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On-Column Ion-Exchange Preconcentration of Inorganic Anions in Open Tubular Capillary Electrochromatography with Elution Using Transient-Isotachophoretic Gradients. 3. Implementation and Method Development

Michael C. Breadmore,[†] Anne S. Palmer,[‡] Mark Curran,[§] Miroslav Macka,[†] Nebojsa Avdalovic,[∥] and Paul R. Haddad*,[†]

Australian Centre for Research on Separation Science, School of Chemistry, University of Tasmania, GPO Box 252-75, Hobart, Tasmania 7001, Australia, Institute for Antarctic & Southern Ocean Studies, University of Tasmania, GPO Box 252-77, Hobart, Tasmania, Australia, Antarctic CRC & Australian Antarctic Division, GPO Box 252-80, Hobart, Tasmania, Australia, and Dionex Corporation, 1228 Titan Way, Sunnyvale, California 94086

A solid-phase extraction method based on an ion-exchange retention mechanism has been used for in-line preconcentration of inorganic anions prior to their separation by capillary electrophoresis (CE). A single capillary containing a preconcentration and a separation zone has been used in a commercial CE instrument without instrumental modification. Analyte anions were retained on a preconcentration zone comprising an adsorbed layer of cationic latex particles, while separation was achieved in a separation zone comprising fused silica modified by adsorption of a cationic polymer. Elution of the adsorbed analytes was achieved using an eluotropic gradient formed by a transient isotachophoretic boundary between a fluoride electrolyte and a naphthalenedisulfonate electrolyte. Optimization of the electrolyte concentrations, sample injection times, and back-flushing times allowed the successful separation of sub-ppb levels of inorganic anions using a 100-min injection at 2 bar pressure, introducing over 40 capillary volumes of sample. A method based on a 10-min injection allowed a 100-fold increase in sensitivity over conventional hydrodynamic injection for Br^-, I^-, NO_3^-, CrO_4^{2-}, and MoO_4^{2-} with a total analysis time of 25 min. Detection limits were dependent on the injection time but were in the range 2.2−11.6 ppb for a 10-min injection time. This approach was used to determine NO_3^- in Antarctic ice cores where the analysis could be performed using a sample volume 100 times less than that used for ion chromatography.

One of the most cited problems with capillary electrophoresis (CE) is its lack of sensitivity when compared to traditional high-performance liquid chromatographic methods. The use of fluorescence, electrochemical, and mass spectroscopic detectors can provide sensitivity that is improved in comparison to the conventional UV absorbance detector, but these detectors can often be too selective for general use or are expensive. A more general approach to improve sensitivity is to preconcentrate the analytes of interest prior to analysis.[1]

Methods for the preconcentration of analytes in CE can be divided broadly into two categories: those based on differences in analyte velocity (usually termed velocity difference-induced focusing (V-DIF)) or those based on chromatographic adsorption (usually termed solid-phase extraction (SPE)). V-DIF is based on analytes having different velocities in two zones (such as a sample zone and an electrolyte zone) of the capillary, causing the analytes to become focused on the boundary between these zones.[2] Common V-DIF methods include stacking (including field-amplified and large-volume sample stacking), isotachophoretic preconcentration, and sweeping.[3−8] One disadvantage of these methods is the limitation that when the sample is injected by pressure prior to preconcentration, the sample volume must be kept below the volume of the capillary. This limitation can be overcome using electrokinetic injection, but this method of sample introduction is often discriminatory between analyte ions and is also susceptible to small differences in the sample matrix. On the other hand, SPE methods can be applied to the preconcentration of more than one capillary volume and in some cases also allows the sample matrix to be removed.[3] The advantages of SPE methods for CE were realized some years ago when packed columns were used for

* To whom correspondence should be addressed: (fax) +61-3-62262858; (e-mail) Paul.Haddad@utas.edu.au.

[†] Australian Centre for Research on Separation Science, School of Chemistry, University of Tasmania.

[‡] Institute for Antarctic & Southern Ocean Studies, University of Tasmania.

[§] Antarctic CRC & Australian Antarctic Division.

[∥] Dionex Corp.

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preconcentration.[3,9−12] Substantial development has occurred since then with methods involving packed and open tubular capillary preconcentrators[13,14] as well as disk-based preconcentrators.[10] While the latter are often preferred due to the high flow rate and low sample elution volume, on-column methods using open tubular or packed beds are becoming increasingly popular due to the ease of automation and implementation. In general, packed bed preconcentrator columns suffer from low flow rates, while open tubular preconcentrators often have a low sample capacity. Most SPE methods for CE reported to date have used reversed-phase interactions to preconcentrate analytes, with elution of the adsorbed analytes typically being performed by injecting a small plug of solvent. A further plug of electrolyte is then used to remove the solvent from the preconcentrator before the voltage is applied.

The preconcentration of inorganic anions by either V-DIF or SPE methods for subsequent CE separation has received only minor attention. Jandik and Jones[4,15] demonstrated the on-line preconcentration of inorganic anions using an isotachophoretic preconcentration step. Chromate was used as both an indirect detection probe and the leading ion for isotachophoresis, while octanesulfonate was added to the sample as the terminating ion and electrokinetic injection was used. A 400-fold decrease in detection limits was obtained with values between 0.3 and 0.8 ppb reported for common inorganic anions. Quirino and Terabe[16] demonstrated large-volume sample stacking (LVSS) and field-enhanced sample injection (FESI) for high-mobility UV-absorbing inorganic anions. LVSS was found to provide a 100-fold increase in sensitivity, while FESI was capable of reducing detection limits by a factor of 1000. Again electrokinetic injection was used to provide detection limits between 1.5 and 7 ppb for Br^-, NO_3^-, and BrO_3^-. Reproducibility was found to be rather poor due to the use of electrokinetic injection, which is also rather sensitive to changes in the ionic strength of the sample.

SPE based on ion-exchange interactions has been reported by Arce et al.,[17−19] who placed the electrode and capillary inlet in the stream of an FIA system containing an ion-exchange preconcentration column. Injection was performed electrokinetically and a 5-fold increase in sensitivity was reported, with detection limits of 10 ppb for NO_2^- and NO_3^-. Novic and Gucek[20] used a similar approach, but employed a carbonate or hydroxide eluent to remove the adsorbed sample anions from the ion-exchange column, followed by protonation of the eluent ions using an ion chromatography suppressor. The effluent from the suppressor was collected into a vial and then injected into the CE. A 10-fold increase in sensitivity was reported for Br, NO_2^-, NO_3^-, and I^- when hydrodynamic injection was using. Both of these on-line SPE approaches require instrumental modification, making automation difficult. A further disadvantage is that not all of the preconcentrated analyte is injected into the capillary and hence the full potential of the preconcentration step is not realized.

Recently, we have developed an on-capillary SPE method for the preconcentration of inorganic anions using a conventional CE instrument without instrumental modification.[21,22] This method utilizes a single capillary in which a short section (∼10 cm) has been coated with nanometer-sized latex particles functionalized with quaternary ammonium groups, with the uncoated remainder of the capillary serving as a conventional CE capillary. The capillary therefore comprises a *preconcentration zone* (the coated section) and a *separation zone* (the uncoated section). The preconcentration zone acts as an open tubular (OT) ion-exchange column, which is used for adsorption of analyte anions. Elution of the adsorbed anions is performed using a compositional gradient of increasing eluotropic strength, formed from a transient isotachophoretic boundary between two electrolytes. The first of these electrolytes contains a competing anion with a low ion-exchange selectivity coefficient (called the weak electrolyte, WE) while the other contains a competing anion with a high ion-exchange selectivity coefficient (called the strong electrolyte, SE). As this gradient moves through the preconcentration zone of the capillary, analytes are simultaneously eluted from the latex layer and are focused into sharp bands. After leaving the preconcentration zone, analyte anions are separated on the basis of electrophoretic mobility in the separation zone. The potential of this method for use as an on-column preconcentration method for CE was demonstrated in an earlier publication,[21] but the number of analytes that could be analyzed was severely limited by the nature of the SE used. In a subsequent study on the manipulation of the isotachophoretic gradients, we examined the potential of 77 anions to function as suitable SE anions.[22] From this study, 1,5-naphthalenedisulfonate (NDS) was found to be a suitable candidate due to its high ion-exchange selectivity coefficient and moderate electrophoretic mobility. The present study addresses the optimization of both the preconcentration and separation steps of the procedure, leading to the implementation of a practical CE method employing preconcentration of UV-absorbing anions using NDS as the SE anion. Method parameters, such as the nature and concentrations of WE and SE, sample loading, and methods for the introduction of WE and SE, have been optimized, and the method is then applied to the determination of ultratrace levels of nitrate in Antarctic ice cores.

EXPERIMENTAL SECTION

Apparatus. The CE instrument used was a Hewlett-Packard 3D-CE (Hewlett-Packard, Waldbron, Germany). Separations were carried out using a Polymicro (Phoenix, AZ) fused-silica capillary (25-μm i.d. with a length of 80.0 cm, 71.5 cm to detector) with detection performed at 195 nm unless otherwise noted. A Dionex DX500 microbore (2 mm) ion chromatograph with a CD20 conductivity detector and GP40 gradient pump (Dionex Corp.,

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Sunnyvale, CA) was used for the IC analysis of Antarctic ice cores using the method of Curran and Palmer.[23]

Reagents. Dionex AS5A latex particles with an approximate size of 75 nm were supplied as an 11% (w/v) suspension. Analytical grade tris(hydroxymethyl)aminomethane (Tris) was obtained from Sigma-Aldrich (Milwaukee, WI) and used without further purification. Standards of 0.1 mM Br^-, I^-, NO_3^-, MoO_4^{2-}, and CrO_4^{2-} were prepared from sodium or potassium salts of analytical reagent grade and were diluted as required. Strong electrolytes were prepared by titration of Tris with 1,5-naphthalenedisulfonic acid to a pH of 8.05. Therefore BGEs with a concentration of 10 mM of NDS will have 40 mM Tris in order to have an electrolyte which has suitable buffering capacity. All weak electrolyte solutions were prepared from aqueous solutions of NaF. Electrolyte solutions were degassed prior to use by vacuum sonication for 1 min.

Capillary Coating Procedure. The latex was cleaned as reported previously.[24] The preconcentration zone of the capillary was prepared by pumping a dilute suspension of latex particles at 50 mbar into the capillary from the detection end until the particles were detected at a window situated 8.5 cm from the end of the capillary. The suspension was then flushed out of the capillary with water using 50 mbar of pressure applied at the injection end. This process was repeated 3 times, with the capillary then being reversed so that the coated section became the injection end. The remainder of the capillary was then flushed with a 0.1% solution of poly(diallyldimethylammonium chloride) (PDDAC) for 5 min to ensure that the electroosomotic flow (EOF) was in the same direction throughout the entire capillary (i.e., toward the anode situated at the detection end of the capillary). The column was then flushed with water for 5 min before further use.

RESULTS AND DISCUSSION

Optimization of Preconcentration Conditions. For the preconcentration step to function effectively, the analyte anions must show strong binding to the stationary phase in the presence of the weak electrolyte and must be eluted rapidly by the strong electrolyte. Using ion-exchange selectivity coefficients (K) to describe the degree of interaction occurring with the stationary phase, the ideal situation occurs when $K_{WE} \ll K_A \ll K_{SE}$, where K_{WE}, K_A, and K_{SE} are the ion-exchange selectivity coefficients for the weak electrolyte, the analyte, and the strong electrolyte, respectively. Previously,[22] we found that, from a group of 77 anions tested, F^- had the lowest ion-exchange selectivity coefficient (arbitrarily assigned $K = 1$) and should therefore be readily replaced by most analyte anions. Naphthalenedisulfonate had a high ion-exchange selectivity coefficient ($K = 16\,900$) and will therefore displace most analyte anions from the stationary phase. A further condition was that the electrophoretic mobilities of the analytes, μ_A, should exceed the mobility of the gradient front so that the separation occurs in the weak electrolyte.[22] Taking this factor into consideration, use of F^- ($\mu = -58.12 \times 10^{-9}$ m^2/V·s) as weak electrolyte and NDS as strong electrolyte ($\mu = -57.38 \times 10^{-9}$ m^2/V·s) should permit the separation of analytes having electrophoretic mobilities higher than about -58×10^{-9} m^2/V·s.

Under such conditions, the preconcentration zone must be converted from the NDS form (at the end of a run) to the F^- form (prior to sample introduction at the start of the next run). Direct conversion between these two forms could not be achieved in practice using electrolyte concentrations suitable for the final separation. It was therefore found necessary to first convert the preconcentration zone from the NDS form to the ClO_4^- form, which could then be converted to the F^- form. This was performed by flushing the capillary successively with one capillary volume each of 250 mM ClO_4^- and finally 250 mM F^-, after which the capillary was flushed with water and the sample injected. It should also be noted that when vials were changed during the preconcentration process, the capillary and electrode tip were dipped into a water vial, which was replenished each time using the on-line replenishing system. If water vials were not replenished after each separation, peak heights decreased substantially due to carry-over contamination from previous separations.

The second step in the preconcentration procedure was to inject the sample and to adsorb the analyte anions onto the stationary phase. The time used for injection governed the final detector response, with longer injection times resulting in a higher response. In practical terms, the injection time that could be used was limited by the ion-exchange capacity of the stationary phase and the need to avoid saturation.[13,14] Figure 1 shows the variation of peak area and efficiency with injection time for a sample of 0.5 μM I^- Br^-, and NO_3^-. Linear calibration was maintained at least up to an injection time of 15 min (the total number of moles injected was 3.63×10^{-12}) indicating that the column capacity had not been exhausted, but the efficiency decreased substantially for injection times longer than 10 min. This result showed that the major limitation on the amount of sample used was not the adsorption step but rather the subsequent elution and focusing steps. Beyond a critical amount of sample, the width of the eluted band of analyte leaving the preconcentration zone increased, leading to loss of separation.

The final step in the preconcentration procedure was to fill the capillary with the WE and to then apply the voltage so that the transient isotachophoretic boundary could be established and the analytes eluted from the stationary phase and focused into compact bands. The concentration of WE (F^-) required to maintain efficiency in the final separation section was 100 mM (see next section). Such a high concentration of WE created the possibility of elution of some of the adsorbed analytes from the preconcentration zone and their possible loss. To prevent this, only 95% of the capillary was filled with WE by back-flushing the capillary (i.e., filling from the detection end), leaving a sample matrix-plug constituting ~5% of the capillary length remaining at the inlet end of the capillary. Initially it was found that variations in the size of the water plug left in the capillary led to significant variations in peak widths and migration times. This is shown in Figure 2, where it can be seen that as the water plug left in the capillary was increased in size, the efficiency of focusing decreased, the peak height was reduced, and the migration time became longer. A water plug occupying ~5% of the total capillary volume was found to provide minimal loss of efficiency and peak height and was selected as the optimal value. To eliminate variations in the size of the water plug caused by slight changes in viscosity with temperature, the temperature of the sample tray

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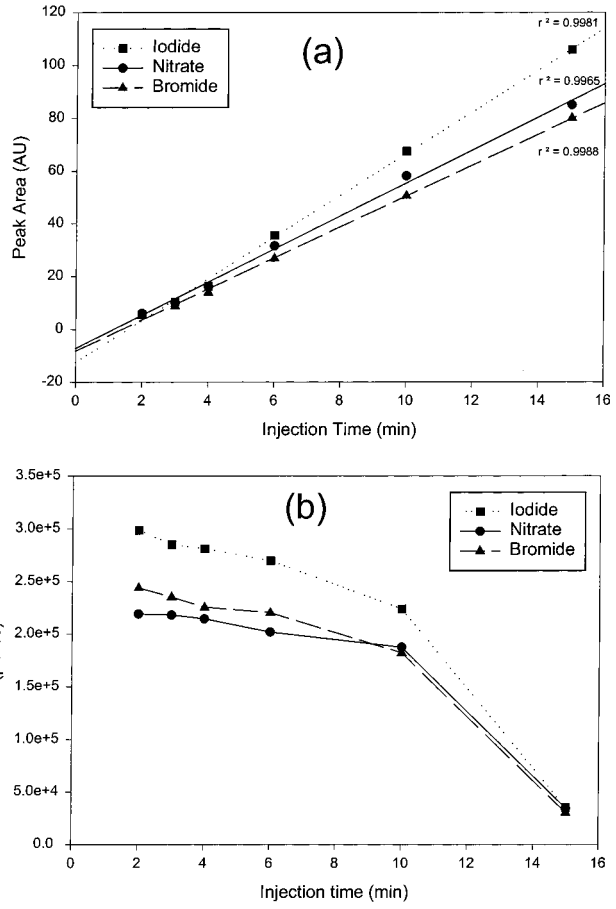

Figure 1. Variation of (a) peak area and (b) peak efficiency (theoretical plates) with injection time for I^-, NO_3^-, and Br^-. Sample, 0.5 μM Br^-, I^- and NO_3^-; injection pressure, 2 bar; capillary, 25 μm i.d., 80.0 cm total; 71.5 cm of PDDAC/8.5 cm of AS5A at 29 °C; WE, 100 mM NaF; SE, 50 mM NDS/200 mM Tris, pH 8.05; injection, as indicated above, followed by back-flush of WE for 1.40 min at −3 bar; voltage, −30 kV.

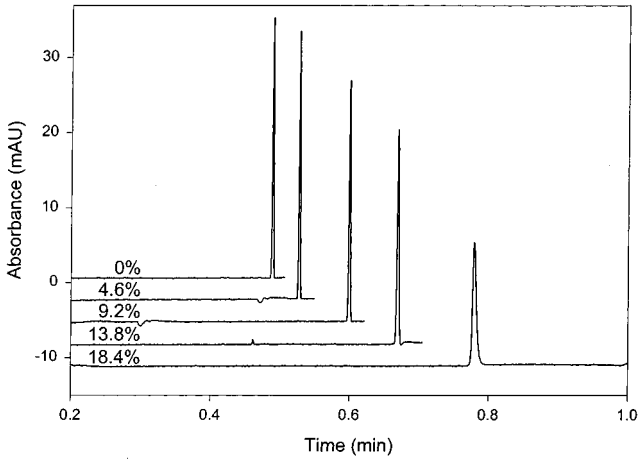

Figure 2. Influence of the size of the water plug in the capillary on efficiency. The percentages indicate the portion of the capillary volume filled with water before application of the voltage. Conditions: 25-μm-i.d. capillary with a length of 34.5 cm (26.0 to detector) fully coated with AS5A latex. Sample was 2 μM I^- in 10 mM NaF and injected for 120 s at 2 bar. WE was 10 mM NaF, and SE was 10 mM ClO_4^-/Tris; voltage, −30 kV. Water was injected after injection of the sample at 2 bar to give the indicated volume.

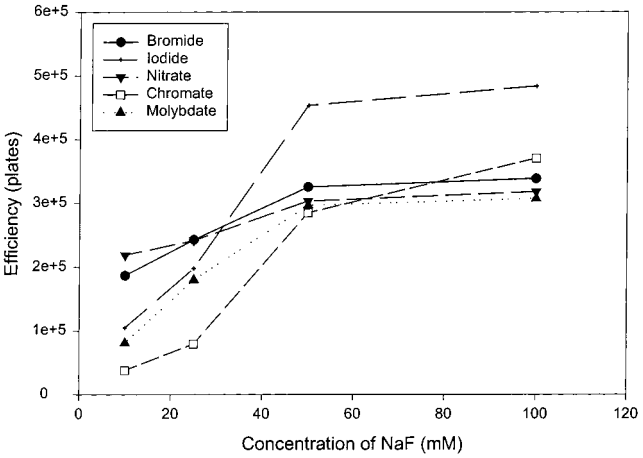

Figure 3. Influence of WE concentration on the separation efficiency of inorganic anions separated in a PDDAC-coated capillary. Conditions: 25-μm-i.d. capillary with a length of 50.0 cm (41.5 cm to detector). Injection of a mixture 0.5 mM of each anion for 20 s at 50 mbar. Voltage was −30 kV.

was regulated using water pumped from a temperature-controlled bath.

Optimization of the CE Separation. The cationic particles adsorbed onto the capillary wall in the preconcentration zone cause a reversal the EOF in this section of the capillary.[24−26] To maintain the separation efficiency in the separation zone, it was important to ensure that the EOF in both sections of the capillary was in the same direction. This was accomplished previously[21] by adding a low concentration of a cationic surfactant (cetyltrimethylammonium chloride) to both the WE and SE. However, this approach could not be used in the present case because of the formation of precipitates between any added cationic surfactant and NDS.

The permanent adsorption of a cationic polymer was investigated as an alternative method for EOF reversal.[27] Flushing the capillary with a dilute solution (0.1% w/v) of PDDAC was found to provide a reproducible and reversed EOF. However, the resultant layer of this cationic polymer coated onto the wall of the separation zone introduced anion-exchange sites that could potentially interact with the anionic analytes during the CE separation stage. Such interactions would be likely to lead to a substantial loss of separation efficiency.[24,28] Anion-exchange interactions could be suppressed by increasing the concentration of WE, thereby providing more effective ion-exchange competition by WE. Figure 3 shows the variation in separation efficiency for a series of analytes separated in a 25-μm-i.d. capillary coated with PDDAC as the concentration of WE (NaF) was increased from 10 to 100 mM. It can be seen that, at lower concentrations of WE, poorer separation efficiencies were obtained due to interaction of the analytes with the PDDAC on the capillary wall. A higher concentration of WE was necessary to suppress the wall interactions and a WE concentration of 100 mM was used with 25 -μm-i.d. capillaries for the remainder of the study.

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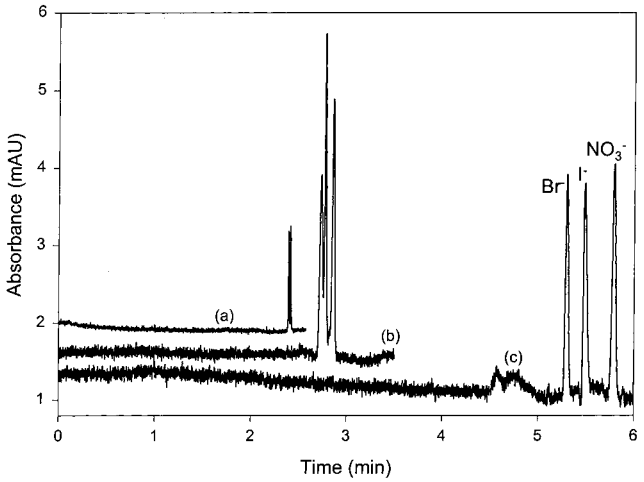

Figure 4. Comparison of separations in (a) 75-, (b) 50-, and (c) 25-μm-i.d. capillaries. All capillaries were 80.0 cm in length (71.5 cm to detector, 8.5 cm coated with AS5A latex particles) and the voltage was -30 kV. Injection was (a) 8×10^{-14}, (b) 2×10^{-13}, and (c) 6×10^{-13} mol of each anion. Back-flushing was for (a) 581 s at -50 mbar, (b) 1309 s at -50 mbar, and (c) 90 s at -3 bar with the appropriate WE. WE concentrations were (a) 1, (b) 20, and (c) 100 mM NaF.

The role of the internal diameter of the capillary was also evaluated. Figure 4 shows the preconcentration and separation of Br^-, NO_3^-, and I^- in 75-, 50-, and 25-μm-i.d. capillaries (note that the injected amounts and the WE were different for each capillary). While the best detection sensitivity was obtained with the 75-μm-i.d. capillary, the best separation was achieved using the 25-μm-i.d. capillary. The reason for this behavior can be found by considering the effects of capillary diameter on the effective ion-exchange capacity of the capillary. In a previous study on open tubular capillary electrochromatographic systems using latex coatings as the stationary phase, we showed that the effective ion-exchange capacity of the capillary increased as the capillary diameter decreased.[24] Thus, for the system presently under study, the concentration of WE needed to suppress wall interactions in the separation zone increased from 1 mM for the 75-μm-i.d. capillary to 100 mM for the 25-μm-i.d. capillary. The EOF was therefore substantially lower in the 25-μm-i.d. capillary, leading to an improved separation. In addition to this effect, it has been shown that a lower EOF will result when the analyte ion has a higher ion-exchange interaction with the wall.[29] Therefore, as the apparent column capacity increases, the EOF should decrease because the anions are interacting more with the capillary wall. The combination of these two factors means that the separation in the 25-μm-i.d. capillary gave the lowest EOF and therefore the best resolution.

A further issue when selecting the optimal capillary diameter is the time required for sample injection and filling the capillary with WE during the preconcentration process. The instrument used in this study was suitable for the use of low pressure (10−50 mbar) or the application of a higher external pressure (2−12 bar) to flush solutions through the capillary. For a fixed capillary length of 80.0 cm, the time required to inject one capillary volume of sample using a pressure of 50 mbar was 581, 1308, and 5237 s for 75-, 50-, and 25-μm-i.d. capillaries, respectively. For the same capillary used with an external pressure of 3 bar (which is the lowest pressure that can be applied to the detection end), the corresponding times were 9.7, 22, and 87 s. A balance needs to be found between reducing the time required for the analysis and maintaining a high degree of precision in the delivery of sample and WE during the process. The latter aspect was found to be the most important consideration, and on this basis and in recognition of the superior resolution obtained, a 25-μm-i.d. capillary used with an external pressure of 3 bar for back-flushing was adopted for the particular analytes addressed in this study. However, different capillary lengths, capillary diameters, and applied pressures could be optimal for different analytes. In particular, the use of 75-μm-i.d. capillaries in which the EOF has been suppressed is a potentially attractive alternative and is currently under investigation.

Analytical Performance Characteristics. Under the optimum conditions discussed above, it is possible to separate a mixture of analyte anions that have moderate ion-exchange selectivity coefficients and electrophoretic mobilities higher than -57×10^{-9} m^2/V·s. Suitable analytes are Br^-, I^-, NO_3^-, CrO_4^{2-}, and MoO_4^{2-}, and Figure 5 shows separations of a mixture of these species where the sample concentration has been decreased progressively as the injection time has been increased. Figure 5a shows the injection of a mixture containing 5 μM of each analyte, injected for 6 s, (b) is the injection of 0.5 μM of each analyte for 60 s, and (c) is the injection of 0.05 μM of each analyte for 600 s. This introduces 0.04, 0.40, and 4.00 capillary volumes of sample, respectively. It can be seen that peak shapes were well maintained and recoveries based on peak areas were 98−102% for the 60-s injection and 92−97% for the 600-s injection. These results indicated that a 100-fold increase in sensitivity could be obtained using a 10-min injection and a total analysis time of 25 min. Analytical parameters based on the 600-s injection time are shown in Table 1, with detection limits in the range 0.018−0.100 μM (2.2−11.6 ppb) being obtained. The precisions for successive preconcentrations of Br^-, NO_3^-, and I^- were 5.4, 3.6, and 5.2% RSD, respectively. Migration time reproducibility was typically 7% RSD, due predominantly to minor variations in temperature causing slight changes in the length of the water plug left at the front of the capillary.

As an illustration of the potential of this technique for the determination of very low concentrations of analytes, Figure 6 shows a 6000-s (100-min) injection of a sample containing anions in the concentration range 0.2−0.6 ppb. This injection introduced 40 capillary volumes of sample, or ∼15 μL, giving a total analysis time of 120 min. Peak efficiency was maintained and recoveries around 90% were obtained for all ions in comparison to an injection of 5 nL of a 1000 times more concentrated sample performed under standard CE conditions. Detection limits were 0.23, 1.4, and 0.31 ppb for NO_3^-, CrO_4^{2-}, and MoO_4^{2-}, respectively, providing more than a 900-fold increase in sensitivity over a conventional injection.

Determination of NO_3^- in Antarctic Ice Cores. One of the major advantages of CE over other liquid chromatographic methods is the small sample size, but the relatively poor sensitivity of CE prevents it being used for many applications. One such situation is the determination of trace ions in Antarctic ice cores in order to provide information on past climatic conditions. The

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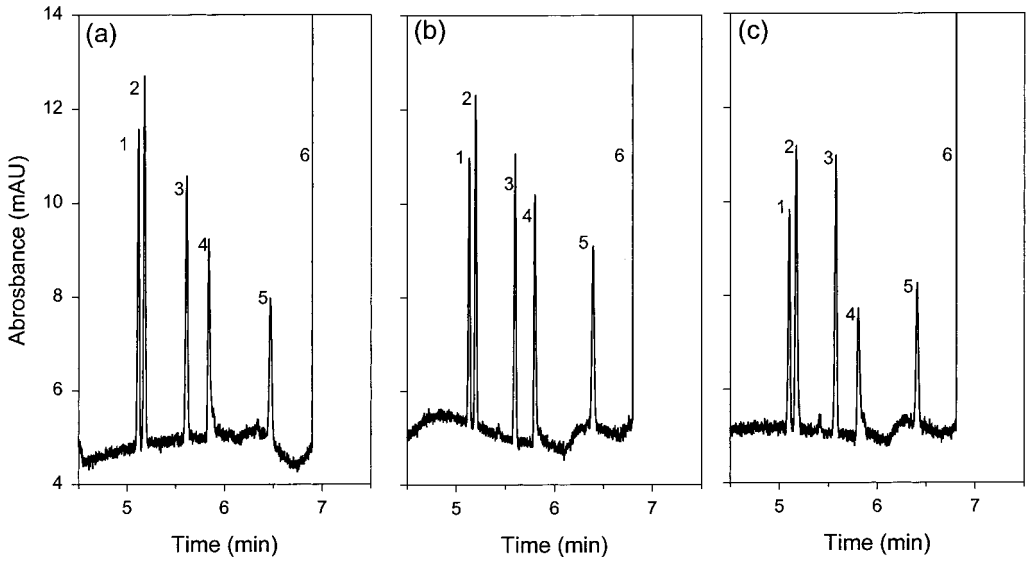

Figure 5. Preconcentration and separation of a mixture of inorganic anions at varying dilutions and injection times. (a) 5 μM Br^-, I^-, NO_3^-, amd CrO_4^{2-} and 1 μM MoO_4^{2-}, injection for 6 s at 2 bar; (b) 1:10 dilution of (a) and a 60-s injection at 2 bar; and (c) 1:100 dilution of (a) and a 600-s injection at 2 bar. Capillary: 25-μm i.d., 80.0 cm total, 71.5 cm of PDDAC/8.5 cm of AS5A at 29 °C. WE, 100 mM NaF; SE, 50 mM NDS/200 mM Tris, pH 8.05. Injection, as indicated above, followed by back-flush of WE for 1.40 min at −3 bar. Voltage, −30 kV. Peaks: (1) Br^-, (2) I^-, (3) NO_3^-, (4) CrO_4^{2-}, and (5) MoO_4^{2-}.

Table 1. Analytical Performance Parameters for the Proposed Preconcentration Procedure[a]

	t_m, min (% RSD)	peak area, mAU_{min} (% RSD)	peak ht, mAU (% RSD)	N plates (% RSD)	LOD, μM (ppb)
Br^-	5.102 (7.5)	6.6 (5.2)	4.6 (7.9)	338 000 (7.6)	0.060 (4.74)
I^-	5.171 (7.4)	9.5 (3.6)	6.0 (8.5)	483 000 (8.6)	0.044 (5.58)
NO_3^-	5.577 (7.2)	8.8 (5.4)	5.9 (8.8)	317 000 (8.6)	0.047 (2.16)
CrO_4^{2-}	5.806 (7.3)	7.8 (3.2)	3.3 (8.2)	370 000 (10.1)	0.100 (11.6)
MoO_4^{2-}	6.408 (7.3)	5.2 (4.1)	3.0 (8.1)	307 000 (8.0)	0.018 (2.88)

[a] A 10-min injection was performed at an external applied pressure of 2 bar, using a 25-μm-i.d. capillary

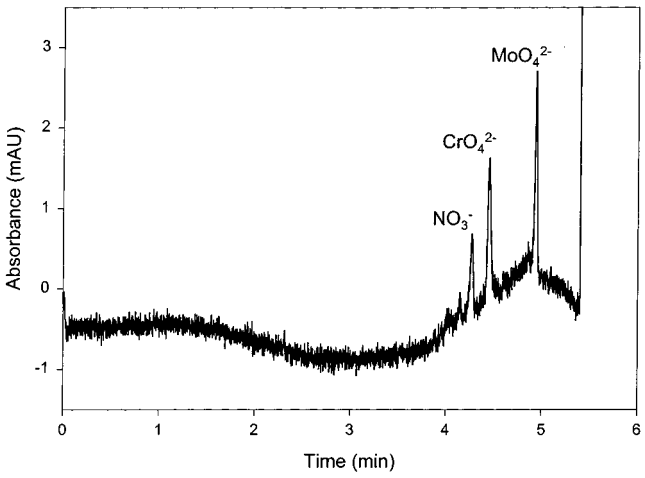

Figure 6. Preconcentration and separation of nanomolar levels of inorganic anions. Injection: 100 min at 2 bar of 5 nM NO_3^-, 10 nM CrO_4^{2-}, and 2 nM MoO_4^{2-}. Other conditions as in Figure 5.

amount of sample available for chemical analysis is limited due to the cost of obtaining such samples, so the development of a method using small sample volumes but high sensitivity would be beneficial in comparison to other methods (e.g., ref 30). Anions including SO_4^{2-}, Cl^-, NO_3^-, and $CH_3SO_3^-$ are typically analyzed using ion chromatographic (IC) methods involving sample preconcentration, with a typical sample volume of 5 mL being used.[23]

NO_3^- is a key ion in polar ice core research, providing information on atmospheric NO_3^- levels and anthropogenic influences,[31] solar activity,[32,33] postdepositional processes,[34] seasonality,[35] and ice core dating.[32] The complexity of the atmospheric NO_3^- cycle and the relative contributions from the various sources and sinks remain poorly understood. The average NO_3^- concentration found in Antarctic ice cores can range between 0.3 and 1.2 μM,[34] and detection at these levels can be attained by the proposed methodology using an injection time of 600 s, giving a total analysis time of 25 min.

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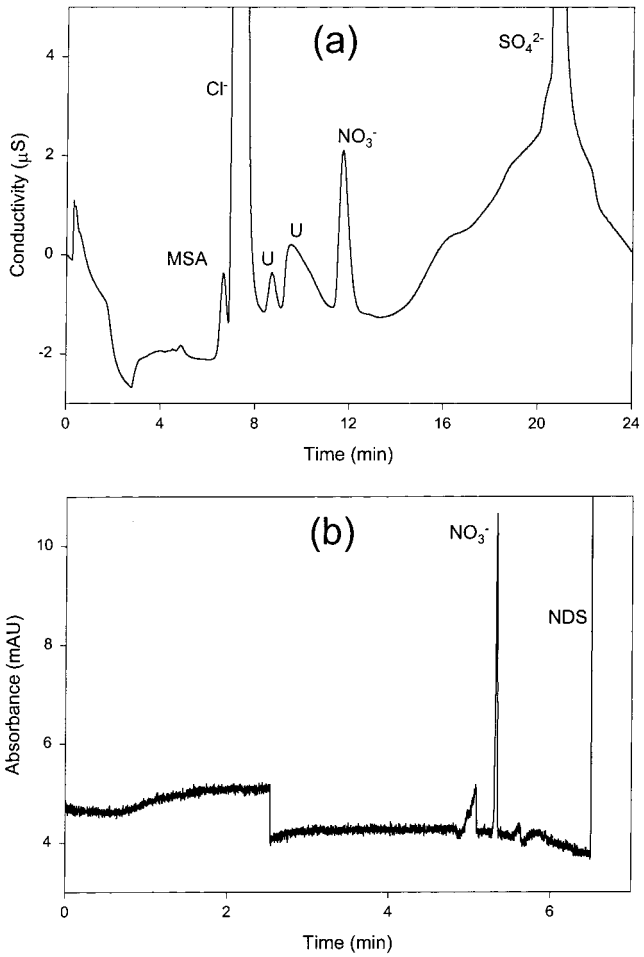

Figure 7. Analysis of ice core sample from Law Dome, East Antarctica (sample DSS99-102-9 by (a) the IC method (details in ref 23) and (b) the CE method (conditions as in Figure 5c).

Analyses of an ice core sample from Law Dome, East Antarctica (sample DSS99-102-9), by both IC and CE are shown in Figure 7, with comparative details of the two methods being shown in Table 2. There is good agreement in the measured concentration of NO_3^- between CE and IC for this sample and the CE method offers performance similar to that of the IC methods with regard to most parameters. However, the major advantage of the CE approach is that it delivers similar sensitivity with a much smaller sample volume. The volume required for CE is less than 50 μL, compared to 5 mL for the IC method,[23] giving a potential 100-fold increase in the number of data points obtainable from a sample. This increase in resolution is immediately applicable to the dating of the Dome Summit South (DSS) ice core using the determination of NO_3^- in annual deposition layers. In the DSS ice core, the depth (age) limit for seasonal NO_3^- dating using current IC techniques is ~700 m (1574 years before present (ybp)) due to the required sample volume. Below this depth, thinning of the annual layers due to ice flow reduces the volume available for IC measurements. Using oxygen isotope ratio analysis, this depth can be increased to 1038 m (4830 ybp),[30] but at greater depths, the signal is lost due to solid ice diffusion of the isotope ratio signal or recrystallization and movement. Analysis of thin ice samples for NO_3^- using CE will provide a unique solution as to the cause of signal loss and potentially increase seasonal dating of the DSS ice core to 1105 m (8100 ybp).

Table 2. Comparison of CE and IC Methods for the Determination of NO_3^- in Antarctic Ice Cores

	CE[a]	IC
detection limit for NO_3^-	0.04 μM	0.005 μM
sample volume	<50 μL	5 mL
analysis time	25 min	24 min
NO_3^- found in sample	0.304 μM	0.314 μM

[a] Using 600-s injections.

CONCLUSIONS

An on-capillary preconcentration method for the CE determination of inorganic anions using anion-exchange solid-phase extraction and transient isotachophoretic gradient elution has been developed. Optimization of the concentration of the weak electrolyte and the method used to introduce it to the capillary prior to application of the voltage was crucial to obtain highly efficient separations. The best separations were obtained in a 25-μm-i.d. capillary due to the improved resolution resulting from a reduction in EOF. Using an optimized method, a 100-min pressure injection allowing 40 capillary volumes of sample to be injected gave an increase in sensitivity by a factor of 900 over standard CE hydrodynamic injection, without any loss in resolution and separation efficiency, and provided sub-ppb detection limits for NO_3^-, CrO_4^{2-}, and MoO_4^{2-}. A more practical method based on a 10-min injection enabled a 100-fold increase in sensitivity to be achieved for Br^-, NO_3^-, I^-, CrO_4^{2-}, and MoO_4^{2-} within a total analysis time of 25 min. This method was used to determine the concentration of NO_3^- in Antarctic ice cores where the CE method allows a 100-fold reduction in sample size.

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