Journal of Chromatography, 546 (1991) 351–367
Elsevier Science Publishers B.V., Amsterdam

CHROMSYMP. 2115

Ion chromatography for the analysis of household consumer products

DAVID MURAWSKI
Church & Dwight Co., Inc., 469 North Harrison Street, Princeton, NJ 08543-5297 (U.S.A.)

ABSTRACT

Ion chromatography (IC) is an indispensable tool for the analysis of household consumer products. Items such as baking soda, laundry detergent, dental care products, mouthwash, etc., can be analyzed quickly and accurately using chemically suppressed IC, single-column ion chromatography (SCIC) or a combination of the two technologies.

In USP baking soda, trace anions can be determined at ppm levels to ensure product quality and conformance to FDA regulations.

In dental care products, the determination and speciation of soluble fluoride compounds will be shown, as well as the determination of the tartar control agent, pyrophosphate. The non-chromophoric sweetener, sodium cyclamate, will be determined in foreign dental care products.

In liquid laundry detergents, chloride is added for viscosity control; silicate, mono-, di- and triethanolamines are added for buffering. Formate is present as an enzyme stabilizer. Citrate and laurate are added for hardness control.

These species can be determined effectively in SCIC systems, as well as chemically suppressed systems. For some applications, the use of traditional SCIC columns along with chemical suppression improves detectability and simplifies sample preparation. The MilliTrap-H^+ membrane cartridge will be evaluated as an aid to sample preparation.

INTRODUCTION

Ion chromatography (IC) has been found to be extremely useful for the analysis of household consumer products. Most of these products contain compounds amenable to IC analysis, whether active ingredients or impurities, the levels of which must be monitored. Church & Dwight, makers of Arm & Hammer brand products, manufactures a variety of consumer products. Analysis of these products is necessary to ensure product quality. Testing of competitive brands is necessary to keep current with emerging trends in the industry, as well as monitor products for patent infringement.

The matrices of these products are as diverse as the species to be determined. Matrices containing largely or solely bicarbonate or carbonate present a challenge to the ion chromatographer. Anion analyses of products with these matrices have traditionally been performed using chemically suppressed IC. Indeed, the rationale behind this is, in many cases, quite valid. At times, sample preparation is simplified due to a compatibility of the sample and eluent. Enhancement of the analyte signal allows for

0021-9673/91/$03.50

greater sensitivity permitting the analyst to sometimes dilute away matrix interference. This is not always necessary, however, since the severity of the bicarbonate/carbonate matrix interference in single-column ion chromatography (SCIC) or non-suppressed IC, is determined by eluent strength, analyte retention, analyte detectability, and the relative concentrations of analyte and bicarbonate–carbonate in the sample.

In some cases, examples will be given of separations performed using both the suppressed and non-suppressed modes of IC. This is to demonstrate the flexibility of IC and not to imply a superiority of one technique over the other.

Many illustrations will be shown using the Hamilton PRP-X100 column with a bicarbonate–carbonate eluent. Although previously shown to produce less than ideal chromatography for bromide and nitrate [1], other anions elute with good peak symmetry. The compatibility of this column with organic solvents is advantageous. With matrices containing a variety of organic compounds including surfactants, rinsing the column with methanol can aid in removing potentially fouling compounds and increase column lifetime.

Ion-pairing and ion-exclusion techniques will be shown as appropriate for larger organic ions and neutral compounds, respectively.

Finally, a separation of two similar compounds —one anionic, one neutral— will be shown on a low-capacity resin-based anion exchanger. This will illustrate a previously reported observation concerning the retention of compounds with a hydrophobic center on a resin-based anion exchanger [2].

INSTRUMENTATION

Several different systems were used in this work. Solvent delivery systems included: Perkin-Elmer Series 10 (Perkin-Elmer, Norwalk, CT, U.S.A.), Altex 110A (Beckman Instruments, San Ramon, CA, U.S.A.), and the Waters 501 (Waters Chromatography Division, Milford, MA, U.S.A.). Conductivity detectors used for SCIC systems were the Perkin-Elmer LC-21 or the Waters 431. For UV absorbance, the Waters 480 variable-wavelength detector was used. Data handling was done by the Spectra-Physics 4270 computing integrator (Spectra-Physics, San Jose, CA, U.S.A.). Where suppressed conductivity was necessary, the Dionex series 4000i (Dionex, Sunnyvale, CA, U.S.A.) was used with the Dionex anion micromembrane suppressor (AMMS).

Analytical columns used were the Hamilton (Reno, NV, U.S.A.) PRP-X100 (250 × 4.1 mm), Wescan (Deerfield, IL, U.S.A.) ion exclusion 269006 (300 × 7.8 mm), Wescan Anion/R guard cartridge 269030, Wescan Cation S (50 × 4.6 mm), Vydac (The Separations Group, Hesperia, CA, U.S.A.) 302IC4.6 (250 × 4.6 mm), Dionex AG4A (50 mm × 4 mm) and AS4A (250 × 4 mm), Supelco (Bellefonte, PA, U.S.A.) LC-8 (150 × 4.6 mm) and LC-CN (150 × 4.6 mm). The MilliTrap-H^+ cartridge (Waters) was also used.

All eluents, standard and sample solutions were prepared using water pretreated via distillation and reverse osmosis, then passed through a Milli-Q Plus (Millipore, Bedford, MA, U.S.A.) water-purification system.

CHLORIDE AND SULFATE IN SODIUM BICARBONATE

Sodium bicarbonate, $NaHCO_3$, or more commonly, baking soda, is one of the most widely used consumer products. For the product to meet USP specifications, it must meet strict requirements for purity. Additionally, trace levels of certain impurities must be determined, as mandated by the USP monograph [3]. Two impurities that must be measured are chloride and sulfate. The USP limit for each of these is 150 ppm as the anion.

This is a particularly difficult situation for the ion chromatographer. First, trace levels of ions are to be measured, requiring maximum sensitivity. Second, the entire matrix is a completely soluble inorganic salt, allowing for potential interferences and severe baseline disturbances. In this particular case, chemically suppressed conductivity is clearly indicated. Conveniently, the Dionex eluent for anion analysis is typically a bicarbonate–carbonate solution chosen for its ability to be chemically suppressed. This eluent closely matches the sample matrix, which will be partially suppressed as well, resulting in a relatively small solvent peak. This is necessary for determination of the early eluting chloride peak. This method is a modification of that for trace anions in sodium carbonate (soda ash). In the latter case, sample preparation consists of a 0.4% (w/v) solution in deionized water. For $NaHCO_3$, a specific amount of NaOH must be added to a 0.32% (w/v) solution to essentially titrate the bicarbonate solution to carbonate. This is necessary to prevent a baseline disturbance that would obscure the chloride peak. A 1*M* NaOH solution is prepared from a 50% (w/w) NaOH solution ("Baker Analyzed" Reagent, J. T. Baker, Phillipsburg, NJ, U.S.A.) and is used to titrate the $NaHCO_3$ sample solution. The levels of chloride and sulfate in the 50% (w/w) NaOH solution are typically less than 10 ppm and can also be determined by ion chromatography. After the addition of NaOH, the concentration of chloride and sulfate in $NaHCO_3$ can easily be determined (see Fig. 1). The method is simple and rapid; the run time is less than 10 min. The minimum detectable limits for chloride and sulfate in sodium bicarbonate are approximately 15 ppm and 30 ppm, respectively.

FLUORIDE AND MONOFLUOROPHOSPHATE IN DENTAL CARE PRODUCTS

Fluoride and monofluorophosphate are active ingredients in dental care products. They function as anti-caries agents. The concentration of fluoride in these products is generally around 1000 ppm.

For dental care products without sodium bicarbonate, many columns and eluents will permit the rapid determination of fluoride. The Hamilton PRP-X100 column was selected for its favorable retention of the fluoride anion. A rather unique eluent consisting of 1.75 m*M* HNO_3 and 1.3 m*M* $Mg(NO_3)_2$ was found to work well. The eluent utilizes nitrate as the driving ion. An eluent consisting solely of dilute HNO_3 (*ca.* 3 m*M*) can be used but the background conductivity is rather high, approximately 1000–1100 μS. The eluent strength is maintained while the conductivity is reduced by *ca.* 30% if $Mg(NO_3)_2$ is substituted in part for the HNO_3. This results in reduced baseline noise [4] and a faster return to baseline prior to fluoride elution. Sample preparation is minimal. A 2% (w/v) slurry of the product is made in deionized water, then filtered. An example of a typical commercial toothpaste analyzed in this way is shown in Fig. 2.

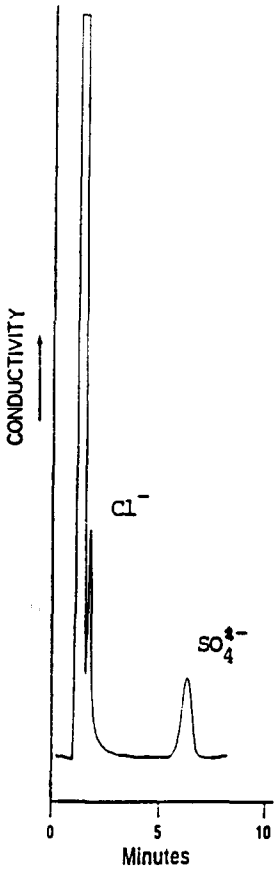

Fig. 1. Determination of trace levels of chloride and sulfate in sodium bicarbonate. Dionex AG4A/AS4A columns are used with a 0.75 m*M* $NaHCO_3$–2.2 m*M* Na_2CO_3 eluent. Flow is 2 ml/min. Range is 3 μS f.s. Regenerant is 6.25 m*M* H_2SO_4 at 3–4 ml/min.

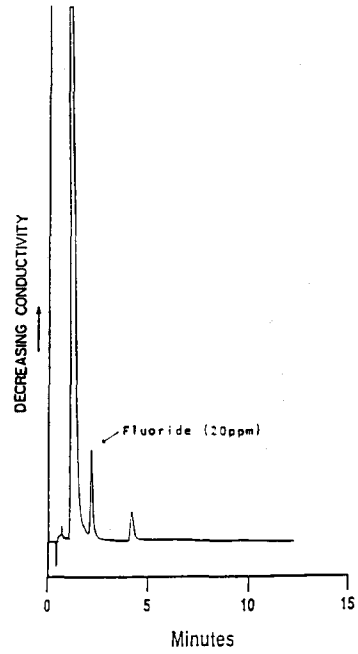

Fig. 2. Fluoride in a commercially available toothpaste. PRP-X100 column is used with an eluent of 1.75 m*M* HNO_3 and 1.3 m*M* $Mg(NO_3)_2$. Flow is 2.5 ml/min. Indirect conductivity detection at 10 μS f.s. is used.

For bicarbonate-based dentifrices with fluoride as the active ingredient, sample preparation to remove the bicarbonate is necessary if SCIC is to be used. This is due to the weak retention of fluoride, the low level of fluoride (*ca.* 0.1%, w/w) in the product and the comparatively large amount of bicarbonate. Sample preparation consists of removing the bicarbonate from an aqueous solution of the product using a thoroughly washed sulfonic acid cation-exchange resin in the hydrogen form. Sample sodium ions are exchanged for resin hydrogen ions, reducing the pH of the solution. At pH 3–4 bicarbonate is removed via CO_2 elution. Helium sparging followed by sub-micron filtration removes essentially all of the bicarbonate from the solution. A chromatogram illustrating the determination of fluoride by the procedure is shown in Fig. 3.

Incomplete removal of bicarbonate results in severe early baseline disturbances and a very large system peak. This is the case when the MilliTrap-H^+ is the only form of sample pretreatment. Passing the sample solution through a MilliTrap-H^+ cartridge did not remove enough of the bicarbonate to allow for the determination of fluoride under the specified conditions. Due to the very weak eluent strength, essentially all of the bicarbonate must be removed from the sample solution for the baseline to appear as shown in Fig. 3.

Although excellent results can be obtained with the above procedure, sample preparation is slow and labor-intensive. An easier and more rapid alternative is to use the same column under conditions typical for anion analysis using chemical suppression. If the Hamilton PRP-X100 column is used with the Dionex series 40000i system, sample preparation is simplified and sensitivity is enhanced. Sample preparation consists of a 0.5% aqueous solution in plastic labware followed by sub-micron filtration, (see Fig. 4).

FLUORIDE/MONOFLUOROPHOSPHATE

Disodium monofluorophosphate (MFP) is used as the active anti-caries agent in many toothpastes. MFP can undergo hydrolysis, however, forming fluoride and

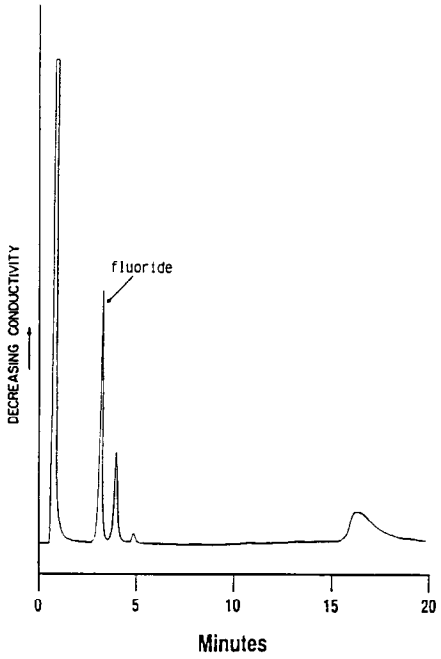

Fig. 3. Fluoride in a bicarbonate-based dentifrice using non-suppressed conductivity detection. PRP-X100 column is used with 3.5 m*M* NaOH–0.5 m*M* sodium benzoate eluent. Flow is 2.5 ml/min. Indirect conductivity detection at 10 μS f.s. is used.

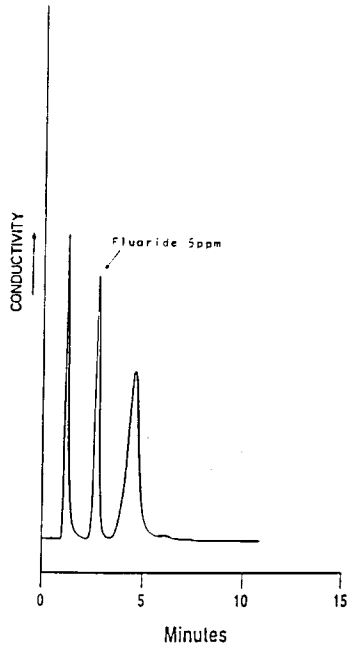

Fig. 4. Fluoride in a bicarbonate-based dentifrice using suppressed conductivity detection. PRP-X100 column is used with a 2.2 m*M* Na_2CO_3–0.75 m*M* $NaHCO_3$ eluent. Flow is 2 ml/min. Range is 10 μS f.s. Regenerant is 6.25 m*M* H_2SO_4 at 3–4 ml/min.

orthophosphate. Once hydrolyzed, the fluoride can react with other ingredients in the sample, such as calcium, thereby rendering it insoluble or "inactive". Therapeutically, there is a minimum level of fluoride a dentifrice may contain below which it is not considered clinically effective. With products containing MFP, it is important to measure the soluble fluoride species to determine the active fluoride level. Although other methods have been previously described [5–7], a new method is now illustrated.

An SCIC system with an HNO_3 eluent with additional NO_3^- driving ion, separates fluoride, orthophosphate and monofluorophosphate. A low pH is necessary to determine MFP as a monovalent ion. Under basic conditions, MFP is divalent and too strongly retained to be determined with the weakly retained fluoride. Sample preparation is designed to keep the extractant/sample ratio as low as practically possible to mimic the actual process a consumer would use while brushing. An example of the chromatography is given in Fig. 5.

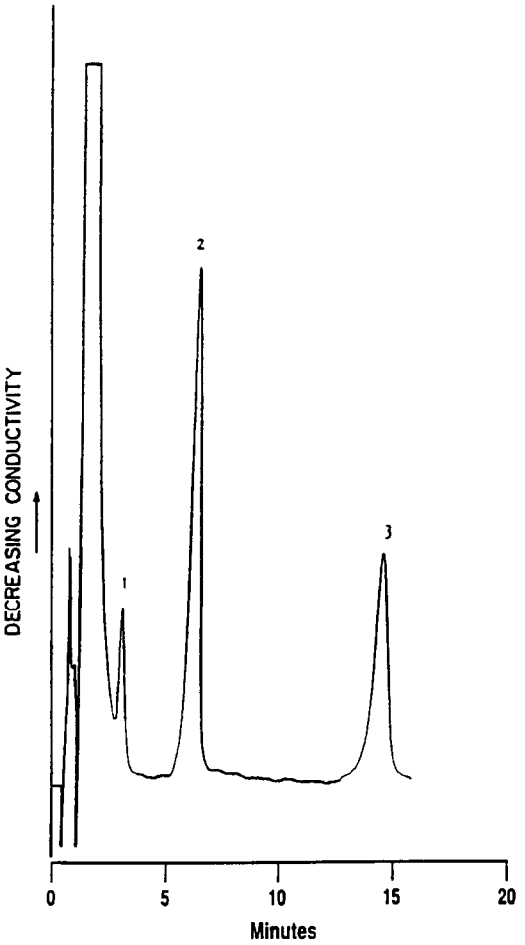

Fig. 5. Fluoride and monofluorophosphate in toothpaste. Sample preparation is 2 g sample with 10 ml water ; mix vigorously for 1–2 min; centrifuge; dilute 2.0 ml to 20 ml; filter through 0.45-μm filter. Conditions as in Fig. 2. Peaks: 1 = fluoride; 2 = orthophosphate; 3 = monofluorophosphate.

PYROPHOSPHATE IN TARTAR CONTROL DENTIFRICES

Pyrophosphate is an excellent hard surface cleaner. The sodium and potassium salts of pyrophosphate are used in a variety of products, such as multipurpose cleaners and automatic dishwasher detergents. In toothpaste, pyrophosphate functions as a tartar control agent.

Since multivalent phosphate species require strong eluents to elute them in a reasonable time, conductivity detectors are not always useful due to the high eluent conductivity [8,9]. For some phosphate species, conductivity detection can be used if the level of the phosphate to be determined is sufficiently large. For our purposes, the simplest system seemed to work adequately. To lower the valency of the pyrophosphate [10], an acidic mobile phase is used, 0.03 *M* HNO_3. With an enormously high conductivity of over 7000 μS, this eluent would seem inappropriate for SCIC. However, because inverse conductivity is used and the level of pyrophosphate in the sample is high enough, excellent results can be obtained without the need for a post column reaction. Fig. 6 illustrates the determination of pyrophosphate in a commer-

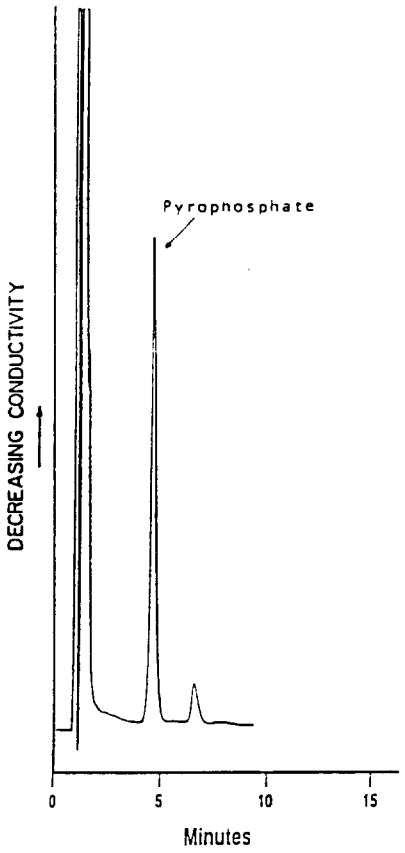

Fig. 6. Pyrophosphate in tartar control toothpaste. PRP-X100 column is used with 0.03 *M* HNO_3 eluent. Flow is 2 ml/min. Indirect conductivity detection is used at 100 μS f.s. Sample is 3% (w/v) solution of toothpaste through 0.45-μm filter.

cially available toothpaste. Sample preparation is simple and the run time is under 10 min.

This scheme will work for tartar control dentifrices containing bicarbonate as well. The sample solution must be slightly less concentrated, approximately 1.0–1.5% (w/v) solution, to minimize the effect of the bicarbonate. Unless additional sensitivity is required, sample pretreatment to completely remove the bicarbonate is not necessary due to the strength of the eluent and the strong retention of the pyrophosphate. If increased sensitivity is a requirement, a more concentrated solution of a bicarbonate-based dentifrice can be prepared and passed through a MilliTrap-H^+ cartridge prior to injection. This is contrary to the determination of fluoride, which necessitated the complete removal of bicarbonate due to the weakness of the fluoride retention and the corresponding eluent strength necessary to determine the weakly retained species.

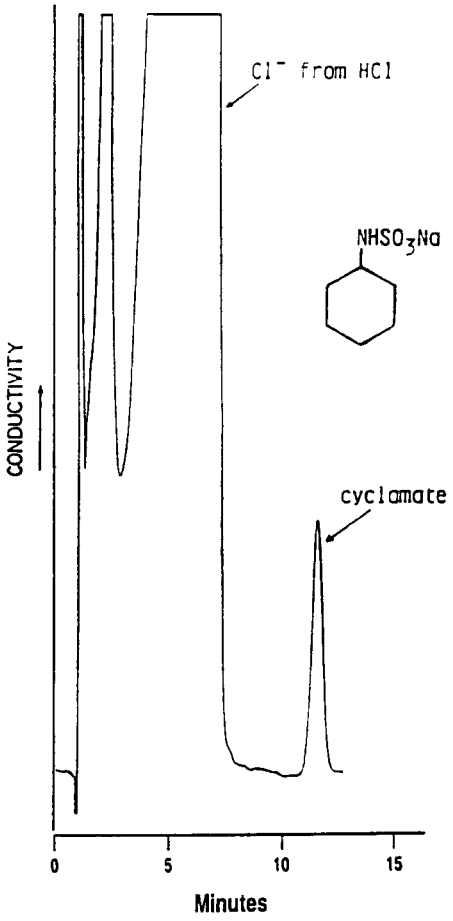

Fig. 7. Cyclamate in dentifrice manufactured in Canada. Vydac 302IC4.6 column with 5 m*M* phthalic acid–methanol (90:10) eluent. Flow is 2 ml/min with direct conductivity detection at 10 μS f.s.

CYCLAMATE IN CANADIAN DENTAL CARE PRODUCTS

Sodium cyclamate is widely used as a sweetener in dentifrices sold in Canada. Unlike its chromophoric counterparts, sodium saccharin and aspartame, it has no appreciable UV absorbance. Being anionic, a sodium salt of a sulfamic acid, it is amenable to ion chromatography and detectable using a conductivity detector. A silica-based anion exchanger, a Vydac 302IC4.6, is used with a phthalic acid–methanol mobile phase. For most products, sample preparation is simply a 1% (w/v) aqueous slurry, filtering any insolubles prior to injection. For bicarbonate-based products, additional sample preparation is necessary. In this particular case, lowering the pH to 2–3 with a minimum amount of 6 *M* HCl proved to be rapid and effective. Though this works well for cyclamate, it will not work for weakly retained anions. Adding an acid to reduce pH inevitably adds a huge amount of the acid anion, in this case, chloride. Most often this will obscure the analyte peak. Cyclamate is strongly retained in this system and the chloride peak, though extremely large, returns to baseline well before the elution of the analyte (see Fig. 7). If HNO_3 or H_2SO_4 were used instead of HCl, the cyclamate peak would be obscured due to the stronger retention and subsequent later elution of nitrate and sulfate.

LAUNDRY DETERGENTS

Ethanolamines are added to liquid laundry detergents as buffering agents. They can be determined by gas chromatography or IC, each method having its own advantages and disadvantages. For our purposes, it was found that ethanolamines can be determined under conditions typical for monovalent cation analysis using the Wescan Cation S column and inverse conductivity detection. Additionally, an entire monovalent cation profile is obtained, giving valuable information as to product formulation. Figs. 8 and 9 illustrate the differences in product composition between competitive brands of liquid laundry detergent. A mixture of ethanolamines was apparently used in the product shown in Fig. 8. Triethanolamine (TEA) is the predominant species, although small amounts of diethanolamine (DEA) and monoethanolamine (MEA) can be detected. The product illustrated in Fig. 9 contains only MEA. Potassium in the formulation can be determined as well. Its presence is due to the use of potassium citrate as a sequestrant.

SILICATE/FORMATE IN LIQUID LAUNDRY DETERGENTS

Silicate is also used as a buffering agent in liquid laundry detergents. Formate is used as an enzyme stabilizer. Both can be determined under similar conditions using a sodium hydroxide–sodium benzoate eluent with the Hamilton PRP-X100 column. Figs. 10 and 11 illustrate the determination of silicate and formate, respectively, in liquid laundry detergents. In each case, sample preparation is simple, requiring only a 0.5% (w/v) dilution in deionized water followed by filtration.

CITRATE IN LAUNDRY DETERGENTS

Citrate is used as a sequestrant in both powdered and liquid laundry detergents.

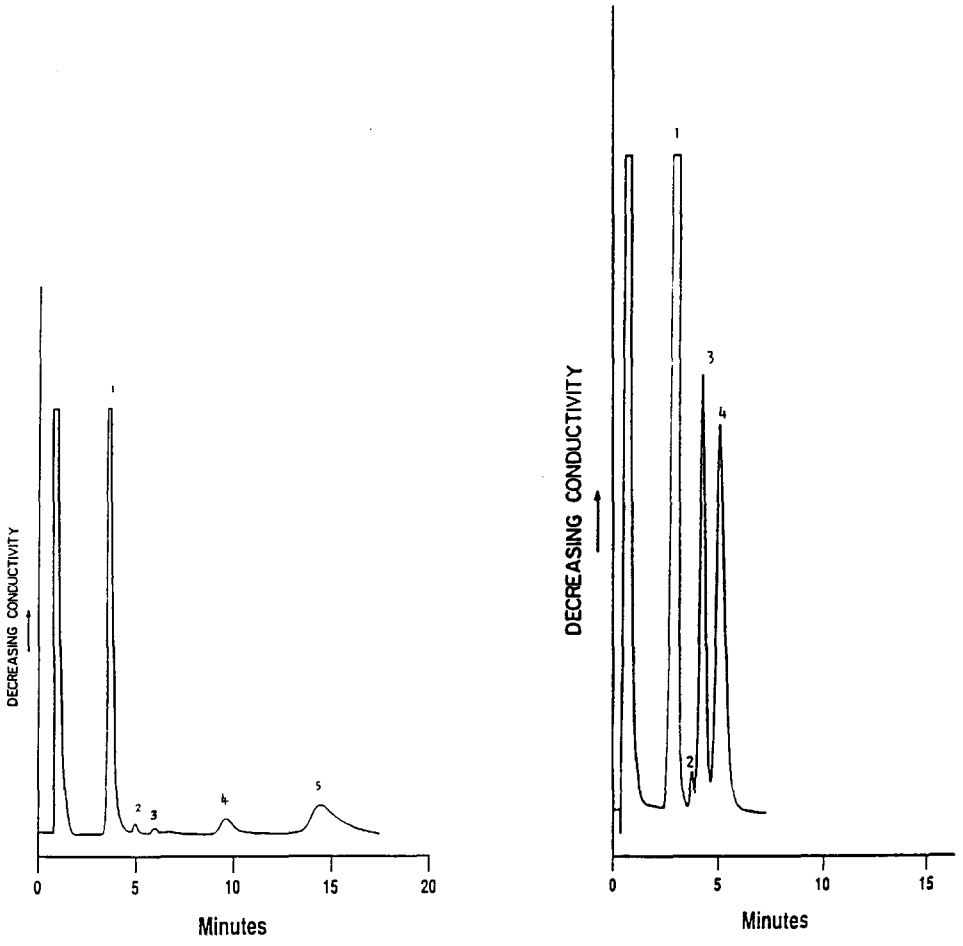

Fig. 8. Ethanolamines in liquid laundry detergent. Wescan Cation S column is used with 3 m*M* HNO_3 eluent. Flow is 1.5 ml/min. Indirect conductivity detection at 10 μS f.s. is used. Sample is 0.1% (w/v) solution. Peaks: 1 = Na^+; 2 = NH_4^+; 3 = MEA; 4 = DEA; 5 = TEA.

Fig. 9. Ethanolamines in liquid laundry detergent. Conditions as in Fig. 8. Peaks: 1 = Na^+; 2 = NH_4^+; 3 = K^+; 4 = MEA.

It can be determined by many methods including ion exclusion and ion exchange. Of the methods we have evaluated, the following has the distinct benefits of easy sample preparation, good resolution and excellent sensitivity [11]. Fig. 12 illustrates the determination of citrate in powdered laundry detergent using the Vydac 302IC4.6 anion column. A phosphate buffer is used as eluent along with UV detection at 220 nm.

SODIUM LAURATE IN LIQUID LAUNDRY DETERGENTS

Sodium laurate, $C_{12}H_{23}O_2Na$, is a relatively large organic anion added to a brand of liquid laundry detergent as a hardness control agent. It can be determined by

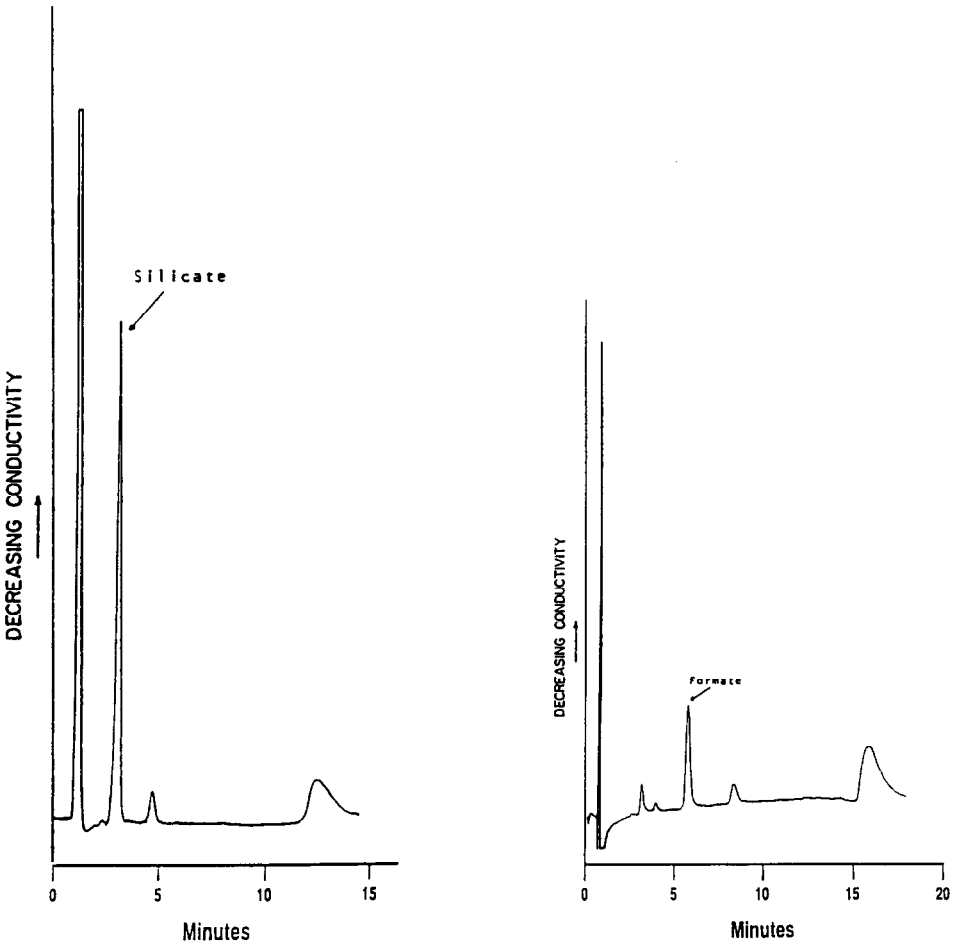

Fig. 10. Silicate in liquid laundry detergent. PRP-X100 column is used with 3.5 m*M* NaOH–0.5 m*M* sodium benzoate eluent. Flow is 2 ml/min with indirect conductivity detection at 10 μS f.s.

Fig. 11. Formate in liquid laundry detergent. Conditions as in Fig. 10.

gas chromatography as well as liquid chromatography. Gas chromatography requires more sample handling, however, as the sodium salt must first be converted to the fatty acid prior to analysis. Attempts at determining sodium laurate on a low-capacity anion exchanger were unsuccessful. Due to its hydrophobic character and low charge to size ratio, reversed-phase ion pairing was chosen. A Supelco LC-C8 reversed-phase column was used along with an eluent of methanol and water. Ammonium acetate was used as the ion pairing agent. Conductivity detection was used due to the lack of UV absorbance of the laurate. Fig. 13 illustrates this procedure.

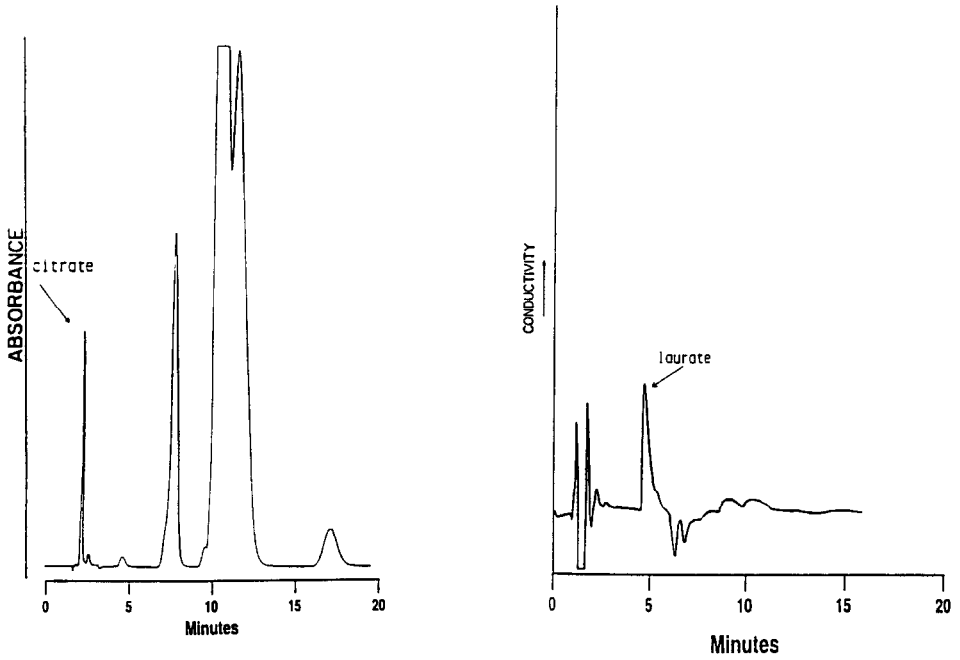

Fig. 12. Citrate in laundry detergent. Vydac 302IC4.6 column is used with 0.1 *M* KH_2PO_4–acetonitrile (90:10), pH 3.2 at 2 ml/min. UV detection at 220 nm is used. Sample is 1% (w/v) solution.

Fig. 13. Sodium laurate in liquid laundry detergent. A Supelco LC-C8 column is used with methanol–water (60:40) and 0.01% ammonium acetate eluent at 1 ml/min. Conductivity detection at 10 μS f.s. is used. Sample is 0.1% (w/v) solution.

ETHANOL AND GLYCERINE IN MOUTHWASH

Both ethanol and glycerine are major ingredients in almost all of the leading brands of mouthwash. Both can be determined by gas chromatography using a suitable thermal gradient. Ion-exclusion chromatography is another alternative, if an anion-exchange precolumn is added in-line immediately prior to the ion-exclusion column. This is done to eliminate an unknown matrix interference found in the mouthwash samples. Without this precolumn, a substantial negative peak appears close to the retention time of glycerine. Quantitative determination is not possible with this interference. The anion precolumn removes this interference.

As discussed earlier, dilute HNO_3 eluents can be useful in determining certain anions with the Hamilton PRP-X100 column. Since the Wescan Anion/R guard column has the same basic chemistry as the PRP-X100, being a resin-based anion exchanger, it was thought that a different retention mechanism in addition to ion exclusion may alter the retention time of these interfering components. Such was found to be the case as these compounds are apparently strongly bound or completely adsorbed by the precolumn. An illustration of the separation is found in Fig. 14.

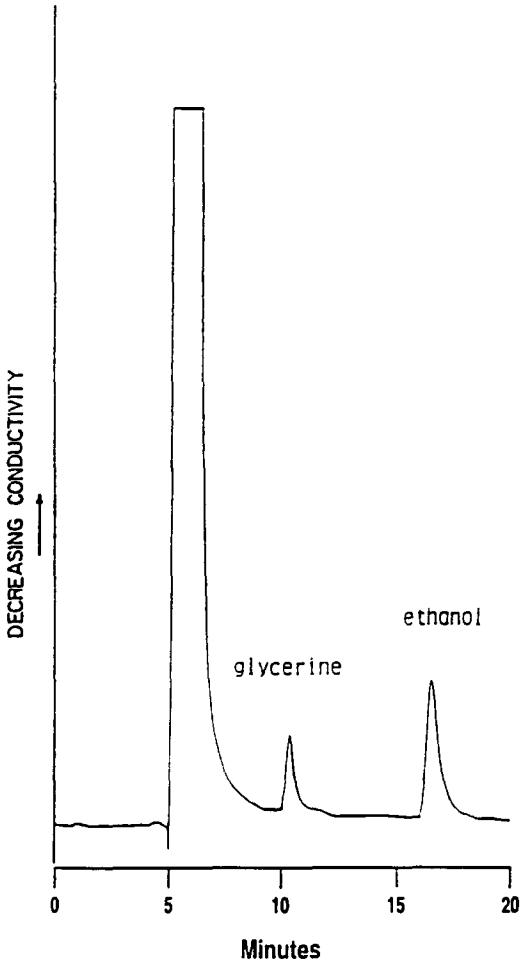

Fig. 14. Glycerine and ethanol in mouthwash using ion-exclusion chromatography. Wescan anion exclusion column No. 269006 with Anion/R Guard precolumn with 4 mM HNO_3 eluent at 0.75 ml/min. Indirect conductivity detection at 10 μS f.s. is used. Sample is 5% (w/v) solution.

CETYLPYRIDINIUM CHLORIDE IN MOUTHWASH

Cetylpyridinium chloride (CPC) is an antibacterial agent added to mouthwash at approximately 0.05%. It is a large organic cation, as shown in Fig. 15. Though opposite in charge, it is similar to sodium laurate in that the charge to molecular size ratio is small, and the large alkyl group adds significant hydrophobic character. Attempts at determining this species using a low capacity cation exchanger were unsuccessful. Instead, an ion-pairing reversed-phase separation was found to work extremely well [12]. Retention of CPC using a C_{18} or C_8 column was found to be too great for short run times even when a large percentage of organic modifier was used in the eluent. A less hydrophobic column, a cyano column was used (Supelco LC-CN,

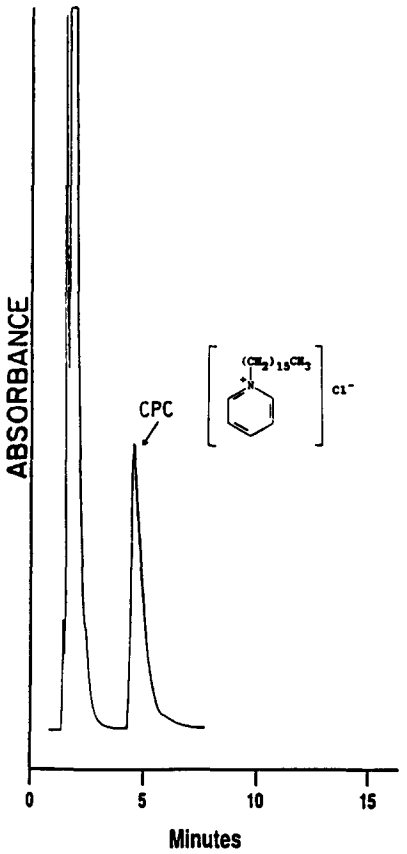

Fig. 15. Cetylpyridinium chloride in mouthwash. Supelco LC-CN column with methanol–water (90:10) and 0.065 *M* acetate (pH 6) is used at 1 ml/min. UV detection at 254 nm is used.

150 × 4.6 mm). This column still required the use of 90% methanol for short analysis time. Sample preparation is simple, a 10% (w/v) solution in methanol–water (90:10). Sensitivity is excellent due to the strong UV absorbance of the CPC cation. Accuracy is more than adequate. Some products contain CPC at 500 ppm, others at 450 ppm. With this method one can quickly and easily distinguish between the two.

NICOTINIC ACID AND NIACINAMIDE

Both nicotinic acid and niacinamide are B complex vitamins. They are used as enriching agents in flour and rice, as nutritional supplements and are even found in at least one commercially available shampoo.

Both have been determined by high-peformance liquid chromatography, although resolution between the two peaks is sometimes difficult to attain and both species respond similarly to changes in organic modifier concentration in the mobile phase. Nicotinic acid can be determined using ion chromatography under a variety of conditions. If niacinamide is present, hydrolysis to nicotinic acid is accomplished

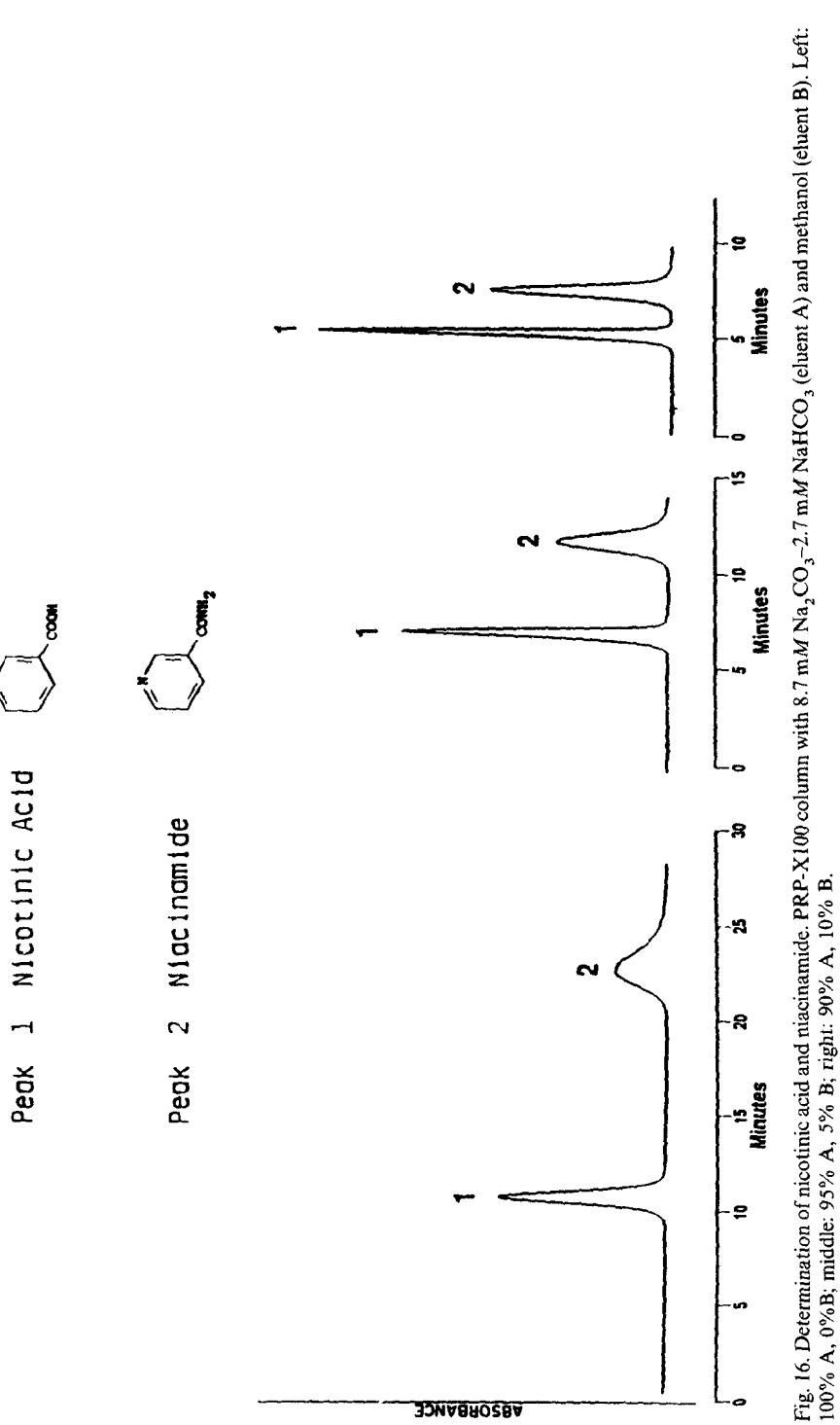

Fig. 16. Determination of nicotinic acid and niacinamide. PRP-X100 column with 8.7 m*M* Na_2CO_3–2.7 m*M* $NaHCO_3$ (eluent A) and methanol (eluent B). Left: 100% A, 0%B; middle: 95% A, 5% B; right: 90% A, 10% B.

using HCl and heat. For our determination, a Hamilton PRP-X100 column was used along with a bicarbonate–carbonate eluent typically used with chemically suppressed detection. Background eluent suppression was unnecessary, however, since UV detection at 263 nm was used.

Upon trying to determine conditions for the complete hydrolysis of the amide to the acid, two peaks were observed in the chromatogram: the first at 10 min, the second at 22 min. The first was easily identified as nicotinic acid using a standard solution. As more severe hydrolysis conditions were used, the nicotinic acid peak grew larger, the second peak smaller. Injection of a niacinamide standard revealed the second peak to be, in fact, niacinamide. The novelty of this separation lies in the fact that under the specified conditions, nicotinic acid is an anion, whereas niacinamide is a neutral species. It was thought that the retention of the amide was due to a hydrophobic interaction with the polymeric support of the column. This was later confirmed by adding an organic modifier (methanol) to the eluent. The addition of 10% methanol to the mobile phase resulted in a threefold decrease in the retention time of niacinamide. At the same time, a similar though less dramatic decrease in retention was observed for the nicotinic acid peak. The retention time of the acid was halved with the addition of 10% methanol to the eluent. Fig. 16 illustrates the effect of the methanol addition to the mobile phase.

A dual mechanism of ion exchange and adsorption is apparently responsible for the retention of the nicotinic acid. This has been observed previously with other organic acids under similar conditions [13]. Organic acids that have a hydrophobic center will exhibit retention due to adsorption with the polymeric support of the column [2]. The retention mechanism of the niacinamide is apparently solely due to adsorption. This method gives the chromatographer a great deal of control in the separation of these two species. Since UV detection is used, it is as sensitive as other high-performance liquid chromatography techniques using the same detection mode, yet affords the analyst great flexibility as to how the final chromatogram will appear.

CONCLUSIONS

Ion chromatography is an extremely useful and flexible tool for the analysis of household consumer products. Many species can be determined in very diverse sample matrices using IC, reversed-phase ion-pairing or ion-exclusion chromatography (IEC). Matrices containing bicarbonate or carbonate pose an additional challenge to the analyst. These products can generally be analyzed using: (1) chemically suppressed IC, (2) sample pretreatment with ion-exchange resin, MilliTrap-H^+, or acidification, (3) an appropriate dilution of the sample if strongly retained analytes of sufficient detectability are to be determined.

The Hamilton PRP-X100 column with a bicarbonate–carbonate eluent provides some interesting separations, including the separation of a neutral species due to a hydrophobic interaction of that compound with the polymeric support of the column.

ACKNOWLEDGEMENT

The author wishes to thank Laura Doskoczynski for her valuable contributions to the development of the method for nicotinic acid and niacinamide.

REFERENCES

1 D. T. Gjerde, in P. Jandik and R. M. Cassidy (Editors), *Advances in Ion Chromatography*, Vol. 2, Century International, Franklin, MA, 1990, p. 171.
2 F. F. Cantwell and S. Puon, *Anal. Chem.*, 51 (1979) 623.
3 *U.S. Pharmacopeia (USP) XXII*, United States Pharmacopeial Convention, Rockville, MD, 1990, p. 1252.
4 H. Small, *Ion Chromatography*, Plenum Press, New York, 1989, p. 139.
5 J. J. Potter, A. E. Hilliker and G. J. Breen, *J. Chromatogr.*, 367 (1986) 423.
6 S. S. Chen, H. Lulla, F. J. Sena and V. Reynoso, *J. Chromatogr. Sci.*, 23 (1985) 355.
7 J. S. Fritz, D. L. DuVal, L. Dean and R. E. Barron, *Anal. Chem.*, 56 (1984) 1177.
8 A. W. Fitchett and A. Woodruff, *LC Mag.*, 1 (1983) 48.
9 T. L. Chester, C. A. Smith and S. Culshaw, *J. Chromatogr.*, 287 (1984) 447.
10 H. Small, *Ion Chromatography*, Plenum Press, New York, 1989, p. 226.
11 D. R. Jenke, *Anal. Chem.*, 56 (1984) 2468.
12 R. C. Meyer and L. T. Takahashi, *J. Chromatogr.*, 280 (1983) 159.
13 T. A. Walker, T. V. Ho and N. Akbari, in P. Jandik and R. M. Cassidy (Editors), *Advances in Ion Chromatography*, Vol. 2, Century International, Franklin, MA, 1990, p. 271.