also given to sample clean-up using reversed pre-electrophoresis. This new rapid on-line desalting procedure utilizes the greater relative mobility of chloride as a principal matrix anion to allow its efficient electrophoretic removal from the sample injected while causing a negligible loss of less mobile analytes.

2. Experimental

2.1. Apparatus and procedure

The CE systems used were a Hewlett-Packard HP^{3D}CE (Waldbronn, Germany) and a Perkin-Elmer (Foster City, CA, USA) Model 270A-HT. Separations were performed on fused-silica capillaries of 72 cm (50 cm effective length)$\times$50 μm I.D. or 48.5 cm (40 cm effective length)$\times$50 μm I.D., respectively, applying a voltage of -10 kV. Prior to each experimental series, the capillary was conditioned by rinsing with 0.1 *M* NaOH for 10 min, water for 2 min, 0.1 *M* HCl for 10 min, water for 2 min, and the electrolyte solution for 20 min. Before each run inlet and outlet electrolyte vials were replenished with the carrier electrolyte to avoid an adverse effect due to electrolytic degradation of non-buffered electrolyte and the capillary was purged with the electrolyte solution for 5 min. Samples were introduced by pressure (50 mbar; HP^{3D}CE) or vacuum (16.9 kPa; 270A-HT). The temperature was maintained at 30°C for capillary cassette during all experiments. The detection wavelength was set as specified below. Electrolytes were filtered through a 0.20-μm pore size membrane filter (Advantec, Tokyo, Japan).

2.2. Carrier electrolyte solutions

As was demonstrated in our previous study [9], a carrier electrolyte solution of 100 m*M* potassium chloride offers the possibility of preventing much of interference from high matrix salinity. Being modified by incorporating 18-crown-6 or tetrabutylammonium (TBA) chloride, the electrolyte compositions developed amend also the separation selectivity for anions possessing different degrees of hydrophobicity. Importantly, both electrolyte additives have little absorbance that avoids appreciable UV absorption background. The pH of the carrier electrolytes used was adjusted to 4.0 with 0.1 *M* HCl. The acidic pH value selected in combination with fairly high electrolyte concentration of cations minimized the electroosmotic flow (EOF) and provided thereby short migration times and an enhanced resolution.

2.3. Standard solutions

All standards (and electrolytes) were prepared with analytical-reagent grade chemicals in distilled deionized water. Stock solutions of inorganic anions (final concentration 0.1 *M* each) were prepared from their corresponding sodium salts. Taking sodium chloride to represent matrix salts in seawater, mixed anion solutions of lower concentrations were prepared by serial dilutions of these standards keeping a constant NaCl concentration of 50 m*M*.

3. Results and discussion

3.1. Performance of direct UV detection

Direct photometric detection of inorganic anions is often underestimated by CE practitioners for the ground that only a limited number of anions are detectable at useful wavelengths [1]. In fact, this number appears to be fairly greater than it is thought. For example, at least 10 UV-absorbing anions exist in seawater at the level of ≥0.1 μg/l [24]. Therefore, in the determination of specific trace anions in samples containing high concentrations of other anions, it is advisable to use direct UV detection provided that the analyte anions show UV absorption whereas the matrix anions do not. However, in reality extreme concentration ratios can be encountered (e.g., the concentration of chloride exceeds the concentrations of other anionic seawater species by at least a factor of 1000); these lead to serious quantification difficulties to be counteracted.

The effect of the concentration of NaCl in the sample was first investigated briefly on the detection of anions. In these experiments taking nitrate as an example, the limit of detection was assessed at decreasing the chloride concentration in the sample injected. As can be seen from the data of Table 1, sample dilution allowed for a somewhat improved detectability. Though this finding looks like controversial to what our common experience shows, a higher sensitivity did result from dilution. A natural reduce in peak height upon diluting the sample solution seems to be overwhelmed with the accompanying lowering of both chloride matrix spectral

Table 1
Chloride matrix effect on the detection of nitrate[a]

NaCl (M)	Relation to seawater matrix[b]	Detection limit (M)[c]	
		in NaCl solution	in seawater
0.50	undiluted	$>5\cdot10^5$	$>5\cdot10^5$
0.25	1:1 diluted	$\geq5\cdot10^5$	$>5\cdot10^5$
0.05	1:10 diluted	$1.3\cdot10^6$	$1.3\cdot10^5$

[a] Conditions: capillary, 48.5 cm (40 cm effective length)×50 μm I.D.; electrolyte, 20 m*M* 18-crown-6, 100 m*M* KCl (pH 4.0); injection, 3 s at 50 mbar; detection at 200 nm.

[b] According to the Japanese standard [25], the chloride concentration in seawater is about 0.46 *M*.

[c] Three times signal-to-noise ratio.

interference and, as justly pointed out one of the reviewers, capillary overloading.

With a 50 m*M* NaCl solution simulating a ten-fold diluted seawater matrix, detection thresholds were measured for other anionic analytes: $1.8\cdot10^{-6}$ *M* I^- (225 nm), $2.3\cdot10^{-6}$ *M* NO_2^- (200 nm), and $3.2\cdot10^{-6}$ *M* IO_3^- (200 nm) using simple pressure injections at 3 s (50 mbar). Increasing the system loadability was considered not practicable in view of inevitable reduction of theoretical plate number count and limited column capacity. Nonetheless ca. a two-fold increased response was observed for iodate when injecting a greater sample volume (4 s or injection length as 7% of the capillary length).

Another attempt to enhance the detectability of the existing CE system was to apply a high sensitivity detection cell available in the Hewlett-Packard CE Capillaries Set. According to the company guidelines, the cell having a pathlength of 1200 μm improves the detection sensitivity for more than 10 times over standard capillaries. However, this was not the case with high-salt sample and carrier electrolyte solutions. In fact, detection performed with the extended light length resulted even in worse sensitivity characteristics (anions at concentrations above 10^{-4} *M* can only be detected). The appearances of high background absorbance and high ionic strength, generating an increased baseline noise, presumably accounted for the limited detectability.

3.2. Sample clean-up by reversed pre-electrophoresis

To address the challenge of chloride matrix interference for direct UV detection, a study was conducted on the use of reversed pre-electrophoresis (RPE). It was believed that chloride, possessing a electrophoretic mobility higher than that of most of target analyte anions, can be removed selectively from the sample zone by the application — after hydrodynamic injection and prior to separation of a low positive voltage for a certain period of time. As at RPE conditions the sample anions move toward the injection (anodic) end of the capillary, both RPE voltage and time should be controlled carefully to prevent the analytes from coming off the capillary. Evidently, the length of the sample plug is also an important parameter since the longer the sample zone, the longer the time and the larger the voltage of RPE can be set, and the greater the amount of analyte can be involved in separation. Increasing the amounts injected becomes in turn arbitrary as it leads to lower detection limits on the one hand and causes diffusion of the analyte zones on the other hand. It is also worthy of noting that the efficiency of RPE depends on the pH of the sample. With a natural, near neutral pH of sodium chloride solutions, a rather strong EOF induced by the positive voltage in the direction opposite to the electrophoretic mobilities tends to facilitate the desalting effect of RPE.

The following general interpretations drawn from Fig. 1 illustrate the action of RPE. With the customary sample introduction/CE separation procedure, the injection of a solution, containing 50 m*M* chloride, $8.5\cdot10^{-5}$ *M* bromide and $5\cdot10^{-6}$ *M* iodide, nitrate, nitrite and iodate, for 3 s resulted in signal responses of the latter four anions close to their detection limits (Fig. 1a). The sample volume increased did not improve detectability but led to a loss of resolution and seriously deteriorated peak shapes (Fig. 1b). With the use of RPE the amounts of analytes participating in separation must have become smaller; that was true for at least the fast anions which migrate more rapidly and, hence, are inclined to be swept to the cathode (cf. Fig. 1a and c for the bromide signals obtained with the injection time of 3 and 10 s, respectively). On contrary an increase in the peak height of iodide took clearly place. The reason for this beneficial effect of RPE can possibly be interpreted in terms of the differing effective mobilities of iodide and chloride. On the other hand, better peak efficiencies for slowly migrating anions are presumably reflecting the action of RPE on the sample plug length.

It should be mentioned here that operational RPE parameters chosen to obtain the electropherogram seen in Fig. 1c, were designed as based on the equation [26]:

$$L_p = \Delta P r^2 t / 8\eta L$$

where L_p denotes the length of the sample plug, ΔP is the pressure across the capillary, r is the inner radius of the capillary, η is the viscosity of electrolyte solution and L stands for the length of the capillary, as well as on the data on migration velocities for anions under investigation.

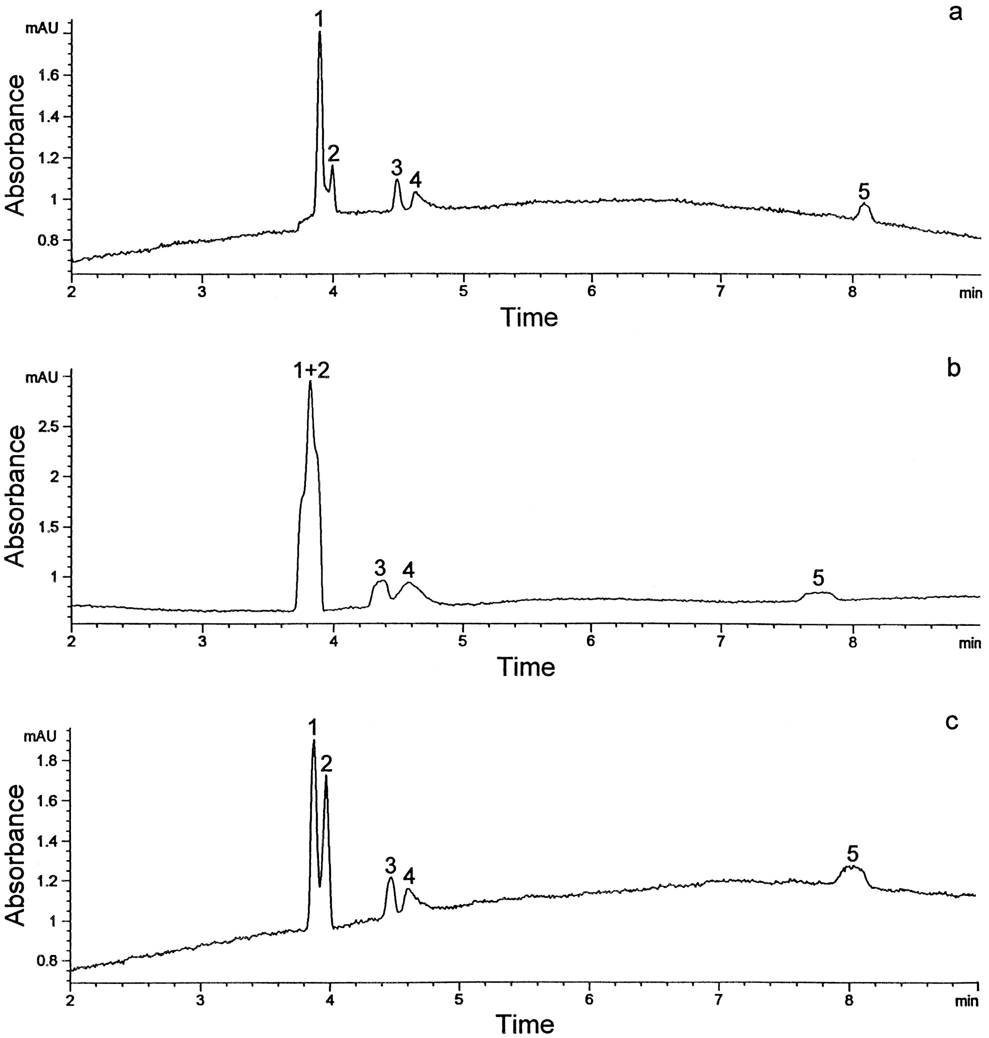

Fig. 1. Detection of low-level anions in (a, b) CE and (c) RPE–CE mode. Capillary, 48.5 cm (40 cm effective length)×50 μm I.D.; electrolyte, 100 m*M* KCl (pH 4.0); injection, pressure, for (a) 3, (b, c) 10 s; detection at 210 nm. RPE, 15 s at 3.0 kV. Sample, (1) $8.5 \cdot 10^{-5}$ *M* Br^-, (2) I^-, (3) NO_3^-, (4) NO_2^-, (5) IO_3^- ($5 \cdot 10^{-6}$ *M* each) in 0.05 *M* NaCl.

3.2.1. RPE with non-modified electrolyte

In order to optimize the performance of RPE, the effects of RPE time and voltage were systematically explored using simple KCl electrolyte. Fig. 2 demonstrates the influence of varying the RPE time on peak heights with the RPE voltage maintained at 3.0 kV (data for nitrite not shown for the sake of simplicity). The responses of fast migrating iodide and bromide were greatly affected, as indicated by a drastic increase in peak heights with decreasing the RPE time from 0.40 to 0.20 min (the latter value is an instrumental parameter which cannot further be reduced). Notably at the shortest possible time of RPE, the iodide peak exhibits nearly the same intensity response as the bromide peak. Conversely, at the longest RPE time studied the RPE swept iodide and bromide to the injection side of the capillary too quickly and no peaks of these anions could be recorded. For other, from moderately to slow mobile anions, having longer residence time on the capillary, the effect of RPE was essentially insignificant. This observation implies that RPE,

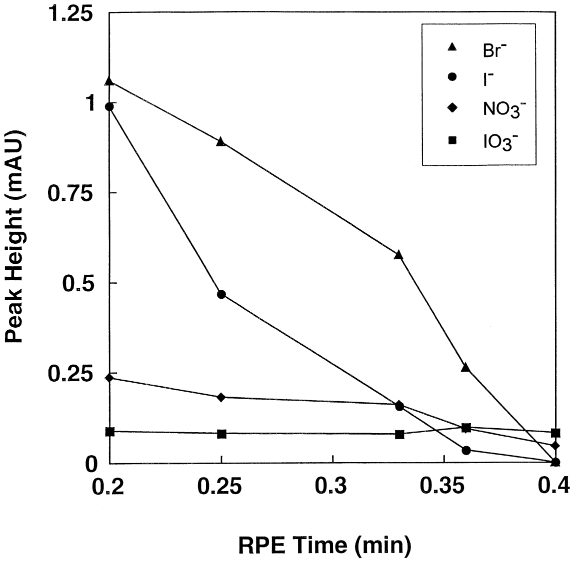

Fig. 2. Anion signal responses vs. RPE time. RPE voltage, 3.0 kV. Other conditions as for Fig. 1c.

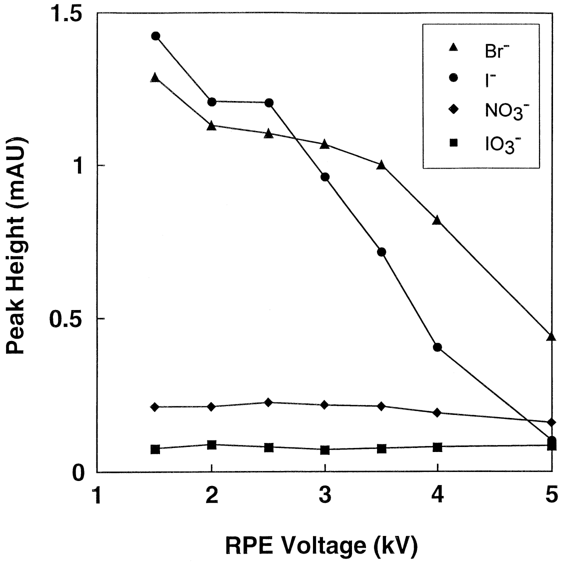

Fig. 3. Effect of RPE voltage on the peak height of anions. RPE time, 12 s. Other conditions as for Fig. 1c.

working in these experiments as a means of sample desalting regarding chloride particularly, exerts a very slight influence on the detection sensitivity of anionic analytes migrating much slower than chloride.

The responses of the four analytes are plotted against the RPE voltage in Fig. 3. To collect the data for Fig. 3 the RPE voltage was applied for 0.20 min. With decreasing the voltage from 5.0 to 1.5 kV, the iodide peak rises gradually from a near-to-detection limit signal to higher than the bromide signal, though the latter anion also experiences a noticeable grow (the bromide concentration in the sample injected is, to remind, 17 times higher). However, at voltages below 2.5 kV the improvement in sensitivity takes place at the expense of resolution. As can also be seen in Fig. 3, changes in the signals of nitrate and iodate with the variation of RPE voltage are negligible as was also true (and for the same reason) when the RPE time was the variable.

From these experiments, the operational RPE voltage and duration selected as the optimum cleanup conditions were 3.0 kV and 0.20 min.

3.2.2. *RPE with TBA-containing electrolytes*

As can be judged from the results of Section 3.2.1, using the RPE step allowed for a ca. five-fold increase in detectability for the iodide ion. All the efforts to detect the iodide signal at concentrations below $5 \cdot 10^{-6}$ *M* were, however, unsuccessful because of inadequate resolving power of non-modified electrolyte. In an attempt to overcome this obstacle, alteration of the resolution between bromide and iodide peaks by adding TBA was studied. The earlier discovered phenomenon of converting the bromide peak into a negative peak at high electrolyte concentrations of TBA [9] was thought to be of a certain benefit for detecting the iodide peak.

To determine whether the RPE acts similarly in the modified electrolyte system, the same anion mixture was monitored under varying the TBA concentration in the electrolyte solution. The baseline resolution between bromide and iodide was achieved at 10 m*M* TBA, and a further increase continued producing a monotonic shift of the iodide peak from bromide to nitrite (Fig. 4). This plot testifies that the best resolution of iodide with respect to both adjusting peaks should be attained at 33 m*M* TBA (as a result of interception of the two linear fits). The corresponding carrier electrolyte did permit an excellent resolution: R_s (Br^-/I^-) and R_s (Br^-/NO_2^-) were 2.07 and 2.13, respectively. However, an

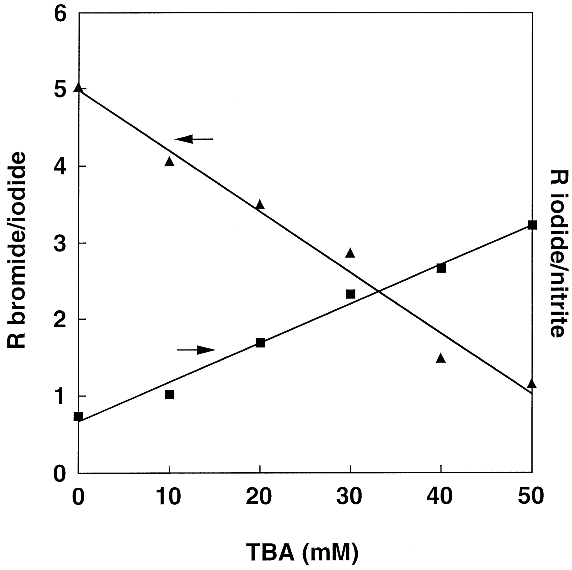

Fig. 4. Resolution between bromide and iodide and iodide and nitrite as a function of TBA concentration. Electrolyte, 100 m*M* KCl (pH 4.0) containing TBA at different concentration. RPE, 15 s at 3.0 kV. Other conditions as for Fig. 1c.

electrolyte solution containing 30 m*M* TBA provided a somewhat better signal response and was thereby recognized as a better choice. The result of this selection is shown in Fig. 5. From the comparison of electropherograms in Figs. 1c and 5 it can, however, be concluded that the influence of RPE on detection sensitivity in the TBA electrolyte system is not so effective.

3.2.3. RPE with 18-crown-6-containing electrolyte

Our final and most successful try to lower the detection limit of iodide, one of the most important trace-level anions for understanding the marine environment, was to conduct RPE–CE measurements in crown-ether electrolyte system. A brief optimization of RPE conditions (data not shown) afforded the best results regarding sensitivity and resolution at a RPE voltage of 3.0 kV. However, because of a mismatch between the EOFs in the sample and electrolyte zones the problem of poor peak area reproducibility was encountered. This problem was solved by modification of the pre-run capillary flushing procedure, that is, using a five-step rinsing with 0.1 *M* NaOH for 2 min, water for 1 min, 0.1 *M* HCl for 2 min, water for 1 min and finally with the electrolyte solution for 5 min.

As a result, iodide was well detected at the level of $2\cdot10^{-6}$ *M* in the presence of more than a 400-fold excess of bromide and at an analyte-to-chloride matrix-ratio of $1{:}2.5\cdot10^{4}$. The minimum detection limit was as low as $9\cdot10^{-7}$ *M* or 110 μg/l that presents a definite sensitivity enhancement over normal CE mode (see Section 3.1).

3.3. Stacking by transient isotachophoresis

Depending on the mobility of sample and analyte ions, isotachophoretic conditions at the beginning of the CE run can be established when the matrix ion acts as leading (or as terminating ion) and the electrolyte co-ion as terminating ion (or leading ion). Analytes with mobilities between those of the matrix ion and the electrolyte ion will undergo focussing at the end of ITP initial stage. This technique has been applied for the determination of inorganic anions in

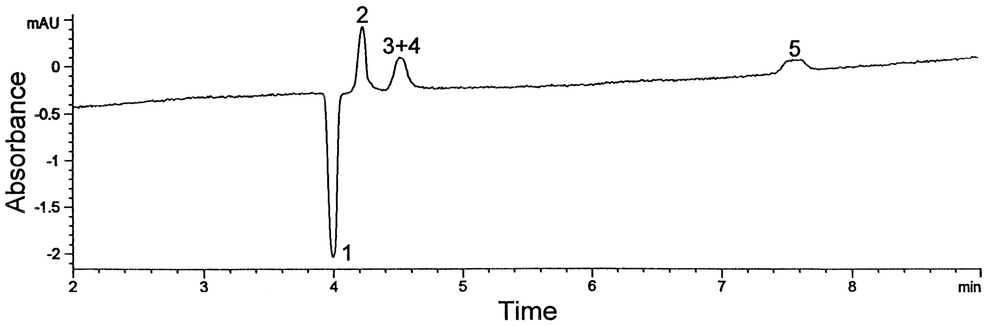

Fig. 5. RPE–CE response of iodide in TBA electrolyte system. Electrolyte, 30 m*M* TBA, 100 m*M* KCl (pH 4.0). Other conditions as for Fig. 4.

samples, containing fluoride [27], hydroxide [28] and chloride [29,30] as matrix ion, with a chromate, salicylate and succinate (phosphate) carrier electrolyte, respectively.

In samples under investigation, the major matrix ion, chloride could perform well the role of a leading anion for the purposes of ITP enrichment. The migration sequence in CE should place an ion serving as a terminating anion at a large distance from the leading chloride. Also importantly, this ion must enable direct UV detection by absorbing only minimally in the low-wavelength range. On these terms fluoride and phosphate were chosen as terminating ions. The result of introducing fluoride into the electrolyte solution can be seen in Fig. 6. For a constant analyte concentration, peak heights of nitrate and nitrite nearly doubled in going from 0 to 10 m*M* fluoride. A minor disadvantage of higher fluoride concentrations was the loss of resolution between the stacked nitrate and nitrite peaks (see Fig. 6b). According to our expectations, only these moderately mobile anions experienced the concentration effect. The mobility of iodide lies at the margin of ionic range used for ITP focussing and thereby iodide expresses a noticeable peak broadening; iodate migrates far after the terminating fluoride. Similar results (but without deliberate intention to establish ITP conditions) were recently reported by Friedberg et al. [12]. The addition of phosphate ions to a saline sample increased the peak height of nitrite and nitrate but not that of bromide (Br^- is the fastest of halide anions).

The increase in sensitivity for nitrate and nitrite by a factor of two brought about by on-column ITP concentration was consistent with that achieved by Bächmann and coworkers [27]. However, whereas such an improvement in detectability is appropriate for other applications, it is outlying for the aims of anion quantification in seawater. It should be emphasized that at acidic pH used fluoride is not favorable for the capillary wall exhibiting large silanophilic interaction. Also tried phosphate performed less efficiently as a transient terminating anion.

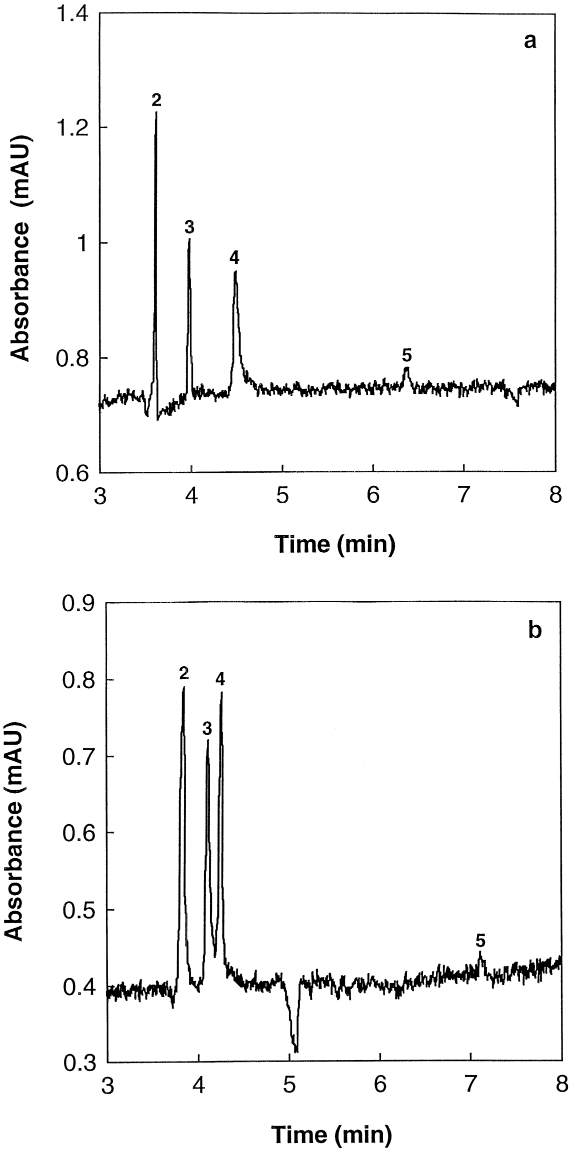

Fig. 6. Detection of low-level anions (a) without and (b) with transient ITP preconcentration. Electrolyte, (a) 20 m*M* 18-crown-6, 100 m*M* KCl (pH 4.0); (b) 20 m*M* 18-crown-6, 90 m*M* KCl–10 m*M* KF (pH 4.0). Sample, $5\cdot10^{-6}$ *M* each I^-, NO_3^-, NO_2^- and IO_3^- in 0.05 *M* NaCl. Other conditions and identification of peaks, as in Fig. 1a.

3.4. Preconcentration by field-amplified sample stacking

One of the most efficient sample stacking procedures (often called large volume sample stacking) implies the injection of a very large volume of the sample solution (of considerably lower ionic strength than the carrier electrolyte) followed by removal of most of the water matrix and focussing the analytes at the sample-carrier electrolyte boundary. The removal takes place under action of EOF directed toward the injection side of the capillary and is typically associated with a polarity-switching step [31,32] or the use of an EOF modifier [33]. For anions with mobilities high enough to overcome the EOF, however, neither would be necessary to pump out the water plug that simplifies the stacking procedure [34,35].

Under basically non-stacking conditions established with the chloride concentration in the sample and carrier electrolyte as 50 and 100 m*M*, respectively, only short injection time can be tolerated without peak distortion and detection signals remain thus rather poor reflecting no zone sharpening effect (Fig. 7a). Increasing the injection time leads to broad peaks (Fig. 7b) despite the fact that the EOF in the sample zone entered the capillary is fairly strong to remove the water plug. On the other hand, when more chloride is added to the electrolyte, to a concentration of 500 m*M*, stacking for all the test anions occurs as illustrated in Fig. 7c. Theoretically the larger the difference in concentrations, the greater the effect of stacking becomes, as the stacking

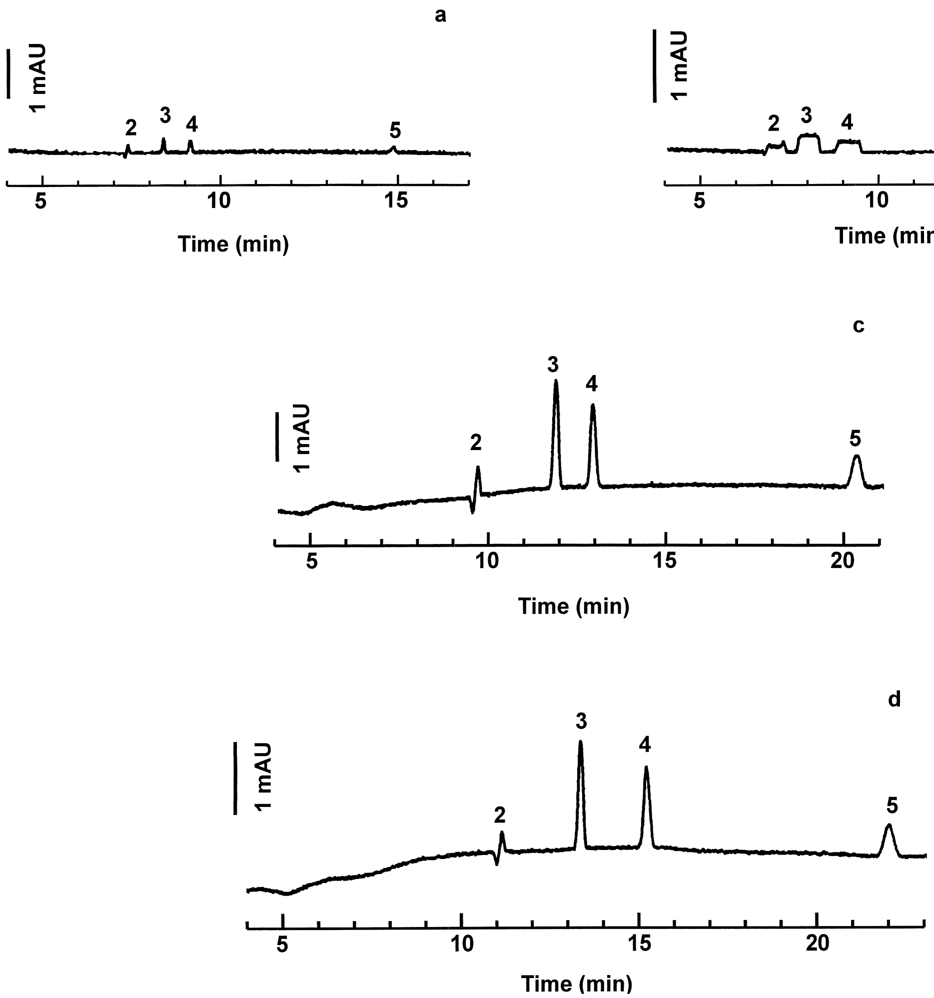

Fig. 7. Effect of field-amplified stacking on the peak height of anions. Capillary, 72 cm (50 cm effective length)×50 μm I.D.; electrolyte, (a, b) 100, (c, d) 500 m*M* KCl (pH 4.0); injection, vacuum, for (a) 3, (b, c) 30, (d) 60 s; detection at 210 nm. Sample (and peak identity), (a–c) same as that in Fig. 6, (d) two-fold dilution of (a).

force is proportional to the field amplification ratio. Accordingly, a two-time longer injection (60 s or about 70% of the capillary length) of a two-fold diluted sample solution can be accomplished without the dispersion effects (Fig. 7d) yielding a further improvement of the detection signal of around two times. This large-volume injection enables to lower the limits of detection down to $1.4 \cdot 10^{-6}$ *M* I^-, $3.2 \cdot 10^{-7}$ *M* NO_3^-, $4.2 \cdot 10^{-7}$ *M* NO_2^- and $1.1 \cdot 10^{-6}$ *M* IO_3^-, i.e., for about an order of magnitude compared to the usual injection conditions. Though enrichment factors of more than 100 have been reported for high-purity matrices [31–33,35], such sensitivity enhancement should be recognized as a step forward in regard to trace anionic seawater analysis. Note that interfering matrix salts are not eliminated but concentrated (by the same factor as the analytes) in the stacking process.

4. Conclusions

Several approaches of compensating for the sensitivity limitations of existing commercial CE system regarding UV detection of inorganic anions in samples of high salt content have been examined in this work. Although inducing improvements of 2–5 times, transient isotachophoresis stacking and reversed pre-electrophoresis do not prove greatly useful for the purposes of seawater analysis. More endorsing results were obtained with field-amplified sample introduction. The up to 10-fold advancements in detection limits make this approach attractive for the determination of trace anions in loaded samples. The power of implementing field-amplified sample stacking could apparently be extended to the analysis of low-level seawater anions (iodide, iodate, molybdate, arsenate, etc.), and this aspect will be the focus of future work.

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