New approach to the analysis of low levels of anions in water

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ABSTRACT

Optimized electromigrative sample introduction improves detection limits for anions in capillary electrophoresis. Reproducible results are achieved for micromolar and nanomolar levels of concentration. The new method offers shorter runtimes, improved resolution and greater simplicity in comparison with ion chromatography. The technique was applied to water samples from the power industry. Trace levels of anions are monitored routinely in water for steam generation in conventional and nuclear power plants. Reproducible and accurate results are presented for pure water samples containing typical concentrations of anions as well as for more specific types of samples, such as water compositions in the primary and secondary circuits of a nuclear power plant.

INTRODUCTION

The detection limits of capillary electrophoresis (CE) with optimized indirect UV detection and hydrostatic sample introduction were shown to be in the micromolar range for common inorganic anions [1–3]. The optimization of indirect UV detection consists of finding carrier electrolyte components of high molar absorptivities and matching their ionic mobility to that of the analyte anions.

The detection limits could be improved even farther, from the micromolar into the nanomolar range, by the application of electromigrative sample introduction under isotachophoretic conditions [4]. Isotachophoretic conditions are achieved by adding a suitable amount of a component of low ionic mobility to the sample. Under properly chosen conditions, the carrier electrolyte acts as an isotachophoretic leading electrolyte, whereas the sample additive fulfills the function of a terminating electrolyte. Analytes of ionic mobilities within the range bracketed by the respective ionic mobilities of the leading and terminating electrolytes are preconcentrated in the narrow zones at the entrance to the separation capillary. As imposed by the Kohlrausch Regulation Function [5], the concentration of ions in the separated isotachophoretic zones is adjusted very close to the concentration of the leading electrolyte (*i.e.* carrier electrolyte). This represents a considerable preconcentration factor with carrier electrolyte in the millimolar range and original concentrations of sample components in the picomolar or nanomolar range.

Nanomolar concentrations of anions are monitored routinely in water for steam generation in power plants, ultrapure water used in semiconductor manufacturing and in many other different types of industrial water samples. In the past ten to fifteen years ion chromatography (IC) has become a method of choice for the analysis of trace anions in water samples. However, it is now widely recognized that a complete analysis of anions in water can be achieved only with relatively complex techniques such as coupled separation modes [6,7] or gradient IC [8,9,10]. Only so was it possible to separate various carboxylates from common inorganic anions or, for example, to analyze trace concentrations of anions in the presence of high concentrations of boric acid [6]. The complexity of IC systems required in many industrial situations prompted us to investigate the usefulness of newly developed CE methodologies for industrial water samples.

EXPERIMENTAL

Instrumentation

The Quanta 4000 capillary electropherograph (Waters Chromatography Division of Millipore, Milford, MA, USA) with a negative power supply and the twelve-position carousel was used in all experiments. The 75 μm I.D. AccuSep (Waters) fused-silica capillary had dimensions of 52 cm (to detection point) and 60 cm (total length). The separations were followed and preceded by 2 min purging of the capillary with the carrier electrolyte to remove the large water peak, migrating at the speed of the electroosmotic flow, which would otherwise reach the point of detection at *ca.* 7 min. Polyethylene vials (2 ml) from Sun Brokers (Wilmington, NC, USA) were utilized as both sample and electrolyte containers. The UV detector settings were 254 nm and 0.1 s time constant. The data were acquired by a Maxima 820 chromatography work station (Waters) using the 20 Hz data acquisition rate.

Chemicals

The sodium octanesulfonate used as an additive to water samples prior to preconcentration was obtained from Kodak (Rochester, NY, USA) and purified by recrystallization in 18 MΩ water. The ultrapure water for recrystallization of octane sulfonate and for the preparation of all solutions used in this study was from a Milli-Q laboratory water-purification system (Millipore, Bedford, MA, USA).

The chromate electrolyte used for capillary electrophoresis was prepared by dilution of two different concentrated stock solutions. The first concentrate contained 100 mM analytical-grade Na_2CrO_4 (Mallinckrodt, Paris, KY, USA) and 0.34 mM Ultrex sulfuric acid (J. T. Baker, Phillipsburg, NJ, USA). The second concentrate was electroosmotic flow modifier (OFM-BT, Waters Chromatography Division of Millipore), a 20 mM solution of a cationic surfactant. All electrolytes for the analysis of low levels of anions were prepared by diluting 10 ml of the first concentrate and 2.5 ml of the second concentrate to 100 ml with 18-MΩ water. Standard mixtures were prepared by diluting 100 μM (inorganic anions) and 1000 ppm (carboxylic acids) stock solutions. Weighed amounts of salts rather than acids were taken for preparation of stock solutions.

Boric acid utilized to prepare compositions similar to primary water in nuclear power plants was of gold label purity (J. T. Baker). Morpholine for simulation of secondary water was an ACS reagent (Aldrich, Milwaukee, WI, USA).

Electromigrative trace enrichment procedure

The final dilutions of standards and samples were placed into 100-ml polypropylene volumetric flasks (VWR, Boston, MA, USA) presoaked 24 h in 18MΩ water. An addition of 100 μl of 70 mM stock solution of purified octanesulfonate was made to each 100.0 ml volume of a sample in volumetric flasks. Disposable laboratory gloves and disposable polyethylene pipettes (Samco Pipettes, Cole Parmer, Chicago, IL, USA) were essential in helping to prevent contamination during the transfer of additive containing samples from the 100-ml volumetric flasks into the 2-ml polypropylene sample vials prior to actual analysis. The sample vials had also to be soaked in 18 MΩ water for 24 h before their use in trace anion analysis. At the 70 μM level of the octanesulfonate additive, two 45-s electromigrative injections at 5 kV yielded comparable ($\pm$ 5%) levels for all analyte anions. At 35 μM of the additive only one electromigrative injection was possible from the 2-ml sample vials. The second injection gave *ca.* 20% lower values than the first injection. The whole sequence, consisting of electromigrative trace enrichment followed by transfer of the capillary to an electrolyte vial and electrophoretic separation, can be carried out automatically by the Quanta 4000. Up to six samples can be analyzed unattended.

RESULTS AND DISCUSSION

Optimized conditions for water analysis

As previously reported [4], a combination of electromigrative trace enrichment, capillary electrophoresis and indirect UV detection, yields detection limits in the nanomolar (ppb) range[a]. The first such results for the seven common inorganic anions were obtained with an electrolyte containing among other things 5 mM chromate. The resolution of fluoride and phosphate after trace enrichment (Fig. 7 in ref. 4) is much less complete than in conjunction with hydrostatic injection (Fig. 2 in ref. 4).

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[a] Throughout this article the American billion (10^9) is meant.

The loss of resolution is caused mainly by the shift of phosphate to shorter migration times. Such a shift can be explained as a consequence of an increase of pH of the chromate electrolyte inside the capillary during the isotachophoretic steady state. An explanation of the underlying mechanism is the subject of another report currently in preparation by the authors. For an easier quantitation of fluoride and phosphate after electromigrative preconcentration it is possible to improve the resolution of the two peaks by increasing the concentration of chromate in the electrolyte [11]. As illustrated by the two electropherograms obtained with hydrostatic sample introduction and shown in Fig. 1, the resolution of fluoride and phosphate is greatly improved in 10 mM chromate. A disadvantage of the higher chromate concentration is the incomplete separation of the sulfate–nitrite peak pair. Since nitrite is absent in most industrial pure water samples, the separation in 10 mM electrolyte with its improved resolution of phosphate and fluoride is of a higher practical value than that with 5 mM chromate. Fig. 2 is an electropherogram in 10 mM chromate after an electromigrative trace enrichment. The fluoride and phosphate peaks are sufficiently separated not only from each other, but also from an additional anion, formate. The formate anion is frequently encountered in pure water samples and the ability to analyze it further increases the usefulness of the higher concentration electrolyte. Other anions frequently present in water samples, such as oxalate, formate, acetate and propionate, are also well separated under these conditions. The two unidentified minor peaks at 3.10 and 3.18 min are impurities stemming from the carboxylate standards. The largest peak at 4.14 min belongs to the carbonate. The concentration of carbonate could not be controlled under the conditions of our experiment and consequently the concentrations of that anion were not evaluated. However, as discussed in one of the following paragraphs, the migration time of the omnipresent carbonate peak can be useful in normalizing of migration time variations caused by fluctuations of certain matrices of industrial water samples.

Another advantage of increased chromate concentration is the higher trace enrichment recovery for analyte anions. The effect is illustrated by the plot of peak areas for one μequivalent per liter of sulfate, nitrate and chloride *versus* mM chromate (Fig. 3). The sensitivity almost doubles for those anions in going from 5 mM to 10 mM chromate. This finding also represents experimental evidence supporting the original assumption of sample pre-
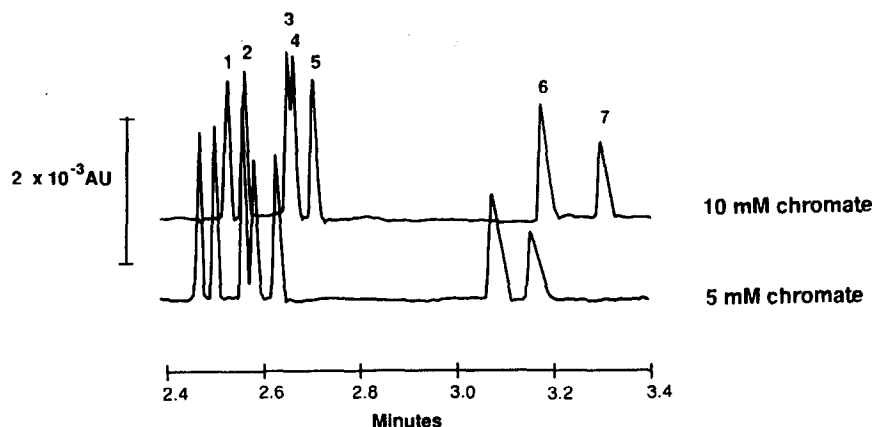

Fig. 1. Influence of the concentration of carrier electrolyte anion. Both separations were obtained after 30 s hydrostatic injection of the same standard mixture at 10 cm height. The standard mixture contained 7.9 ppm bromide (peak 1), 3.5 ppm chloride (peak 2), 4.8 ppm sulfate (peak 3), 4.6 ppm nitrite (peak 4), 6.2 ppm nitrate (peak 5), 1.9 ppm fluoride (peak 6) and 3.2 ppm phosphate (peak 7). Carrier electrolyte concentration was 0.5 mM NICE-Pak OFM anion-BT, 5 mM (lower trace) or 10 mM (upper trace) sodium chromate. The electrolyte was adjusted to pH by an addition of a suitable volume of dilute sulfuric acid. The 75-μm I.D. fused-silica capillary had dimensions of 60 cm (total length) and 52 cm (sample entry to detector). The separations were carried out with -20 kV separation voltage and the peaks were detected by indirect photometric detection at 254 nm.
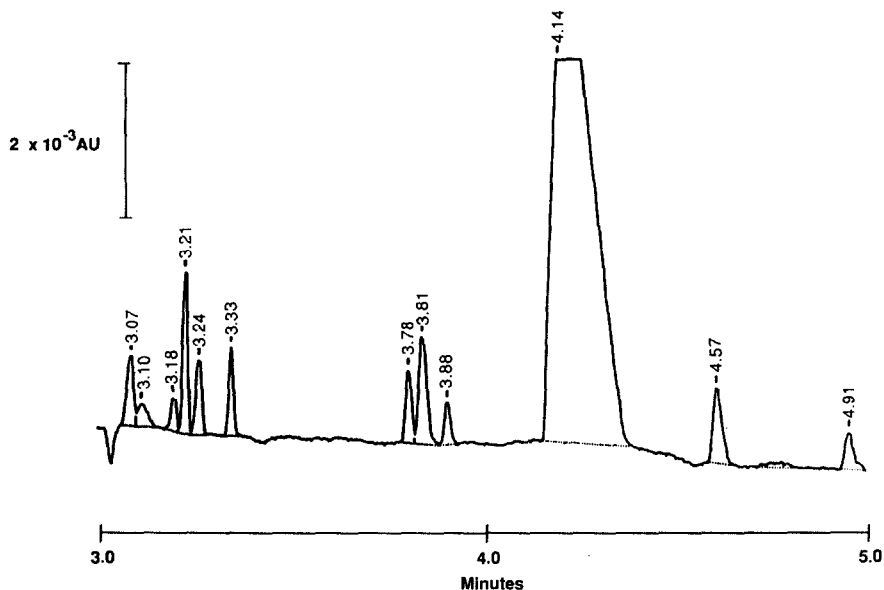
Fig. 2. Trace analysis of common inorganic and organic anions in pure water. The separation was recorded after an electromigrative trace enrichment, 45 s at 5 kV and with 75 μM octanesulfonate additive in the sample (see Experimental for a detailed description of the electromigrative trace enrichment procedure). The sample contained 3.5 ppb chloride (3.07 min), 4.8 ppb sulfate (3.21 min), 6.2 ppb nitrate (3.24 min), 5 ppb oxalate (3.33 min), 1.9 ppb fluoride (3.78 min), 5 ppb formate (3.2 min), 3.2 ppb phosphate (3.88 min), 5 ppb acetate (4.57 min) and 5 ppb propionate (4.91 min). The carrier electrolyte consisted of 10 mM sodium chromate and 0.5 mM NICE Pak OFM anion-BT, adjusted to pH 8 with dilute sulfuric acid. The separation voltage was − 15 kV. The capillary dimensions and detection technique were the same as in Fig. 1.
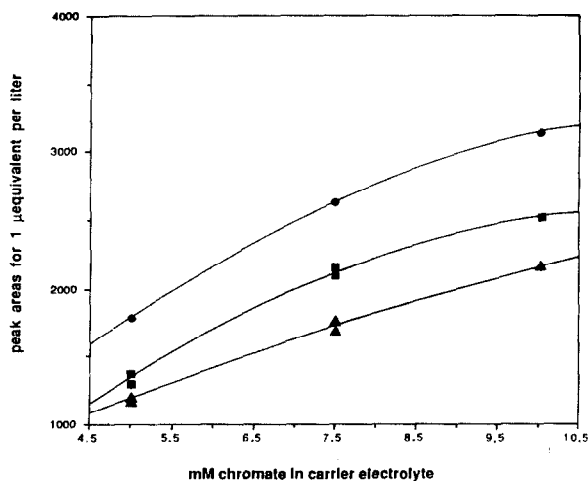

Fig. 3. Influence of chromate concentration in the carrier electrolyte on the sensitivity (peak areas) for three anions. Analytical conditions were as indicated in Fig. 2, except for the concentration of chromate in the electrolyte which was 5, 7.5 or 10 mM. The analyte anion concentrations were 48 ppb sulfate (●), 62 ppb nitrate (▲) and 35 ppb chloride (■).

concentration due to an isotachophoretic steady state [4].

According to the Kohlrausch Regulation Function however, the relationship between the concentration of sample zones on one the hand and the chromate concentration on the other hand (Fig. 5 in ref. 4) should be linear under the conditions of isotachophoretic trace enrichment. The non-linear behavior above ca. 7.5 mM is most likely caused by an increased rate of electroosmotic flow leading to a decreasing efficiency of the electromigrative trace enrichment.

The applied voltage of 15 kV in Fig. 2 is lower than the 20 kV utilized in our initial work. The lower voltage was adapted to eliminate low-frequency baseline oscillations caused by overheating of the electrolyte. An improved sensitivity at 15 kV separation voltage and 45 s trace enrichment time is compared with an electropherogram using 20 kV separation voltage and 30 s trace enrichment time in Fig. 4. Under the latter set of conditions the peak
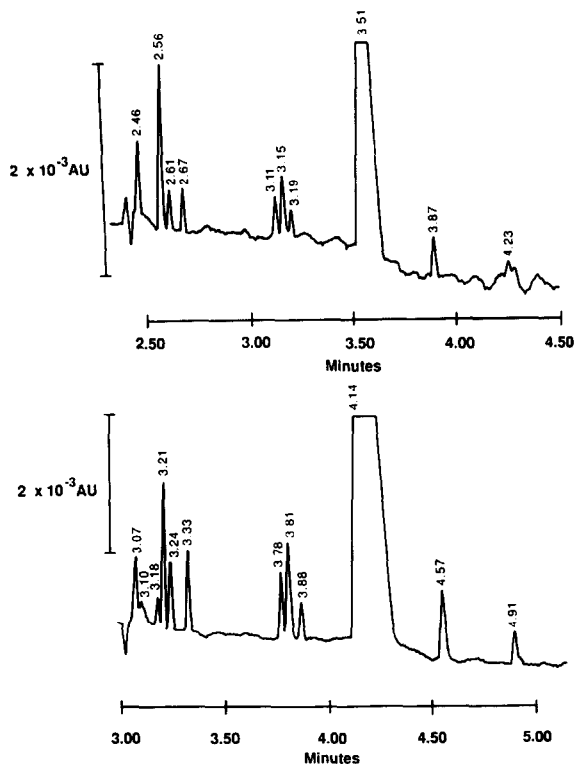
Fig. 4. Influence of separation voltage and sampling time on the sensitivity for traces of common inorganic and organic anions. Analytical conditions, except for separation voltage and preconcentration time, are given in Fig. 2. The separation voltage was 20 and 15 kV for the upper and lower separation, respectively. The upper chromatogram was obtained after electromigrative trace enrichment lasting 30 s, while the lower electropherogram is the result of a 45-s long trace enrichment. The peak identities are the same as in Fig. 2.

for 5 ppb propionate (4.23 min) is approaching its detection limit. At the lower separation voltage of 15 kV the sensitivity has clearly increased beyond the factor of 1.5 given by the longer trace enrichment time. The long-drawn and relatively regular ocillations lasting about 0.25 min, that are clearly present at 20 kV, are not encountered in the 15-kV electropherogram. Table I gives the values of detection limits determined under the optimized conditions for water samples.

IC is capable of similar or better detection limits in matrix-free pure water samples, but it requires trace enrichment times much longer than 45 s — typically 5–10 min.

TABLE I

DETECTION LIMITS FOR TRACE ANIONS IN WATER

Trace enrichment at 5 kV and 45 s. See Experimental for a complete description of analytical procedure.

Anion	ppb
Chloride	0.5
Sulfate	0.3
Nitrate	0.8
Oxalate	0.6
Fluoride	0.3
Formate	0.5
Phosphate	0.3
Acetate	0.8
Propionate	0.6

It is also appropriate to comment on the interesting selectivity of CE separations of anions in comparison with IC. The complete separation of short-chain alkyl carboxylates from fluoride, simultaneously with anions strongly retained on ion-exchange columns, such as sulfate and oxalate (Fig. 2), is achieved within only *ca.* 6 min using comparatively simple instrumentation. The same kind of separation by IC takes always longer than 15 min and requires either coupled separation modes or gradient elution.

Quantitation of trace anions in aqueous samples

The usefulness of the method for quantitative monitoring of anions in pure water was evaluated by means of calibration and reproducibility experiments. As shown in Table II, valid calibration plots could be obtained for all anions separated in Fig. 2.

TABLE II

CALIBRATION DATA BETWEEN 0.1 TO 1 μM FOR NINE ANIONS IN WATER

Anion	Correlation coefficient	Slope	y intercept
Chloride	0.999	8423	394
Sulfate	0.998	21 159	649
Nitrate	0.999	8832	−11
Oxalate	0.999	18 520	−116
Fluoride	0.999	7796	223
Formate	1.000	9700	795
Phosphate	0.993	12 686	−17
Acetate	0.999	8503	888
Propionate	0.997	7781	293

The calculated correlation coefficients for analyte concentrations between 0.1 and 1 μM were in the range of 0.993 to 1.000. The y intercept values were the highest for sulfate, formate and acetate. All three anions were subsequently detected as contaminants in the purified octane sulfonate employed as an additive for the electromigrative trace enrichment [11]. Additional purification steps planned for the octanesulfonate can thus be expected to decrease the values of y intercepts in future experiments.

The values of slope were similar within ± 10% for monovalent and divalent anions, respectively. A "universal" calibration by one anion standard can thus be expected to give useful, approximate results in equivalents per liter for all known and unknown peaks in the electropherogram. The possibility of "universal" calibration with indirect detection in IC was first evaluated by Yeung [12]. The above calibration data indicate that a "single standard calibration" may also be possible in CE, if indirect detection is employed.

The precision of six consecutive determinations was evaluated at 0.5 μM for inorganic anions and 0.4–0.5 μM carboxylates. In each analytical run only one electromigrative trace enrichment was carried out from a 2-ml volume of standard anion mixture containing 70 μM sodium octanesulfonate. All analytical conditions were as described in the Experimental section. The results, calculated as relative standard deviations (R.S.D.) of peak areas along with the anion concentrations in the standards used for the repetitive runs, are listed in Table III.

TABLE III

PRECISION DATA FOR SIX CONSECUTIVE RUNS

Anion	ppb	R.S.D. (%)
Chloride	17.5	4.3
Sulfate	24	3.3
Nitrate	31	2.7
Oxalate	25	2.9
Fluoride	9.5	2.5
Formate	25	2.0
Phosphate	15.5	2.6
Acetate	25	7.5
Propionate	25	7.2

Trace anions in water samples containing high levels of other components

In many industrial situations trace anion determinations have to be performed in aqueous samples containing much larger concentrations of various ionic and non-ionic components. Nuclear pressurized water reactors (PWRs) provide two important examples of such water samples.

The first example is so-called primary water (PW). PW is an aqueous solution of 500–2000 ppm boron added as boric acid (2855–11420 ppm H_3BO_3), it also contains maximum 3 ppm Li, added as LiOH. The boric acid can be expected to fluctuate strongly within the specified limits. Our study was carried out at a constant level of 1.7 ppm Li and at several different levels of boron. Values of 5 ppb are recognized as normal levels for the most common inorganic anions: chloride, sulfate, nitrate and fluoride. The maximum admissible levels for any of the inorganic anions are approximately 40 ppb.

Given the relatively high concentration of boric acid, we first had to clarify the role of borate anion in the electromigrative trace enrichment. A possibility that could not be dismissed without a clarifying experiment, is that through a pH increase in the electrolyte due to isotachophoresis, sufficient amounts of borate would be generated to act as a terminating electrolyte contributing to the trace enrichment of other anions according to the mechanism postulated in our earlier work [4]. The series of three enrichment experiments is depicted in Fig. 5. The presence of boric acid in the sample did not contribute to preconcentration of analyte anions. The analysis of spiked levels became possible only after an addition of octanesulfonate resulting in 25 or 75 μM levels in the sample before the preconcentration step.

The feasibility of calibration for standard anion concentrations ranging from 0.1 to 2 μM in a constant PW matrix was evaluated next. The corresponding calibration data are summarized in Table IV. As in the case of matrix free, pure water samples (Table II), meaningful calibraton plots can also be obtained for water samples containing high levels of boric acid. The single standard calibration, for example by chloride, appears to be feasible for normalities (equivalent per liter) of the remaining three anions, with absolute values of errors not exceeding 10%. The calibration equations for chloride and
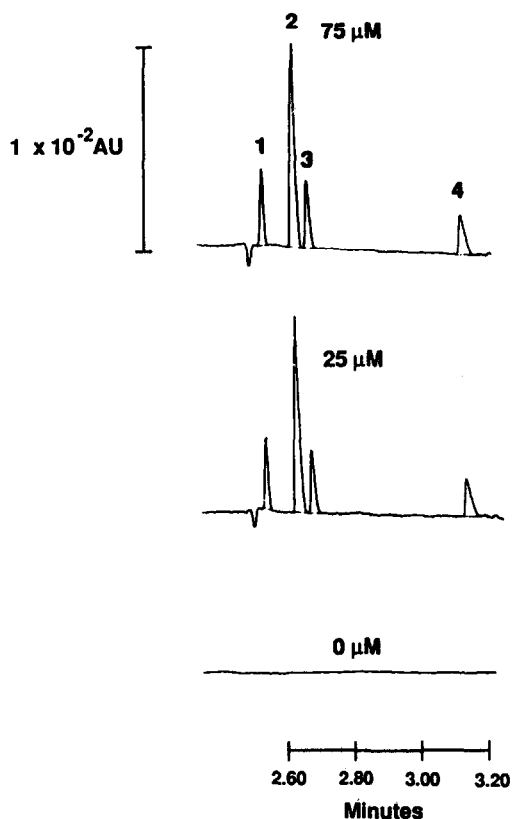
Fig. 5. Results of electromigrative trace enrichment from samples containing 5710 ppm boric acid (1000 ppm boron). The trace enrichment was carried out first at 5 kV, 30 s, without any addition of octanesulfonate (bottom trace). The upper two separations were generated also at 5 kV, 30 s, but with 25 (electropherogram in the middle) and 75 μM octanesulfonate (upper electropherogram) in the sample solution. The peak identities and concentrations were as follows: chloride 35 ppb (peak 1), sulfate 48 ppb (peak 2), nitrate 62 ppb (peak 3) and fluoride 19 ppb (peak 4). All other analytical conditions were as indicated in Fig. 2.

TABLE IV

CALIBRATION IN PRIMARY WATER (1000 ppm BORON AND 1.7 ppm LITHIUM)

0.1 to 2.0 μM anions.

Anion	Correlation coefficient	Slope	y intercept
Chloride	0.999	2161	541
Sulfate	1.000	4307	1020
Nitrate	1.000	1930	158
Fluoride	0.999	1875	200

sulfate show higher values of y intercepts than those for nitrate and fluoride. This indicates a presence of noticeable levels of sulfate and chloride impurities from the octanesulfonate additive or from the boric acid.

Can variations of boric acid concentration be expected to affect the reproducibility of measured migration times and peak areas of trace anions present in primary water samples? The plot of measured migration times *versus* boron concentration for the four anions and carbonate is presented in Fig. 6A. The actual variations of the migration times within the range of 500 to 2000 ppm boron are relatively minimal. However, a clear trend toward longer migration times is observed within a broader range from 500 to 3000 ppm boron. The increasing boron concentration in the samples causes decreasing sample pH (pH 7.3 at 500 ppm, pH 6.85 at 1000 ppm, pH 5.65 at 2000 ppm), if the concentration of lithium hydroxide remains constant. In boric acid solutions, the lower pH increases electrical resistance of the sample segment in the initial stages of the CE separation. The higher resistance leads to a slower increase of current immediately after the application of separation voltage and in consequence to slower migration times.

The observed shifts of migration times can be eliminated by normalization. We have carried out a normalization by dividing the migration times of sulfate, nitrate, fluoride and chloride at a given concentration of boron by the migration time of the carbonate peak obtained in the respective separations. The plot in Fig. 6B shows constant values of normalized migration times throughout the entire range of 500 to 3000 ppm boron. Carbon dioxide equilibrates at several hundreds ppb in water. After the trace enrichment of anions from samples exposed to the atmosphere, a peak for carbonate is always present in the electropherogram and no addition of an internal standard has to be made to obtain a reference peak for migration times. An automatic normalization of migration times by calculated ratios of analyte *versus* reference value can be performed by most internal standardization routines in commercial data acquisition and reduction software.

The data for variations of peak areas with changing boron concentrations are presented in Fig. 7. With increasing boron concentration the response
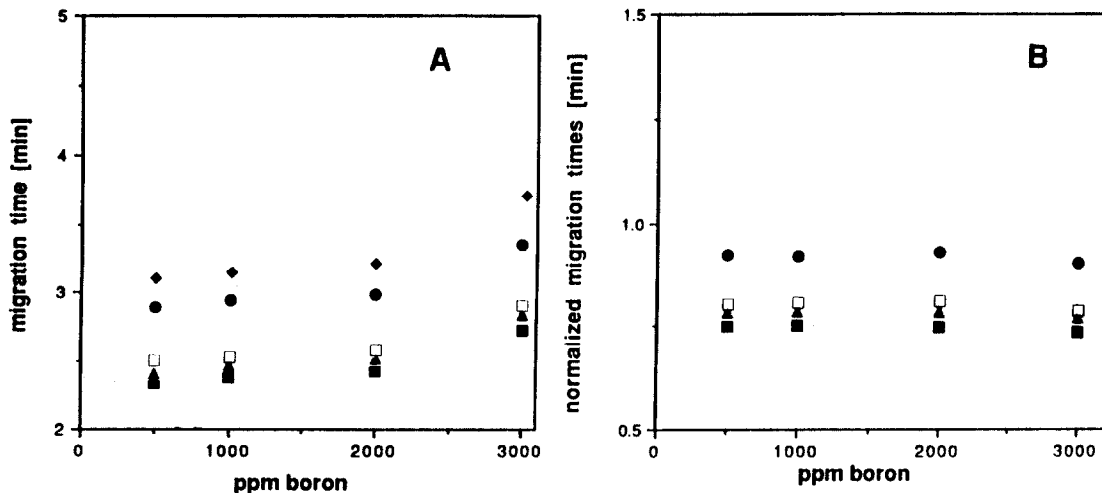
Fig. 6. Changes of migration times with changing concentration of boron (added as boric acid). (A) Directly measured migration times *versus* ppm boron; (B) migration times divided (normalized) by migration times of the carbonate peak at the same concentration of boron. The concentration of Li (added as LiOH) was kept constant at 1.7 ppm. The anion concentrations were also constant at the following levels: ■ = chloride, 35 ppb; ▲ = sulfate, 48 ppb; □ = nitrate, 62 ppb; ● = fluoride, 19 ppb. The level of carbonate (◆) was as obtained by adsorption from the atmosphere (several hundred ppb) and quantitative evaluation of peak areas was made for this anion. The trace enrichment was carried out at 30 s, 5 kV and 75 μM octanesulfonate. All other conditions were as in Fig. 2.
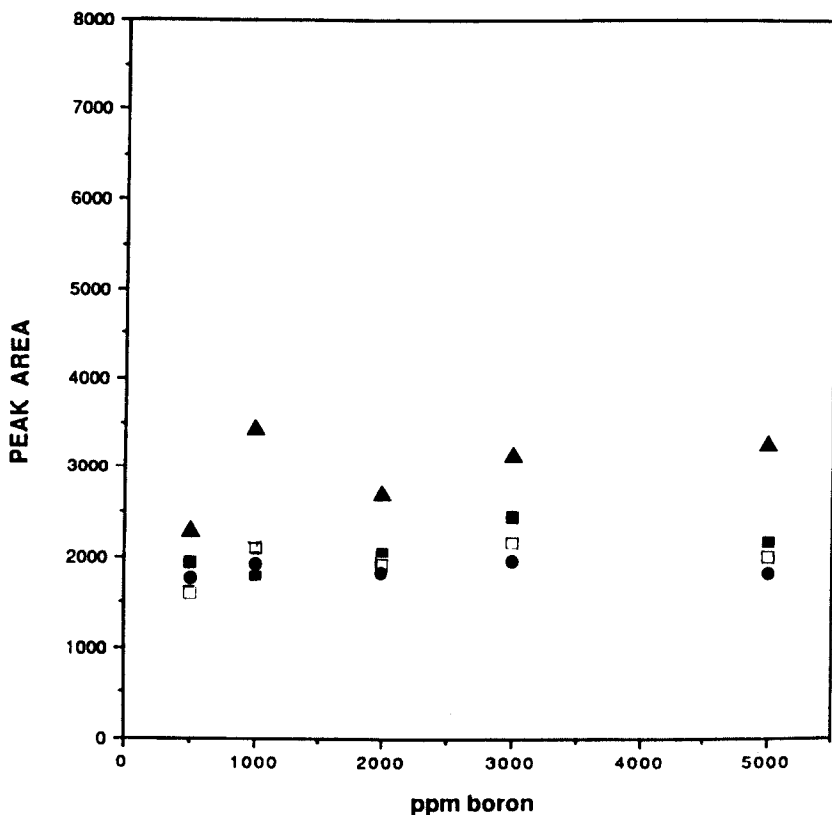

Fig. 7. Changes of peak areas for common inorganic anions with changing concentrations of boron (added as boric acid). The samples were prepared as indicated in Fig. 6 and analytical conditions were as indicated in Fig. 2, except for the trace enrichment conditions which were modified to 5 kV and 30 s. ■ = chloride (R.S.D. 10.9%); ▲ = sulfate (R.S.D. 14.0%); □ = nitrate (R.S.D. 6.7%); ● = fluoride (R.S.D. 3.2%).
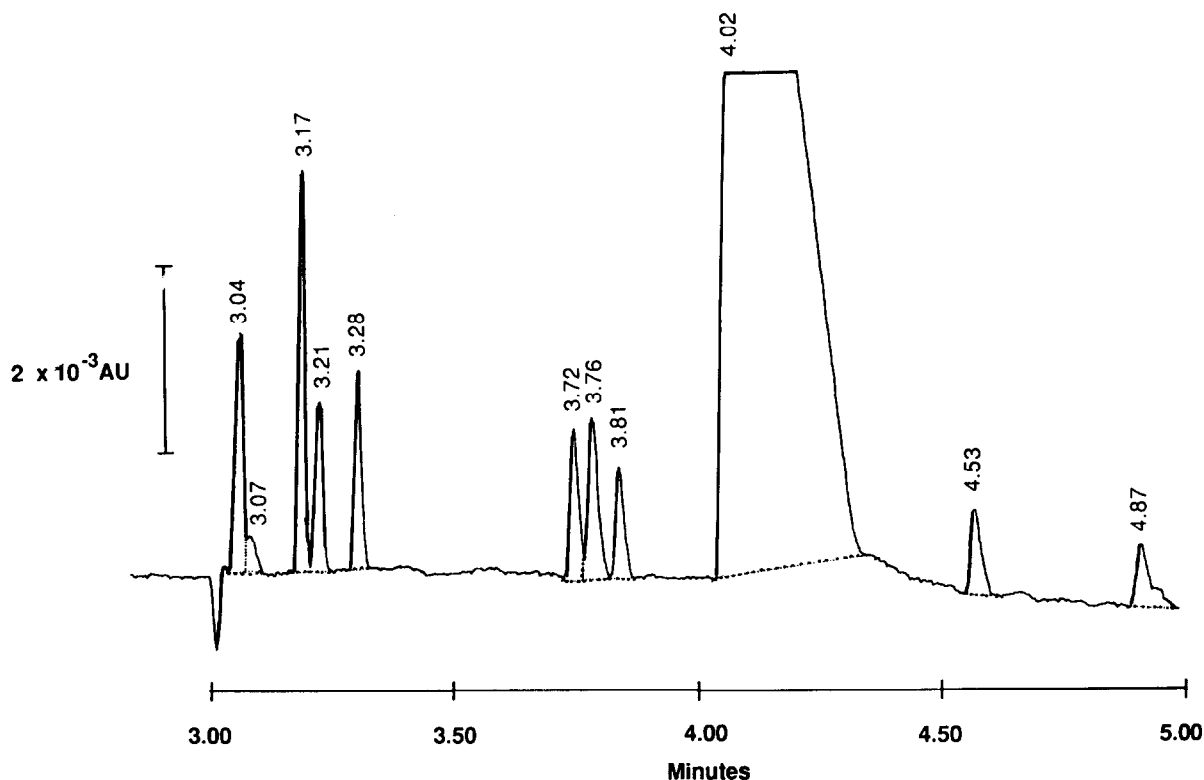
Fig. 8. Trace anions in the presence of 3 ppm morpholine. The separation was generated after electromigrative trace enrichment, 45 s at 5 kV and with 75 μM octanesulfonate additive in the sample. A complete description of the procedure is given in the Experimental section. The sample contained 7 ppb chloride (3.04 min), 9.6 ppb sulfate (3.17 min), 12 ppb nitrate (3.21 min), 10 ppb oxalate (3.28 min), 3.8 ppb fluoride (3.72 min), 10 ppb formate (3.76 min), 6.2 ppb phosphate (3.81 min), 10 ppb acetate (4.53 min) and 10 ppb propionate (4.87 min). The carrier electrolyte consisted of 10 mM sodium chromate and 0.5 mM NICE Pak OFM anion-BT, adjusted to pH 8 with dilute sulfuric acid. The separation voltage was -15 kV. The capillary dimensions and detection technique were the same as in Fig. 1.

for sulfate and chloride increases more rapidly than that of nitrate and fluoride. The higher values of y intercepts for sulfate and chloride, obtained in calibration plots at 1000 ppm boron (Table IV), support the preliminary conclusion of observed increases of peak areas for these two anions being caused by a relatively higher levels of these impurities in boric acid. The actual level of variance would than be less than 10% for 500 to 5000 ppm boron as indicated by the R.S. D. values of nitrate and fluoride. All practically possible samples of primary water (500 to 2000 ppm boron, *ca.* 1.7 ppm Li, detection limit up to 40 ppb inorganic anions) could thus be analyzed using a calibration at a single level of boron.

The second investigated example of an industrial

water sample containing elevated levels of ionic matrix is the secondary water (SW) in PWR. SW normally contains ammonia or morpholine at *ca.* 3 ppm. Also present are the reaction products (amines, carboxylates, etc.) of the basic additives and ion-exchange resins. Maximal admissible levels of inorganic anions and carboxylates are at 40 ppb. Normally encoutered concentrations of these ionic impurities are less than 5 ppb. An electropherogram of all anions usually monitored in SW, obtained in the presence of 3 ppm morpholine, is shown in Fig. 8.

The separations in the presence of morpholine are virtually identical with those obtained in the absence of the additive, the only noticeable differences being firstly, the larger areas of carbonate peaks due

to higher pH of the samples, and secondly, a slight shift towards longer migration times in morpholine-containing samples in comparison to pure water samples. Despite that, the calibration and precision data in synthetic SW samples are very similar to those shown in Tables II and III for matrix-free pure water samples and are for that reason not presented here.

CONCLUSIONS

The CE approach to the analysis of trace anions offers shorter run times per sample, improved resolution of sample components and a greater simplicity in comparison with IC. Validity of calibration curves is demonstrated in pure water samples containing common anions at trace levels as well as for some more specific samples such as water compositions in a nuclear power plant.

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