

Elimination of matrix interferences in ion chromatography by the use of solid-phase extraction disks

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Abstract

The use of solid-phase extraction disks as a sample clean-up device is described. The disks contain a membrane composed of resin beads permanently enmeshed in a polytetrafluoroethylene membrane, housed in a medical-grade polypropylene housing. The resin within the membrane is functionalized to retain specific types of components from the sample. Several chemistries are developed to remove various interfering components. The recovery of the ions after sample treatment is examined.

1. Introduction

Ion chromatography (IC) has become a popular analytical method for the determination of anions and cations. The method is simple, fast, and requires minimum sample preparation. For most samples, only dilution and filtration are required before injection. In certain cases where the sample contains components that can damage the column, are too acidic or too basic, or one or more components are present in great excess, a more sophisticated technique is usually necessary to eliminate matrix interferences.

Solid-phase extraction (SPE) is one of the most common techniques for eliminating matrix interferences in chromatography [1]. It is easy to use, requires small sample volume, and a wide variety of stationary phases are available commercially in convenient disposable cartridges. In previous work, we discussed the use of SPE cartridges for eliminating matrix interferences in

IC [2,3]. These cartridges are packed with IC-grade resin functionalized to retain or neutralize certain components in the sample matrix. Matrix interferences such as acidic or basic solutions, high level of halides, or sulfates, or hydrophobic components are successfully eliminated using these cartridges. Two major drawbacks of the packed bed SPE cartridges are bed channeling and higher back pressure. Bed channeling results in non-uniform flow, reducing the full capacity of the cartridge. The narrow internal diameter of the cartridge sometimes causes high back pressure, complicating the sample clean-up process.

This paper examines the use of SPE disks as a sample clean-up device for ion chromatography. The disks contain a membrane composed of resin beads permanently enmeshed in a polytetrafluoroethylene (PTFE) membrane, housed in a medical grade polypropylene housing. The resin within the membrane is functionalized to retain specific types of components from the sample. Several chemistries are developed to remove various interfering components. The

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recovery of the ions after sample treatment is examined.

2. Experimental

2.1. Instrumentation

Chromatography was performed on an Alltech (Deerfield, IL, USA) IC system that consists of a Model 325 high-performance liquid chromatography (HPLC) pump, a Model 330 column heater, a 335 suppressor module, and a Model 350 conductivity detector. Sample introduction was done with a Model 9125 Rheodyne (Cotati, CA, USA) injector. All data were recorded on a Spectra-Physics (Santa Clara, CA, USA) SP 4400 Chromjet integrator. The Alltech Universal Anion column (150 mm × 4.6 mm) and the Alltech Universal Anion 300 columns (150 mm × 4.6 mm and 100 mm × 4.6 mm) were used to separate the anions.

Fig. 1 shows the construction of the SPE disk. The 25-mm membrane impregnated with ion-exchange media is housed in a medical-grade polypropylene housing. The inlet and outlet of the housing accepts a luer-hub syringe and needle, respectively. The ion-exchange capacity of the 25 mm disk is 1.5 mequiv. The membrane is rigid, eliminating the need for additional frits.

2.2. Reagents

Standards and eluent buffers were made from reagent-grade chemicals obtained from Aldrich

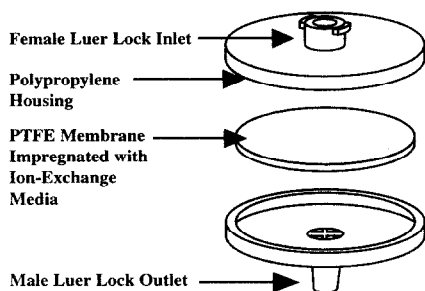


Fig. 1. The construction of the SPE disk.

Chemical (Milwaukee, WI, USA). Distilled deionized water was used throughout.

2.3. Procedure

Before applying sample, the disk is pre-conditioned by passing 5–10 ml of IC-grade water through the device using a luer-hub syringe. The sample (approximately 3 ml) is then passed through the disk at a flow-rate of 1.0 ml/min or less. The first 1 ml of the eluate is discarded to avoid partial dilution of the analytes. The remaining eluate is collected for analysis. The amount of contaminants that need to be removed from the sample must not exceed the total capacity of the disk. More than one SPE disk can be used in series to increase its capacity.

3. Results and discussion

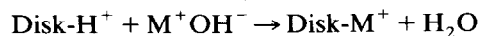
SPE disks are a new generation of solid-phase extraction device. They have been used widely for extracting environmental pollutants from aqueous matrices [4–6], and for the purification and separation of biological fluids [7]. This paper describes the first application of SPE disks for eliminating matrix interferences in ion chromatography.

The membrane disk used for the applications described here are composed of 60% cation-exchange resin and 40% PTFE. The resin is styrene–divinylbenzene with a sulfonic acid functional group. Three forms of SPE disks, cation exchange in the hydrogen, silver and barium form, are used for various applications. The ion exchange capacity for the 25-mm disk is 1.5 mequiv. Because of the styrene–divinylbenzene based resin, the membrane is stable from pH 1 to 14.

As sample is passed through the packing, specific chemical interactions take place which selectively retain certain components of the matrix while other components pass through unchanged. The chemical characteristics of the membrane determine which sample components are retained.

3.1. SPE disk in the H^+ form

The SPE disk in the H^+ form provides a reliable method to neutralize samples containing high concentration of hydroxide ions or to remove cations before anion analysis. The disk neutralizes hydroxide from the sample through an acid–base neutralization reaction:



where M^+ = cations. The cations from the sample exchanges with the hydrogen ion from the disk. The released hydrogen ion reacts with hydroxide to form water. Anions pass through the disk unchanged.

Fig. 2a and b show applications of the SPE disk in the H^+ form to neutralize hydroxide. The high hydroxide concentration in the process cleaning solution overloads the low-capacity column and masks the peaks of interest. It also causes a large system peak which requires almost 40 min to subside. After passing the sample through the disk, the hydroxide is neutralized to water and the fluoride, chloride, and sulfate can be quantitated easily. In Fig. 2b, a suppressor-based IC system was used. The high hydroxide concentration causes a large negative water dip, which interferes with the peaks of interest. After treatment with the IC- H^+ disk, the ions of interest are easily quantified.

SPE disk in the H^+ -form may also be used to remove excess cations from samples. Fig. 3 shows an application of SPE disk in the H^+ form to remove an amine. The high amine concentration interferes with the early eluting chloride peak and causes a large system peak. After treatment with the disk, the chloride and sulfate is easily quantified. The size of the system peak is also reduced.

3.2. SPE disk in the Ag^+ form

The SPE disk in the Ag^+ form provides a reliable method to remove or reduce excess halides from the sample before analysis of other anions. The silver contained on the membrane

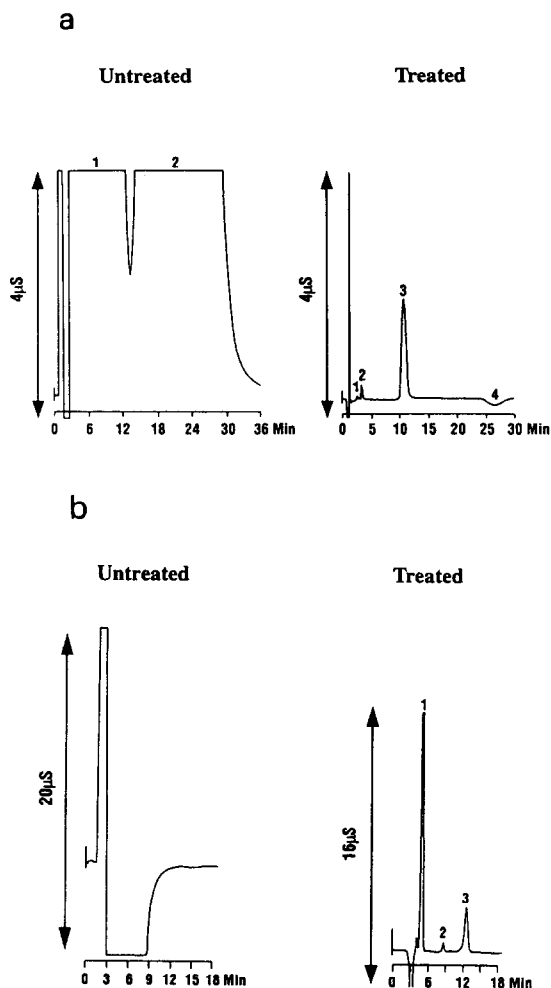
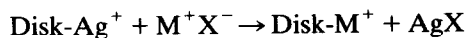


Fig. 2. (a) Process cleaning solution (ammonium hydroxide). Peaks: 1 = fluoride; 2 = chloride; 3 = sulfate; 4 = system peak. Column, Universal Anion (150 mm \times 4.6 mm); eluent, 4 mM phthalic acid, pH 4.5 with LiOH; flow-rate, 1.0 ml/min; detector, conductivity; injection volume: 100 μ l. (b) Battery electrolyte (potassium hydroxide). Peaks: 1 = chloride; 2 = nitrate; 3 = sulfate. Column, Universal Anion 300 (100 mm \times 4.6 mm); eluent, 1.7 mM NaHCO_3 –1.8 mM Na_2CO_3 ; flow-rate, 1.0 ml/min; detector, chemically suppressed conductivity; injection volume, 100 μ l.

functional group reacts with halides from the sample to form insoluble silver salts:



where $X = \text{Cl}, \text{Br}, \text{I}$. Anions that form insoluble or partially soluble silver salts such as chloride, bromide, iodide, and carbonate will be removed

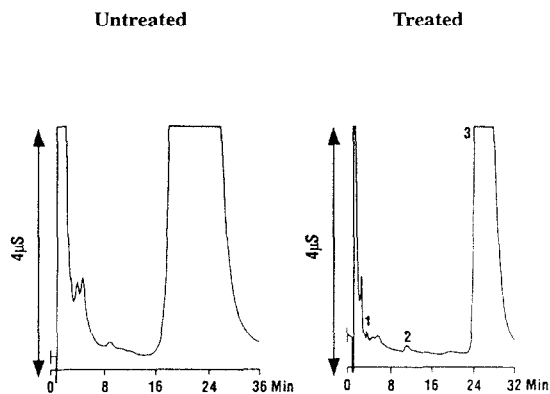


Fig. 3. Trace anions in technical grade hexamethylene tetramine. Peaks: 1 = chloride; 2 = sulfate; 3 = system peak. Column, Universal Anion (150 mm × 4.6 mm); eluent, 4 mM phthalic acid, pH 4.5 with LiOH; flow-rate, 1.0 ml/min; detector, conductivity; injection volume, 100 μ l.

completely or partially from the sample. Other anions such as fluoride, nitrite, nitrate, phosphate, and sulfate will pass through unchanged.

Fig. 4 shows an application of the SPE disk in the Ag^+ form in removing excess chloride. Chloride in the untreated sample masks the nitrate peak, making it impossible to quantitate. After the treatment, the nitrate and sulfate can be determined easily.

When carbonate–hydrogencarbonate eluent is used for the anion analysis using suppressor-based IC, the use of SPE devices in the Ag^+

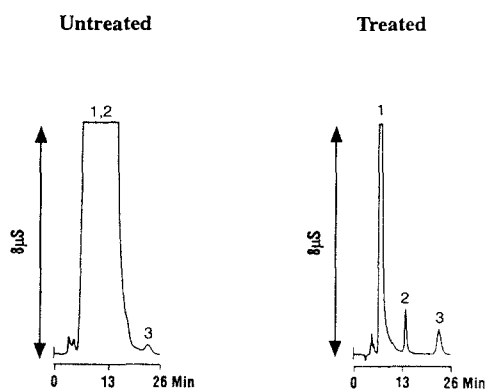
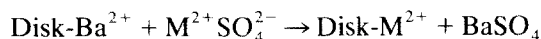


Fig. 4. Anions in HCl digest paper coating. Peaks: 1 = chloride; 2 = nitrate; 3 = sulfate. Column, Universal Anion 300 (150 mm × 4.6 mm); eluent, 1.7 mM NaHCO_3 –1.8 mM Na_2CO_3 ; flow-rate, 1.0 ml/min; detector, chemically suppressed conductivity; injection volume, 100 μ l.

form is not recommended. Since silver carbonate is sparingly soluble [8], the silver from the sample after the treatment process may form a precipitate in the analytical column. Since the amount of sample injected is very small, it will not block the column. However, when chloride or other halides are injected onto the column in subsequent analyses, the peak may disappear or the sensitivity may decrease due to the formation of silver halides in the column. Excess silver in the analytical column can be removed by passing dilute nitric acid through the column. For applications that require the use of the SPE devices in the Ag^+ form, non-suppressed IC methods should be used. If a suppressor-based IC method must be used, eluents other than carbonate–hydrogencarbonate should be used.

3.3. SPE disk in the Ba^{2+} form

The SPE disk in the Ba^{2+} form is used to remove sulfate before analysis of other anions. The sulfate is removed from the sample through the formation of barium sulfate:



where M = cations. Since barium phosphate is sparingly soluble, this disk may also reduce phosphate concentration if it is present in high concentrations. The concentration of other an-

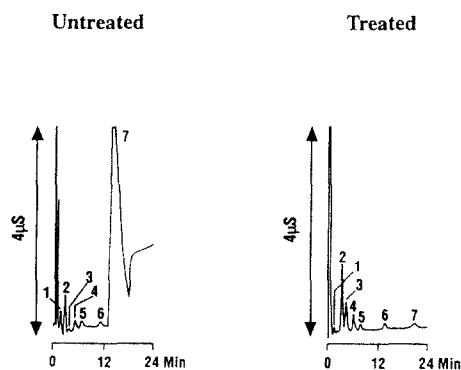


Fig. 5. Anions in battery acid. Peaks: 1 = fluoride; 2 = chloride; 3 = nitrite; 4 = bromide; 5 = nitrate; 6 = phosphate; 7 = sulfate. Column, Universal Anion (150 mm × 4.6 mm); eluent, 5 mM *p*-hydroxybenzoic acid, pH 7.9 with LiOH; flow-rate, 1.0 ml/min; detector, conductivity; injection volume, 100 μ l.

Table 1
Recovery of anions with SPE disks

Anions (mg/l)	Average recovery (%) (n = 3)	R.S.D. (%)
<i>SPE disk in the H⁺ form</i>		
Fluoride (10)	97	0.52
Chloride (20)	98	1.03
Nitrite (20)	40	3.78
Bromide (20)	102	0.91
Nitrate (20)	104	1.34
Phosphate (30)	86	1.21
Sulfate (30)	99	0.64
<i>SPE disk in the Ag⁺ form</i>		
Fluoride (5)	106	0.83
Chloride (500)	–	–
Nitrite (10)	97	1.32
Bromide (10)	–	–
Nitrate (10)	105	0.35
Phosphate (15)	93	1.41
Sulfate (15)	110	1.56
<i>SPE disk in the Ba²⁺ form</i>		
Fluoride (10)	95	1.11
Chloride (20)	101	0.25
Nitrite (20)	92	1.15
Bromide (20)	95	0.89
Nitrate (20)	95	0.75
Phosphate (30)	104	1.72
Sulfate (30)	–	–

ions such as fluoride, chloride, nitrite, bromide, and nitrate will not be affected. Fig. 5 shows an application of the SPE disk in the Ba²⁺ form for removing excess sulfate before the analysis of trace anions in battery acid. The battery acid was diluted 50 times before passing through the disk. Sulfate in the untreated sample produces baseline disruption and reduces the retention time of other anions.

3.4. Recovery of anions with SPE disks

Table 1 shows the recovery data of the SPE disks. The data were obtained by comparing standard solutions analyzed before and after treatment with the SPE disks. With the exception of nitrite (with the SPE disk in the H⁺ form), the recoveries of other anions are reasonably good. The poor recovery of nitrite with all sample

pretreatment devices is well known [3,9]. In the presence of hydrogen ion, nitrite forms nitrous acid, which in water will quickly convert to nitric oxide (gas) and nitric acid (nitrate). As presented in Table 1, the recovery of nitrate is higher than 100%, due to the oxidation of nitrite.

The recovery data obtained using the SPE disks are comparable to the data obtained using the packed bed SPE cartridges studied earlier [3]. No recovery advantage is observed with the SPE disk. However, the highly uniform packing of the SPE disks eliminate bed channeling often encountered with packed bed SPE devices. Because of the thinner and wider bed, the back pressure is lower, making it easier to push the sample through the disks. Several samples may be processed simultaneously using a vacuum manifold.

4. Conclusions

SPE disks provide a reliable method for eliminating matrix interferences in ion chromatography. Matrix interferences such as basic solutions and high level of halides and sulfate are successfully eliminated using these SPE disks. With the exception of nitrite, the recovery of all anions are reasonable good.

5. References

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