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Electrodialysis for clean-up of strongly alkaline samples in ion chromatography

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ABSTRACT

An electrodialysis method is described for the off-line neutralization of strongly alkaline samples containing trace levels of common inorganic anions. This method uses an electrodialysis cell comprising three compartments separated from each other by cation-exchange membranes. These compartments comprise an anode compartment housing, a platinum wire anode and 10 ml of a suitable hydrogen ion donating medium, a sample compartment which contains 1 ml of the alkaline sample, and a cathode compartment housing a platinum wire cathode and a dilute solution of sodium hydroxide. During electrodialysis at either constant applied current or constant applied power, hydrogen ions from the anode compartment displace sodium ions from the sample, thereby effecting neutralization.

Experimental parameters, such as the magnitude of the applied current or power, the type of cation-exchange membrane used and the design of the cell have been studied and optimum results were obtained using a Neosepta CM-2 membrane, of area 616 mm^2 supported between two perspex discs, with an applied current of 150 mA or applied power of 3 W. Under these conditions, a 1 ml sample of 1 *M* sodium hydroxide could be neutralized in 11 min. The most effective hydrogen ion donating medium consisted of a 2:1 (w/v) slurry of BioRad AG 50W-X8 (200–400 mesh, H^+ form) cation-exchange resin in 1 m*M* octanesulfonic acid. Recoveries of solute anions (3–10 μg/ml) from the dialysed solution were close to quantitative, except for fluoride and nitrite, which gave recoveries of less than 60%. It is suggested that low recoveries for these ions are due to formation of neutral, protonated species within the membrane with subsequent loss by diffusion.

INTRODUCTION

Dialysis is a technique based on a diffusion process in which selected sample components are transferred across a membrane. The technique can be divided into passive dialysis and active (or Donnan) dialysis. Passive dialysis involves the diffusion of particles of a specified molecular mass range through a neutral membrane and is a slow process that often requires a large volume of sample and normally results in severe sample dilution. On the other hand active or Donnan dialysis involves the transfer of ions of a specified charge through an ion-exchange membrane. It is a much faster and more reliable process than passive dialysis. Active dialysis has been used to achieve both matrix normalization and sample preconcentration when used for sample clean-up in ion chromatography (IC) [1,2]. In previous work, we have successfully employed active dialysis with a membrane fibre device for the treatment of strongly alkaline samples prior to IC analysis [3].

Further refinement to active dialysis methods can be achieved by coupling electric fields with membranes; this process is known as electrodialysis. The electrodialytic process has been used for many years in industry for water purification, wastewater treat-

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ment and desalination procedures [4–7]. On the analytical scale, the method has been used as an extraction method in drug analysis [8,9] and has been reported for the treatment of strongly acidic samples prior to the determination by IC of magnesium(II) and calcium(II), using a dual anion-exchange membrane tube device [10]. In this work, concentric anion-exchange membrane tubes were used to form the sample and electrolyte compartments and migration of anions was induced under conditions of constant current. Cations were prevented from movement between compartments as a result of the permselectivity of the membranes. These authors have also suggested the potential applicability of electrodialysis using the same experimental arrangement for the pre-treatment of alkaline samples prior to analysis using IC. Electrodialysis coupled on-line with HPLC has also been described for the determination of basic and acidic compounds in environmental samples [11,12], but no study has been reported on the use of this technique for inorganic anions determination by IC.

In the present work electrodialysis is used for the off-line pre-treatment of alkaline solutions prior to their analysis by anion-exchange IC. Such samples are traditionally difficult to analyze by IC because of the severe baseline disturbances generally caused when the sample is injected onto the column. Simple neutralization with acid is not practicable because of the resultant high concentration of the acid anion introduced into the sample. Electrodialysis can be achieved by arranging two sheets of cation-exchange membrane in a stack to form a three-compartment cell comprising compartments for anode, cathode and sample. The anode compartment contains a hydrogen ion donating medium, the cathode compartment contains a dilute alkaline solution (which acts as a receiver) and the sample compartment is filled with a mixture of inorganic anions in a sodium hydroxide solution. Application of a dc electrical field causes cations (especially sodium ions) to move from the sample compartment towards the cathode, and to be replaced by hydrogen ions from the anode compartment. Anions do not move between compartments. The net effect of this process is the neutralization of the alkaline sample solution. During the electrodialysis, water will be oxidized at the anode to produce O_2 and H_3O^+ and will be reduced at the cathode to form H_2 and OH^-. The concentration of OH^- in the cathode compartment therefore increases, whilst the amount of water in the anode compartment decreases at the end of the process.

The stability of the membrane to changes in pH and temperature during electrodialysis is an important factor for the ultimate success of the process, as are the changes in shape of the membrane which will directly affect the electrodialysis time. Chemical stability and high permselectivity of the membrane also play a significant role in the recovery of inorganic ions present in the sample. In this work, the electrodialysis technique is applied to the neutralization of alkaline samples, with particular attention to the design of a cell suitable to minimize the electrodialysis time and to optimize the electrodialysis conditions.

EXPERIMENTAL

Instrumentation

The ion chromatograph consisted of a Millipore-Waters (Milford, MA, USA) Model 510 pump, Model U6K injector and Model 430 conductivity detector, operated in both the suppressed and non-suppressed modes. The column used for non-suppressed IC was a Millipore-Waters IC Pak A anion column, 50 × 4.6 mm I.D., packed with polymethacrylate anion-exchange resin. The column used for suppressed IC was a Dionex HPIC AS-4A anion separator with AG-4A guard column, connected with an AMMS membrane suppressor. A Waters reagent delivery module was used to pass the regenerant of 12.5 m*M* H_2SO_4 through the suppressor. Sodium ion was determined using a Millipore-Waters IC Pak C cation column, 50 × 4.6 mm I.D., packed with styrene–divinylbenzene resin. Chromatography was carried out at room temperature with an eluent flow-rate of 1.2 ml/min.

The electrodialysis cell used is shown schematically in Fig. 1. The cell was constructed as a series of cylindrical perspex components held together by two plates compressed with longitudinal threaded rods (Fig. 2). Electrodes were constructed from platinum wires (60 × 0.25 mm O.D.), clipped to the cell and connected to the power supply. The cation-exchange membranes (see Table II for thickness) were supported on each side with perspex discs (not shown in Fig. 2), 0.9 mm in thickness, through

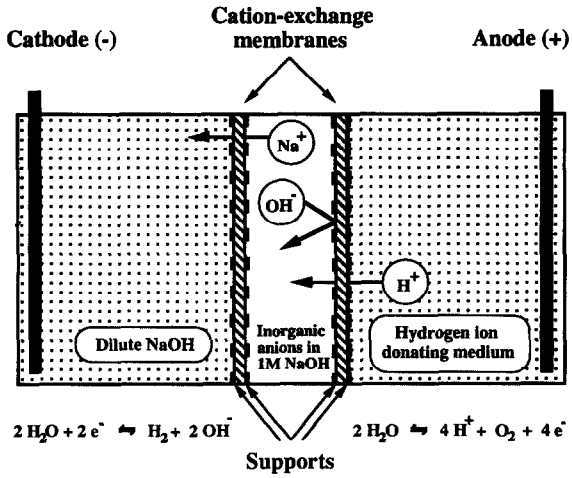

Fig. 1. Schematic diagram of the electrodialysis process.

which had been drilled closely spaced 3.2 mm diameter holes covering a circular area 28 mm in diameter. Under these conditions, the surface area of the membrane in contact with the sample and electrode solutions was 616 mm^2. The perspex disc supports added no significant increase to the electrodialysis time and their use virtually eliminated buckling of the membrane due to heat production. The volume of both the anode and cathode compartments was 10 ml, whilst the sample compartment contained 1 ml. Samples were introduced into the sample compartment by means of a 500-μl glass microsyringe.

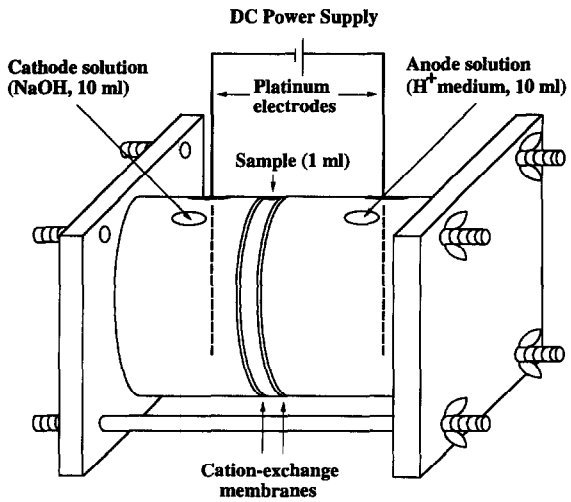

Fig. 2. Electrodialysis cell.

A Bio-Rad (Richmond, CA, USA) microprocessor-controlled electrophoresis power supply (Model 3000 Xi) was used in the fixed potential, fixed current and fixed power modes. When an applied current in excess of 300 mA was required, a GoodWill (Taiwan) laboratory dc power supply (Model GPR-7530D) was used.

Reagents

All chemicals used were of analytical reagent grade and the water employed for the preparation of standard solutions and eluents was purified on a Millipore (Bedford, MA, USA) Milli-Q water treatment system. Samples and eluents were filtered through a Millipore 0.45 μm membrane filter and degassed in an ultrasonic bath prior to use. The eluent used for non-suppressed IC analysis of the treated samples contained 1.3 m*M* sodium tetraborate, 5.8 m*M* boric acid and 1.4 m*M* potassium gluconate adjusted to pH 8.5 and made up in water–acetonitrile (88:12, v/v). The eluent for the suppressed system contained 2 m*M* sodium bicarbonate and 2 m*M* sodium carbonate. The eluent for sodium determination contained 0.5 m*M* EDTA and 2 m*M* nitric acid.

Standard stock solutions of inorganic anions were prepared by dissolving appropriate amounts of the sodium salts in water. Working solutions of these ions were obtained by diluting the stock solutions with sodium hydroxide to give final concentration of 1 *M* NaOH. The concentration of inorganic anions in these solutions was in the range 30–100 μg/ml for the non-suppressed system and in the range of 3–10 μg/ml for the suppressed system.

Hydrogen ion donating solutions for use in the anode compartment of the electrodialysis cell were prepared using 0.0005–0.05 *M* sulfuric acid, methanesulfonic acid (MSA), octanesulfonic acid (OSA), camphorsulfonic acid (CSA) and *p*-toluenesulfonic acid (TSA). All were obtained from Sigma (St. Louis, USA) with the exception of octanesulfonic acid which was prepared by passing a solution of sodium octanesulfonate through a glass column packed with 100 g Bio-Rad AG 50W-X8 hydrogen form cation-exchange resin, 200–400 mesh. This same cation-exchange resin was also used as hydrogen-ion donating medium and prior to its use for this purpose, was washed thoroughly with Milli-Q water.

The cation-exchange membranes used in this work were obtained from Asahi Glass, Japan (CMV), Du Pont (Wilmington, DE, USA) (Nafion 324, Nafion 901), Ionics Incorp., USA (CZL-386, AZL-389), Tokuyama Soda, Japan (Neosepta CM-2, CMS, C66-10F, CLE-E), Pall RAI, USA (Raipore R-5010-M) and Asahi Chemical Company, Japan (K-101).

Procedures

The determination of co-ion concentrations present in a particular membrane was carried out by first soaking the membrane in Milli-Q water for 24 h to remove any residual ions, after which it was equilibrated in 100 ml of 0.1 *M* sodium salt solutions (*e.g.*, NaF, NaCl, NaBr, $NaNO_3$, Na_3PO_4, Na_2SO_4) for a further 24 h period and then blotted to dryness. The co-ions present in the membrane were displaced by soaking the membrane for 24 h in 20 ml of 0.3 *M* potassium chloride for sulfate ion or in 20 ml of 0.2 *M* potassium sulfate for other anions. The displaced anions were determined by suppressed IC and the displaced sodium ion (which is a measure of the cation-exchange capacity of the membrane) was measured by non-suppressed IC.

RESULTS AND DISCUSSION

Selection of electrodialysis conditions

Preliminary tests showed that the mechanical stability of the membranes was a major consideration in that distortion of the membrane as a result of the heat generated in the cell was the most common source of failure. Since the electrodialysis can be performed by applying the electrical field in three ways, namely constant potential, constant current or constant power, these methods were evaluated with respect to heat evolution in the cell.

The constant potential mode was found to give rapid temperature rises, even at the start of the electrodialysis. For example a constant potential of 30 V applied to a sample of 20 ml of 1 *M* NaOH caused the temperature of the sample solution to reach 80°C within the first few min of electrodialysis. Lowering the applied potential reduced heat production but neutralization of the sample could not be achieved. For these reasons, dialysis at constant potential was not performed further.

Dialysis at constant current proved to be suitable in that both the current and voltage (and hence the temperature) could be held fairly constant over most of the dialysis, with significant changes occurring only as neutralization was approached and the conductance of the sample decreased. The time required for a particular dialysis was found to be inversely proportional to the current density, which in turn was dependent on the surface area of the membrane and the magnitude of the applied current. Currents in the range 100–200 mA were found to give effective dialysis without excessive heat production under the experimental conditions used. Similarly, dialysis at constant power was also suitable, provided that the applied power did not produce currents outside the working range indicated above. For this reason, the applied power was restricted to about 3 W. More aggressive conditions always caused pronounced buckling of the membrane (even when mechanical supports were used) and loss of sample through volatilization.

Cell design

The cell was designed to optimize the dialysis of a sample solution containing up to 1 *M* sodium hydroxide since most samples occurring in practice should be dilutable to this level. Varying volumes of sample were dialysed under differing applied currents until neutralization was reached. This point was indicated by either a rapid increase of applied potential or by the change in colour from blue to yellow of bromothymol blue indicator (pK_a = 7.0) added to the sample compartment. Tests indicated that there was no penetration of the indicator through the cation-exchange membrane nor did the presence of the indicator interfere in the analysis of the inorganic anions by non-suppressed or suppressed IC. The cathode compartment of the cell was filled with 20 ml of 0.1 *M* sodium hydroxide and the anode compartment was filled with 10 ml of 0.05 *M* sulfuric acid. The membrane used in this experiment was Asahi CMV, a cation-exchange membrane with an ion-exchange capacity of 2.1 mequiv./g.

Table I shows the dialysis time required under different experimental conditions and indicates that this time was directly proportional to the moles of hydroxide in the sample and inversely proportional to the applied current (note that the membrane area was constant for all experiments). Moreover, the

TABLE I

ELECTRODIALYSIS TIMES AT CONSTANT APPLIED CURRENT FOR NEUTRALIZATION OF SAMPLES TO pH 6

Sample volume (ml)	[NaOH] (*M*)	Current (mA)	Voltage (V)	Time (min)
20.0	0.1	15	6–50	220
20.0	0.1	150	10–50	25
10.0	0.1	15	6–50	115
10.0	0.1	150	10–50	12
10.0	1.0	150	10–100	90
10.0	1.0	450	17–100	30
10.0	1.0	750	26–100	15.3
1.0	1.0	150	10–100	11.1
1.0	1.0	450	18–100	3.9
1.0	1.0	750	24–100	2.1

dialysis times obtained were in close agreement with those calculated using the current density and the known number of moles of hydroxide in the sample, showing that the cell was performing efficiently. In practical terms, an electrodialysis time of 11 min could be achieved in the neutralization of 1 ml of 1 *M* NaOH solution by applying a constant current of 150 mA, without the production of excessive heat and resultant distortion of the membrane. Electrodialysis could be performed on two samples simultaneously by coupling two identical cells in parallel to the same power supply. The applied total current was distributed evenly to both cells and each sample reached the neutralization point at the same time. For example, the electrodialysis time for a single sample containing 1 ml of 1 *M* NaOH with a current of 150 mA was 11 min, whilst 22 min was required for two parallel cells, each containing 1 ml of the same sample. Increasing the current to 300 mA for the parallel cells reduced the dialysis time to 11 min.

Selection of the membrane

The cation-exchange membranes used in the construction of the cell must show a high permselectivity towards cations and be able to withstand the heat generated in the cell. A range of membranes was evaluated and the important properties of each are listed in Table II. These membranes were soaked in water for at least 24 h prior to use, except for Nafion 901 which was soaked in 2% NaOH so-

TABLE II

PROPERTIES OF THE COMMERCIAL CATION-EXCHANGE MEMBRANES USED IN THIS STUDY

Supplier	Type	Electrical resistance (Ω cm^2)	Total cation transport number	Burst strength (kg/cm^2)	Exchange capacity (mequiv./g)	Thickness (mm)
Asahi Glass	CMV	2.0–3.5	>0.92	3–5	2.1[a]	0.13
Du Pont	Nafion 901	2.8	n.a.[b]	n.a.	n.a.	0.45
Du Pont	Nafion 324	4.5	n.a.	n.a.	o.6[a]	0.32
Ionics	CZL-386	13	n.a.	8	2.7	0.60
Ionics	ZAL-389	28	n.a.	27	2.6	1.20
Tokuyama Soda	Neosepta CM-2	2.0–3.0	>0.98	3–5	2.2[a]	0.14
Tokuyama	Neosepta	1.5–2.5	>0.98	3–4	2.4[a]	0.16
Tokuyama Soda	Neosepta C66.10F	5.0–8.0	>0.98	6–8	1.7–2.2	0.30
Tokuyama Soda	Neosepta CLE-E	15–25	>0.98	8–10	1.3–1.8	1.10
Pall RAI	R-5010-M	4–8	0.92	n.a.	n.a	0.17
Asahi Chemical	K-101	n.a.	n.a.	n.a.	n.a.	0.20

[a] Value determined experimentally.
[b] n.a. = Data not available.

TABLE III

PERCENTAGE RECOVERY OF ANIONS (3–10 μg/ml) FROM 1 *M* NaOH SOLUTION AFTER ELECTRODIALYSIS AT 3 W USING VARIOUS CATION-EXCHANGE MEMBRANES

The range derived from 5 replicates is shown in parentheses.

Membrane	F^-	Cl^-	Br^-	NO_3^-	HPO_4^{2-}	SO_4^{2-}
Neosepta CM-2	4.4 (2.1)	96.1 (4.2)	94.1 (4.4)	97.3 (3.2)	98.5 (1.4)	89.5 (5.4)
Asahi CMV	30.0 (4.3)	87.2 (6.5)	85.7 (6.9)	87.4 (6.2)	85.6 (3.6)	66.5 (7.8)
Asahi K-101	55.0 (5.0)	79.4 (8.1)	75.6 (3.8)	80.9 (3.4)	80.6 (4.2)	80.7 (6.3)
Neosepta CMS	9.2 (3.6)	86.8 (8.7)	88.9 (7.3)	87.5 (6.3)	83.6 (3.6)	78.7 (2.4)
Raipore R-5010-M	19.4 (6.0)	78.8 (2.5)	83.2 (4.3)	83.8 (4.8)	82.8 (2.6)	80.3 (6.8)
Nafion 324	35.0 (2.0)	73.0 (5.2)	86.8 (4.1)	90.4 (3.5)	85.3 (3.6)	76.8 (3.8)
Nafion 901	33.3 (4.5)	69.2 (7.0)	83.6 (6.5)	91.2 (5.6)	83.2 (4.2)	76.6 (3.4)

lution as suggested by the manufacturer. When the membranes were supported with the porous perspex discs (as described under Experimental), all showed adequate mechanical stability with the exception of the Neosepta CMS membrane. The Neosepta CM-2 membrane was tested by repeated usage for the neutralization of 1 *M* NaOH sample solutions and showed minimal distortion even after 20 h use.

The permselectivities of the membranes were assessed by determining the recoveries for a range of inorganic anions initially added to 1 *M* NaOH before the samples were subjected to electrodialysis at 3 W constant power until neutralized. Some of the thicker membranes (*e.g.*, Ionics AZL-389 and CZL-386, Neosepta CLE-E and Nafion 901) showed insufficient permselectivity, leading to low recoveries. The results for some of the more successful membranes are given in Table III, which shows that with the exception of fluoride, the Neosepta CM-2 membrane gave recoveries which were close to quantitative. Recovery data of the type determined here are governed by the degree to which the anionic solutes (*i.e.*, solutes having the same charge as the membrane, or "co-ions") can diffuse into the negatively charged membrane. This diffusion for any specified co-ion can be measured by equilibrating the membrane with a solution of that anion (generally by soaking for 24 h), drying the membrane by blotting and then displacing any co-ion from the membrane using a relatively concentrated solution of another anion. For example, the diffusion of fluoride into the membrane could be measured by first soaking the membrane in 0.1 *M* sodium fluoride and then displacing with 0.2 *M* potassium sulfate. The displaced fluoride can be measured by IC, as can the concentration of sodium displaced, which is a measure of the ion-exchange capacity of the membrane.

Table IV shows the co-ion concentrations found in some of the membranes shown earlier to have promise for electrodialysis. It can be seen that these

TABLE IV

CO-ION CONCENTRATIONS FOR DIFFERENT CATION-EXCHANGE MEMBRANES

Anion	Co-ion concentration (mequiv./g)			
	Neosepta CM-2	Neosepta CMS	Asahi CMV	Nafion 324
F^-	0.13	0.07	0.05	0.02
Cl^-	0.002	0.003	0.007	0.002
Br^-	0.001	0.001	0.008	0.006
NO_3^-	0.001	0.002	0.009	0.009
SO_4^{2-}	0.001	0.003	0.009	0.004
HPO_4^{2-}	0.022	0.022	0.020	0.025

concentrations vary significantly, illustrating that there are substantial differences in the permselectivities of the membranes. Comparison of Tables III and IV highlights the fact that an elevated co-ion concentration for a particular membrane is reflected by a reduced recovery for that ion after electrodialysis. For example, the Neosepta CM-2 membrane gave the highest concentration of fluoride and the lowest recovery for this ion. Despite this, the CM-2 membrane gave the best overall performance and, with some supplementation by the Asahi CMV membrane, was used in further studies.

The consistently low recoveries obtained for fluoride for all membranes merits comment. The most plausible explanation for the low recoveries is that partial protonation leads to the formation of neutral hydrofluoric acid which can then diffuse through the membrane. The electrodialysis was terminated when the sample solution reached pH 6, so it would not be expected that there would be any significant formation of hydrofluoric acid (pK_a = 3.17). However, it must be remembered that the pH inside the membrane is likely to be much lower than that existing in the bulk external solution because under the Donnan effect, there is an accumulation of cationic species inside the membrane compared to the bulk solution. This accumulation ratio is often very high [13], so that protonation of fluoride is therefore quite probable. In a similar manner, losses of nitrite can be predicted due to the formation of nitrous acid (pK_a = 3.14). Recovery studies obtained from electrodialysis of alkaline nitrite solutions with the Neosepta CM-2 membrane gave an average recovery of 20.9%, in accordance with this prediction. A further complication observed in this particular experiment was the appearance of a small nitrate peak in the final chromatogram (equivalent to 5.4% of the original nitrite), presumably from oxidation of nitrite. Losses of both fluoride and nitrite during electrodialysis could be reduced by terminating the electrodialysis at a higher pH value (*e.g.* pH 10), but in all cases the recoveries for these two ions were less than 60%. These results suggest that under the conditions used in this paper, electrodialysis is unsuitable for samples containing fluoride and nitrite, and perhaps also for other anions of weak acids.

Selection of hydrogen ion donating medium

After design of a suitable cell and selection of the optimal electrodialysis mode and membrane type, the next step was to determine the best composition of the hydrogen ion donating medium used to fill the anode compartment. Important factors to be considered in the choice of the hydrogen ion donating medium are the degree of sample contamination resulting from penetration of the acid anion through the cation-exchange membrane, and the effect on performance parameters such as the time of dialysis and the amount of heat produced. As in our previous studies on treatment of alkaline samples using Donnan dialysis, a range of aliphatic and aromatic sulfonic acids was compared with sulfuric acid and with slurries of cation-exchange resin in acid solution.

All of the hydrogen ion donating media gave similar performance (with the CMV membrane) in terms of dialysis time and heat production, but significant differences were observed in the degree of the incursion of acid anion into the sample. Table V shows the penetration of acid anions from solutions of hydrogen ion donating media into the sample after electrodialysis at different fixed currents. The degree of incursion increased with concentration of the hydrogen ion donating solution and with the applied current. The concentration of the acid anions found in the sample solution after dialysis is expressed as a percentage of the initial concentration of this anion in the solution of hydrogen ion donating medium. Surprisingly, sulfate showed less penetration than the larger sulfonate anions.

One possible means to reduce penetration of the acid anion is to use a cation-exchange resin in the hydrogen form as the hydrogen ion donating medium [14]. This approach has been utilized successfully in our previous studies on Donnan dialysis [3]. However, these studies also showed that resin beads can act as effective hydrogen ion donating media only when they are used as a slurry with a suitable acid solution. The interstitial acid solution is necessary for site-to-site transport of hydrogen ion from the bulk slurry to the membrane surface. Some penetration of the anion of the slurrying acid is therefore possible, but this can be minimized by keeping the concentration of this acid as low as practicable. Studies showed that Bio-Rad AG 50W-X8 (200–400 mesh, H^+ form) slurried in a 2:1 (w/v) ratio

TABLE V

PENETRATION OF ANION FROM THE HYDROGEN ION DONATING MEDIUM (ANODE COMPARTMENT) INTO THE SAMPLE, EXPRESSED AS A PERCENTAGE OF THAT INITIALLY PRESENT IN THE ANODE COMPARTMENT

The CMV Membrane was used.

H^+-donating medium	0.05 *M*			0.025 *M*		
	150 mA	300 mA	450 mA	150 mA	300 mA	450 mA
Sulfuric acid	0.06	0.06	0.09	0.09	0.03	0.03
Methanesulfonic acid	2.7	4.3	4.6	2.1	2.3	2.5
Toluenesulfonic acid	2.7	3.6	8.6	0.1	0.2	0.2
Camphorsulfonic acid	1.0	1.7	2.5	0.3	0.5	0.5
Octanesulfonic acid	1.7	2.5	6.7	0.05	0.1	0.1

with 1 m*M* toluenesulfonic acid, octanesulfonic acid or camphorsulfonic acid acted as a suitable hydrogen ion donating medium, without any measurable penetration of the acid anion into the sample solution during electrodialysis. Dialysis times were increased marginally (approximately 5-10%) over those obtained with the solutions of hydrogen ion donating media of higher concentration used for Table V, but this was considered to be a minor drawback. Therefore 1 m*M* octanesulfonic acid was used as the slurrying solvent in further work.

Application

A chromatogram showing the application of the electrodialysis system to the treatment of a 1 *M* sodium hydroxide solution containing fluoride, chlo-

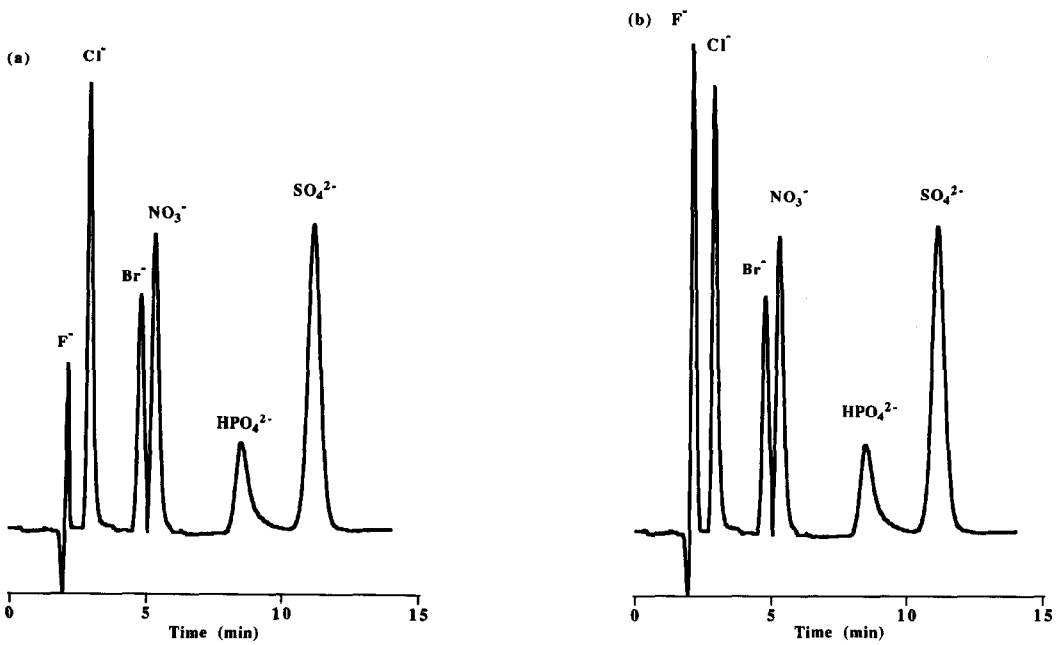

Fig. 3. Chromatogram of inorganic anions (3–10 μg/ml) in (a) 1 *M* NaOH after electrodialytic treatment and (b) Milli-Q water. Injection volume: 10 μl; eluent: 2.0 m*M* Na_2CO_3–1.8 m*M* $NaHCO_3$; column: Dionex HPIC-AS4A with AG4A guard column and AMMS suppressor.

ride, bromide, nitrate, phosphate and sulfate in the concentration range 3–10 μg/ml is given in Fig. 3. Fig. 3a shows the treated sample, whilst Fig. 3b shows a chromatogram for the same initial concentrations of anions in Milli-Q water. The two chromatograms are virtually identical, except for the low recovery of fluoride in the treated sample. By contrast, the chromatogram obtained for the original sample before electrodialysis showed no solute peaks whatsoever, but rather only a single, large solvent peak which obscured the entire chromatogram.

CONCLUSIONS

Provided correct attention is paid to the design of the cell and the manner in which the current (or power) is applied, electrodialysis can be used for the rapid neutralization of strongly alkaline samples as a clean-up step for IC. A 1 ml sample of 1 *M* sodium hydroxide could be neutralized in about 10 min, without loss of strong acid anions present in trace amounts in the sample. Weak acid anions, such as fluoride and nitrite, gave poor recoveries probably due to protonation reactions occurring within the membrane leading to the formation of neutral species which could diffuse from the sample compartment. Electrodialysis under the conditions used in this study is therefore not recommended for these ions. Multiple samples can be treated simultaneously without extending the dialysis time by using several cells arranged in parallel.

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