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On-line sample preparation techniques for ion chromatography

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Abstract

New on-line sample preparation techniques using electrochemically-regenerated ion suppression and sample neutralization are described. These techniques describe the removal of matrix interferences and the neutralization of acidic and basic samples before ion chromatographic analysis. Both methods treat samples on-line as they are being analyzed, simplifying sample preparation. Time and cost associated with off-line solid-phase extraction techniques are eliminated. The device for sample neutralization also can be used for on-line sample preconcentration of ultra-trace level samples for ppb and ppt levels detections. All sample pretreatment and concentration techniques described can be easily automated for continuous operation with any ion chromatography system. Several applications are presented to show the capabilities of on-line sample preparation. Linearity, reproducibility, and recovery data are presented. © 1998 Elsevier Science B.V.

Keywords: Sample preparation; Ion suppressor, electrochemically regenerated; Inorganic anions; Inorganic cations

1. Introduction

Sample preparation has been a growing area in chromatography over the past several years. Samples containing interfering substances can affect chromatographic performance. These substances may mask peaks of interest or irreversibly retain on the analytical column, permanently damaging the column. To eliminate these problems, such samples need to be treated before injection.

Several sample preparation devices are commercially available. The most widely used are packed bed solid-phase extraction (SPE) cartridges [1]. This technique is easy to use and requires only small sample volumes. A variety of stationary phases are readily available to solve many matrix interference problems. The use of SPE cartridges to eliminate matrix interferences in ion chromatography (IC) has been discussed previously [2,3]. The cartridges are packed with neutral and functionalized resins that remove matrix acids, bases, halides, sulfates, or hydrophobic components that would otherwise interfere with analysis of the components of interest. Membrane-based SPE disks are also available and use the same functionalized resins permanently enmeshed in a polytetrafluoroethylene (PTFE) filter membrane [4].

The above SPE techniques are done off-line, requiring extra time and labor. Each sample is passed manually through the cartridge or disk with a syringe and then injected to the ion chromatograph. Since each cartridge or disk is discarded after processing just one sample, this technique can be expensive over time.

This article describes new on-line methods for sample preparation using two different devices. One of the two devices is an electrochemically regenerated ion suppressor (ERIS Autosuppressor) which is commonly used for improving detection sensitivity of anions and cations in IC [5,6]. This self-regenerat-

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ing suppression device uses the detector effluent to electrochemically regenerate the suppressor. This article describes its application for removing components that would damage the analytical column.

The second on-line method describes the usage of a sample concentrator and neutralizer (SCAN Sample Processor), a derivative of the ERIS Autosuppressor. This technique neutralizes acidic or basic samples before ion analysis with an on-line ion-exchange neutralizer cell. Upon sample neutralization, the neutralizer cell is then regenerated by the previously described electrochemical process [5,6]. The same device also can be used for the preconcentration of trace level samples for increased sensitivity. Applications of both ERIS Autosuppressor and SCAN Sample Processor for sample pretreatment along with analytical data such as reproducibility, linearity, and recovery are presented.

2. Experimental

2.1. Instrumentation

The IC System used was the Alltech (Deerfield, IL, USA) Odyssey System. The system consists of a Model 526 HPLC Pump, 530 Column Heater, ERIS 1000HP Autosuppressor, and 550 Conductivity Detector. The sample neutralization and concentration were performed with the SCAN 1000 Sample Processor. The analytical columns used for the anion separations were the Allsep Anion (100×4.6 mm) and the Sarasep AN1 (250×4.6 mm) (Sarasep, Santa Clara, CA, USA). The concentrator column used for the anion analysis was the Anion Concentrator column (7.5×4.6 mm) and the ERIN (Electrochemically Regenerated Ion Neutralizer) cell packed with cation-exchanger in the hydrogen form was used to neutralize the basic samples. Cation separations were performed with the Universal Cation (100×4.6 mm) column. The concentrator column used for the cation analysis was the Cation Concentrator column (7.5× 4.6 mm) and the ERIN cell packed with anion-exchanger in the hydroxide form was used to neutralize the acidic samples. The organic acid separation was performed using the Bio-Rad Aminex HPX-87H (300×7.8 mm) (Bio-Rad, Hercules, CA, USA). All data were recorded using the TSP 4400 Chromjet integrator (Thermo Separation Products, San Jose, CA, USA).

2.2. Reagents

Standards and mobile phase buffers were prepared from reagent-grade chemicals obtained from Aldrich (Milwaukee, WI, USA). Solutions were made by dilution of these chemicals in 18.2 MΩ water, obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA).

2.3. Procedures

2.3.1. Sample pretreatment to protect analytical columns

Sample treatment before ion analysis is necessary to protect expensive analytical columns. An example of this is the determination of organic acids on a high-capacity sulfonic acid cation-exchange column. Many organic acid samples contain high concentrations of transition metals. These metal ions will contaminate the column packing, causing a gradual loss in capacity and eventually, column failure. Therefore, the removal of these metal ions will dramatically increase column lifetime. This report focuses on an on-line SPE technique for organic acid analysis using the ERIS Autosuppressor.

In this report, the suppressor is placed between the injection valve and the analytical column. Therefore, it acts as a sample preparation device for removing components that would damage the analytical column. In this case, transition metals in organic acid samples can bind to the cation-exchange sites lowering the capacity of the column. Fig. 1 shows the ERIS Autosuppressor valve configuration. ERIS Autosuppressor has cells that are packed with strong cation-exchanger in the hydrogen form. When the sample passes through a suppressor cell, transition metals are retained on the cell and removed from the sample. In effect, the ERIS Autosuppressor acts as an electrochemically regenerated guard column. The components of interest (organic acids) pass through the suppressor cell unchanged. While one cell is removing the metals from the sample, the other cell is electrochemically regenerated. The electrochemical regeneration process was described previously [5]. The valve configuration within the ERIS Au-

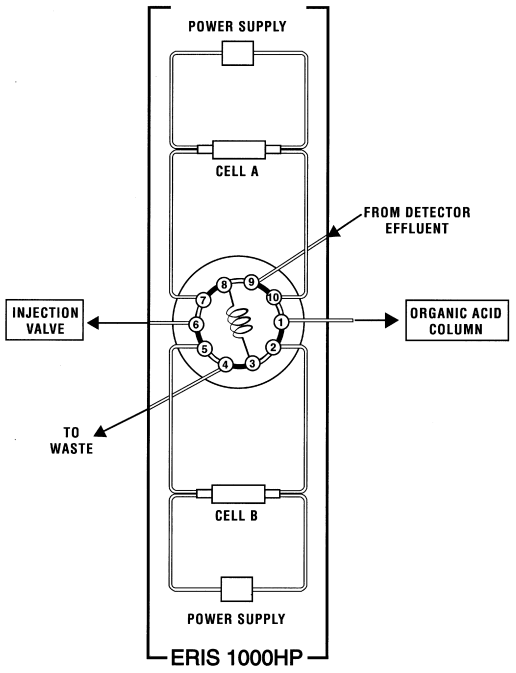

Fig. 1. The valve configuration for the ERIS autosuppressor. The shaded and unshaded portions within the valve diagram represent which ERIS cell is in use. If the sample follows the shaded portion then cell B is treating the sample. Cell A is treating the sample when the unshaded portion is in use.

tosuppressor allows for endless cycling between two suppressor cells for continuous operation.

2.3.2. Sample neutralization

Some samples, such as concentrated acids or bases, are high in acidic or basic content. However, it still may be important to analyze the ionic content of these samples. If so, then some sort of sample neutralization must be performed, otherwise the high H^+ or OH^- ions will cause large baseline shifts, masking the peaks of interest. A focus of this report is to determine the concentrations of anions and cations in concentrated bases and acids respectively.

The SCAN Sample Processor is a dual-purpose instrument, designed for **s**ample **c**oncentration **a**nd **n**eutralization (SCAN). It is installed between the analytical column and the autosampler. It uses an electrically-actuated ten-port valve, a concentrator column, a neutralization cell, and a constant current power supply. The neutralization cell is used to neutralize acidic and basic samples. The cell is packed with either anion or cation-exchange resin, depending upon the application.

Fig. 2 shows the liquid flowpath of the on-line application. An autosampler loads sample into a sample loop (a manual injection valve also may be

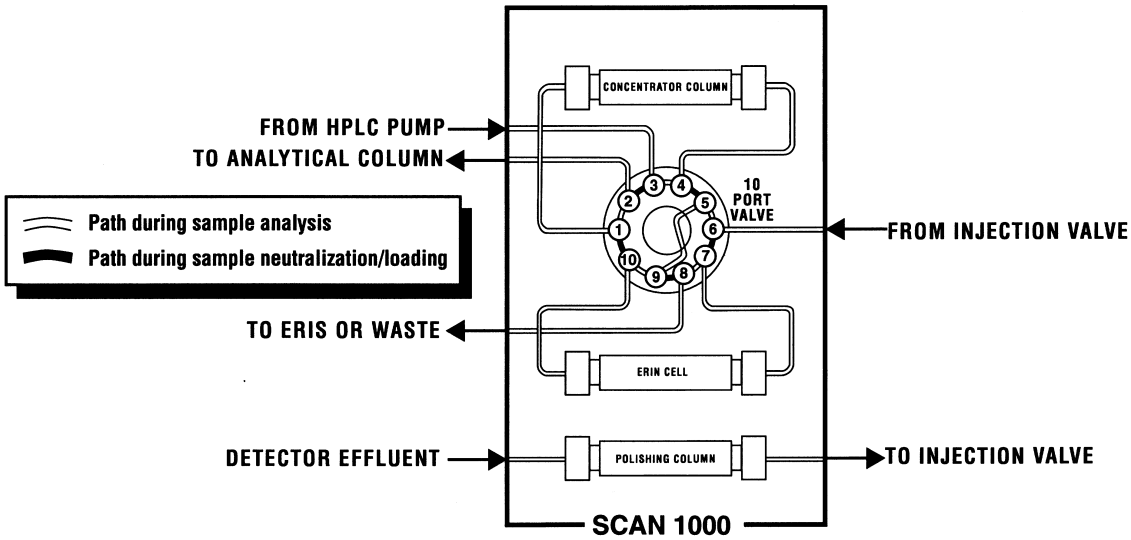

Fig. 2. The valve configuration for the SCAN 1000 sample processor. The shaded portion of the valve diagram represents the liquid flowpath during sample neutralization/concentration. The unshaded portion shows the liquid flowpath during sample analysis.

used). Next, the IC system's detector effluent, which first flows through a polishing column to remove ionic contaminants, pushes the sample from the sample loop into the SCAN sample processor. The sample flows through the neutralizer cell and onto the concentrator column where the anions or cations from the sample are retained through ion-exchange. Next, the SCAN valve rotates, directing the mobile phase through the concentrator column, eluting the sample ions onto the analytical column and the rest of the IC system for separation and detection. During the separation process, the neutralizer cell is electrochemically regenerated back to its original form and equilibrated so it's ready to neutralize the next sample. This process is repeated for each sample. Fully automated, unattended operation is possible when an autosampler is used to load the sample.

2.3.3. Sample concentration

A final application described here is the analysis of low-level analytes by sample preconcentration. Sample preconcentration is a technique used to dramatically increase the sensitivity of the analytes of interest. Traditional sample concentration is performed by pumping a large volume of a dilute sample onto a short ion-exchange column that traps the analytes of interest while the rest of the sample flows to waste. Sample ions are then eluted from the preconcentration column onto an analytical column and the rest of the IC system for detection and/or quantification [7]. In this technique, the preconcentration column is installed within a six-port sample injection valve and the sample is delivered onto the column with a pump.

A new sample preconcentration technique is described which uses the SCAN Sample Processor. This new technique is simpler than traditional methods. The instrument setup is the same as in Fig. 2 with the exception that a union is used in place of the neutralization cell and the electrochemical regeneration process doesn't take place. The instrument works in the same manner as in the neutralization mode. A large volume of sample is loaded into the sample loop either manually or with an autosampler. The deionized, polished detector effluent is used to push the sample from the sample loop to the sample concentrator. The sample is directed to the concentrator column where the anions or cations are retained by ion-exchange. The SCAN valve then rotates directing mobile phase through the concentrator column, eluting the sample ions onto the analytical column and the rest of the IC system for separation and detection.

3. Results and discussion

3.1. Sample pretreatment to remove components that would damage an analytical column

Organic acid columns are easily damaged by samples containing transition metals. Traditionally, a guard column or off-line SPE products are used to remove these metals from the sample before they reach the column. The electrochemically regenerating ion suppression technique simplifies the sample pretreatment process by removing the sample contaminants on-line. The ERIS Autosuppressor acts as electrochemically regenerated guard column. The suppressor cell is electrochemically regenerated after each analysis, purging accumulated sample contaminants to waste. Each sample sees a fresh cell that has maximum removal capacity. The suppressor cell dimensions are optimized to minimize dead volume. Fig. 3a and b show the organic acid chromatograms without and with treatment of the sample using ERIS Autosuppressor. Identical chromatograms are obtained, demonstrating that the ERIS Autosuppressor doesn't cause significant band-broadening. In Fig. 3a, a good separation is obtained even though the sample was not treated. However, under these conditions, column performance degrades with each injection as transition metals build-up on the packing. Columns typically fail after two weeks of use. A single column is still operating after eight months of continuous use with the new electrochemically regenerated ion suppression technique.

3.2. Sample pretreatment to neutralize basic samples

Analyzing anions in basic samples is often difficult because high matrix hydroxide concentrations interfere with separation and detection. The described on-line sample neutralization method neutralizes samples containing high hydroxide concentra-

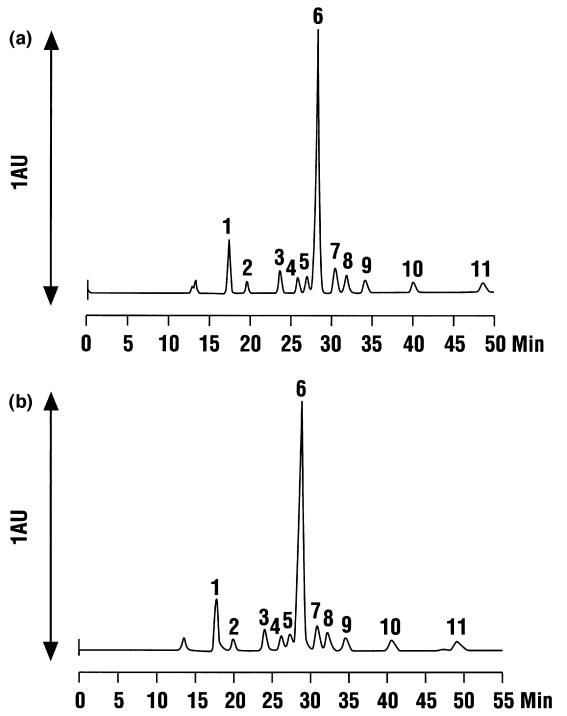

Fig. 3. (a) Untreated organic acids. Bio-Rad Aminex HPX-87H, 300×7.8 mm, mobile phase: 0.00125 *M* H_2SO_4, flow-rate: 0.5 ml min^{-1}, column temperature: 60°C, detector: UV at 210 nm. Peaks: 1=pyruvate; 2=malonate; 3=glycerate; 4=succinate; 5=glycolate; 6=lactate; 7=formate; 8=2hydroxybutyrate; 9=acetate; 10=propionate; 11=butyrate. (b) Treated organic acids. Conditions and peaks as in (a).

tions before anion analysis. A neutralizer cell packed with cation-exchanger in the H^+ form is used. As sample passes through the neutralizer cell, hydroxide in the sample is neutralized by the following acid–base reaction.

$$R\text{-}SO_3^-\text{-}H^+(\text{cell}) + M^+\text{-}OH^-(\text{sample}) \rightarrow R\text{-}SO_3^-\text{-}M^+ + H_2O$$

where M^+=cations. The countercations from the sample exchange with the hydrogen ions from the neutralizer cell. The released hydrogen ions react with the hydroxide from the sample to form water. The sample anions are converted to their acid forms and pass through the cell onto the concentrator column.

Fig. 4a and b show an application of on-line sample neutralization for analyzing a rock fusion

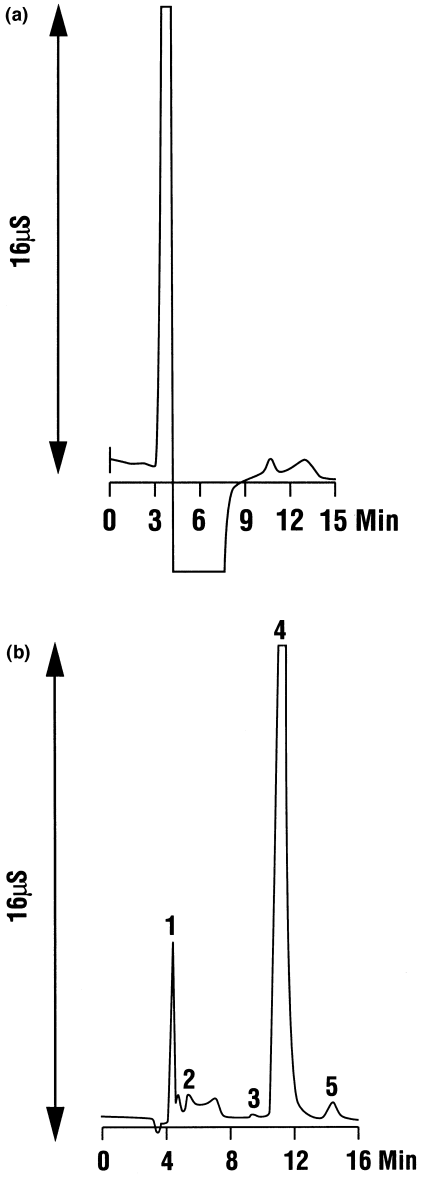

Fig. 4. (a) Untreated rock fusion sample. Sarasep AN1, 250×4.6 mm, mobile phase: 1.7 m*M* $NaHCO_3$–1.8 m*M* Na_2CO_3, flow-rate: 1.0 ml min^{-1}, detector: suppressed conductivity. (b) Treated rock sample. Conditions as in (a). Peaks: 1=fluoride, 4.5 ppm; 2=chloride, 2.5 ppm; 3=nitrate, 1.4 ppm; 4=phosphate, 723 ppm; 5=sulfate, 5.0 ppm.

sample where sodium hydroxide was used as the flux material in the fusion process. In the untreated sample, the high hydroxide concentration causes a large negative peak that interferes with the peaks of

interest. In the treated sample, the neutralizer cell neutralizes the matrix hydroxide before the sample enters the analytical column, making anion separation and detection possible. This analysis was done using a suppressor-based IC method. This sample pretreatment technique also works with single-column IC methods.

Table 1 shows recovery data of spiked anions in basic samples using the on-line sample neutralization technique. The data were obtained by comparing anion peak areas before and after the sample treatment. The neutralized sample was 0.5 *M* NaOH spiked with anion standards. All recoveries are reasonably good with the exception of the nitrite. The low nitrite recovery has been well documented [8]. In the presence of H^+, nitrite will form nitrous acid, HNO_2. In water, HNO_2, converts to nitric oxide and nitrate. As shown in Table 1 the nitrate recovery is greater than 100% probably from the nitrite oxidation to nitrate. The high recovery of chloride may be from contamination within the caustic matrix.

3.3. Sample pretreatment to neutralize acidic samples

Analyzing cations in acidic samples is often difficult because high matrix hydronium ion concentrations interfere with separation and detection. An on-line sample treatment technique can also be used to neutralize samples containing high hydronium ion concentration before cation analysis. A neutralizer cell packed with anion-exchanger in the OH^- form is used. As sample passes through the neutralizer cell, hydronium ion is neutralized by the following acid–base reaction.

$$R\text{-}(NH_3)_3^+\text{-}OH^-(\text{cell}) + H^+\text{-}X^-(\text{sample}) \rightarrow R\text{-}(NH_3)_3^+\text{-}X^- + H_2O$$

where X = anions. The counteranions from the sample exchange with the hydroxide from the neutralizer cell. The released hydroxide ions react with the hydronium ions from the sample to form water. The sample cations are converted to their hydroxide forms and pass through the cell onto the concentrator column.

Fig. 5a and b show an application of on-line sample neutralization for analyzing trace cations in 12 *M* HCl diluted 1:1 with deionized water. In the untreated sample, the high hydronium ion concentration causes a large negative peak that interferes with the peaks of interest. In the treated sample, the neutralizer cell neutralizes the matrix hydronium ions before the sample enters the analytical column, making cation separation and detection possible. This analysis was done using a single-column IC method. This sample pretreatment technique also works with suppressor-based IC methods.

Table 2 shows recovery data of spiked cations in acidic samples using the on-line sample treatment technique. The data were obtained by comparing cation standards before and after sample treatment. The neutralized sample was 0.9 *M* HCl spiked with cation standards. Excellent recovery and R.S.D. results were obtained for all of the cations analyzed.

3.4. Sample concentration to analyze trace anions and cations

Trace anions and cations in the low ppb and ppt levels can only be analyzed using preconcentration. Fig. 6 shows a chromatogram of trace anions in an ultrapure water sample obtained using on-line sample preconcentration. Sulfate and chloride are detected at less than 1 ppb. The on-line sample concentration technique uses the detector effluent to carry the sample to the concentrator column, eliminating the separate sample pump required for conventional preconcentration techniques. This new preconcentration technique is easily automated for unattended multisample runs. This technique is applicable for

Table 1
Recovery of spiked anions in NaOH

Anions (ppm)	Average recovery (% $n=5$)	R.S.D. (%)
Fluoride (1)	98	1.84
Chloride (2)	110	1.42
Nitrite (2)	84	3.18
Bromide (2)	93	2.68
Nitrate (2)	104	2.75
Phosphate (3)	86	3.62
Sulfate (3)	96	0.90

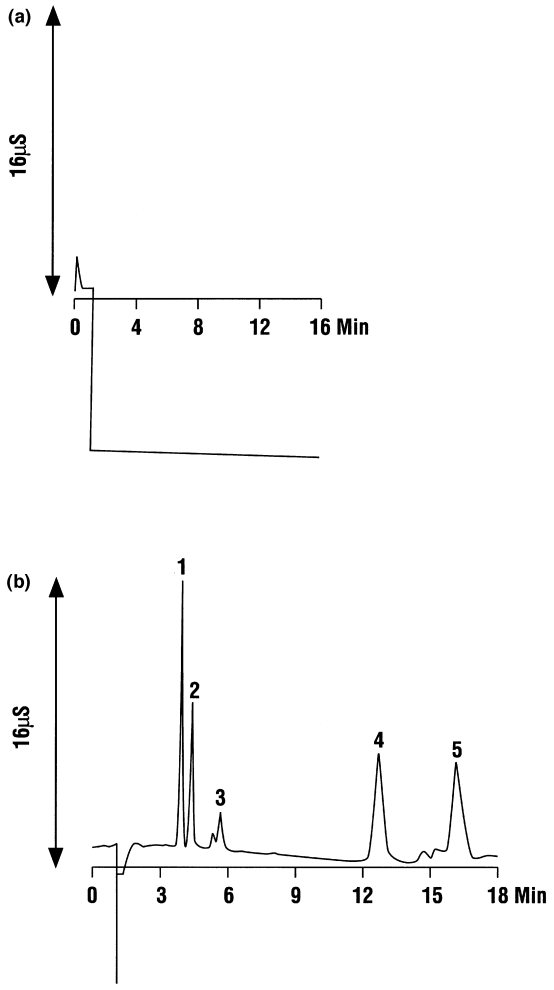

Fig. 5. (a) Untreated concentrated HCl. Universal Cation, 100×4.6 mm, mobile phase: 3 m*M* methanesulfonic acid, flow-rate: 1.0 ml min^{-1}, column temperature: 35°C, detector: conductivity. (b) Treated concentrated HCl. Conditions as in (a). Peaks: 1=sodium, 0.5 ppm; 2=ammonium, 0.3 ppm; 3=potassium, 0.2 ppm; 4=magnesium, 0.4 ppm; 5=calcium, 0.8 ppm.

Table 2
Recovery of spiked cations in HCl

Cations (ppm)	Average recovery (% $n=7$)	R.S.D. (%)
Lithium (0.2)	91	1.89
Sodium (1.5)	100	1.28
Ammonium (1.5)	94	3.52
Potassium (2.5)	99	2.67

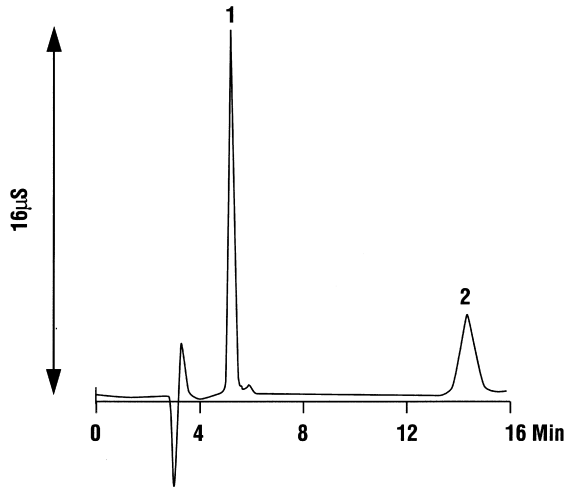

Fig. 6. Trace anions in ultrapure water. Sarasep AN1, 250×4.6 mm, mobile phase: 1.7 m*M* $NaHCO_3$/1.8 m*M* Na_2CO_3, flow-rate: 1.0 ml min^{-1}, detector: suppressed conductivity. Peaks: 1=chloride, 0.5 ppb; 2=sulfate, 0.5 ppb.

Table 3
Calculated detection limits using on-line sample preconcentration.

Anion	Detection limit (ppt)
Bromide	19
Nitrate	56
Phosphate	69
Sulfate	40

anion and cation analyses by both single-column and suppressor-based methods.

The linearity of anions using this concentration technique was studied by injecting different concentrations of different amounts of the anions studied. Injection volumes of 2.0 ml–4.0 ml were made with concentrations ranging from 5 ng ml^{-1} to 15 ng ml^{-1}. The anions which were studied were Br^-, NO_3^-, HPO_4^{2-}, and SO_4^{2-}. The linearity obtained based on seven injections was 0.9999, 0.9998, 0.9990, and 0.9987 respectively. Detection limits with 4 ml sample volumes are listed in Table 3. The detection limits are based on three times signal to noise ratio.

4. Conclusions

On-line sample preparation techniques offer many

advantages over traditional packed-bed solid-phase extraction devices. All three methods: on-line sample matrix interference removal, on-line sample neutralization, and on-line sample concentration are easily automated and eliminate costly, time-consuming off-line techniques. The suppressor and neutralizer cells are regenerated electrochemically, eliminating disposable SPE cartridge costs. Recovery data shows that on-line sample neutralization is an excellent method for the determination of anions or cations in bases and acids respectively. In addition, reproducibility was found to be excellent. Finally, sample preconcentration also can be performed on-line to give much better detection limits than direct injection IC.

References

[1] J. Horack, R.E. Majors, LC–GC 11 (1993) 74.
[2] R. Saari-Nordhaus, J.M. Anderson Jr., I.K. Henderson, Am. Lab. 22(8) (1990) 18.
[3] I.K. Henderson, R. Saari-Nordhaus san, J.M. Anderson Jr., J. Chromatogr. 546 (1991) 61.
[4] R. Saari-Nordhaus, L.M. Nair, J.M. Anderson Jr., J. Chromatogr. A. 671 (1994) 159–163.
[5] R. Saari-Nordhaus, J.M. Anderson Jr., Am. Lab. 28(3) (1996) 33N.
[6] L.M. Nair, R. Saari-Nordhaus, Am. Lab. 29(4) (1997) 33FF.
[7] A.L. Heckenberg, P.R. Haddad, J. Chromatogr. 330 (1985) 95.
[8] P.R. Haddad, S. Laksana, R.G. Simmons, J. Chromatogr. 640 (1993) 135.