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Membrane-based solid-phase extraction as a sample clean-up technique for anion analysis by capillary electrophoresis

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Abstract

The use of membrane-based solid-phase extraction disks as a sample clean-up technique for anion analysis by capillary electrophoresis is discussed. The polytetrafluoroethylene membrane is impregnated with high-purity polystyrene–divinylbenzene sulfonated cation-exchange resin beads. Three different chemistries are used to remove various interfering components from the sample. The applications of this technique for the analysis of various anions in difficult samples are demonstrated.

1. Introduction

Capillary electrophoresis (CE) is an emerging ion separation and analysis technique [1,2]. It is attractive because it offers speed, high theoretical plates, and small sample and solvent requirements. Consumable costs are insignificant since the separation is done in an open tubular capillary as compared to a packed column in ion chromatography (IC). In most cases, sample preparation in CE is minimal. There is no expensive column to protect. Cations migrate in the opposite direction and do not interfere in the anion separation. Organic acids and neutral compounds migrate much later than the inorganic anions and are removed from the inorganic anions migration band.

However, as in IC, the separation of certain components can be complicated by the presence of interfering components in the sample matrix. The complications becomes particularly severe

when the sample is contaminated with a high level of ionic species. Although it may be possible to separate the ionic matrix components from the analytes of interest, this separation becomes difficult to achieve when the concentration of the matrix ion is high. The interfering components can mask, broaden (reduces the efficiency), or change the migration time of the peaks of interest. Therefore, some type of sample clean-up is usually necessary to remove the interfering components.

Solid-phase extraction (SPE) is a widely used sample preparation technique. It is easy to use, requires small sample volume, and a wide variety of chemistries are readily available. In recent years, membrane-based SPE has become a popular and growing technique for sample clean-up [3–5]. It offers several advantages over the traditional packed-bed SPE cartridges such as higher flow-rates (because of the wide and thin membrane), less plugging (due to its larger surface area), and elimination of channeling (due to its uniform and stable extraction matrix). SPE has been used widely for sample clean-up in IC.

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Both traditional packed-bed cartridges [6,7] and the new membrane-based disk have been used [8]. This paper examines the use of SPE disks as a sample clean-up technique for the analysis of anions by CE.

2. Experimental

2.1. Instrumentation

The CE system employed was a Crystal 300 (ATI, Unicam, Madison, WI, USA) interfaced with a Linear (Thermo Separation Products, San Francisco, CA, USA) Model 204 UV-Vis detector. Indirect UV detection at 254 nm was used. Electropherograms were recorded on a SP 4400 Chromjet integrator (Thermo Separation Products, Santa Clara, CA, USA). The separations were carried out using polyimide-coated fused-silica capillaries obtained from Polymicro Technologies (Phoenix, AZ, USA). The dimension of the capillary used through out this work was 70 cm (effective length 60 cm) \times 75 μ m I.D. Sample introduction was by hydrodynamic injection (dynamic pressure injection) at 25 mbar, for 30 s.

Alltech's (Deerfield, IL, USA) Novo-Clean IC disks were used as the membrane-based SPE device. Fig. 1 shows the construction of the Novo-Clean IC disk. The 25-mm polytetrafluoroethylene (PTFE) membrane is impregnated with high-purity polystyrene-divinylbenzene sulfonated cation-exchange resin beads. The pore size of the disk is approximately 5 μ m. It is housed in a high-purity polypropylene housing to eliminate ionic contaminations. The inlet and outlet of the housing accepts a luer-hub syringe and needle, respectively. As the sample passes through the membrane, specific ion-exchange interactions selectively retain matrix interferences while analytes pass through unchanged. Three chemistries in the hydrogen (Novo-Clean IC-H), silver (Novo-Clean IC-Ag) and barium (Novo-Clean IC-Ba) forms were used for the work discussed here. Table 1 summarizes the characteristics of each disk and its applications.

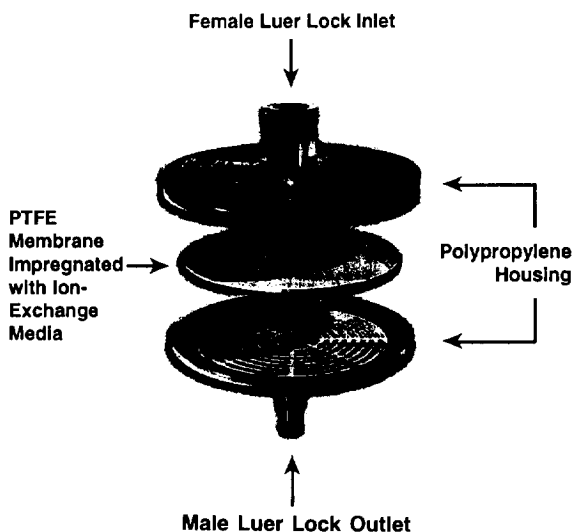


Fig. 1. The construction of the Novo-Clean IC disk.

2.2. Chemicals

The carrier electrolyte was prepared from sodium chromate (Aldrich, Milwaukee, WI, USA). Cetyltrimethylammonium bromide (CTAB) (Aldrich) was used as the electroosmotic flow (EOF) modifier. Sulfuric acid (5 M) was obtained from Fisher Scientific (Pittsburgh, PA, USA). Sodium hydroxide was obtained from Aldrich. Anion standards were prepared by diluting the 1000 ppm Certified IC Standard from Alltech. Deionized water was used for preparing all solutions.

2.3. Procedures

Before applying sample, the disk was pre-conditioned by passing 5–10 ml of deionized water using a luer-hub plastic syringe. The water was left in the device for 5 min to swell the membrane. Excess water was removed by pushing air through the disk. The sample was then passed through the disk at a flow-rate of 1.0 ml/min or less. The first 1 ml of the eluate was discarded to eliminate partial dilution of the analytes. The remaining eluate was collected for

Table 1
Characteristics of the Alltech Novo-Clean IC disks

Disk	Membrane	Retains	Applications
IC-H	Strong cation exchanger in the hydrogen form	Cations	Exchanges cations for hydrogen. Removes or concentrates sample cations or reduces pH of basic samples
IC-Ag	Strong cation exchanger in the silver form	Cations, chloride, iodide, bromide	Exchanges cations for silver. Removes excess halides through formation of silver halide salts
IC-Ba	Strong cation exchanger in the barium form	Cations, sulfate	Exchanges cations for barium. Removes excess sulfate through formation of barium sulfate

Capacity of all (25-mm) disks: 2.0 mequiv.

analysis. During removal of matrix interferences through precipitation reactions, the precipitates are retained on the disk while the soluble analytes passed through. No blockage of the extraction disk due to the precipitates was observed through out these experiments.

Each disk contains 2.0 mequiv. of either hydrogen (IC-H), barium (IC-Ba) or silver (IC-Ag). Under ideal conditions, it will remove an equal amount of hydroxide or carbonate (IC-H), sulfate (IC-Ba) or halides (IC-Ag) from the sample. In practice, the maximum capacity of the disk will be affected by the nature of the sample (concentration and ionic strength) and the rate at which the sample is loaded into the disk. The amount of contaminants that need to be removed from the sample must not exceed the total capacity of the disk. More than one disk can be used in series when the contaminant concentration is higher than the disk capacity. Also, it is possible to use the disk repeatedly as long as the contaminant concentration does not exceed the disk capacity. For best results, the sample size should not exceed 50% of the disk absolute capacity.

The electrolyte was 5 mM sodium chromate and 0.5 mM CTAB. The electrolyte was made

from concentrated stock solutions containing 100 mM sodium chromate/0.69 mM sulfuric acid, and 20 mM CTAB. The pH of the electrolyte was adjusted with either 100 mM sodium hydroxide or 100 mM sulfuric acid.

3. Results and discussions

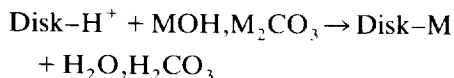
Unlike IC, very little information is available on sample clean-up for CE. Several approaches have been suggested to overcome simple problems. Optimizing the electrolyte conditions for a particular analysis by controlling the electrolyte pH, composition and ionic strength have been shown to solve a limited range of problems [9,10]. As an example, by increasing the concentration of the EOF modifier from 0.5 to 1.5 mM, 1 ppm chloride can be separated from 1000 ppm sulfate [10]. Adding organic solvents to the carrier electrolyte is another way to change the separation selectivity and is found useful for analyzing small amount of iodide in the present of large excess of sulfate [11]. The work described here uses a sample clean-up technique to remove the interfering components. Three

chemistries are used to solve a variety of interference problems.

The anions are separated using an electrolyte condition published elsewhere [12]. The electrolyte condition was not optimized for a specific matrix interference problem since the purpose of this work was to eliminate the interfering components using a sample pretreatment device, rather than changing the electrolyte condition.

3.1. Membrane-based SPE for removing hydroxide and carbonate

The Novo-Clean IC-H membrane contains sulfonic acid-functionalized resin in the hydrogen form. As sample passes through the disk, cations in the sample exchanges with hydrogen. The released hydrogen reacts with hydroxide or carbonate to form water or carbonic acid. The ion-exchange reaction that takes place in the disk is:



where M = cations. This SPE disk is ideal for

removing hydroxide or carbonate from samples before the analysis of other anions. Strong-acid anions are not effected by this treatment. The recovery of strong acid anions after treatment with the Novo-Clean IC-H membrane was discussed in an earlier publication [8] using IC as the analytical technique. A similar result is expected in CE since the sample pretreatment is done prior to the analytical technique.

Fig. 2 shows electropherograms of technical-grade sodium carbonate. The sample contains 2 g sodium carbonate dissolved in 100 ml water. In the untreated sample, only the carbonate peak was observed. After treating the sample with a Novo-Clean IC-H, trace levels of chloride, sulfate, nitrite, nitrate and phosphate were found in the sample. Dilution is not suitable for this application since the concentration of the anions is very low compared to carbonate.

Fig. 3 shows another application of the Novo-Clean IC-H disk to remove excess hydroxide. Fig. 3a shows an electropherogram of a caustic solution. High hydroxide concentration masks the peaks of interest. The migration time for fluoride is also shortened by the highly conductive hydroxide ion. By treating the sample with

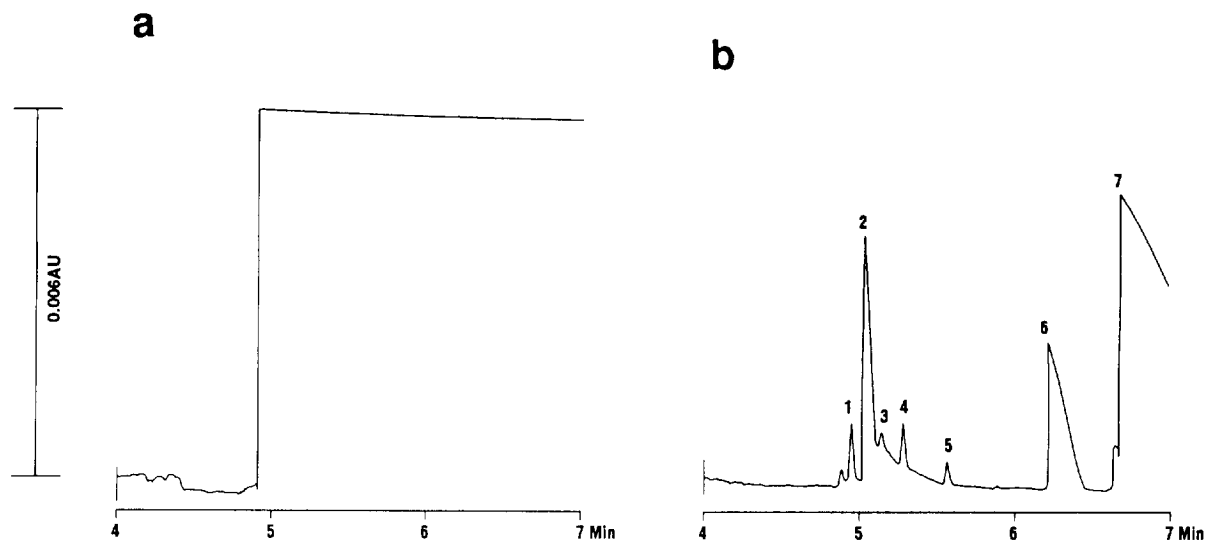


Fig. 2. Electropherograms of a technical-grade sodium carbonate. (a) Untreated; (b) treated with Novo-Clean IC-H. Conditions: fused silica 60 cm \times 75 μ m; 15 kV (negative); 5 mM sodium chromate with 0.5 mM CTAB, pH 8.0; indirect UV detection at 254 nm. Peaks: 1 = chloride (5 ppm); 2 = sulfate (32 ppm); 3 = nitrite (12 ppm); 4 = nitrate (10 ppm); 5 = unknown; 6 = phosphate (18 ppm); 7 = carbonate.

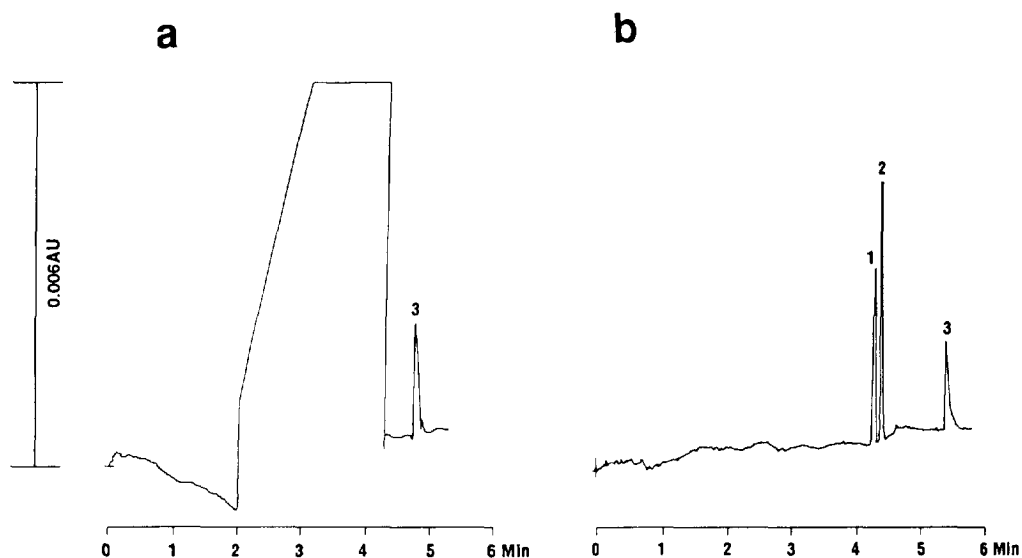
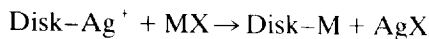


Fig. 3. Electropherograms of a caustic solution. (a) Untreated; (b) treated with Novo-Clean IC-H. Conditions: fused silica $60 \text{ cm} \times 75 \text{ }\mu\text{m}$; 15 kV (negative); 5 mM sodium chromate with 0.5 mM CTAB, pH 7.9; indirect UV detection at 254 nm. Peaks: 1 = chloride (18 ppm); 2 = sulfate (29 ppm); 3 = fluoride (9 ppm).

the Novo-Clean IC-H disk, the ions of interest are easily quantified as shown in Fig. 3b. The migration time returns to normal after hydroxide is removed.

3.2. Membrane-based SPE for removing halides

Novo-Clean IC-Ag membrane contains sulfonic acid-functionalized resin in the silver form. It is useful for removing excess halides from samples before the analysis of other anions. The Novo-Clean IC-Ag disk removes halides from the sample through the formation of insoluble silver halides. The ion-exchange reaction that take place in the IC-Ag disk is:



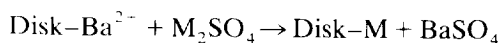
where M = cations and X = Cl, Br, I. When sample is passed through the disk, the sample cations exchange with silver. The released silver reacts with the anions in the sample. Anions that form insoluble or partially soluble silver salts will be removed completely or partially from the sample depending on their solubilities. Other anions that form soluble silver salts such as fluoride, nitrite, nitrate, phosphate and sulfate

will pass through unchanged. The recovery of these other anions after sample pretreatment with the Novo-Clean IC-Ag membrane was discussed earlier [8].

Fig. 4 shows electropherograms of a hydrochloric acid digest paper coating. The sample (0.1 g) was dissolved in 1.0 ml concentrated HCl and diluted to 100 ml with water. In the untreated sample, the chloride peak masks the peaks of interest. After treating the sample with the Novo-Clean IC-Ag membrane, chloride is completely removed and nitrate, fluoride and phosphate peaks are easily quantified.

3.3. Membrane-based SPE for removing sulfate

Novo-Clean IC-Ba membrane contains sulfonic acid-functionalized resin in the barium form. It is useful for removing excess sulfate from samples before the analysis of other anions. The Novo-Clean IC-Ba disk removes sulfate from the sample through the formation of insoluble barium sulfate. The ion-exchange reaction that takes place in the IC-Ba disk is:



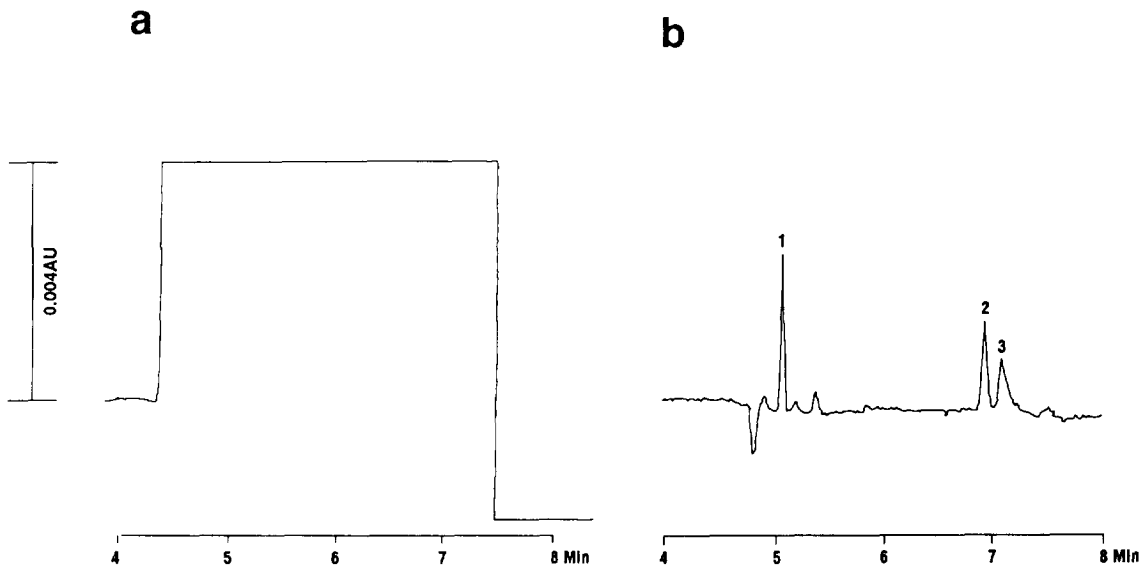


Fig. 4. Electropherograms of a hydrochloric acid digest paper coating. (a) Untreated; (b) treated with Novo-Clean IC-Ag. Conditions: fused silica 60 cm \times 75 μ m; 15 kV (negative); 5 mM sodium chromate with 0.5 mM CTAB, pH 7.9; indirect UV detection at 254 nm. Peaks: 1 = nitrate (6 ppm); 2 = fluoride (2 ppm); 3 = phosphate (5 ppm).

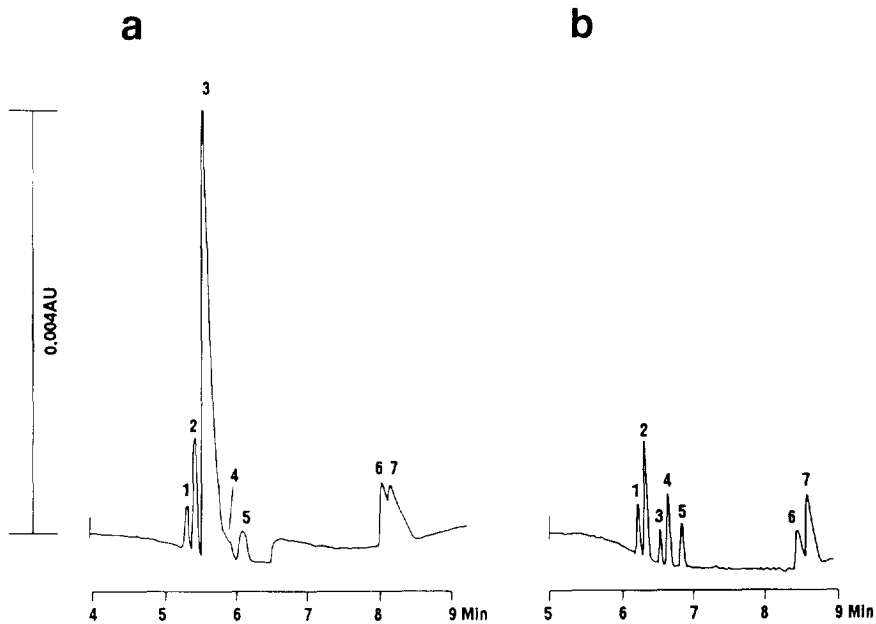


Fig. 5. Electropherograms of a standard of anions containing 500 ppm sulfate. (a) Untreated; (b) treated with Novo-Clean IC-Ba. Conditions: fused silica 60 cm \times 75 μ m; 15 kV (negative); 5 mM sodium chromate with 0.5 mM CTAB, pH 7.9; indirect UV detection at 254 nm. Peaks: 1 = bromide (10 ppm); 2 = chloride (10 ppm); 3 = sulfate; 4 = nitrite (10 ppm); 5 = nitrate (10 ppm); 6 = fluoride (5 ppm); 7 = phosphate (15 ppm).

where M = cations. When sample is passed through the disk, sample cations exchange with barium. The released barium reacts with sulfate in the sample to form insoluble barium sulfate. Since barium phosphate is partially soluble, some phosphate may be removed by this disk. Other anions that forms soluble barium salts such as fluoride, chloride, nitrite, bromide and nitrate will pass through unchanged. The recovery of these anions after sample pretreatment with the Novo-Clean IC-Ba membrane was discussed earlier [8].

Fig. 5 shows electropherograms of a standard of anions containing 500 ppm sulfate. In the untreated sample, the sulfate peak masks the chloride and nitrite peaks. Other anion peaks are broad and the resolution between fluoride and phosphate is poor. After treating the sample with the Novo-Clean IC-Ba disk, a large quantity of sulfate was removed and the separation efficiency and resolution are improved.

4. Conclusions

Membrane-based SPE is useful as a sample clean-up technique for removing high concentration of ionic contaminants before anion analysis by CE. The chemistries described here pro-

vide a selective method for removing hydroxide, carbonate, halides and sulfate. This technique provides a reliable method for eliminating matrix interferences in CE.

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