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Dialytic clean-up of alkaline samples prior to ion chromatographic analysis

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ABSTRACT

Membrane-based devices for the neutralization of alkaline samples prior to ion chromatographic analysis are studied. These devices use a cation-exchange membrane fibre (either hollow or packed with polystyrenedivinylbenzene beads) immersed in a hydrogen ion-donating medium. As the sample is passed through the lumen of the fibre, a dialysis reaction involving exchange of sodium ions in the sample with hydrogen ions from the surrounding medium occurs, resulting in total or partial neutralization of the sample. Several hydrogen ion-donating media are evaluated on the basis of neutralization efficiency and penetration of the acid anion through the membrane. Octanesulfonic acid (OSA) at a concentration of 0.1 *M* gave optimal performance. Dual ion-exchange using hydrogen-form cation exchange resins slurried with water or 0.1 *M* OSA are also evaluated. The resin slurries provide much larger neutralization capacities than the acid solutions and are not subject to problems of penetration of the acid anion into the sample. When the resin is slurried in OSA and is stirred occasionally, the total theoretical neutralization capacity of the resin can be achieved.

INTRODUCTION

Samples of extreme pH (*i.e.* outside the pH range 3–11) often pose problems in ion chromatographic (IC) determinations because of deleterious effects on the column life and performance [1]. In particular, strongly alkaline samples may give distorted analyte peaks, system peaks and severe baseline perturbations due to the effect of the injected sample on the acid–base equilibria existing in the eluent in both suppressed and non-suppressed IC. Whilst these problems can sometimes be circumvented through the use of selective detectors or specially designed eluents, adequate sample clean-up steps are generally required to ensure the ultimate success of the analysis.

Sample clean-up may involve the removal of undesired particulate matter, the reduction in concentration or complete removal of potential interferences, or concentration of the analyte of interest to improve detection. Samples of high ionic strength are often troublesome due to the large response and long recovery times of the conductivity detectors. When the high ionic strength of the sample is due to the presence of elevated levels of sodium hydroxide, simple neutralization of the sample is unsuitable because the resultant high level of the acid anion would also be likely to cause interference problems. However, two alternative methods of sample clean-up are applicable.

The first involves treatment of the sample with a cation-exchange resin in the hydrogen form, which results in replacement of sodium in the sample with hydrogen ions from the resin, leading to neutralization of the sample. This treatment can be accomplished using a batch method wherein the ion-exchange resin is added to the sample, or using a column method wherein the sample is passed through a small column packed with suitable resin [2]. The second approach to sample clean-up uses a dialysis treatment with a suitable membrane. In this case, the membrane is usually functionalized with sulfonic acid groups to impart cation-exchange characteristics and dialysis occurs between the sample solu-

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tion on one side of the membrane and an acidic solution on the other side. Again, exchange of sodium ions for hydrogen ions leads to sample neutralization and the mechanism of operation is identical to that used in membrane-based suppressors employed in suppressed IC. The physical form of the membrane may vary, with flat sheets [3] or hollow fibres [4] being used.

The dialysis process involves the transfer (diffusion) of ions of positive charge through the cation-exchange membrane. Anions possess the same charge sign as the exchange site and, in theory, are excluded from diffusion through the membrane by electrostatic repulsion. The extent of exclusion (referred to as the permselectivity of the membrane) depends on the concentration of the external electrolyte with which the membrane is in equilibrium, and decreases as this concentration is increased [5]. Permselectivity may also decrease when the membrane shows excessive swelling in water, due to the resultant low charge density of functional groups on the membrane. Thus, the concentration of the acidic medium used as a source of hydrogen ions for the dialysis process is limited by the permselectivity of the membrane towards the anion of the acid employed. One method which may be used to overcome this problem is described as "dual ion-exchange" dialysis [6]. Here, an aqueous slurry of cation-exchange resin in the hydrogen form is used as the source of hydrogen ions instead of an acidic solution. The acid anion is now a resin bead and its incursion through the membrane is physically precluded. Moreover, the change in concentration of an analyte ion in the sample solution either through contamination effects, adsorption losses or sample volume change which commonly feature in conventional ion-exchange is also minimized.

In this paper we examine membrane dialysis procedures for treatment of alkaline solutions prior to IC analysis. The efficiency and neutralization capacity of various hollow-fibre cation-exchange membranes used with a range of hydrogen ion-donating media (including cation-exchange resins) are evaluated.

EXPERIMENTAL

Instrumentation

The ion chromatograph consisted of a Millipore-Waters (Milford, MA, USA) Model 510 pump, Model U6K injector and Model 430 conductivity detector. The column used was a Millipore-Waters IC Pak A anion column, 50 × 4.6 mm I.D., packed with polymethacrylate anion-exchange resin. Chromatography was carried out at room temperature with an eluent flow-rate of 1.2 ml/min.

Two sample treatment devices were constructed. The first, shown in Fig. 1, utilized a length of cation-exchange hollow fibre (30 cm × 1.2 mm I.D. fibre protected by a woven polymer sheath) housed in a 10 cm × 24 mm I.D. glass tubing. A syringe was fitted to the inlet end of the tubing and was used to pass the sample through the membrane, with the effluent being collected. The outside of the fibre was bathed in a solution of a suitable hydrogen ion-donating medium. This apparatus was similar in construction to that described by Jones and Jandik [4]. The second device, shown in Fig. 2, used cation-exchange membrane fibre (345 cm × 0.5 mm I.D.

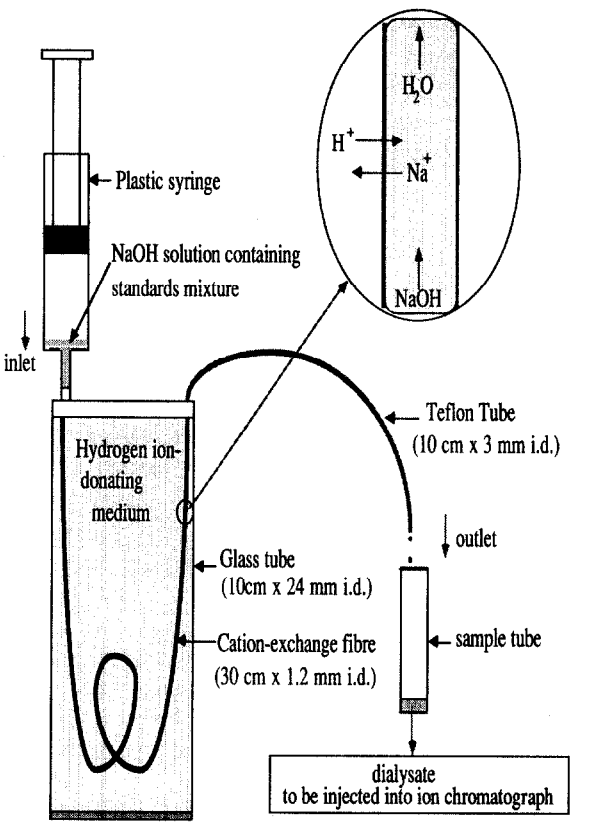

Fig. 1. Dialysis device used for comparison of hydrogen ion donating media.

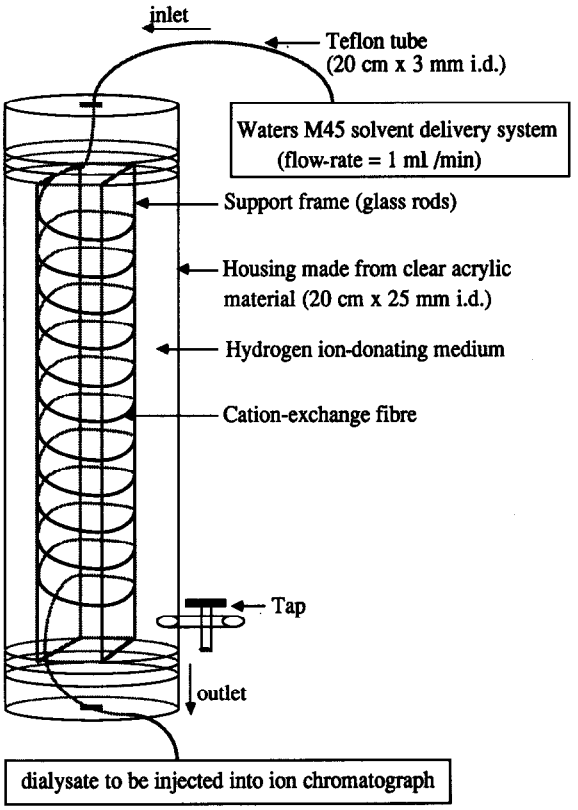

Fig. 2. Dialysis device used for comparison of fibre types and for determination of maximum neutralization capacity.

DuPont Nafion tubing or 160 cm × 0.6 mm I.D. DuPont Nafion tubing packed with polystyrene–divinylbenzene beads) coiled on glass rods and housed in an acrylic container 20 cm × 25 mm I.D. A Millipore-Waters M45 pump was used to pass sample through the membrane fibre and the effluent was collected. Again, the outside of the fibre was bathed in a solution of a suitable hydrogen ion-donating medium.

Reagents

All chemicals used were of analytical-reagent grade and the water used in 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 IC analysis of the treated samples contained 1.3 mM sodium tetraborate, 5.8 mM boric acid and 1.4 mM potassium gluconate adjusted to pH 8.5 and made up in water–acetonitrile (88:12).

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 to give 10^{-1}–10^{-4} M sodium hydroxide in the final solution. The concentration of inorganic anions in these solutions was in the range 30–100 ppm.

Hydrogen ion-donating solutions were prepared using 0.1–1.0 M sulfuric acid, methanesulfonic acid (MSA), octanesulfonic acid (OSA), camphorsulfonic acid (CSA) and *p*-toluenesulfonic acid (TSA). All were obtained from Sigma (St. Louis, MO, USA), with the exception of OSA 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. Dual ion-exchange experiments were performed using the following cation-exchange resins, all of which were used in the hydrogen form: Bio-Rad AG 50W-X8, 200–400 mesh; Bio-Rad AG 50W-X2, 200–400 mesh; Amberlite IRC-50, 50–100 mesh and Amberlite IR-120, 50–100 mesh. Resin was pretreated by thorough washing with Milli-Q water.

Procedures

The apparatus shown in Fig. 1 was used as follows. Before dialysis, the fibre was flushed thoroughly with Milli-Q water and a plastic syringe was used to pass 1 ml of sample through the fibre at a flow-rate of 1 ml/min. The first 10 drops of dialysate were discarded with the remaining dialysate being collected in 50-μl fractions for IC analysis. The pH of the samples was measured before and after dialysis using pH indicator sticks. The apparatus shown in Fig. 2 was used in a similar manner, except that a pump was used to deliver the sample at a flow-rate of 1 ml/min. The resin slurries were made by adding 25 ml of either Milli-Q water or 0.1 M OSA into 80 g of resin which had been soaked in Milli-Q water and filtered on a Buchner funnel.

RESULTS AND DISCUSSION

Comparison of hydrogen ion donating media

The first step in the design of a suitable sample

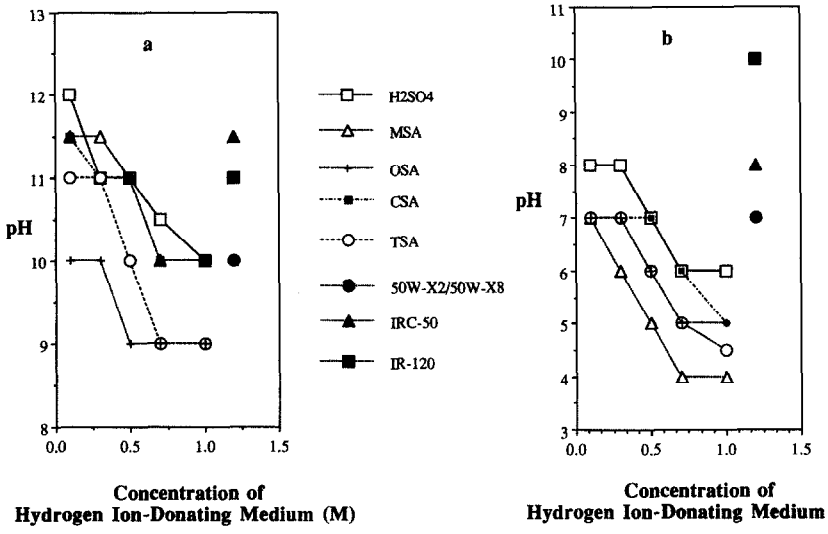

Fig. 3. Dialysate pH from (a) 10^{-1} *M* NaOH and (b) 10^{-2} *M* NaOH samples using various hydrogen ion donating media. MSA = Methanesulfonic acid; OSA = octanesulfonic acid; CSA = camphorsulfonic acid; TSA = *p*-toluenesulfonic acid.

treatment device was to determine the optimum composition of the hydrogen ion-donating solution. A range of sulfonic acids and cation-exchange resins was compared with sulfuric acid. Fig. 3 shows the pH of 0.1 and 0.01 *M* NaOH solutions after dialysis using the apparatus shown in Fig. 1. In all cases the pH of the sample was lowered significantly and the extent of pH reduction increased when the concentration of the hydrogen ion-donating medium was increased. All of the sulfonic acid solutions were more effective in lowering pH than sulfuric acid and some differences in performance between the different sulfonic acids can be noted. The four cation-exchange resins used in the dual ion-exchange approach were less effective in lowering the sample pH; however, Bio-Rad AG 50W-X8 gave the best performance.

The incursion of the acid anion into the sample must also be considered since anions normally have non zero transport numbers in cation-exchange membranes [6]. Sulfate shows typical penetration behaviour (Fig. 4), with the degree of incursion increasing with concentration of the hydrogen ion-donating medium. At a concentration of more than 0.3 *M*, each of the sulfonic acids was found to penetrate the membrane giving negative peaks in the final chromatogram. The penetration of MSA was most severe, whilst OSA and CSA showed least

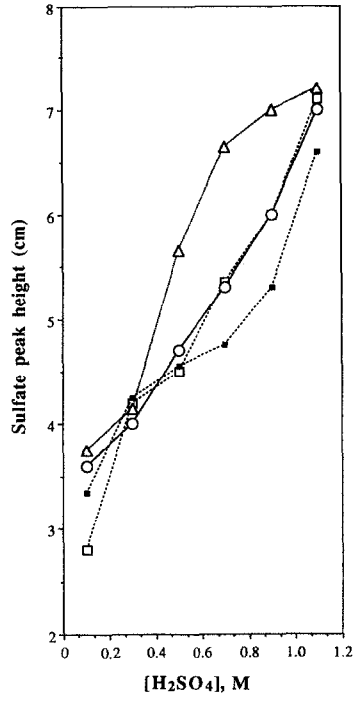

Fig. 4. Sulfate incursion from H_2SO_4 medium after dialysis. NaOH concentration: □ = 10^{-1} *M*; △ = 10^{-2} *M*; ○ = 10^{-3} *M*; ■ = 10^{-4} *M*.

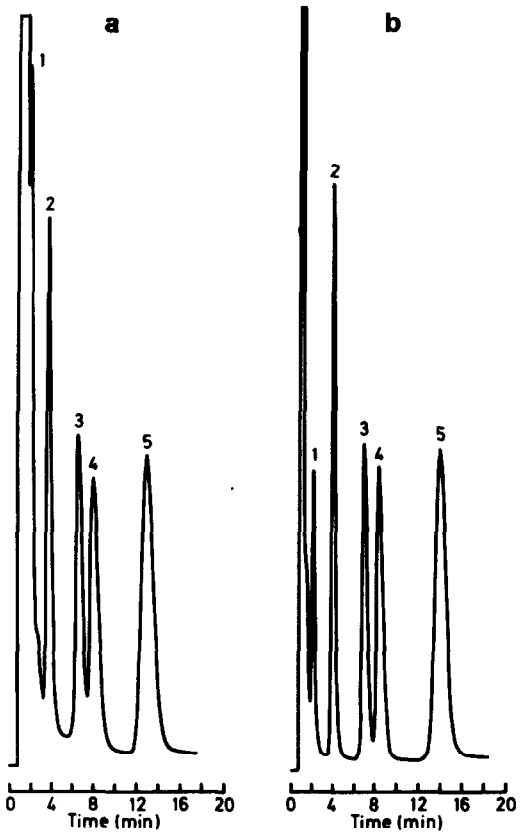

Fig. 5. Chromatogram obtained before (a) and after (b) Donnan dialysis of 10^{-2} *M* NaOH solution containing anions. Injection volume: 50 µl. Eluent: gluconate–borate, pH 8.5. Column: Waters IC Pak A, 50 × 4.6 mm I.D. Peaks: 1 = fluoride; 2 = chloride; 3 = bromide; 4 = nitrate; 5 = sulfate.

penetration. The efficacy of sample clean-up by dialysis can be seen in Fig. 5, which shows chromatograms for a mixture of anions in 10^{-2} *M* NaOH before and after dialysis with 0.1 *M* OSA. The fluoride peak is partially obscured prior to dialysis but can be quantitated after sample treatment.

Loss of analyte during dialysis is a further important consideration. Average recovery data are given in Table I and show that no significant loss of analyte occurred. High apparent recoveries were observed for fluoride in 0.1 *M* NaOH solution due to the fact that the pH of the dialysed solution was above 9, causing distortion of the fluoride peak. The high recoveries of sulfate when sulfuric acid was used as the hydrogen ion-donating medium were due to penetration of sulfate through the membrane.

Comparison of fibre types

Two types of cation-exchange fibres, namely Nafion tubing both with and without polystyrenedivinylbenzene beads, were compared using OSA, CSA and Bio-Rad AG 50W-X8 cation-exchange resin as hydrogen ion-donating media. The results showed that the packed fibre was most efficient since 160-cm fibre of this type performed virtually identically to a 345-cm unpacked fibre. For example, a 0.1 *M* NaOH sample after dialysis with 0.1 *M* OSA, 0.1 *M* CSA and Bio-Rad AG 50W-X8 cation-exchange resin gave pH values after dialysis of 4.5, 4.0 and 4.0, respectively, for the packed fibre, whilst the corresponding pH values for the unpacked fibre were

TABLE I

AVERAGE RECOVERIES (%) OF SOLUTE ANIONS IN 10^{-1}–10^{-4} *M* NaOH AFTER DIALYSIS TREATMENT

The range derived from 20 replicates is shown in parentheses.

Medium	F^-	Cl^-	No_2^-	Br^-	NO_3^-	SO_4^{2-}
H_2SO_4	126 (4)	103 (14)	93 (18)	99 (14)	103 (18)	182 (77)
MSA	123 (55)	101 (19)	94 (8)	98 (19)	98 (17)	95 (9)
CSA	106 (28)	99 (14)	89 (15)	94 (8)	93 (19)	99 (9)
TSA	127 (62)	97 (14)	93 (10)	89 (14)	90 (7)	100 (11)
OSA	106 (38)	94 (12)	92 (8)	90 (5)	94 (11)	98 (10)
AG 50W-X8	116 (49)	96 (9)	93 (11)	102 (10)	95 (7)	89 (9)
AG 50W-X2	130 (44)	92 (9)	88 (8)	91 (10)	90 (6)	91 (12)
IRC-50	130 (78)	93 (13)	89 (18)	85 (16)	86 (12)	89 (12)
IR-120	118 (63)	90 (10)	90 (10)	86 (20)	85 (15)	88 (9)

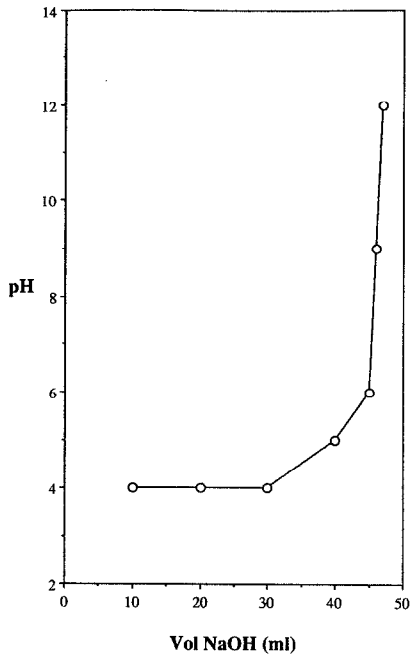

Fig. 6. Breakthrough curve for the packed fibre using 100 ml of 0.1 *M* octanesulfonic acid as hydrogen ion-donating medium and 0.1 *M* NaOH as sample.

each 4.0. The superior performance of the packed fibre is in accordance with the results obtained in previous studies using such fibres [7]. It was also noted that CSA showed greater penetration of the unpacked fibre.

Neutralization capacity of sample clean-up devices

Clean-up devices of the type described in this paper will have a finite life (expressed as the volume of sample of known concentration which can be treated) governed by the volume and concentration of the hydrogen ion-donating solution and the diffusion kinetics across the membrane. This lifetime can be determined by breakthrough experiments by measuring the pH of the effluent and noting the volume of sample which may be treated until the pH of the effluent shows a sharp rise. Fig. 6 shows such a breakthrough curve for the packed fibre using 100 ml of 0.1 *M* OSA as hydrogen ion-donating medium and 0.1 *M* NaOH as sample. The breakthrough point is 47 ml, which corresponds to 47% of the total theoretical capacity of the device.

The neutralization capacity cannot be increased substantially simply by increasing the concentration of hydrogen ion-donating medium because of the likclihood of penetration of the acid anion, even when OSA is used. However, resin slurries offer very high theoretical neutralization capacities. For example, direct titration of 5 g of Bio-Rad AG 50W-X8 cation-exchange resin with 0.1 *M* NaOH using phenolphthalein indicator gave an end-point corresponding to 127.5 ml of NaOH. A slurry containing 80 g of resin therefore has a theoretical total neutralization capacity corresponding to 2040 ml of 0.1 *M* NaOH. The problem with such resin slurries is that their neutralization efficiency is low, as shown in Fig. 3. This suggests that the transfer of hydrogen ions from one resin particle to the next and ultimately through the membrane is rather slow when water is used as the slurrying solvent. One possible solution to this problem is to use an acid solution as the slurrying solvent, at a concentration

TABLE II

NEUTRALIZATION CAPACITY OF THE DIALYSIS DEVICE

The 345 cm × 0.5 mm I.D. unpacked Nafion fibre was used.

Hydrogen ion-donating medium (total volume 100 ml)	Volume 0.1 *M* NaOH neutralized (ml)
0.1 *M* OSA	47
Bio-Rad AG 50W-X8 resin (80 g) in water	25
Bio-Rad AG 50W-X8 resin (80 g) in 0.1 *M* OSA	300
Bio-Rad AG 50W-X8 resin (80 g) in 0.1 *M* OSA, stirred	2000
As above, regenerated with 1 *M* OSA	450
0.45 *M* SPR-H^+ reagent, stirred	220

below which penetration of the acid anion through the membrane occurs.

Table II shows the neutralization capacities obtained with a number of resin slurries with the unpacked fibre. Data for the packed fibre showed similar trends but in each case the neutralization capacities were less than those for the unpacked fibre, presumably due to the greater length of the former. From Table II it can be noted that resin slurried in water has a particularly low neutralization capacity, however, this can be increased by a factor of 12 when 0.1 *M* OSA is used as slurrying solvent. Even in the latter case, the neutralization capacity is only approximately 15% of the theoretical total of the hydrogen ions contained in the resin and the OSA slurrying solvent. We found that occasional stirring of the slurry greatly improved performance, with capacity now reaching 97% of the theoretical value. *In situ* regeneration of the exhausted resin was attempted by passing 50 ml of 1 *M* OSA through the device. Although some neutralization capacity was restored, the original performance was not recovered, suggesting that more thorough regeneration is necessary.

The particle size of the resin is also likely to exert some influence on performance. This aspect was not studied in detail, however a solution of ultra-fine (approximately 50 nm in diameter) cation-exchange resin was examined as a hydrogen ion-donating medium. The particular reagent used was Millipore-Waters SPR-H^+ reagent, which has been used for post-column addition to IC eluents as a means of reducing their conductance through protonation reactions [8]. When titrated with base, this solution was found to contain 0.45 *M* of H^+, so that 100 ml provides a theoretical neutralization capacity corresponding to 0.45 l of 0.1 *M* NaOH. As shown in Table II, the SPR-H^+ reagent gave a low neutralization capacity (approximately 50% of the theoretical value), even when the solution was stirred. Examination of the fibre by electron microscopy after use of the SPR-H^+ reagent showed particles of resin imbedded in the pores of the fibre, suggesting that physical blockage of the fibre could be responsible for the observed low neutralization capacity.

CONCLUSIONS

This study has shown that clean-up of strongly alkaline samples prior to IC analysis can be achieved with the aid of membrane fibre devices. The hydrogen ion-donating solution into which the fibre is immersed must be chosen carefully to avoid penetration of the acid anion into the sample. Hydrophobic sulfonic acids, such as OSA and CSA give best results. The neutralization capacity of the clean-up devices can be increased greatly by using a slurry of cation-exchange resin in the hydrogen form as the hydrogen ion-donating medium. If a suitable acid (such as 0.1 *M* OSA) is used as the slurrying solvent and the slurry is stirred during use, the neutralization capacity approximates the theoretical maximum value dictated by the total ion-exchange capacity of the resin.

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