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Elimination of Matrix Interferences in Ion Chromatographic Analysis of Difficult Aqueous Samples

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Abstract

Several different methods of eliminating matrix-related chromatographic interferences are compared. Modification of the borate–gluconate eluent composition improves the appearance of chromatograms of anions from either acidic or alkaline sample matrices. The pH range of possible samples can be further extended by the employment of procedures utilizing ion-exchange resins or ion-exchange membranes. Membrane-based ion exchangers are found to give better recoveries for analyte anions after sample pretreatment than ion-exchange resins. It is also found that samples pretreated on ion-exchange membranes contain less ionic contamination than those treated with ion-exchange resins.

Introduction

Ion chromatography (IC) has become a widely utilized method for determination of anions in various kinds of water samples (1,2). Hardly any sample pretreatment, except filtration, is required in the majority of cases for concentrations as low as micrograms per liter. Even nanograms per liter levels can still be routinely measured, provided thirty or more milliliters of the sample are available and can be preconcentrated on a suitable precolumn before injection onto an anion-exchange column. However, widespread use of IC has also made it obvious that in certain cases some sample pretreatment may be mandatory. As typical examples, one can consider aqueous samples outside the pH range of 3 to 11 or those containing elevated levels of divalent cations (3). In agreement with the fundamental acido-basic equilibria, adjustments of pH are easily accomplished by ion exchange. Strongly acidic samples are adjusted by exchanging protons for alkaline cations or hydroxides for acid anions, whereas alkaline samples are usually acidified by using a protonated cation exchanger. Cation exchange for H^+ is also preferred for the removal of divalent cations.

The first applications of resin-based cation exchangers containing sulfonic groups were reported fifty years ago (4,5). Increased availability of polymeric ion exchangers has contributed to the widespread utilization of the method in subsequent years (6,7). One advantage of pH adjustments by ion exchangers is of great importance for separation methods such as IC. With an ion exchanger, pH is adjusted by changing the H^+ or OH^- concentrations (as well as decreasing the levels of exchanged ions, e.g., sodium for H^+). It is not necessary to introduce excessive amounts of an interfering counterion as in the case of strong acid or strong base addition (8). This report compares the usefulness of cation-exchange resins and of hollow fiber cation exchangers for sample preparation prior to anion chromatography. It provides application examples obtained with the help of a newly developed membrane-based sample pretreatment device. The possibility of eliminating pH-related artifacts by modification of the borate–gluconate mobile phase, the most common eluent presently used in single column IC, is also discussed.

Experimental

Equipment. All chromatographic components were from Waters Chromatography Division of Millipore. The IC system consisted of an M590 dual piston pump, a U6K injector, and an M431 conductivity detector connected to an M840 data system. Three different anion-exchange columns, all based on aminated polymethacrylate resin (exchange capacity ca. 30 μequiv/g), were used for our investigation. These were IC Pak Anion™ (dimensions, 0.46×5.0 cm; particle size, 10 μm), IC Pak Anion HC™ (dimensions, 0.46×15 cm; particle size, 10 μm), and IC Pak Anion HR™ (dimensions, 0.46×7.5 cm; particle size, 7 μm).

Eluents. Two different compositions of the mobile phase, referred to as standard or modified borate–gluconate, were evaluated. Standard borate–gluconate eluent was prepared by diluting 20 mL of a concentrate and 120 mL of acetonitrile to 1 L with 18-megohm water. The concentrate contained 34 g/L boric acid, 23.5 mL/L gluconic acid (50% w/w), 8.6 g/L lithium hydroxide monohydrate, and 125 mL/L glycerol. Modified composition of borate–gluconate was as reported by McClory and Warren (9). The concentrate contained 25.5 g/L boric acid, 13.2 mL gluconic acid (50% w/w), 7.2 g/L lithium hydroxide monohydrate, and 94 mL/L glycerol. The actual mobile phase was prepared by mixing 20 mL of concentrate, 120 mL acetonitrile, and 860 mL 18-megohm water. Both types of mobile phase were filtered and degassed with a Waters Solvent Clarification Kit.

Chemicals. Eighteen-megohm water for all solutions was generated by Milli-Q® Laboratory Water Purification System (Millipore). D-Gluconic acid (50% in water w/w) was purchased from Sigma. Boric acid (98% ACS reagent) and lithium hydroxide monohydrate were obtained from Aldrich. Acetonitrile (HPLC grade) and glycerol (USP-FCC) were supplied by J.T. Baker Inc. Strong organic acid free of ionic contamination utilized in the membrane-based device was obtained from Waters. The properties of the strong organic acid were chosen to minimize the contamination of the sample by the counterion-donating solution (CID). The exact chemical identity of the CID acid is proprietary to Waters Chromatography Division of Millipore. All other chemicals including those used for preparation of standards were of reagent grade quality and were used as obtained from a variety of commercial sources.

Sample pretreatment with cation-exchange resin. Virtually all commercial analytical grade cation-exchange resins leach traces of ions well above the detection limits of ion chromatography. The following resin cleanup procedure was developed specifically for the AG50W-X12 cation exchanger supplied by Bio-Rad. The same procedure should be applied to any commercial resin before use in an ion chromatographic sample preparation. The bottle containing the resin was filled with enough 18-megohm water to create a slurry that could be stirred by a large (3–4-cm) magnetic stirring bar. The rate of stirring was kept high enough to prevent settling of the resin. After 15 minutes of stirring, the resin was allowed to settle and the supernatant was decanted. A new portion of 18-megohm water was then added, and the above process was repeated. Water additions, stirring, and decanting were repeated several times, typically four times for a 1-lb resin container.

The prerinsed resin was then stored in an excess of water. Immediately before usage, ca. 4 mL of the wet resin was packed into a 10-mL polyethylene syringe (Becton, Dickinson). The syringe outlet was fitted with a Millex® HV filter (Millipore) to keep the resin inside the barrel. Approximately 4 mL of the water sample was added to the syringe and pushed through the resin and the Millex filter with the plunger. The repeated use of the same 4-mL batch of resin can be recommended only for repetitive treatment of an identical sample, provided the composition (pH, polyvalent cation levels) is known and is exceeded by the ion exchange capacity of the resin (2.3 mequiv/mL for AG 50W-X12).

Ion-exchange capacity of the hollow fiber material. The cation-exchange hollow fiber (0.51 mm o.d. and 0.36 mm i.d.) was from Nafion perfluorosulfonate (manufactured to our specifications by Permapure Products Inc.). The fiber was converted to H^+ form before use and subjected to a "break-through" test described by Samuelson (7). The test consisted of pumping a measured volume of 0.01 N NaOH through 91 cm of the fiber at 1 mL/min. The pH of the effluent was monitored by a calibrated pH electrode placed in contact with it in a homemade flow-through cell. The resulting semilogarithmic plot of pH versus mL 0.01N NaOH is converted by calculation to a break-through plot (ratio of normalities of OH^- ions influent/effluent versus mL 0.01 N NaOH).

Sample pretreatment with hollow fibers. The improvised experimental arrangement shown in Figure 1 was utilized in the beginning of our study. A Luer-Tip syringe (Becton, Dickinson) was connected to the fiber through a three-part assembly consisting of a Luer-Lok adapter, a plastic union (Upchurch Scientific), and a homemade part (retainer) that connected the fiber

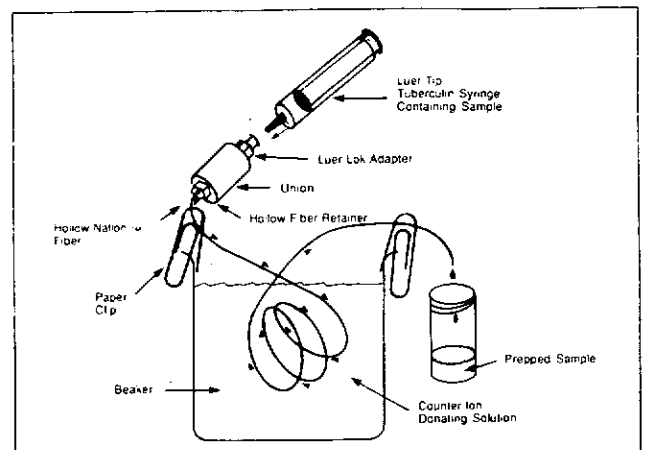

Figure 1. Experimental configuration for sample pretreatment with a hollow fiber cation exchanger immersed in 0.025 N sulfuric acid solution.

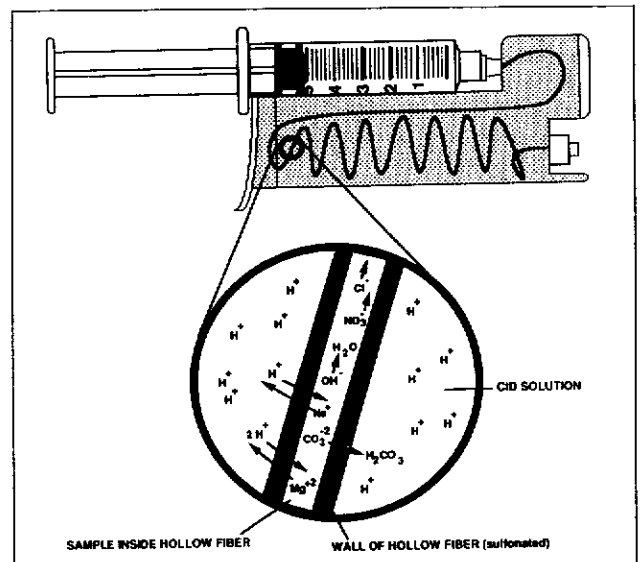

Figure 2. Sample pretreatment cartridge with the same hollow fiber as in Figure 1. The counterion-donating solution is a strong organic acid, 0.025 N. In the pretreatment of samples containing NaCl, NaOH, $Mg(NO_3)_2$, and Na_2CO_3, the sample components are converted to hydrochloric acid, nitric acid, and water. A considerable portion of the carbonate is removed from the sample.

to the plastic union. The inner diameter of the hollow fiber retainer was 0.50 mm.

The commercial device, MilliTrap™ (patent pending, Waters), shown in Figure 2, was developed as a result of these investigations. This device contains 151 cm of Nafion nonporous hollow fiber immersed in a dilute solution of an ultrapure strong organic acid. Only those batches of the purified acid in which the concentrations of common inorganic ions are below the detection limits of ion chromatography are used. The housing is made of a polypropylene material presoaked in 18-megohm water.

The uniform quality of the hollow fiber is controlled by break-through tests as well as by electron microscopy. The latter procedure was introduced after a report by Lamb et al. (10) concerning irregular Donnan exclusion on some commercial fibers.

According to this report, the defects are caused by 10-μm pinholes detectable by electron microscopy. An electron micrograph is shown in Figure 3.

Results and Discussion

Matrix interferences in ion chromatography are commonly overcome by modifications of separation or detection techniques. Another alternative is sample preparation. We have investigated three different approaches to the analysis of samples having extreme pH levels or high concentrations of polyvalent cations. The first approach consisted of the optimization of a mobile phase.

Figure 3. Electron micrograph of a cross-section of the hollow fiber. The bar at the bottom of the photograph indicates the dimension of 23.6 μm.

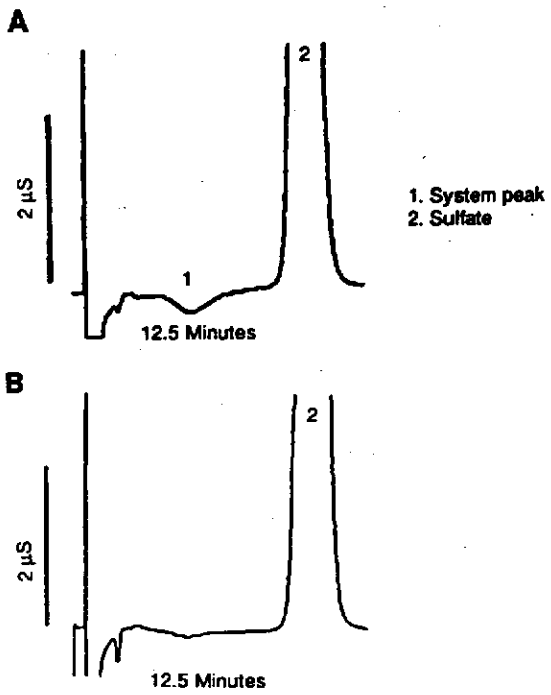

Figure 4. Chromatograms after injection of (A) 100 μL 0.01 N sulfuric acid into a standard composition of borate–gluconate eluent, and (B) 100 μL 0.01 N sulfuric acid injected into the modified borate–gluconate eluent. Flow rate, 1.2 mL/min; column, IC Pak A; detector, M430 conductivity.

Changes of pH artifacts in two different compositions of borate–gluconate

Borate–gluconate is a mobile phase that permits sensitive detection and efficient separation in single-column ion chromatography with aminated polymethacrylate columns (11). According to recent reports (3,12,13), several different complexes between borate and gluconate may be present in this eluent. The prevailing species is determined by the molar ratios of the constituents of the eluent and by the eluent's pH. In the standard borate–gluconate eluent, changes of complexation with pH lead to significant artifacts after injections of acidic (Figure 4A) or alkaline (Figure 5A) samples.

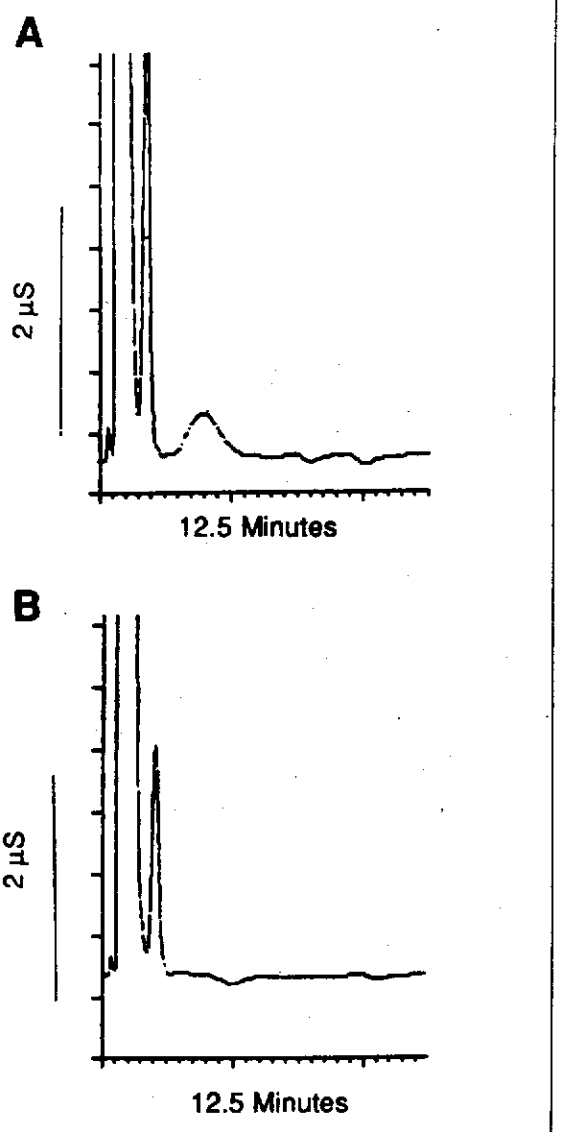

Figure 5. Chromatograms obtained after an injection of (A) 100 μL 0.01 N sodium hydroxide into a standard borate–gluconate eluent (the broad peak appearing between 4 and 6 minutes is an artifact caused by a disturbance of dynamic equilibria between the borate and gluconate anions) and (B) 100 μL of 0.01 N sodium hydroxide injected into the modified borate–gluconate eluent. Other experimental conditions are the same as in Figure 4.

The exact nature of the equilibria involved has not been clarified. However, from the directions of the acidic and alkaline disturbances, it is possible to arrive at some preliminary conclusions. The conductivity decrease in Figure 4A indicates a shift in the pH-dependent borate-gluconate equilibrium, for example (gluconate indicated as L), $BL^{2-} + H^+ \rightarrow BH + L^-$, while the positive peak in Figure 5A may be due to an increase in complexation according to $BH + L^- \rightarrow BL^{2-} + H^+$. McClory and Warren (9) described elimination of artifacts encountered in the analysis of ground water samples by using a modified composition of the borate-gluconate eluent. In Figures 4B and 5B we show our results with such a mobile phase after injections of acidic and alkaline samples. Clearly, by changing the ratio of gluconate and borate concentrations, the useful range of the borate-gluconate eluent could be extended beyond the originally specified region of pH 3–11.

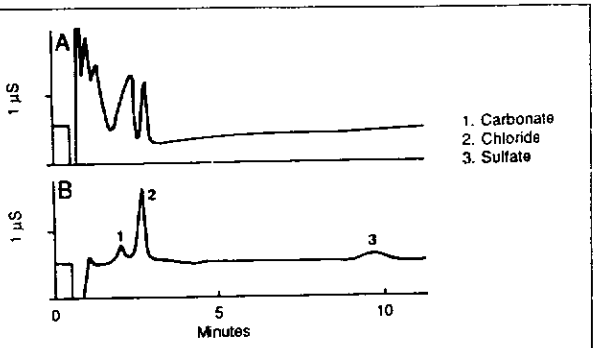

Figure 6. Contaminated groundwater samples. (A) 100 µL injected, no sample preparation. (B) 100 µL pretreated by a cation-exchange resin in H^+ form. Chromatographic conditions were as in Figure 4A.

Sample preparation by a cation-exchange resin in H^+ form

The second alternative in dealing with extremely alkaline or acidic samples is pretreatment by a suitable ion-exchange resin. This approach is demonstrated in Figures 6A and 6B. Samples to be analyzed consisted of groundwater collected near a petrochemical industrial facility. They were of red-brown color, with pH between 12 and 14. The color was found to be due to dissolved iron, but the exact source of the groundwater contamination remained unknown. A distinct alkaline artifact, which rendered any quantitation unreliable, was observed upon injecting an untreated sample (Figure 6A). The separation was markedly improved by the cation-exchange pretreatment outlined in the experimental section (Figure 6B). The wet resin was taken out of the storage container, and three milliliters of pure water were put through it prior to the application. Of immediate concern were the observed increase in the peak height for chloride relative to Figure 6A and the emergence of a sulfate peak in Figure 6B. A parallel determination (with 4 mL prewashed resin in a syringe, rinsing with 3 mL water, pushing 4 mL of pure water through the resin, and injecting an aliquot of the eluate) confirmed that the observed increases in chloride and sulfate concentrations were due to a contamination of the treated sample by the resin. Twenty milliliters of pure water were necessary to reduce the chloride and sulfate contamination to levels that did not interfere with the quantitation of ppm concentrations of the same anions from the sample (<0–50 ppb). A study of recoveries for the standard eight inorganic anions was then carried out with the same volume of cation-exchange resin (4 mL), the same sample volume (4 mL), and an increased rinsing volume (20 mL). A chromatogram of an 8-anion standard, before the resin treatment, is presented in Figure 7A. Figure 7B shows an injection of the same standard after it had been pushed through the prerinsed cation-exchange resin. The values for the recoveries are given in Figure 7.

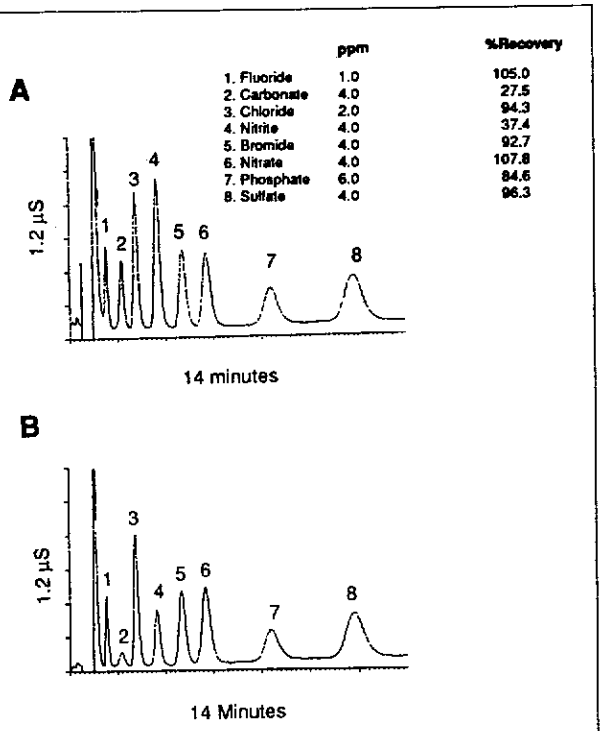

Figure 7. Chromatograms of an 8-anion standard. (A) 100 µL injected. (B) The same standard after passage through the prerinsed cation exchanger. Analytical conditions were as in Figure 4A. The values of recoveries compare peak areas from 7A and 7B.

The low results for nitrite and phosphate can be explained by partitioning of the undissociated conjugated acids into the bulk of the resin material, an effect that is well documented for suppressed ion chromatography with packed column suppressors (14). The higher than 100% value for nitrate suggests an oxidative contribution to the loss of nitrite. The increased value for fluoride after the cation-exchange treatment is most likely due to the better resolution of this anion from the preceding matrix peak. Low recovery for carbonate can potentially be exploited for the selective removal of high carbonate levels in certain types of water samples before the quantitation of other anions. On the other hand, the losses for chloride, bromide or sulfate are not excessive, and the estimated relative standard deviation (ca. 5%) for the recoveries of all anions is well within the acceptable range for many applications.

Sample pretreatment with hollow fiber cation exchangers

The above results with the cation-exchange resin prompted us to search for another form of sample treatment that would give a more uniform recovery of all the standard anions. Cox and co-workers have recently demonstrated the use of hollow fibers for the pretreatment of concentrated samples in ion chromatography (15). They also discuss the relative advantages of their method based on Donnan dialysis and "dual ion exchange" as compared to the use of ion-exchange resin for the same type of sample preparation. According to their conclusions, hollow fibers are more suitable mainly because of the smaller surface area, which results in fewer adsorptive losses. In order to determine

the optimal experimental configuration for our type of sample matrices (low concentrations of anions, 1–100 ppm divalent cations, and pH below 2 or above 12) the ion-exchange capacity of the fiber with and without a counterion-donating solution (CID) was evaluated. Following the procedure described in the experimental section, we generated two different break-through curves (Figure 8). As recommended by Samuelson (5), the ion-exchange capacity should always be defined with a particular application in mind. For the majority of cases of sample pretreatment, only a rate of removal of interferences exceeding 90% (or 0.9 c/c_0) can be considered satisfactory. Based on this, the ion-exchange capacities can be determined as ca. 0.1 mequiv for the 91 cm of fiber and as 1 mequiv for the same length of the fiber immersed in 80 mL of 0.025 mN sulfuric acid. Therefore, we concluded that the fiber alone had too low a capacity for the application in question and that only about one-half of the number of equivalents of counterions in the fiber or in the counterion-donating solution give the value of ion-exchange capacity useful for the sample preparation.

With the ion-exchange capacity available, 100 mL of a pH 12, 10 mL of a pH 13, or 250 mL of a neutral aqueous solution containing 50 ppm or less calcium can be successfully pretreated for injection into an ion chromatographic system that uses the standard borate-gluconate eluent. Significantly larger sample volumes can be used if the modified eluent is employed.

The minimum prerinsing volume for sample pretreatment was established by analyzing portions of pure water put through the hollow fiber that was immersed in a CID solution (0.025 N strong acid). When the CID solution was sulfuric acid, sulfate was detectable by ion chromatography. Sulfuric acid appears to penetrate past the negative charges of sulfonic groups of the

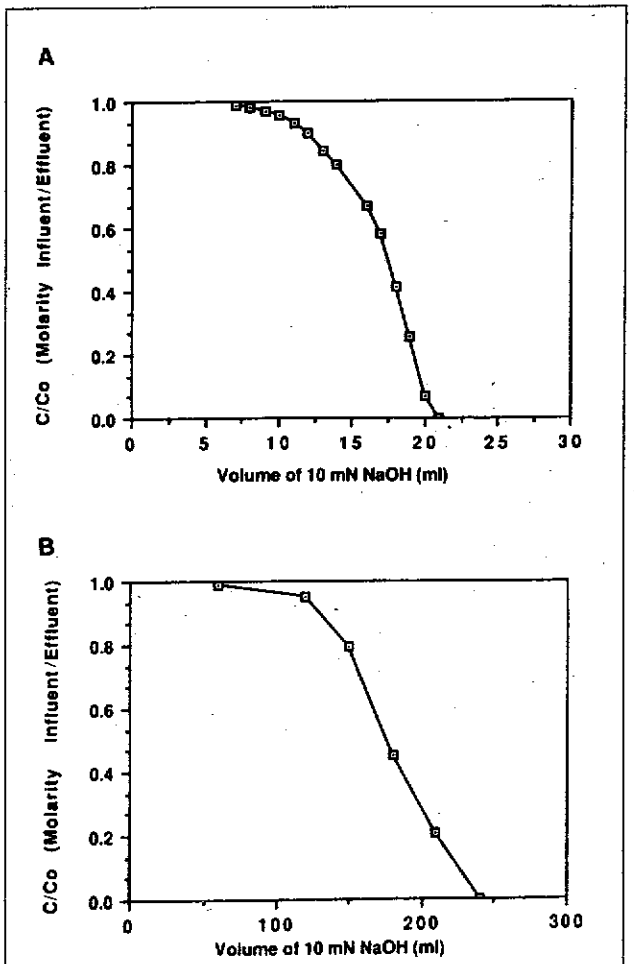

Figure 8. Ion-exchange break-through curves obtained for 91-cm hollow fiber. (A) No CID solution used. (B) Immersed in 80 mL of 0.025 N sulfuric acid solution.

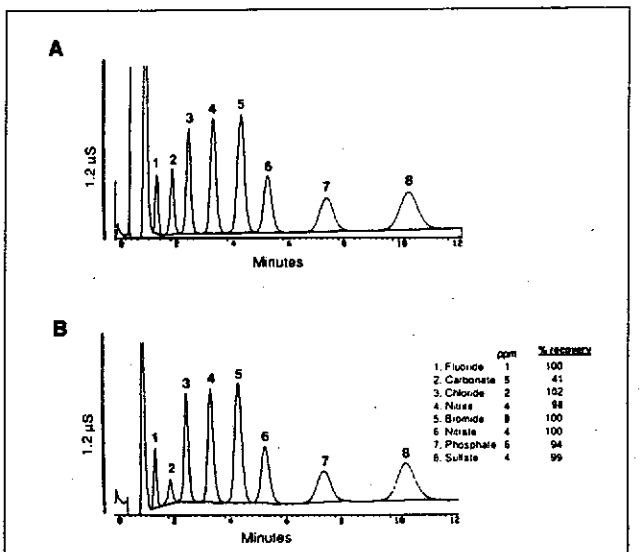

Figure 9. Recoveries of anions after passage through a hollow fiber immersed in 80 mL of 0.025 N CID solution and prerinsed by 1 mL of 18-megohm water. The values of recoveries were calculated as percentage ratios of peak areas in the two chromatograms. (A) 100 µL of an 8-anion standard injected directly. (B) The same volume of the anion standard after a passage through the hollow fiber. Chromatographic conditions are identical with those in Figure 4A.

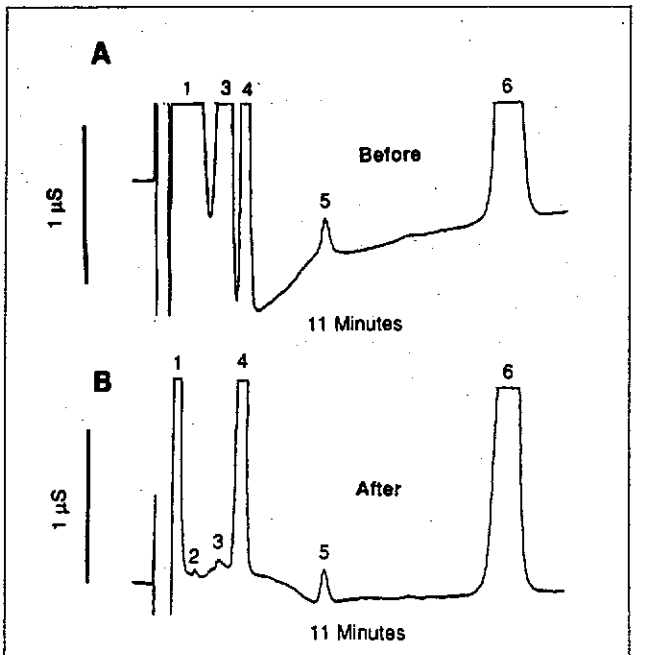

Figure 10. Injections of 100 µL of a drinking water sample containing 12 ppm magnesium and 68 ppm calcium, (A) before and (B) after the treatment by the hollow fiber device shown in Figure 2. Column, IC Pak A HR; eluent, modified borate-gluconate; other conditions as in Figure 4A. Peaks: (1) cation peak; (2) organic acid; (3) carbonate; (4) chloride, 17.6 ppm; (5) nitrate, 1.3 ppm; (6) sulfate, 32 ppm.

membrane into the sample stream. The levels of sulfate contamination were influenced more by the time of residence of samples inside the hollow fiber than by the rinsing volume. Accordingly, the sulfate concentration in the effluent varied between ca. 0.4 and 8 ppm after the fiber was prewashed with 1 mL of pure water or the sample.

More acceptable results were obtained with the 0.025 N proprietary strong organic acid as a CID solution. The chromatograms of a standard before and after sample pretreatment are shown in Figures 9A and 9B, respectively. Before its use to generate the chromatogram in Figure 9B, the fiber device was rinsed with only 1 mL of 18-megohm water. The recoveries are relatively uniform. The reduction of carbonate concentration is useful for samples containing too high levels of that anion, as already discussed in connection with the cation-exchange resin.

The device has been tested on a variety of water samples. Pretreatment of a drinking water sample containing 12 ppm magnesium and 68 ppm calcium is shown in Figure 10. As reported by Erkelens and co-workers (3), the presence of alkaline earth cations in water samples leads to distortions in chromatograms if borate-gluconate is used as a mobile phase in the ion chromatographic system (see Figure 10A). Such calcium- and magnesium-related artifacts could be largely eliminated by the use of a hollow fiber cation exchanger (Figure 10B). Another example is a waste water sample from an industrial facility taken on the influent side of the waste water treatment plant (Figure 11). In this particular sample, the quantitation of fluoride was impossible without the use of the membrane device. The large negative base line perturbation extending from the water dip to the center of the chromatogram in Figure 11A was attributed to the presence of divalent cations.

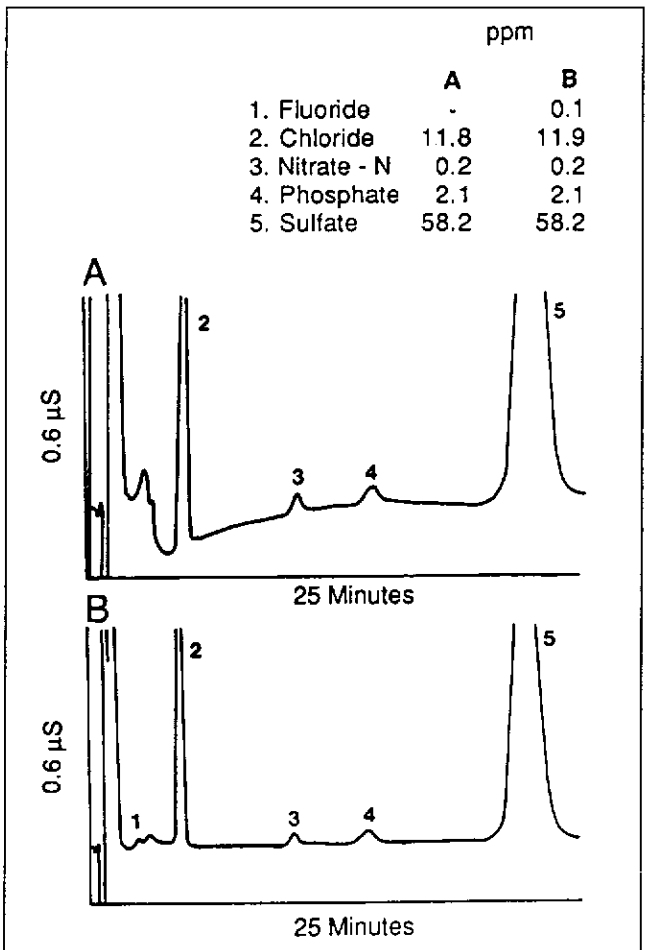

Figure 11. Chromatograms of a waste water sample obtained (A) before and (B) after preparation with a hollow fiber cartridge from Figure 2. The column was an IC Pak A HC with the standard composition of the borate-gluconate as mobile phase. All other conditions were as in Figure 4A.

Conclusions

The new technique, using sample preparation devices with hollow fiber cation exchangers in conjunction with a modified borate-gluconate elution buffer, offers a simple and efficient approach to the pretreatment of highly acidic, highly alkaline, and high-calcium or high-magnesium water samples. Various base line disturbances investigated in this study, as well as those reported by other authors, are eliminated. Evaluation of peak heights and peak areas especially by automatic integrators is thus made easier and more reliable. The removal of polyvalent cations as well as the moderation of extreme pH values leads to prolonged column lifespans. In consequence, a reduction of operating costs is realized in the ion chromatographic analysis of water samples.

Acknowledgments

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