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Short communication

Ion exchange-based preconcentration for the determination of anions by capillary electrophoresis

Milko Novič[a,*], Marjan Guček[b]

[a]*National Institute of Chemistry, Hajdrihova 19, SI-1000 Ljubljana, Slovenia*

[b]*Faculty of Chemistry and Chemical Technology, University of Ljubljana, Aškerčeva 5, SI-1000 Ljubljana, Slovenia*

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Abstract

In the present paper a capillary zone electrophoresis (CZE)-compatible preconcentration technique for anions, based on ion exchange, is described. The described preconcentration approach has found limited use until recently because of the inherent elution step that leads to contamination of the sample with eluent components. In this paper, we describe an improved anion exchange-based preconcentration technique in which contamination of the sample with the eluent constituents, which occurs during anion elution from the preconcentration column, is eliminated by on-line chemical suppression on a packed-bed suppressor column. In the present communication, the basic principles of the proposed anion enrichment system are presented. The system was optimized, resulting in a minimal additional dilution of the eluted sample plug. This was achieved by the use of a computer-controlled, sensing/switching system. The effectiveness of the developed method was later tested on the determination of some anions in a synthetic sample using CE apparatus.

Keywords: Preconcentration; Anions

1. Introduction

Capillary electrophoresis (CE) is widely applied, particularly for separating complex mixtures of importance in biochemistry, environmental studies and in the pharmaceutical industry. Despite this, obstacles still limit the use of CE as a universal analytical technique and much effort is being devoted to developing suitable pretreatment techniques so as to achieve sample clean-up, diminish matrix effects and to concentrate the analyte of interest [1]. Generally, organic components can be efficiently concentrated on-line by using membranes, but the preconcentration of inorganic anions and cations is still a challenge [2]. Currently, CE is rapidly expanding within the field of inorganic ion analysis of environmental samples, reaching the same status as ion chromatography (IC) – a standard tool for the determination of anions [3]. However, regardless of its excellent separation efficiency, sample enrichment is an essential pretreatment step in CE. One way to achieve a moderate sample preconcentration is electrokinetic injection, which can produce a tenfold increase in sensitivity [4]. Alternatively, sample stacking within the capillary can also lead to a substantial enrichment. The features of electrostack-

*Corresponding author. Tel.: +386-61-1760-253; fax: +386-61-1259-244.

E-mail address: milko.novic@ki.si (M. Novič)

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ing are of interest for determining trace inorganic anions [5]. Capillary isotachophoresis (ITP) coupled with CE is a proven combination, leading to a 1000-fold increase in concentration [6,7]. Flow injection analysis (FIA) offers elegant sample pretreatment in routine applications [8] and can be successfully combined with CE, especially with other sample pretreatment techniques such as gas diffusion [9], solid-phase extraction [10] or ion exchange [11]. Undoubtedly, on-line sample preconcentration on an ion-exchange column in a FIA system with CE is a promising strategy. Nevertheless, the limiting factor preventing its wider application is the elution step, which results in the contamination of the enriched sample by eluent components.

In the present communication, we present a general ion preconcentration technique based on ion exchange, the subsequent elution of analytes and on-line removal of eluent components by chemical suppression on a packed-bed suppressor column. To our knowledge, there have been no reports on the use of ion suppression for the elimination of the effect of the eluent. The enriched samples are collected in sample vials and analyzed by CE, using indirect UV detection. We determined anions in purified water to test the optimized system.

2. Experimental

2.1. Instrumentation

2.1.1. Sample preconcentration system

The sample preconcentration system is shown in Fig. 1. It comprised a high-performance pump

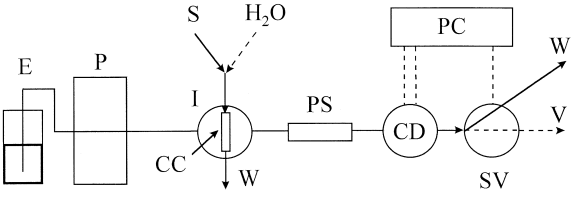

Fig. 1. Schematic showing the apparatus for the preconcentration of anions in CE for the analysis of purified water. P, High-pressure pump; E, eluent; H_2O, Milli-Q water; I, injector; CC, anion concentrator column; S, sample; PS, packed-bed suppressor column; CD, conductivity detector; SV, selection valve; V, vial; PC, personal computer with I/O ports; W, waste.

(Spectra SYSTEM 400, Spectra-Physics, San Jose, CA, USA), a pneumatically driven injector (Rheodyne 9010, Cotati, CA, USA), a conductivity detector with a flow-through cell (Shodex CD-5, Japan) and an electrically driven six-port selection valve (LabPRO PR100-105-01, Rheodyne). The IonPac TAC-LP1 (Dionex, USA) anion concentrator column (35×4 mm) with total capacity of 25 μequiv./column (20 μm styrene–divinylbenzene copolymer) and a void volume of approximately 250 μl was used throughout the experiments. As a suppressor column CTC-1 (Dionex) packed-bed suppressor column (24×9 mm) with 3.0 mequiv./column of total capacity (divinylbenzene–styrene copolymer of a diameter of 500 μm with sulfonic acid as the functional group) and column void volume of 500 μl, was used. CTC-1 column was prepared (regenerated) by pumping through it 50 mmol/l HCl or 25 mmol/l H_2SO_4 for 1 h at flow-rate 1 ml/min and consequent its rinsing for 1 h with Milli-Q water at the same flow-rate.

The preconcentration system was computer-controlled through a D/A converter (CIO-DDA06/Jr) and a 16-channel 12 bit A/D converter (CIO-DAS16/Jr), both produced by ComputerBoards, Mansfield, USA. A 50 mmol/l NaOH solution was used as the eluent.

2.1.2. Capillary electrophoresis

For analysis we employed a 270A-HT capillary electrophoresis system (Applied Biosystems, Perkin-Elmer) equipped with Turbochrom software and fitted with a 50 μm I.D.×360 μm O.D. capillary (Supelco, Bellefonte, PA, USA). The total length was 72 cm with 50 cm between the injector and the UV detector. Detection was made spectrophotometrically at 200 nm, and injection made hydrodynamically for 5 s at 0.169 bar. The applied voltage was −20 kV, producing a 278 V/cm electric field.

The capillary was conditioned daily, first with deionized water (5 min), followed by 0.1 mol/l NaOH (20 min), then again with deionised water (5 min) and finally with freshly prepared buffer (30 min). To achieve reproducible analyses, we rinsed the capillary with 0.1 mol/l NaOH (5 min) and with buffer (10 min) after each run. The buffer consisted of 20 mmol/l sodium tetraborate (Kemika, Zagreb, Croatia) and $9 \cdot 10^{-5}$ mol/l cetyltrimethylammonium

bromide (CTAB), used to reverse the electroosmotic flow (EOF) under negative electrophoretic voltages.

3. Results and discussion

3.1. Sample preconcentration procedure

The scheme of the proposed anion preconcentration system is presented in Fig. 1. Because of the nature of the stationary phase filled into the concentration column (CC, Fig. 1), the column could be used either with hydroxide- or carbonate-based eluents. Due to the instrumental set-up installed in our laboratory, NaOH was chosen as the eluent in all experiments (E, Fig. 1).

During each individual preconcentration cycle, the preconcentration column CC (Fig. 1) was first rinsed with Milli-Q water. During that step the pump P was switched off in order to save the suppressor column capacity. Regardless of its rather high total capacity (3.0 mequiv.), its dynamic capacity allows only about 40 min of total operating time at eluent (NaOH) flow-rate of 1 ml/min and its concentration of 50 mmol/l. A known volume of sample (5 ml) is then purged through the preconcentration column (installed in the injector I) by using a hand-driven syringe. The sample loading time was approximately 1.5 min. In the next step, in the injector position LOAD, the eluent was pumped through the system (flow-rate 1.0 ml/min) until constant detector response was reached (below 1 μS). After that the injector was switched to the INJECT position and the detector response was recorded through an A/D converter installed in the computer (PC, Fig. 1). Selection valve SV (Fig. 1) was later switched to the vial position (V) when increased eluent conductivity (above 2 μS) was detected. The selection valve was in the V position until eluent conductivity was not diminished below 5 μS, which means that the preconcentrated anions were eluted almost quantitatively into the collection vial V. The selection valve SV remained in the V position to complete the time interval (0.5 min) in order to obtain a well determined volume (500 μl) of the preconcentrated sample in the vial. Later the selection valve was switched to waste (W) and the pump remained switched on until background conductivity was diminished to below 1 μS. With switching the pump off, the preconcentration cycle was finished. The sample collected into the vial was later analyzed by CE. The preconcentration repeatability was tested using a synthetic sample composed of F^- (0.01 mg/l), Cl^- (0.01 mg/l), NO_2^- (0.05 mg/l), NO_3^- (0.05 mg/l), HPO_4^{2-} (0.1 mg/l) and SO_4^{2-} (0.1 mg/l). The preconcentration repeatability was tested in such a way that the area of the eluted peak was measured in the time interval the selection valve SV was in the V position. The relative standard deviation of five consecutive measurements was calculated to be 4.6%.

3.2. Separation of anions by CE

The direct UV detection of anions can be problematic, but fortunately, nitrate, nitrite, bromide and iodide exhibit sufficient absorptivities around 200 nm to allow direct UV detection. For the sensitive detection of analytes, we require electrolyte buffers of high transparency at the detection wavelengths. Thus, we chose a buffer system containing tetraborate [12] with a concentration of 20 mmol/l. Additionally, under negative applied voltages, we used an EOF modifier (CTAB) to reverse the direction of EOF. The concentration of the modifier was kept low ($9 \cdot 10^{-5}$ mol/l) to avoid systematic peaks caused by the presence of bromide present in the modifier.

At an applied voltage of −20 kV, it is possible to achieve a fast (<3 min) separation of bromide, nitrite, nitrate and iodide. To check the performance of the developed preconcentration system, a synthetic sample containing 1 mg/l of Br^-, 0.5 mg/l of NO_2^-, 1 mg/l of NO_3^- and 1 mg/l of J^- was analyzed directly and after preconcentration. The injection was performed hydrodynamically. The results are presented in Fig. 2, where a positive effect of the sample preconcentration, using the proposed chemically suppressed ion exchange-based system, can be observed. About five- to eightfold increase in individual peak height can be observed what correlates well with the expected theoretical tenfold sample enrichment. What was even more important however was the fact that there was no matrix effect

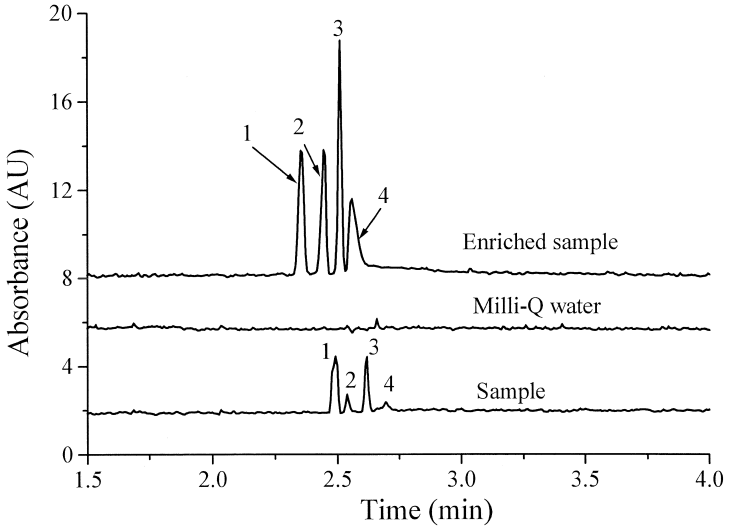

Fig. 2. Electropherograms of a sample of Milli-Q water, of a synthetic sample (containing 1 mg/l of Br^-, 0.5 mg/l of NO_2^-, 1 mg/l of NO_3^- and 1 mg/l of J^-) and an electropherogram of the same but enriched sample using the developed preconcentration technique. Conditions: 72 cm (50 cm from injector to detector)×50 μm I.D. capillary, direct detection at 200 nm, buffer: 20 mmol/l tetraborate, $9 \cdot 10^{-5}$ mol/l CTAB, injection: 5 s at 0.169 bar, applied potential −20 kV. Peaks: 1=bromide, 2=nitrite, 3=nitrate, 4=iodide.

caused by the eluent (50 mmol/l NaOH), which additionally confirmed the general applicability of the proposed preconcentration procedure.

4. Conclusions

Sample preconcentration based on ion-exchange for the CE separation of anions is promising when combined with on-line eluent chemical suppression on a packed-bed suppressor. In comparison with the other preconcentration approaches used as a sample pretreatment step for capillary zone electrophoretic analysis of some anions, the described method was found to be simple, effective and it ensured sample enrichment without any discrimination between individual ions, as is the case for example in electrokinetic preconcentration. Because of the nature of this approach, we could also apply our procedure to cation preconcentration. The main limitation of this system at the moment remains the limited capacity of the suppressor column and the need for its frequent regeneration, resulting in a rather poor reproducibility. In our future work, these drawbacks will be eliminated by the development of a preconcentration system including continuously regenerated micromembrane suppressors. Further improvement in repeatability is expected also by replacing syringe sample loading with a second injector containing a sample loop with exchangeable volume.

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