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Short Communication

Hollow-fibre membrane-based sample preparation device for the clean-up of brine samples prior to ion chromatographic analysis

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ABSTRACT

    A hollow-fibre membrane-based sample preparation device was investigated for the removal of chloride from brine samples prior to ion chromatographic analysis. A device consisting of 150 cm of sulphonated Dupont Nafion® fiber immersed in a counter-ion donating solution of 0.050 M silver p-toluenesulphonate can remove greater than 99% of chloride and bromide in a sample while giving quantitative recoveries for other inorganic anions of interest. This sample pretreatment approach combined with conventional non-suppressed ion chromatography using conductivity detection gives a detection limit for nitrite of approximately 0.1 ppm in brine samples containing up to 5000 ppm chloride.

INTRODUCTION

    Ion chromatography (IC) is now widely used for the determination of anions in water samples [1,2]. While many natural and industrial water samples often only require filtration and/or dilution prior to injection, the determination of trace anions in brines and other samples containing high levels of chloride has typically been achieved using a variety of approaches.
    The most common approach is to reduce the chloride concentration by precipitation as the silver salt. This is usually achieved either by directly adding silver form cation-exchange resin to the sample or by passing the sample through a silver form cation-exchanger [3–5]. Any cation-exchange resin used must first be converted to the silver form, usually by soaking in silver nitrate, then rinsed extensively to avoid contamination [3]. Alternatively, a column packed with silver form resin can be placed on-line so that it acts as a halide suppressor, however the halide suppressor only has a finite lifetime as silver chloride precipitation in the column results in increasing backpressure as the column becomes exhausted [6].
    Selective detection, such as direct UV absorption or amperometry, has been used

to achieve the determination of specific anions [7,8] in brines; and the use of a sodium chloride eluent in conjunction with selective detection [9,10] further enhances the ability to determine trace anions in high chloride matrices. Reinjection of unresolved column effluent fractions back into the IC system by means of switching valves has also been shown to allow determination of trace level anions in brine [11], however, all these approaches are somewhat limited in general utility.

It has recently been shown that hollow-fiber ion-exchange membranes offer some advantages over resin-based ion-exchangers for sample pretreatment in terms of ease of use for small sample volumes [12], better recoveries and less ionic contamination [13]. In this paper we discuss the use of a silver form, cation-exchange, hollow-fiber device for reducing chloride interference in the analysis of anions in brines and similar samples by ion chromatography with conductivity detection.

EXPERIMENTAL

Instrumentation
The liquid chromatograph consisted of a Waters (Milford, MA, U.S.A.) Model 510 pump, U6K injector, Model 430 conductivity detector, Model 441 UV detector and either a Waters 840 data station or 745 integrator. The analytical column used was a Waters IC-Pak™ anion HC (150 × 4.6 mm I.D.) methacrylate-based anion-exchanger. The eluent used was the Waters standard borate–gluconate buffer which consisted of 1.3 mM gluconate, 1.5 mM tetraborate, 5.8 mM boric acid, 120 ml/l acetonitrile, 20 ml/l n-butanol, pH 8.5 operated at a flow-rate of 2.0 ml/min. The eluent was prepared daily, filtered and degassed with a Waters solvent clarification kit.

Reagents
Eighteen-MΩ water purified using a Millipore Milli-Q™ water purification system (Bedford, MA, U.S.A.) was used for all solutions. Sodium D-gluconate (97%), boric acid (98% ACS reagent) were obtained from Sigma and sodium tetraborate (99% ACS reagent) was obtained from Aldrich. Acetonitrile and n-butanol [both high-performance liquid chromatography (HPLC) grade] were obtained from J. T. Baker, as were the analytical grade sodium salts used for the preparation of all the anion standards. Silver nitrate (99%) and silver p-toluenesulphonate (99%) used for the counter-ion donating (CID) solutions were also obtained from Aldrich.

Hollow-fiber sample pretreatment device
The strong cation-exchange hollow-fiber (0.87 mm O.D., 0.72 mm I.D.) was made from Nafion® perfluorosulphonate fiber obtained from Permapure Products (Toms River, NJ, U.S.A.). The sample pretreatment device was simply a 150 cm length of this fiber immersed in the CID solution which was housed in a 80-ml plastic sample storage bottle, similar to the experimental device described by Jones and Jandik [13]. A female plastic Luer-Lok® fitting was attached at one end of the fiber to enable the sample to be passed through the fiber with a disposable Luer-tip syringe. A male Luer-Lok fitting was attached at the outlet end of the fiber to allow a Millipore Millex® GV disposable filter to be incorporated into the device to remove any silver chloride precipitation prior to injection.

RESULTS AND DISCUSSION

Selection of an appropriate CID solution

For this application, co-cations in the sample (sodium, potassium, magnesium, etc.) are exchanged across the membrane for silver ions from the CID solution. The silver then precipitates as the chloride salt, to be passed through the fiber along with the sample stream. Silver nitrate (60 ml of 0.025 M) was initially selected as the CID solution as this silver salt is typically used for converting cation-exchange resins to the silver form [3]. The fiber was initially rinsed with 20 ml of Milli-Q water then 1 ml of a standard anion mix (10 ppm fluoride, 20 ppm chloride, 40 ppm nitrite, 40 ppm bromide, 40 ppm nitrate, 60 ppm phosphate and 40 ppm sulphate) was passed through the fiber at approximately 1 ml/min with a disposable Luer-tip syringe. The last 0.5 ml of the effluent was retained for injection. This procedure was repeated four times and the average recoveries (%) for the anions in the effluent are shown in Table I.

As was expected, the device completely removed chloride and bromide from the solution. However, the recovery for nitrate was higher than expected, while the remaining anions gave quantitative recoveries. The same anion mix was then allowed to reside in the fiber for 30 min before collection and injection into the IC. Similar recoveries were obtained to those shown in Table I for all ions, except that the recovery for nitrate was 345%. The nitrate ion evidently permeates into the sample from the CID solution, even though the fiber was negatively charged. A similar contamination problem was observed by Jones and Jandik [13] when using sulphuric acid as the CID solution with a hydrogen form, cation-exchange fiber device. The amount of nitrate permeating the fiber was found to be dependent upon the residence time of the sample in the fiber and the concentration of the CID solution.

Silver p-toluenesulphonate was then investigated for use as the CID solution, as it has been demonstrated that the greater the molecular weight of the scavenger (or CID co-anion in this case) the less leakage through the membrane occurs [14]. The recoveries for the seven anion mix were determined as previously for the device but using 60 ml of 0.025 M silver p-toluenesulphonate as the CID solution. Similar recoveries were obtained to those shown in Table I, except that the average recovery (of five) for nitrate was 96.3%. The p-toluenesulphonate anion did not appear to permeate the fiber at this CID concentration as no chromatographic peak was ever observed on the UV detector (operated at 214 nm) at the retention time corresponding to that of p-toluenesulphonate (*ca.* 15 min). The silver p-toluenesulphonate CID

TABLE I

RECOVERIES FOR A SEVEN-ANION MIX PASSED THROUGH THE HOLLOW-FIBER SAMPLE PRETREATMENT DEVICE WITH 60 ml OF 0.025 M SILVER NITRATE AS THE CID SOLUTION

The (%) relative standard deviation of the recovery is shown in parenthesis.

Average recovery ($n = 5$)

F^-	Cl^-	NO_2^-	Br^-	NO_3^-	PO_4^{3-}	SO_4^{2-}
98.9 (0.4)	0.0	94.2 (1.8)	0.0	117.3 (4.6)	96.6 (0.1)	98.6 (0.9)

solution proved to be light sensitive but was stable for several weeks if stored in the absence of light.

Performance of fiber sample pretreatment device for chloride removal

A standard solution containing a high chloride concentration (5000 ppm chloride and 50 ppm each of nitrite, nitrate and sulphate) was prepared to test the performance of the fiber sample pretreatment device. The device was prepared as above (except using 0.050 M silver p-toluenesulphonate as the CID solution) and rinsed with 5 ml of Milli-Q water before use. The high chloride solution (1 ml) was passed through the device at approximately 1 ml/min, with the last 0.25 ml being retained for injection into the IC. Fig. 1 shows a chromatogram (20 μl injection) of the high chloride solution before being passed through the fiber sample pretreatment device and Fig. 2 shows a chromatogram of the same solution after being passed through the device. The chloride concentration was reduced by over 99% while the other anions all gave quantitative recoveries. Also, the chromatography was greatly
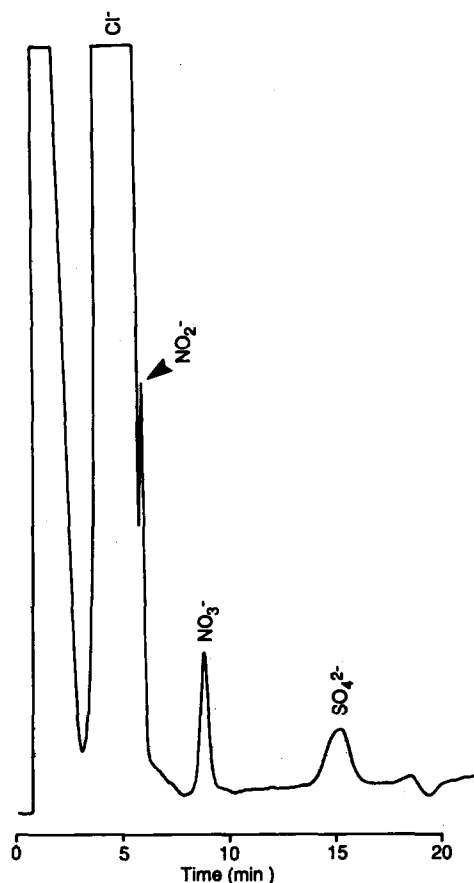

Fig. 1. Chromatogram of standard containing 5000 ppm chloride and 50 ppm each of nitrite, nitrate and sulphate. See Experimental section for conditions.
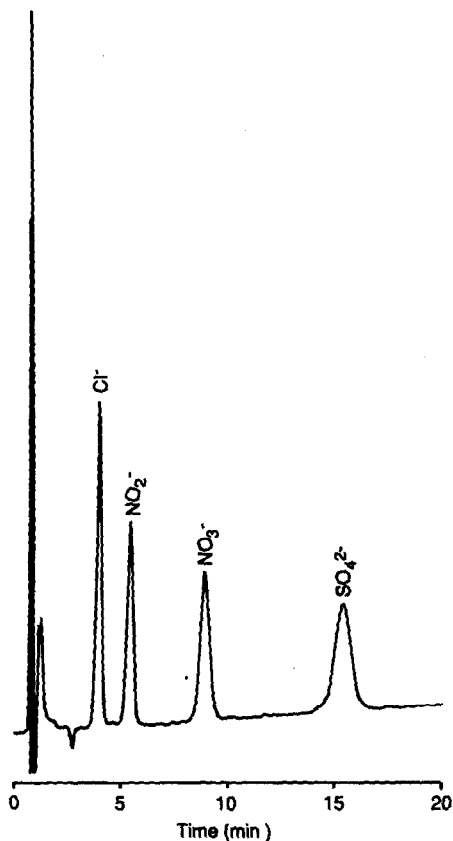
Fig. 2. Chromatogram of standard containing 5000 ppm chloride and 50 ppm each of nitrite, nitrate and sulphate after being passed through fiber sample pretreatment device. See text for details. See Experimental section for conditions.

improved due to the reduction in ionic strength of the sample after being passed through the device.

The fiber sample pretreatment device was applied to the determination of nitrite and nitrate in an industrial brine. A device was prepared as above and 1 ml of the sample was passed through the fiber at approximately 1 ml/min with the last 0.25 ml being retained for direct injection. Fig. 3 shows a chromatogram (20 µl injection) of the brine before being passed through the fiber sample pretreatment device and Fig. 4 shows a chromatogram of the same solution after being passed through the device. The sample contained approximately 1500 ppm chloride, which was almost totally removed (along with bromide) by passage through the device. The detection limit (3 × signal-to-noise) for nitrite in the presence of up to 5000 ppm chloride is *ca.* 0.1 ppm.

Capacity of fiber sample pretreatment device for chloride removal

The capacity of the device was limited to the removal of approximately 0.5 mequiv. of chloride as the fiber become blocked by precipitated silver chloride with use. However, it was possible to clean-up the fiber *in situ* by passing 2 ml of 1.0 *M*
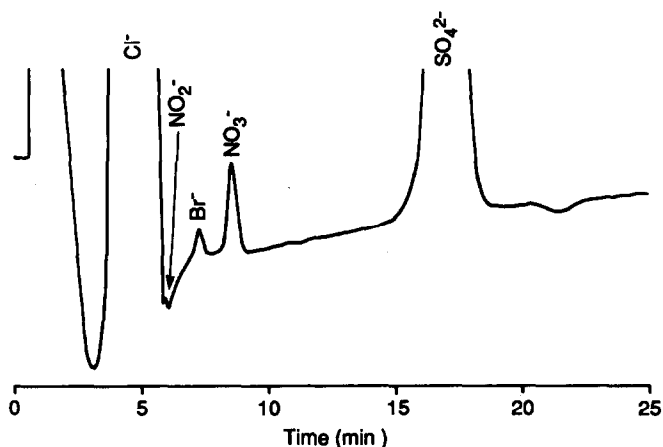
Fig. 3. Chromatogram of industrial brine. See Experimental section for conditions.

ammonium hydroxide through the device via a Luer-Lok syringe. The fiber was then rinsed with 5 ml of Milli-Q water before a new sample was applied and this procedure could be carried out until the CID solution was depleted of free silver ions.

CONCLUSIONS

The removal of chloride from brine samples prior to ion chromatographic analysis can be accomplished using a sample pretreatment device consisting of 150 cm of sulphonated Nafion fiber immersed in a CID solution of 0.050 M silver p-toluenesulphonate. The device can remove > 99% of chloride and bromide at levels up to 5000 ppm in a sample while giving quantitative recoveries for other inorganic anions. The silver chloride which precipitates in the hollow-fiber tubing can be
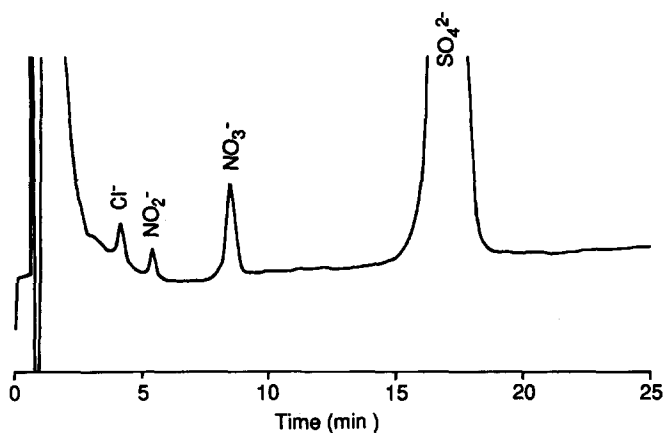

Fig. 4. Chromatogram of industrial brine after being passed through fiber sample pretreatment device. See text for details. See Experimental section for conditions. Nitrite and nitrate were present at 1.4 and 9.6 ppm, respectively.

removed *in situ* with ammonium hydroxide enabling the device to be regenerated and reused until the CID solution is exhausted. This sample pretreatment approach allows the determination of trace levels of nitrite (*ca.* 0.1 ppm) in brine samples containing up to 5000 ppm chloride when using conductivity detection.

REFERENCES

1 O. A. Shpigun and Yu. A. Zolotov, *Ion Chromatography in Water Analysis*, Ellis Horwood, Chichester, 1989.
2 D. T. Gjerde and J. S. Fritz, *Ion Chromatography*, Huthig, Heidelberg, 2nd ed., 1987.
3 R. M. Merril, *Technical Report SAND-84-2297*, Sandia National Laboratories, Albuquerque, NM, 1985.
4 R.-D. Wilken and H. H. Kock, *Fresenius Z. Anal. Chem.*, 320 (1985) 477.
5 M. H. Gaffney and M. Cooke, *Anal. Proc.*, 22 (1985) 25.
6 P. F. Kehr, B. A. Leone, D. E. Harrington and W. R. Bramstedt, *LC · GC*, 4 (1986) 1118.
7 R. G. Gerritse and J. A. Adeney, *J. Chromatogr.*, 347 (1985) 419.
8 K. Itoh and H. Sunahara, *Bunseki Kagaku*, 37 (1988) 292.
9 T. Okada, *Bunseki Kagaku*, 36 (1987) 702.
10 P. Pastore, I. Lavagnini, A. Boaretto and F. Magno, *J. Chromatogr.*, 475 (1989) 331.
11 P. F. Subosa, K. Kihara, S. Rokushika, H. Hatano, T. Murayama, T. Kuboto and Y. Hanaoka, *J. Chromatogr. Sci.*, 27 (1987) 680.
12 J. A. Cox, E. Dabek-Zlotorzynska, R. Saari and N. Tanaka, *Analyst (London)*, 113 (1988) 1401.
13 W. R. Jones and P. Jandik, *J. Chromatogr. Sci.*, 27 (1989) 449.
14 Y. Hanaoka, T. Murayama, S. Muramoto, T. Matsuura and A. Nanba, *J. Chromatogr.*, 239 (1982) 537.