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On-line analysis of alkaline samples with a flow-through electrodialysis device coupled to an ion chromatograph

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Abstract

A flow-through device suitable for on-line neutralization of strongly alkaline samples using electrodialysis is described. This device comprises an anode compartment filled with a slurry (2:1, w/v) of 1 m*M* octane sulfonic acid and hydrogen-form cation-exchange resin, a 300 μl sample chamber bounded by two cation-exchange membranes, and a cathode compartment filled with dilute sodium hydroxide. An alkaline sample (up to 1 *M* sodium hydroxide) passed through the device at a rate of 0.1 ml/min is neutralized and with the aid of a switching valve, the treated sample can be routed directly to a suppressed ion chromatographic system for determination of inorganic anions. The design parameters for the electrodialysis devices have been studied, including the type of membrane used, the size of the electrodes, the shape of the sample compartment, and the applied power. Optimal performance was obtained with planar stainless-steel electrodes and with 2 W of power. Recoveries of inorganic anions from treated samples were close to quantitative with the exception of nitrite, for which losses were observed. The on-line electrodialysis is shown to be suitable for the treatment of sodium hydroxide solutions, but was less successful when applied to solutions of sodium carbonate and sodium tetraborate. The system has been used for the determination of fluoride in forage vegetation after preparation of the sample by fusion with sodium hydroxide. Good agreement was obtained with results from colorimetric determination of fluoride.

1. Introduction

Donnan dialysis, in which ions of a specified charge pass selectively through an ion-exchange membrane, has been used for matrix normalization [1], sample preconcentration [2] and sample clean-up [3] in ion chromatography (IC). Electrodialysis, wherein an electric field is applied to enhance the performance of a conventional Donnan dialysis experiment, has also recently found use in IC [4–7] and in high-performance liquid chromatography [8,9]. The IC applications of electrodialysis include the treatment of strongly acidic samples prior to the determination of magnesium(II) and calcium(II) using a dual anion-exchange membrane tube device [4], and the treatment of alkaline samples (up to 1 *M* sodium hydroxide) prior to the determination of trace levels of inorganic anions by suppressed IC [5]. In both cases, the electrodialysis was performed off-line. A flow-through electrolytic device has been reported [6] which has the primary function of suppression of IC eluents prior to conductivity detection. This device, called a "self regenerating suppressor (SRS)", uses a similar configuration of membranes to that employed in the micromembrane suppressor [10], but with the addition of two electrodes. The SRS employs

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the electrolysis of deionized water as a source of hydronium ions which are then involved in a conventional suppression reaction [11] capable of neutralizing sodium hydroxide eluents as concentrated as 150 m*M*. Whilst the primary role of the applied power is to provide a source of hydronium ions for the suppression reaction, it is probable that electrodialysis also plays a significant role in the operation of this device. The SRS has also been shown to be applicable to the treatment of concentrated acids and bases prior to IC analysis [7]. Since the SRS does not have the necessary capacity to neutralize such samples during a single passage through the device, the sample is recycled a sufficient number of times until the pH reaches a level appropriate for the subsequent IC analysis. When a current of 500 mA was used, a 50% sodium hydroxide solution could be neutralized using three cycles through the SRS.

For some time we have been studying the use of dialytic methods for the treatment of alkaline samples, chiefly because of the importance of alkaline fusion as a sample dissolution method in IC [11]. An off-line electrodialysis cell was developed which achieved neutralization of a 1 *M* sodium hydroxide sample in 11 min without loss of solute anions, except for fluoride and nitrite [5]. Losses of these two ions were attributed to the formation of neutral, protonated species inside the membrane, with subsequent egress from the sample chamber by diffusion through the cation-exchange membrane used. Careful choice of the membrane enabled such losses to be minimized. In the present work, modifications to the off-line electrodialysis cell have been made to produce a flow-through electrodialysis cell which permits on-line treatment of the sample, followed by direct injection onto the IC. Variations to the shape of the sample chamber, the size of the electrodes and the nature of the cation-exchange membrane are examined in order to optimize the flow-through cell design and to minimize the heat generated inside the cell. In addition, the utility of the procedure for use with samples containing high levels of carbonate or borate is studied and the method is applied to the determination of fluoride in vegetation samples prepared by hydroxide fusion. The results are compared with those obtained by colorimetry.

2. Experimental

2.1. 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 the suppressed mode was a Dionex HPIC AS-4A anion separator with AG-4A guard column, connected to an anion micromembrane suppressor. A Waters Reagent Delivery Module was used to pass the regenerant of 12.5 m*M* sulfuric acid through the suppressor. The column used for the non-suppressed mode was a Millipore-Waters IC Pak HR anion-exchange column (75 × 4.6 mm I.D.). Sodium ion was determined using a Millipore-Waters IC Pak C cation column, 50 × 4.6 mm I.D. All chromatographic separations were carried out at room temperature with an eluent flow-rate of 1.2 ml/min and chromatograms were recorded on a Millipore-Waters Maxima 820 data station.

2.2. Flow-through electrodialysis device

The flow-through electrodialysis cell was developed from the two-membrane static electrodialysis cell described previously [5] and was constructed as a series of perspex blocks held together with longitudinal screws to form a three-compartment cell separated by cation-exchange membranes, as depicted in Fig. 1.

The sample chamber was designed to allow the sample to flow during the electrodialysis process. Electrodes were constructed from stainless-steel plates (60 × 25 × 0.7 mm), inserted into the electrode compartments and connected to the power supply. The membranes were supported with a perspex sheet attached to each electrode solution compartment, through which had been drilled numerous closely spaced holes, 2 mm in diameter. The volume of both the anode and cathode compartments was 15 ml, whilst the

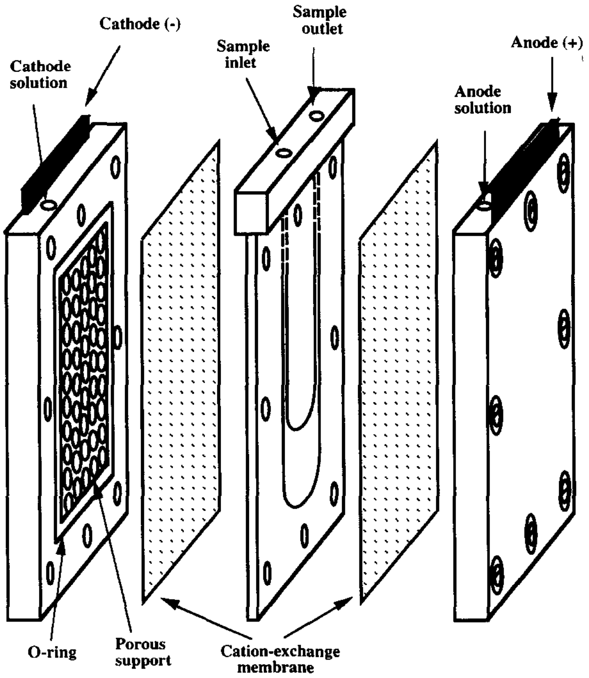


Fig. 1. Flow-through electrodialysis cell.

sample compartment contained 300 μl. A BioRad (Richmond, CA, USA) microprocessor-controlled electrophoresis power supply (Model 3000 Xi) was used in the fixed power and fixed current modes.

The sodium hydroxide sample solution was passed through the sample compartment of the cell at a constant flow-rate of 0.1 ml/min using a syringe pump (Razel Scientific Instruments, Stamford, CT, USA), whilst a d.c. potential was applied at constant power (2 W) to the electrodes at the two ends of the cell. The outlet of the sample compartment was connected to a six-port switching valve fitted with a standard 20-μl sample loop so that direct injection of the neutralized sample solution onto the IC system was possible.

2.3. 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 the suppressed IC mode contained 2 m*M* sodium bicarbonate and 2 m*M* sodium carbonate. The eluent used for the non-suppressed IC system contained 0.1 *M* boric acid and 1.9 m*M* tartaric acid adjusted to pH 4.5 with the addition of sodium hydroxide solution. The eluent for sodium determination contained 0.5 *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 a final concentration of 1 *M* NaOH. The inorganic anion concentrations in the sample solution were fluoride (3 μg/ml), chloride (3 μg/ml), nitrite (6 μg/ml), bromide (6 μg/ml), nitrate (6 μg/ml), sulfate (8 μg/ml) and phosphate (10 μg/ml). A standard solution containing the same concentrations of anions was made up in water and was used to calibrate the instrument.

The hydrogen ion donating medium used in the anode compartment was a slurry of BioRad AG 50W-X8 hydrogen form cation-exchange resin, 200–400 mesh, in 1 m*M* octanesulfonic acid (2:1, w/v). The cathode compartment was filled with 0.1 *M* sodium hydroxide. Octanesulfonic acid solution was prepared by passing a solution of sodium octanesulfonate through a glass column packed with 100 g of BioRad AG 50W-X8 hydrogen form cation-exchange resin, 37–74 μm. The cation-exchange resin was washed thoroughly with Milli-Q water prior to use. The cation-exchange membranes used in this work were obtained from Tokuyama Soda Company (Tokyo, Japan) (Neosepta CM-2 and CMS) and Asahi Glass Company (Tokyo, Japan) (CMV).

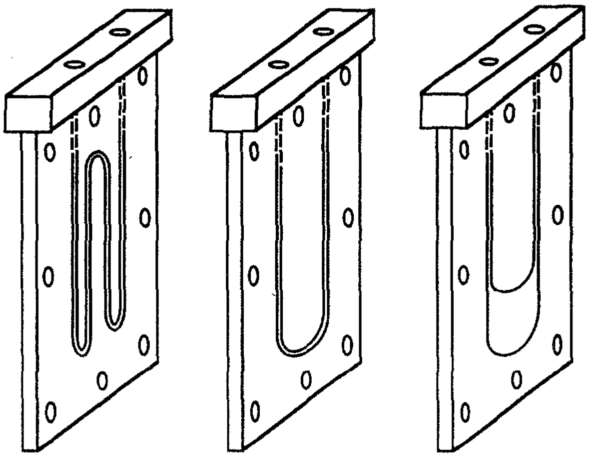
2.4. Sample preparation procedures

Vegetation samples for this work were obtained from the vicinity of an aluminium smelter and were prepared as follows. Approximately 2.0 g of ground, dried sample was weighed into a nickel crucible and 10 ml of 5 g/l calcium oxide was added to form a slurry. The crucible was placed on a hotplate, charred for 1 h and transferred to a muffle furnace at 600°C for 2 h. Sodium hydroxide pellets (3 g) were added and the fusion continued for 3 min at 600°C. The crucible was then removed from the furnace and swirled carefully to suspend the particulate matter until the melt solidified. After cooling, the fused sample was dissolved and diluted with water in a 100 ml volumetric flask to give a final hydroxide concentration of 0.75 *M*.

3. Results and discussion

3.1. Design of the flow-through electrodialysis device

The first goal of this work was the design and construction of a flow-through cell suitable for the neutralization of strongly alkaline solutions, while at the same time allowing the cell to be connected directly to an IC system. The cell requires compartments for housing the sample, the hydrogen ion donating medium (anode compartment) and the receiver solution (cathode compartment). This configuration was obtained by modifying our previous static electrodialysis cell design [5] to include a sample compartment made by cutting a flow-path into a perspex sheet, both sides of which were covered by planar cation-exchange membranes. The upper part of the perspex sheet was drilled and threaded to make an inlet and outlet so that the sample was able to flow during the electrodialysis process. Three types of sample compartments were made, as shown in Fig. 2. The electrode compartment was constructed by machining a chamber in the centre of a perspex block. Several holes were drilled from the upper section of the perspex block for introducing the electrode and the required solution into the compartment. Mechanical support for the membrane was required and was provided by perforated perspex sheets which formed one wall of each electrode chamber. The components of the cell were held together with longitudinal screws, to form the flow-through electrodialysis cell shown in Fig. 1.



Compartment A Compartment B Compartment C

Fig. 2. Sample compartments constructed for the flow-through electrodialysis cell.

Previous work had demonstrated that the neutralization process could be achieved by applying either constant current or constant power. Preliminary tests on the flow-through cell using sample compartment A (shown in Fig. 2), a Neosepta CM-2 cation-exchange membrane and platinum wire electrodes (50 × 0.2 mm O.D.) showed that a constant current in the range of 110–130 mA or a constant power of at least 4 W was required to neutralize a solution of 1 *M* NaOH at a flow-rate of 0.1 ml/min. A higher sample flow-rate could be accommodated by applying a greater constant current or power, but this also caused the sample solution to heat up which ultimately distorted the membranes. Fig. 3 shows the current required for neutralization at different sample flow-rates. Recovery studies were undertaken to assess the loss of anions from the sample during dialysis at constant currents of 110, 120 and 130 mA. The recovery values were generally higher at lower applied current but the most consistent results were obtained when 120 mA was used as the applied current. Under the experimental conditions described above, a considerable amount of heat was generated inside the flow-through cell after several cycles of sample neutralization, resulting in pronounced buckling of the membranes. Increasing the total conductivity of the

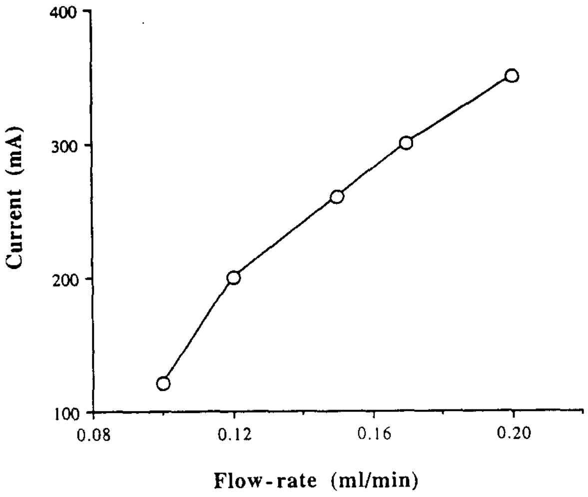


Fig. 3. Constant current required for the neutralization of 1 *M* NaOH using the flow-through electrodialysis cell at different flow-rates.

cell by addition of cation-exchange resin beads (AG 50W-X8, H^+ form, 37–74 μm) to the sample flow-chamber was attempted but this actually caused heat production to increase.

Two alternative sample compartments (B and C in Fig. 2) were evaluated as a means to reduce the heat generated inside the cell. Despite differences in the accommodated sample volume (290, 155 and 300 μl for compartments A, B and C, respectively, in Fig. 2), the thickness and the contact area of the flow gallery, all compartments required approximate currents of 120 mA for the neutralization of 1 *M* NaOH sample solution. However, the sample compartments showed varying resistance, as indicated by the differences in power and potential when a constant current of 120 mA was applied to each of the three sample compartments. Compartment C (300 μl), which had the greatest contact area to the sample solution, gave the best performance and was used for all further work.

The resistance of the cell, and hence the amount of heat generated, is influenced by the size of the electrodes. For this reason, two platinum wire electrodes (50 mm long with diameters of 0.2 and 0.3 mm) and a series of stainless-steel plate electrodes (thickness 0.7 mm, length 45 mm and widths in the range 3–15 mm) with different surface areas were evaluated in an effort to decrease the cell resistance. The results obtained showed that the plate electrodes gave superior performance to wire electrodes and that an electrode of 12 mm width generated the highest current at lowest potential when constant power was applied to the cell. Increasing the size of the electrode to 15 mm gave only a marginal change in performance. The final design of the flow-through cell incorporated stainless-steel plates (0.7 × 25 × 60 mm) as electrodes, with which a current of 120 mA was generated when a constant power of 2 W was applied to the cell. These conditions were shown to have no detrimental effects on the mechanical stability of the membrane, even after 8 h of continuous neutralization (to pH 7) of 1 *M* NaOH solution flowing at 0.1 ml/min through the cell.

3.2. Selection of the membrane

Previous work [5] has shown that the permselectivities of the membranes, assessed by determining the recoveries of a range of inorganic anions initially added to NaOH solution before the samples were subjected to electrodialysis, played an important role in ensuring the success of the process. Recovery experiments using three different types of membranes (Neosepta CM-2, Neosepta CMS and Asahi CMV) were undertaken using a constant power of 2 W (which correlated to a current of 120 mA). The results are given in Table 1, from which it can be seen that suitable recoveries were obtained for all ions except for nitrite, with the Neosepta CM-2 membrane giving the best overall performance. The ability to successfully treat samples containing fluoride with the CMS membrane is an improvement over the static electrodialysis cell described previously and is attributable to the fact that loss of fluoride by diffusion of hydrogen fluoride through the membrane does not occur to any significant extent since this species is formed only when the sample is about to exit the cell. Chromatograms showing a mixture of inorganic anions in Milli-Q water and in 1 *M* NaOH after electrodialytic treatment using the Neosepta

Table 1

Percentage recovery of anions (present in the range 3–10 μg/ml) from 1 *M* NaOH solution after electrodialysis at 2 W using various cation-exchange membranes in the flow-through cell

Anion	Membrane		
	Neosepta CM-2	Neosepta CMS	Asahi CMV
F^-	84.3 (3.5)	95.8 (3.0)	73.4 (5.2)
Cl^-	99.2 (2.1)	89.0 (4.8)	84.7 (4.2)
NO_2^-	53.0 (4.2)	53.3 (2.6)	48.4 (3.8)
Br^-	94.6 (2.5)	92.5 (3.5)	72.5 (2.7)
NO_3^-	98.4 (3.0)	88.5 (5.3)	74.5 (6.1)
HPO_4^{2-}	99.6 (1.0)	93.2 (4.5)	84.6 (3.4)
SO_4^{2-}	98.5 (2.4)	94.0 (5.2)	85.2 (5.0)

The range derived from 8 replicates is shown in parentheses.

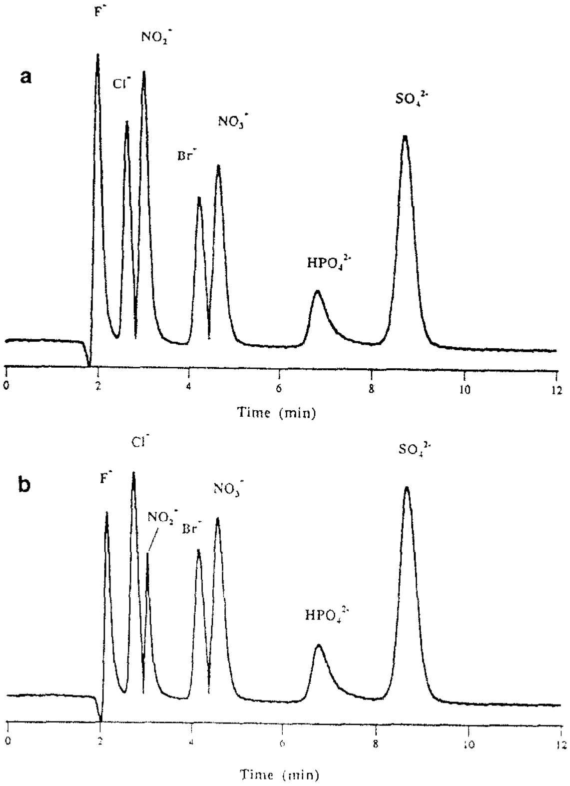


Fig. 4. Chromatograms of inorganic anions (3–10 μg/ml) in (a) Milli-Q water and (b) 1 *M* NaOH after electrodialytic treatment using Neosepta CM-2 membranes. Injection volume: 20 μl. Eluent: 2.0 m*M* Na_2CO_3–2.0 m*M* $NaHCO_3$. Column: Dionex HPIC-AS4A with AG4A Guard Column and AMMS Suppressor.

CM-2 membrane are given in Fig. 4. The two chromatograms are virtually identical, except for the low recoveries of fluoride and nitrite in the treated sample.

3.3. Electrodialysis of carbonate and tetraborate solutions

Alkaline fusion techniques commonly involve alkalis other than sodium hydroxide, for example sodium carbonate and sodium tetraborate. These have been used for the dissolution of samples such as glass [12], insoluble waste-water precipitate [13] and rock materials [14] prior to IC determination. The electrodialysis method described in this paper has been applied successfully to the neutralization of sodium hydroxide solutions and we now consider its utility for the neutralization of sodium carbonate and sodium tetraborate solutions.

Electrodialysis of 1 *M*, 0.5 *M* and 0.2 *M* sodium carbonate solutions was carried out at varying values of constant applied power using the flow-through cell. The pH of these solutions after the electrodialytic treatment are shown in Table 2, from which it can be seen that relatively high values of applied power were required to bring the pH reached of the dialysate to approximately 7. This can be attributed to the fact that the electrodialysis results in the formation of bicarbonate and carbonic acid, producing a buffered system. The high concentration of residual carbonate and bicarbonate in the final solution caused saturation of the suppressor system when

Table 2

pH of Na_2CO_3 solutions after electrodialysis using the flow-through cell at various values of applied power

Applied power (W)	pH		
	1.0 *M* Na_2CO_3	0.5 *M* Na_2CO_3	0.2 *M* Na_2CO_3
2.0	9.0	8.5	8.0
3.0	9.0	8.0	7.5
4.0	8.5	7.5	7.0
5.0	8.0	7.0	7.0

the dialysed sample was analyzed by suppressed IC, producing severe baseline distortions in the chromatogram. The electrodialysis of 0.1 *M* sodium tetraborate was also carried out using the flow-through electrodialysis cell and the pH of this sample was reduced from 9.5 to 6. However, the chromatogram obtained for the treated solution again showed severe distortion due to boric acid produced by the dialysis.

The displacement efficiency of the electrodialysis technique, which usually governs the capacity of the neutralization process, was examined by determining the concentration of residual sodium in the dialysate solutions after treatment of samples of sodium hydroxide, sodium carbonate and sodium tetraborate. The results are shown in Table 3. Displacement efficiencies close to 100% were obtained for 1 *M* sodium hydroxide and 0.1 *M* sodium borate, with much lower efficiencies being observed for sodium carbonate.

The above results suggest that the electrodialysis procedure has practical application only when sodium hydroxide is used as the flux for fusion procedures involving IC analyses.

3.4. Determination of fluoride in forage vegetation samples

Fluoride is a major environmental pollutant from an aluminium smelter and can be absorbed and accumulated in the tissues of plants which grow in the vicinity of the smelter. Whilst there is no standardised method yet for sample preparation prior to fluoride analysis, acid leaching and hydroxide fusion are the most commonly employed techniques. These processes are frequently followed by distillation and colorimetric determination after reaction with alizarin fluorine blue-lanthanum reagent [15]. Other determination procedures, such as potentiometry [16–18], have also been reported.

The determination of fluoride in a highly alkaline sample matrix has been approached using ion-exclusion chromatography [19], however problems associated with this method when applied to the determination of fluoride in vegetation samples after hydroxide fusion have been reported recently [20]. Elevated levels of silica present in the samples resulted in a build-up of silica on the column, reducing column performance. An ion-exchange separation approach combined with solid-phase reagent conductivity detection, following dilution and neutralization steps using hydrogen ion cartridges, was selected as being most appropriate.

In the present work, vegetation samples obtained from the vicinity of an aluminium smelter were prepared by hydroxide fusion and the sample solution then neutralized using the flow-through electrodialysis cell connected to a suppressed IC system. The flow-rate of the sample through the cell was 0.1 ml/min, a constant power of 2 W was applied for the neutralization process, and Neosepta CMS membranes were used. The results obtained by IC were compared with those obtained by colorimetry following sample preparation by hydroxide fusion, and the results are shown in Table 4. Two standard reference materials (powdered timothy grass) are

Table 3
Residual sodium present in various alkaline solutions after electrodialytic treatment

Solution	Na^+ in original solution (μg/ml)	Na^+ in dialysed solution (μg/ml)	Displacement efficiency (%)
1 *M* NaOH	23 000	108 (56)	99.5 (0.2)
1 *M* Na_2CO_3	46 000	20 500 (700)	55.4 (0.5)
0.5 *M* Na_2CO_3	23 000	2250 (65)	90.2 (0.3)
0.2 *M* Na_2CO_3	9200	216 (42)	97.7 (0.5)
0.1 *M* $Na_2B_4O_7 \cdot 10H_2O$	4600	28 (8)	99.4 (0.2)

The range derived from 5 replicates is shown in parentheses.

Table 4
Comparative results for fluoride in vegetation samples

Sample	Ion chromatography (μg/g)	Colorimetry (μg/g)
Vegetation 1	156 (3)	135
Vegetation 2	554 (12)	560
Vegetation 3	7.6 (1.0)	7
Vegetation 4	106 (4)	110
Standard timothy grass 1	68.1 (1.6)	64
Standard timothy grass 2	269 (9)	277

Results are expressed in terms of the dry mass of the sample. The range derived from 5 replicates is shown in parentheses.

included in Table 4 and the fluoride content of these has been determined using a number of methods, such as titration with thorium nitrate following fusion and distillation, colorimetry following fusion and microdistillation from sulfuric acid, and ion-selective electrode measurement after oxygen bomb decomposition [21]. It has been suggested that the colorimetric measurement with on-line distillation determines the "total" fluoride while IC determines only "free" fluoride in the hydroxide fused sample [20], hence some difference between the results might be anticipated. However, the data in Table 4 show good correlation between the two methods.

The chromatogram obtained for an electrodialysed sample solution using suppressed IC with a carbonate/bicarbonate eluent is shown in Fig. 5. The fluoride present in the sample is well resolved from other anions and can be quantified readily. It was also noticed that there was no interference from the elevated level of silica in the fused sample, either in the electrodialysis cell or on the chromatography column throughout the analyses. This represents an advantage in using the electrodialysis cell over hydrogen ion neutralization cartridges.

The feasibility of employing non-suppressed IC for the determination of fluoride in the electrodialysed sample solution was also investigated. The presence of carbonate (from CO_2) in the neutralized solution often causes interference with the determination of early eluted anions, such as fluoride and chloride, when non-suppressed IC is employed. Such interference has been overcome by the use of tartrate/borate eluents operated in the pH range 3–5 [22,23], since at this pH the carbonate is completely protonated and is therefore eluted at the void volume. However, when the eluent strength was adjusted to 0.1 *M* boric acid and 1.9 m*M* tartaric acid (at pH 4.5) in order to give adequate retention of fluoride, poor detection sensitivity resulted and analysis of the electrodialysed samples by this method was not practicable.

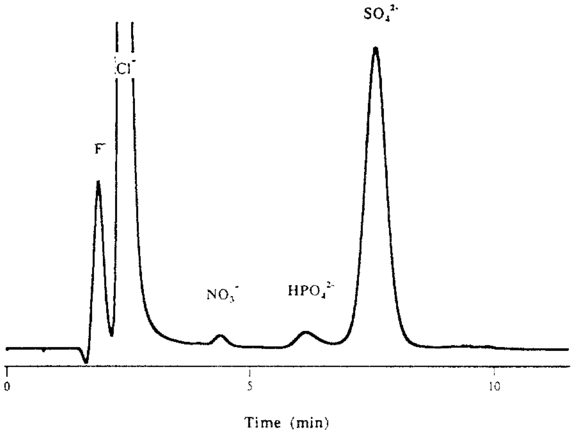


Fig. 5. Chromatogram of electrodialysed vegetation sample. Conditions as for Fig. 4, except that Neosepta CMS membranes were used.

4. Conclusions

This study has shown that clean-up of strongly alkaline solutions prior to ion chromatographic analysis can be achieved on-line with the aid of a flow-through electrodialysis device fitted to a six-port switching valve. Optimum performance of the flow-through electrodialysis device was achieved by employing a sample chamber which accommodated 300 μl of sample, using stainless-steel plate electrodes (0.7 × 25 × 60 mm), and by passing the sample at a constant flow-rate of 0.1 ml/min through the cell while applying a constant power of 2 W. Under these conditions, 1 *M* NaOH sample solution could be neutralized in approximately 3 min.

The electrodialytic treatment was found to be applicable to sodium hydroxide solutions only, but this is considered to be a minor drawback of the technique since many insoluble solid samples can be dissolved by fusion with sodium hydroxide. The flow-through cell could be used to successfully treat samples containing fluoride without loss when Neosepta CMS membranes were used. This represents an advantage over the static electrodialysis cell reported earlier. The system was used successfully to determine fluoride in forage vegetation samples after sample preparation by hydroxide fusion.

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