

Membrane-based sample preparation device for the pretreatment of acidic samples prior to cation analysis by ion chromatography[☆]

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ABSTRACT

A hollow-fiber, membrane-based sample preparation device was investigated for the pretreatment of acidic samples prior to (separate) mono- and divalent cation analysis by ion chromatography. A device consisting of aminated DuPont Nafion fiber immersed in a counter-ion donating solution of either tetrabutylammonium hydroxide (for monovalent cations) or tetrabutylammonium borate (for divalent cations) can effectively neutralize samples with a pH as low as 1. No contaminants are added to the sample using this approach and quantitative recoveries are obtained for standard solutions of alkali metal and alkaline earth cations after passage through the device.

INTRODUCTION

The analysis of alkali metal and alkaline earth cations by ion chromatography (IC) is becoming accepted as an alternative to the more traditional atomic absorption and emission techniques [1,2]. The determination usually involves an ion-exchange separation followed by conductimetric detection. The eluents used for cation-exchange chromatography are typically mineral acids in the 1–10 mM range for monovalent cations [3] and amines at pH 4–6 for divalent cations [4]. Both of these separations are adversely affected in a number of ways by the injection of very acidic samples; shifts in analyte retention times occur due to the acidic sample acting as an internal eluent, the resulting large void peak may mask early eluting cations and the high ionic strength of the sample may result in poor peak shape

due to column overloading. Dilution of the sample may not always be appropriate, especially if the analytes are present in the original sample at very low levels and direct addition of base to the sample is not generally permitted due to the contamination from the co-cation. A commonly used sample pretreatment method is to pass the sample through an anion-exchanger in the hydroxide form [5], however, this approach requires a relatively large sample volume and each portion of resin may only be used once per sample before regeneration and cleaning.

It has been demonstrated that hollow-fiber ion-exchange membranes offer advantages over resin-based ion-exchangers for sample pretreatment, especially for ease of use with small sample volumes [6]. In some applications they may also give better recoveries and less ionic contamination [7,8]. In this paper we discuss the use of a re-usable hydroxide form, anion-exchange, hollow-fiber device for the neutralization of acidic samples prior to mono- and divalent cation analysis by IC.

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EXPERIMENTAL

Instrumentation

The liquid chromatograph consisted of a Waters Chromatography Division of Millipore (Milford, MA, USA) Model 510 pump, U6K injector, Model 430 conductivity detector and either a Waters 745 integrator or 840 data station. The analytical column used was a Waters IC-Pak Cation (50 × 4.6 mm I.D.) polystyrene-based cation exchanger. The eluent used for monovalent cation analysis was 2 mM nitric acid (Ultrex) operated at a flow-rate of 1.2 ml/min. The eluent used for divalent cation analysis was 0.5 mM ethylenediamine adjusted to pH 6.0 with nitric acid (Ultrex), also operated at a flow-rate of 1.2 ml/min. An IC-Pak Cation Guard Column (50 × 4.6 mm I.D.) was placed between the pump and injector for monovalent cation analysis. The eluents were prepared daily, filtered and degassed with a Waters solvent clarification kit.

Reagents

Water purified (18 MΩ) using a Millipore Milli-Q water purification system (Bedford, MA, USA) was used for all solutions. Ethylenediamine and boric acid were obtained from Sigma (St. Louis, MO, USA), Ultrex nitric acid and tetrabutylammonium hydroxide (30%) were obtained from J. T. Baker (Phillipsburg, NJ, USA), as were the analytical grade chloride salts used for the preparation of all the cation standards.

Hollow-fiber sample pretreatment device

The strong anion-exchange hollow-fiber (0.87 mm O.D. × 0.5 mm I.D.) was made from Nafion perfluorosulfonate fiber obtained from Permapure Products Inc. (Toms River, NJ, USA). The sample pretreatment device was a 150 cm length of this fiber immersed in the counter-ion donating (CID) solution which was housed in an 80-ml plastic sample storage bottle, similar to the experimental device previously described by Jones and Jandik [7]. A female plastic Luer-Lok fitting was attached at one end of the fiber to enable sample to be passed through the fiber with a disposable Luer-Tip syringe. The fiber was rinsed with 10 ml of Milli-Q water prior to each sample application.

RESULTS AND DISCUSSION

Selection of CID solution for monovalent cation analysis

For an anion-exchange fiber device to neutralize acidic samples, hydroxide ions in the CID solution are exchanged for anions in the sample (forming water in the sample) and ideally, no cations should cross the membrane. It has previously been demonstrated that the greater the molecular weight of the CID co-cation, the less leakage of the forbidden ions (cations in this case) through the membrane occurs [9]. For this reason, tetrabutylammonium hydroxide (TBAOH) was initially chosen as the CID solution as the relatively large, positive tetrabutylammonium ion would not be expected to penetrate the anion-exchange membrane. The anion-exchange fiber was immersed in the CID solution (60 ml of 25 mM TBAOH) and initially rinsed with 20 ml of Milli-Q water. A standard monovalent cation mix (2.5 ml of a solution containing 1 ppm lithium, 5 ppm sodium, 10 ppm ammonium and 10 ppm potassium) was then passed through the fiber at approximately 1 ml/min with a disposable Luer-Tip syringe. The 2.5 ml of effluent from the device was collected in successive 0.5 ml fractions and the monovalent cations in the fractions were quantitated using a nitric acid eluent and an IC-Pak C column with conductivity detection. Recoveries for the cations were calculated relative to the influent and are shown in Table I.

The results from Table I indicate that essentially

TABLE I

MONOVALENT CATION RECOVERIES OF SUCCESSIVE 0.5-ml FRACTIONS OF A FOUR-CATION MIX PASSED THROUGH THE HOLLOW-FIBER SAMPLE PRETREATMENT DEVICE WITH 60 ml OF 25 mM TETRABUTYLAMMONIUM HYDROXIDE AS THE CID SOLUTION

Fraction (ml)	Cation recovery (%)			
	Li	Na	NH ₄	K
0.5	45.5	51.7	41.3	37.4
1.0	97.1	102.2	94.1	89.9
1.5	103.1	104.9	97.5	99.5
2.0	102.4	104.2	95.4	105.6
2.5	103.5	106.9	96.8	103.6

quantitative recoveries were attained within 1 ml of sample being passed through the hollow-fiber sample preparation device and that once the interstitial volume of the fiber had been flushed with sample, consistent recoveries were obtained for the cations in subsequent 0.5-ml fractions. The capacity of the hollow-fiber device to neutralize an acidic sample solution was then measured using a breakthrough technique. A 150 cm length of aminated Nafion fiber was placed in 60 ml of 25 mM TBAOH as the CID solution. Nitric acid (10 mM) was pumped through the fiber at 1.0 ml/min and 0.5-ml effluent fractions were collected every 2 min. The pH of the fractions was measured using a glass pH electrode and a breakthrough curve was plotted as % removal of acid *versus* volume of acid passed through the fiber. Defining effective ion-exchange capacity as 50% breakthrough gave a capacity of 0.137 mequiv. for the device, or expressed simply, the device could neutralize 13.7 ml of 10 mM nitric acid before 50% breakthrough was achieved. Unfortunately, this capacity was too low considering that the sample preparation device was intended to be used for the pretreatment of multiple samples. A number of fiber lengths, solution volumes and concentrations were investigated and it was found that a device prepared using a 150 cm length of aminated Nafion fiber and 30 ml of 100 mM TBAOH as the CID solution provided reasonable capacity. The breakthrough curve was measured as described previously and to reach 50% breakthrough required 220 ml of 10 mM nitric acid, which corresponded to a capacity of 2.2 mequiv. for the device. Also, the shape of ion-exchange breakthrough curve was sigmoidal with this CID solution, as would be expected for a strong ion exchanger [10], which was not the case when the CID solution was 25 mM TBAOH.

The recoveries of the four cations through a device prepared using the aminated Nafion fiber and 30 ml of 100 mM TBAOH as the CID solution were then measured as described previously. The same monovalent cation standard (12 ml) was passed through the device with the first 2 ml being discarded to waste. The remaining 10 ml was collected in 1-ml fractions and the concentrations of the four cations in the fractions were determined using the conditions described previously. The average recovery for each of the four cations in the ten fractions was determined to be 98.8% for lithium, 103.2% for

sodium, 94.6% for ammonium and 97.5% for potassium. The recovery for the ammonium ion was slightly low as it appeared that a small percentage was converted (or neutralized) to form ammonia in the fiber at a TBAOH concentration of 100 mM. Fig. 1 shows chromatograms of the monovalent cation standard before (a) and after (b) passage through the optimized hollow-fiber, sample preparation device. No breakthrough of the tetrabutylammonium through the fiber was evident in any of the chromatograms.

Selection of CID solution for divalent cation analysis

The optimized hollow-fiber, sample preparation device was then used to test the recoveries for a

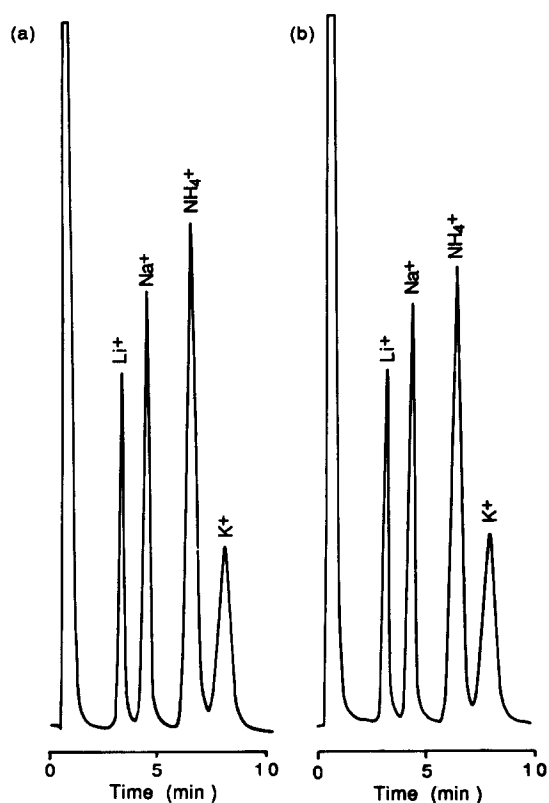


Fig. 1. Chromatogram of monovalent cation standard before (a) and after (b) being passed through an aminated fiber, hydroxide-based sample preparation device. Conditions: column, Waters IC-Pak Cation; eluent, 2.0 mM nitric acid; flow-rate, 1.2 ml/min; injection volume, 20 μ l; detection, conductivity. Solutes: lithium (1 ppm), sodium (5 ppm), ammonium (10 ppm) and potassium (10 ppm).

mixture of divalent cations using the same procedure as for the monovalent cations. A divalent cation standard (2.5 ml of a solution containing 10 ppm magnesium, 20 ppm calcium, 30 ppm strontium and 80 ppm barium) was passed through the fiber immersed in a CID solution of 100 mM TBAOH at approximately 1 ml/min. The 2.5 ml of effluent was collected in successive 0.5-ml fractions and the divalent cations in the fractions were quantitated using an eluent of 0.5 mM ethylenediamine at pH 6.0 with an IC-Pak C column and conductivity detection. Recoveries for the cations were calculated relative to the influent and are shown in Table II. The recoveries for calcium, strontium and barium were essentially quantitative after 1 ml of the standard had been passed through the device, however poor recovery was obtained for magnesium. It appeared that magnesium was being precipitated as its hydroxide inside the fiber, hence the poor recovery.

It was evident that hydroxide was not appropriate for the CID solution due to the poor recovery obtained for magnesium. Sodium tetraborate was then investigated for use as the CID solution, however the sodium cation penetrated the anion-exchange fiber quite readily, resulting in a relatively large void peak which interfered with the quantitation of the magnesium peak. While the magnesium could not be accurately quantitated under these conditions the peak area was approximately quantitative. As the tetrabutylammonium cation did not appear to penetrate the fiber, it appeared that

TABLE II

DIVALENT CATION RECOVERIES OF SUCCESSIVE 0.5-ml FRACTIONS OF A FOUR-CATION MIX PASSED THROUGH THE HOLLOW-FIBER SAMPLE PRETREATMENT DEVICE WITH 30 ml OF 100 mM TETRABUTYLAMMONIUM HYDROXIDE AS THE CID SOLUTION

Fraction (ml)	Cation recovery (%)			
	Mg	Ca	Sr	Ba
0.5	4.3	93.7	94.5	95.2
1.0	14.3	92.6	91.7	92.5
1.5	28.6	96.3	95.7	99.9
2.0	27.1	98.3	98.5	95.2
2.5	12.9	95.4	97.2	94.8

tetrabutylammonium borate would be an appropriate CID solution for the sample preparation device when being used for divalent cation analysis. A solution of tetrabutylammonium borate was prepared by the neutralization of 100 mM TBAOH with 100 mM boric acid to pH 10.7. The recoveries for the divalent cation standard after passage through the fiber immersed in a CID solution of 100 mM tetrabutylammonium borate were then measured for ten successive 1-ml fractions as described previously. The average recovery for each of the cations in the ten fractions was determined to be 95.0% for magnesium, 95.2% for calcium, 100.2% for strontium and 97.8% for barium. Fig. 2 shows

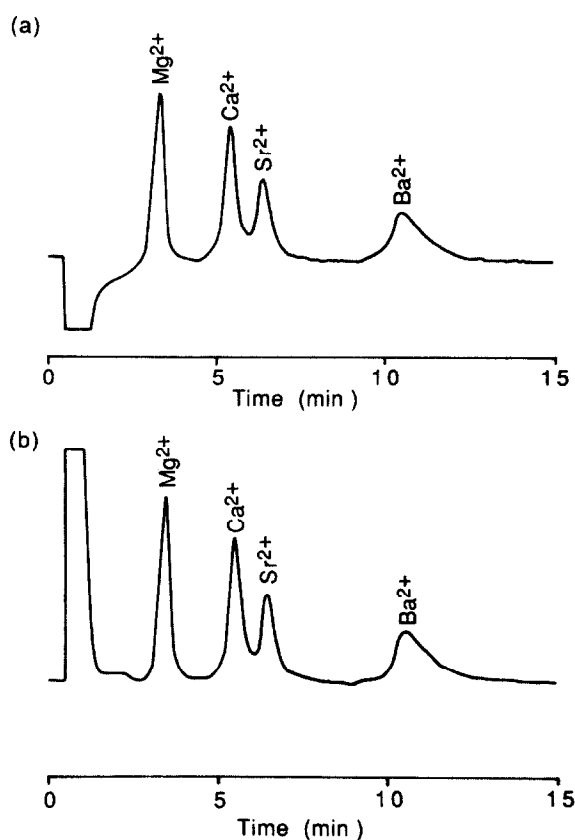


Fig. 2. Chromatogram of divalent cation standard before (a) and after (b) being passed through an aminated fiber, borate-based sample preparation device. Conditions: column, Waters IC-Pak Cation; eluent, 0.5 M ethylenediamine adjusted to pH 6.0 with nitric acid; flow-rate, 1.2 ml/min; injection volume, 50 μ l; detection conductivity. Solutes: magnesium (10 ppm), calcium (20 ppm), strontium (30 ppm) and barium (80 ppm).

chromatograms of the 10–80 ppm divalent cation standard before (a) and after (b) passage through the hollow-fiber, sample preparation device using tetrabutylammonium borate as the CID solution.

The capacity of the tetrabutylammonium borate hollow-fiber device to neutralize an acidic sample solution was then measured as described previously. The aminated Nafion was placed in 30 ml of a 100 mM tetrabutylammonium borate CID solution. Nitric acid was passed through the fiber, effluent fractions were collected and the pH of the fractions was measured using a glass pH electrode. The 50% breakthrough point required only 130 ml of 10 mM nitric acid in this instance, which corresponded to a capacity of 1.3 mequiv. for the device. This was significantly lower than the 50% breakthrough point for the corresponding sample preparation device which used 100 mM TBAOH as the CID solution. This lower capacity occurred as a result of the breakthrough curve for the borate device being less steep than was the case for the hydroxide-based device. This was to be expected as borate, being a weaker base than hydroxide, should give a less steep titration (or breakthrough) curve.

Application of hydroxide and borate-based devices for sample pretreatment

The application of a hydroxide-based, hollow-fiber device for the neutralization of acidic samples prior to monovalent cation analysis was then investigated. The device was prepared as previously using aminated Nafion fiber and 30 ml of 100 mM TBAOH as the CID solution. A monovalent cation standard (2 ml) containing 0.5 ppm lithium, 2.5 ppm sodium, 5 ppm ammonium and 5 ppm potassium made up in 50 mM nitric acid was passed through the device with the last 0.5 ml being retained for injection into the liquid chromatograph. Fig. 3 shows the chromatograms obtained (using a nitric acid eluent and an IC-Pak C column with conductivity detection) of the acidic standard before (a) and after (b) passage through the hydroxide-based sample preparation device. Fig. 3a clearly illustrates the deleterious effect of acidic samples on the chromatography of the monovalent cations as both lithium and sodium are eluted near the large void peak and all the cations exhibit poor peak shape due to column overloading. Fig. 3b shows that there was a dramatic improvement in the chromatography

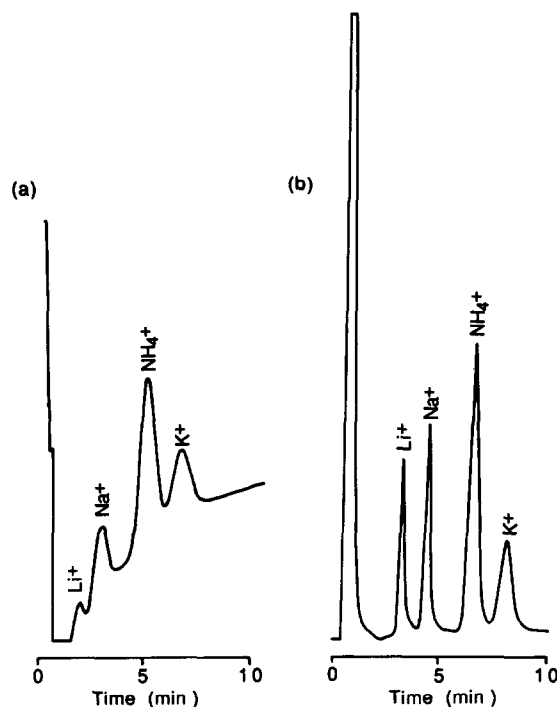


Fig. 3. Chromatogram of acidic monovalent cation standard before (a) and after (b) being passed through an aminated fiber, hydroxide-based sample preparation device. Solutes: lithium (0.5 ppm), sodium (2.5 ppm), ammonium (5 ppm) and potassium (5 ppm) in 50 mM nitric acid. Other conditions as in Fig. 1.

after the acidic standard was passed through the hydroxide-based sample preparation device. The pH of the acidic cation solution changed from 1.23 to 3.69 after being passed through the device; samples as concentrated as 100 mM acid could be treated before any significant disturbance of the chromatography was evident. A 2-ml sample of an acid copper plating bath, diluted 1:50, was then passed through the same device with the last 0.5 ml being retained for injection. Fig. 4 shows the chromatograms of the diluted acid bath before (a) and after (b) passage through the device. The hollow-fiber device enabled quantitation of the low levels of monovalent cations (0.87 ppm sodium, 0.26 ppm ammonium and 0.19 ppm potassium) in a sample which otherwise could not have been analyzed using the chromatographic conditions employed.

A borate-based, hollow-fiber device was then used for the treatment of acidic samples prior to divalent cation analysis. A divalent cation standard

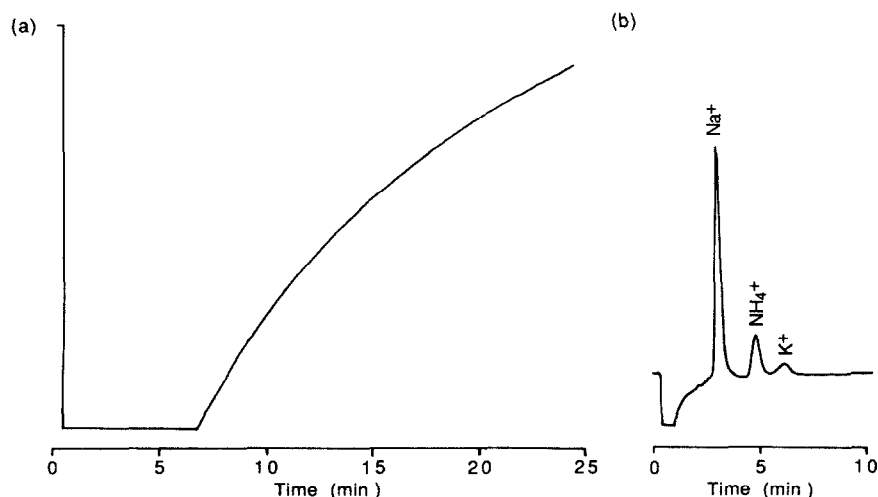


Fig. 4. Chromatogram of a diluted acid copper plating bath before (a) and after (b) being passed through an aminated fiber, hydroxide-based sample preparation device. Conditions as for Fig. 1 except: sample, acid copper plating bath diluted 1:50. Solutes: sodium (0.87 ppm), ammonium (0.26 ppm) and potassium (0.19 ppm).

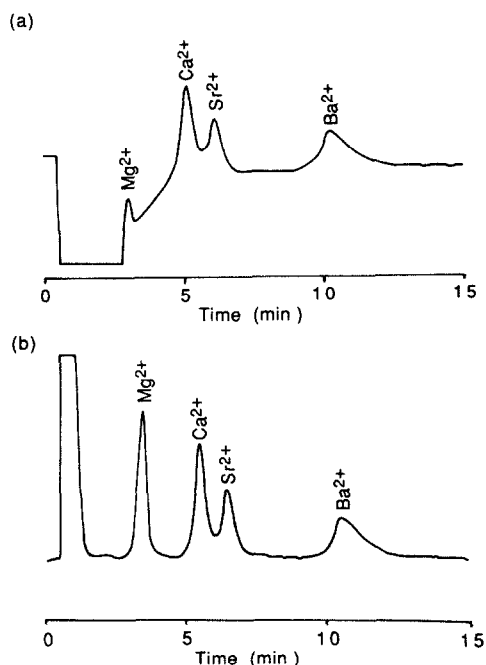


Fig. 5. Chromatogram of acidic divalent cation standard before (a) and after (b) being passed through an aminated fiber, borate-based sample preparation device. Solutes: magnesium (10 ppm), calcium (20 ppm), strontium (30 ppm) and barium (80 ppm) in 25 mM nitric acid. Other conditions as in Fig. 2.

of 10 ppm magnesium, 20 ppm calcium, 30 ppm strontium and 80 ppm barium acidified with 25 mM nitric acid was passed through the device (30 ml of 100 mM tetrabutylammonium borate as the CID solution) and 0.5 ml was retained for injection into the liquid chromatograph. Fig. 5 shows the chromatograms obtained (using an eluent of 0.5 mM ethylenediamine at pH 6.0 with an IC-Pak C column and conductivity detection) of the acidic standard before (a) and after (b) passage through the borate-based device. Again, there was a dramatic improvement in the chromatography after the acidic standard was passed through the hollow-fiber sample preparation device. The maximum acid concentration which could be tolerated with the borate-based device was approximately 40 mM as the divalent cation analysis method was more affected by low pH samples than was the monovalent cation analysis approach. The borate-based device was also effective for neutralizing acidic monovalent cation solutions, however the capacity (and efficiency) of the device was not as high as a hydroxide-based device with a CID solution of equivalent concentration. The borate-based device was applied to the clean-up of a calcium salt lipid active drug. The drug formulation was only soluble in a solution of 30% tetrahydrofuran acidified to pH 4 with nitric acid. Fig. 6 shows the chromatograms of the drug formulation

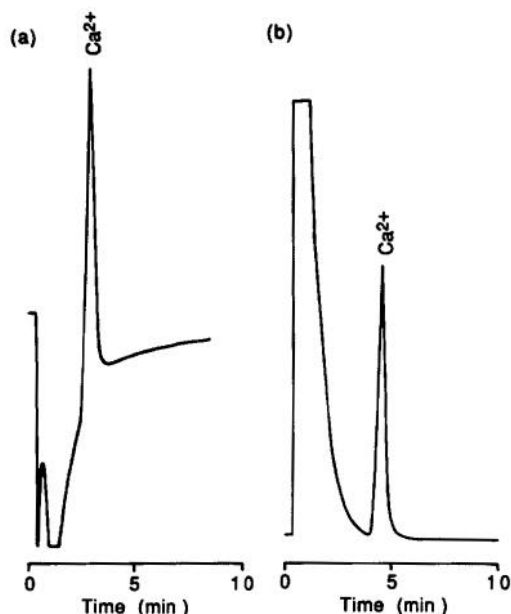


Fig. 6. Chromatogram of a calcium salt lipid active drug formulation before (a) and after (b) being passed through an aminated fiber, borate-based sample preparation device. Sample: dilution 1:100 in 30% tetrahydrofuran acidified to pH 4 with nitric acid. Solute: calcium (21.4 ppm). Other conditions as in Fig. 2.

solution before (a) and after (b) passage through the borate-based device. With the untreated sample, the calcium peak suffers interference from the large baseline disturbance at the void, making quantitation difficult. After passage through the sample preparation device, accurate quantitation was obtained for calcium, which was well resolved from the void peak.

CONCLUSIONS

The neutralization of acidic samples prior to the IC analysis of mono- and divalent cations can be accomplished using a sample pretreatment device consisting of 150 cm of aminated Nafion fiber immersed in a CID solution of either TBAOH or

tetrabutylammonium borate. Minimal sample volumes are required (approximately 1 ml) for use with the hollow-fiber based device, no contaminants are added to the sample and quantitative recoveries are obtained for monovalent cations using a CID solution of tetrabutylammonium hydroxide (or borate), while quantitative recoveries are obtained for divalent cations using a CID solution of tetrabutylammonium borate. The device(s) can be prepared to have an ion-exchange capacity as high as 2 mequiv. which enables them to be used for the treatment of many samples with only a deionized water rinsed required between successive sample applications. Regeneration of an exhausted device can be achieved simply by replacing the CID solution and this sample pretreatment approach allows the IC determination of trace levels of mono- and divalent cations in samples with a pH as low as 1.

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