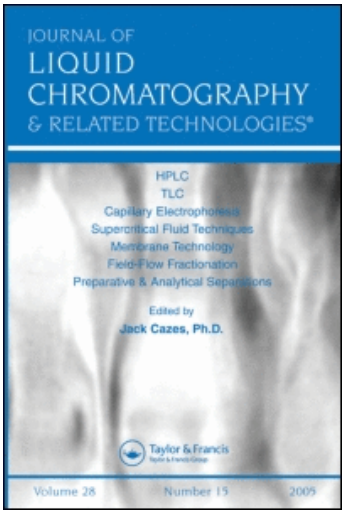

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Karen Johnson[a]; Dee Cobia[a]; James G. Tarter[a]
[a] Department of Chemistry, North Texas State University, Denton, Texas

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NARROW BORE ION CHROMATOGRAPHY WITH COMMERCIALLY AVAILABLE ION CHROMATOGRAPHIC EQUIPMENT

Karen Johnson, Dee Cobia, and James G. Tarter

Department of Chemistry
North Texas State University
Denton, Texas 76203-5068

ABSTRACT

The use of narrow bore separator columns (inner diameter less than 1 μM) in high performance liquid chromatography has become a well established technique which has obvious advantages in specific situations over the use of traditional size separator columns. The work reported here investigates the use of traditional ion chromatographic equipment (essentially unmodified) for use in narrow bore ion chromatography. The only adjustments made to the equipment were some arrangements in the placement of valves and tubing in order to minimize extra-column dead volume. The columns used in this work were glass capillary columns of 1.0 mm inner diameter. A selected group of ion exchange resins were slurry packed into the column and the retention and separation characteristics of the narrow bore column were determined. The results of this investigation indicate that in certain cases the commercially available equipment is adequate for performing narrow bore ion chromatography. The distinct advantage of the use of narrow bore ion chromatography is the lower flow rates used in the chromatographic procedure with a corresponding decrease in eluant consumption, eluant cost, and eluant disposal.

INTRODUCTION

Ion Chromatography is a developing branch of high performance liquid chromatography. Many of the theoretical and practical aspects of HPLC can also be applied to ion chromatography. One of the recent advances in HPLC which should have applicability in IC is the use of narrow bore, or microbore, columns to perform the separation. A detailed book on microcolumn separations has been published which should be standard reading for any individual in this area (1). One chapter within this book edited by Novotny and Ishii deals with microcolumn separations using ion chromatography. In general, the results were quite good but were obtained with the aid of high priced specialty equipment manufactured for HPLC microcolumn work (2). There are numerous excellent references which discuss both the theoretical and practical aspects of microbore separations (3-7)

The problems encountered in the use of narrow bore ion chromatography columns, or in the use of HPLC columns, center on extra-column band broadening. This band broadening occurs in the tubing used to connect the various components as well as in the detector cell itself. Thus, it is traditionally considered of key importance to minimize all extra-column dead volume to minimize the band broadening. The objective of much of the original research as reported in the literature was to determine the optimum conditions to achieve maximum separation and resolution usually by optimizing the theoretical plate height.

The object of this study was to determine whether useful information could be obtained using commercial IC equipment under conditions which would not be considered the optimum analytical conditions.

EXPERIMENTAL

Equipment

The equipment used for this work consisted of a Dionex Model 10 Ion Chromatograph which was essentially in the original working condition as when received from the factory. Minor adjustments were made to the positions of the valves in order to minimize tubing used in connections, but the original valves, detector cell, etc. were used in this research. We used the LDC-Milton Roy MiniPump to pump the eluant through the narrow bore column and onto the detector. The flow rate was measured to be 0.4 mL/Min. The injection volume was 4.4 μL. The detector used for this work was the original detector in the Model 10 with the original detector cell and detector electronics.

The narrow bore analytical column was constructed from a piece of 1 mm inner diameter glass tubing which was 8.2 cm in length. The internal volume of this column is approximately 64 μL as calculated mathematically. The fittings which were used for the glass column were taken from old Dionex columns. The fittings were held in place on the glass column by placing the fitting on

the column and then adding a small ring of glass near the end of the column to keep the fitting in place. This is a very easy and rapid procedure for any one reasonably adept at glass blowing techniques.

The narrow bore capillary column was packed using a slurry type technique. A Dionex AS3 separator column, which was no longer useful, was used as a slurry reservoir. The old column was emptied of the original resin and then a water-new resin mixture was placed into the empty column without column frits using a Pasteur pipet. The slurry reservoir was then connected between the MiniPump on the IC and the glass narrow bore column. The MiniPump was turned on and the slurry passed from the reservoir into the narrow bore column. The pump was operated at the lowest possible flow until the glass column was filled with resin as determined visually. The pump speed was then increased until the pressure was approximately 600 PSI. The pump was operated at this pressure to pack the column for approximately five minutes. During this research, we packed this particular column approximately 10 times. In all cases the packing appeared uniform as evidenced by flowrate-pressure relationships and by visual inspection after packing.

Reagents

The reagents used in this work were all reagent grade quality salts, either the sodium or potassium salt for the anions or the chloride or nitrate salt for the cations. The water used in the

preparation of the eluant and all of the solution was distilled-deionized water which was prepared in our laboratory.

RESULTS AND DISCUSSION

Anion Determinations

Two different resins were used in the investigation of the anions. One resin was a low capacity ion exchange resin (Dionex HPIC-AS3 resins, capacity of 0.03 meq/gram) and a high capacity ion exchange resin (Bio-Rad Dowel 1-X 200-400 mesh, 3.2 meq/gram capacity).

The initial work was performed with the high capacity resin. During the course of this work, no conditions were found which provided useful separation and resolution. It was determined that the concentration of the eluant necessary to cause elution in a reasonably short period of time was so high that the background conductance would distinctly reduce sensitivity. In fact, with the model 10 detector, the largest linear operating scale, 1K S, was not sufficient for the background conductance.

The next step of the work was to use the low capacity ion exchange resin. Our initial attempts at an eluant were to use distilled-deionized water as the eluant and let the absorbed carbon dioxide in the water act as the eluant ions. We encountered difficulty in this procedure due to the fact that the water in use was produced and used in a variable time frame thus

producing changes in the concentration of absorbed CO_2 in the water. Also, it was difficult to determine the pH of these solutions to verify consistency due to the problems inherent in measuring the pH of pure water. The next eluant choice was a dilute acetic acid eluant. We tested various concentrations of acetic acid, primarily 1-20 drops of glacial acetic acid as measured from a Pasteur pipet in one liter of distilled-deionized water. The optimum chromatographic eluant was the solution with 2 drops glacial acetic acid, approximately 1.5 mM. Using this eluant, distinct retention times could be obtained for several common anions as given in Table 1. A simple chromatogram is shown in Figure 1.

According to the theories governing narrow bore HPLC, one of the main problems is extra-column band broadening. In traditional work injection volumes of less than 1 μL are used along with detector cell volumes of less than 1 μL. In our work, neither of these guidelines were followed and the peaks shown in Figure 1 are broader than one would want in many applications. However, the fact that separation is obtained between the species and that the retention times of the anions do differ as shown in Table I indicates that the traditional theory and rules are not inflexible. Useful results can be obtained from what would be classified as non-optimum working conditions. Another area of band broadening occurs when tubing of different diameters is used. In our work, all tubing was of the same diameter and the column

TABLE I

RESULTS OF ANION DETERMINATIONS

RESIN: Dionex AS3

ELUANT: 2 drops glacial acetic acid in one liter atmosphere equilibrated distilled-deionized water

DETECTOR: 3 S Full Scale

ION	RETENTION TIME	DETECTION LIMITS
F	1.0 min	**
Cl	2.0 min	0.1 ppm
Br	3.5 min	0.5 ppm
NO_3	3.75 min	0.5 ppm
SO_4	4.00 min	1.0 ppm

** co-elutes with water dip

was approximately the same diameter. We used 0.7 mm ID tubing and a 1 mm ID column. This would minimize the effect of bore changes upon the chromatographic results.

It would seem reasonable to expect that a larger column, one with more resin, would produce even better results. The key point in this discussion is that it may be possible to obtain useful narrow bore ion chromatographic results using inexpensive equipment.

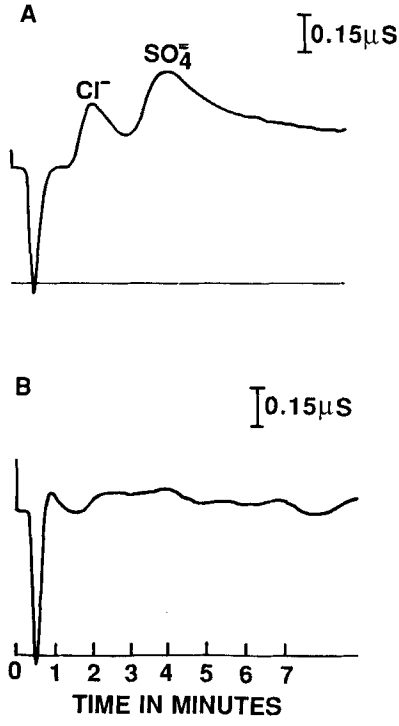

Figure 1: The separation of chloride and sulfate ions using narrow bore ion chromatography with conventional ion chromatography equipment. The eluant was 1.5mM acetic acid at a flow rate of 0.4 mL/Min. The column was 1.0 mm ID by 82 mm in length packed with Dionex HPIC-AS3 resin using slurry techniques.

Cation Determinations

Two different resins were also used in the investigation of the cations. One of the resins was a low capacity resin (Dionex HPIC-CS1 resin, capacity 0.2 meq/gram capacity) and the other resin was a high capacity resin (Bio-Rad, Dowel 50W-X8 resin, 5.1 meq/gram).

As with the anion work, distilled-deionized water was quickly ruled out as an eluant due to the problems in reproducing an eluant. We next tried a dilute acetic acid eluant without being able to obtain any resolution between sodium and potassium ions. A stronger eluant, composed of 3 drops of concentrated nitric acid per liter of water, approximately 2.4 mM, did produce two peaks for sodium and potassium ions. Unfortunately, there was not baseline resolution between the peaks. There appeared to be insufficient resin to produce complete separation.

We investigated both the low capacity resin and the high capacity resin with respect to potential applicability for alkaline earth ions. In neither case was there significant chromatographic separation at an eluant strength compatible with the detector in use. We also looked for the possibility of determining both monovalent and divalent metal cations with the high capacity resin but were unsuccessful.

CONCLUSION

The results in this manuscript indicate that under certain conditions it is possible to separate several inorganic anions using a 1.0 mm ID column and traditional equipment normally used for larger columns. Although a completely successful cation separation was not achieved, the results indicate that separation and detection are possible if longer columns are used.

It would seem that the theoretical material which has been developed for narrow bore chromatography is not necessarily the only case in which useful results can be obtained, just the best case. We feel that useful ion chromatography, where just three or four ions are involved, can be performed using easily constructed narrow bore columns and reduced flow rates. The resulting savings in cost of eluant and cost of resin could easily become significant in many areas where routine analysis of only a few ions is performed. An alternate application of this procedure would be the testing of new separations or new samples on a standard procedure. Should the column be ruined, the cost of replacement of a column with a volume of approximately 100 μL would be much smaller than the replacement of a larger separator column. Normal HPLC pumps with flow rates in the tenths of a milliliter per minute are adequate as are detector cells with volumes well in excess of 1 μL.

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