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Automated dual capillary electrophoresis system with hydrodynamic injection for the concurrent determination of cations and anions

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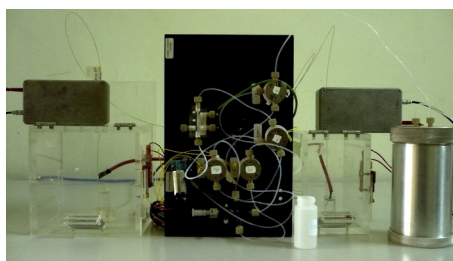
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HIGHLIGHTS

- Concurrent determination of cations and anions was carried out by electrophoretic separation.
- Optimized conditions for each class of analytes was possible by using separate capillaries.
- Simultaneous hydrodynamic injection was carried out.
- Pneumatic actuation was used for flushing and sample handling.
- The denitrification of drinking water was successfully demonstrated.

GRAPHICAL ABSTRACT



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ABSTRACT

The capillary electrophoresis instrument developed for the concurrent determination of cations and anions features two separate capillaries and individual detectors to allow independent optimization for each group of ions. The capillaries are joined in a common injector block. The sample is drawn into the injector with a small membrane pump and automated simultaneous injection into both capillaries is achieved by pressurization of the fluid with compressed air. Flushing of the injector and of the capillaries with the background electrolyte is also carried out automatically by the same means. The buffer consisted of 12 mM histidine and 2 mM 18-crown-6 adjusted to pH 4 with acetic acid and was suitable for the contactless conductivity detection employed. The system was optimized for the determination of cationic NH_4^+ and anionic NO_3^- and NO_2^- , and linear calibration curves from about 20 μM up to about 1.5 mM were obtained for these ions. In a test run over 8 h, the reproducibility for the peak areas was within $\pm 7\%$. For demonstration, the instrument was successfully applied to the concurrent monitoring of the concentrations of the three ions during the biological removal of ammonium from contaminated groundwater in a sequencing batch reactor, where NO_3^- and NO_2^- are formed as intermediate products.

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1. Introduction

Capillary electrophoresis (CE) is a relatively simple method as basically only a capillary and a high voltage power supply are

needed for the separation of the analyte ions. It is, therefore, possible to construct compact and inexpensive portable instruments for field analysis [1–3]. Sample injection into the separation capillary can easily be automated by employing a flow-injection analysis (FIA) front end [4–6]. The use of a sequential injection analysis (SIA) manifold as an alternative fluid handling method for capillary electrophoresis [7,8] is a bit more complex, but its higher degree of versatility allows, for example, the implementation of extended unattended monitoring [9], or automated preconcentration [10].

In CE the separation of both, cations and anions is possible. However, if both types of ions must be determined in the same sample this usually has to be done in two separate runs with opposite polarity of the applied voltage. In order to simplify the analysis, *i.e.* to enable concurrent separation of both types of ions, the method of dual opposite end injection has been developed [4,11–17]. In this approach, analyte cations and anions migrate in opposite direction through the capillary. The need to inject at both ends is, however, a complication. It may be overcome by pumping a sample plug from one capillary end to the other before separation [18]. Nevertheless, these methods require careful optimization in order to avoid peak overlaps arising from the opposite movement of cations and anions. Alternatively, concurrent separation is carried out in two separate capillaries, following simultaneous injection from the same sample container. This was demonstrated by Bächmann et al. in 1992 [19] employing two fluorescence detectors and simultaneous manual hydrostatic sample injection.

More recently, Huang et al. [20] reported a dual capillary system for the determination of inorganic cations and anions in an aerosol sample. However, this system was improvised and was based on two completely separate injections into the two capillaries. Gaudry et al. [21] reported an automated dual capillary system connected to a manifold based on a peristaltic pump and a miniature piston pump. The former was used for flushing of the system, including the capillaries, with background electrolyte, and the latter for sample aspiration followed by concurrent electrokinetic injections into both capillaries from the same sample plug. The application of the instrument to the monitoring of inorganic cations and anions in industrial and municipal water samples was demonstrated. Contactless conductivity detection (C^4D) was employed for both of these systems. Among other advantages, one of the features of this detection method is low cost, so that the need for two detectors in dual capillary electrophoresis is not a limitation. For fundamental aspects of C^4D see, for example, [22–28]. Applications of C^4D for CE have been described in several reviews [29–32].

The alternative automated dual CE system reported herein is also based on contactless conductivity detection, uses a simple pneumatic mechanism for the pumping of background electrolyte and a small membrane pump for sample aspiration. The pneumatic pressurization system also allowed the implementation of hydrodynamic injection. This is generally preferred to the electrokinetic injection employed by Gaudry et al. in their dual capillary system [21]. Electrokinetic injection is easier to implement than hydrodynamic injection but suffers from a sampling bias. The system was successfully applied to the simultaneous monitoring of the concentrations of NH_4^+ , NO_3^- and NO_2^- during the biological removal of ammonium from contaminated groundwater in Hanoi, Vietnam.

2. Experimental

2.1. Chemicals and materials

All chemicals were of analytical or reagent grade and purchased from Fluka (Buchs, Switzerland) or Merck (Darmstadt, Germany). For the preparation of the stock solutions (10 mM) of chloride, nitrate,

sulfate and nitrite their sodium or potassium salts were used. Similarly, those of the inorganic cations (NH_4^+ , Na^+ , Ca^{2+} , Mg^{2+} , K^+ , Li^+) were prepared from the chloride salts. The separation buffer consisted of 12 mM L-histidine (His) and 2 mM 18-crown-6 adjusted to pH 4 with acetic acid. Before use, the capillaries were preconditioned with 1 M NaOH for 15 min, 0.1 M NaOH for 5 min and deionised water for 10 min prior to flushing with the buffer. The groundwater contaminated with ammonium was collected from Van Phuc village (Hanoi, Vietnam). Deionised water purified using a system from Millipore (Bedford, MA, USA) was used for the preparation of all solutions and for sample dilution if required.

2.2. Instrumentation

The solenoid valves were purchased from NResearch (116T021 and 116T031, Gümligen, Switzerland) and the micro-graduated needle valve from IDEX (P-470, Oak Harbor, WA, USA). The membrane pump for sample aspiration was obtained from KNF (NF-5-DCB, Balterswil, Switzerland). All fluidic connections were made with 0.02 in. i.d. and 1/16 in. o.d. Teflon PFA tubing unless otherwise stated and with $1/4$ -28 UNF fittings (IDEX). The interface accommodating the capillaries and the ground electrode was machined in a PMMA (poly(methyl methacrylate)) block (3 cm \times 2 cm \times 2 cm) and is a modification of the split injector reported by Kubán et al. [5]. Pneumatic pressurization was achieved with a standard cylinder of compressed nitrogen at 200 bar. The outlet pressure was adjusted to 1 bar with a regulator.

The electrophoresis section was based on two dual polarity high voltage power supplies (Spellman CZE2000, Pulborough, UK) with ± 30 kV maximum output. The high voltage electrodes were contained in insulated cages fitted with safety switches. Polyimide coated fused silica capillaries of 50 μ m i.d. and 365 μ m o.d. (from Polymicro, Phoenix, AZ, USA) were used for the separations. The high voltage ends of the capillaries were isolated with safety cages made from PMMA, which were equipped with microswitches to interrupt the high voltage on opening. Detection was carried out with two miniaturized high-voltage C^4D cells built in-house. For excitation, a sine wave of 400 kHz and 20 V_{p-p} was produced with a function generator integrated circuit (XR2206, Exar, Fremont CA, USA). This was boosted to 200 V_{p-p} using purpose-built transformers made from two E 13/7/4, N87 ferrite cores with matching E 13/7/4 coil formers. These components were obtained from EPCOS (Munich, Germany) (product nos. B66305-G-X187 and B66306-C1010-T1). The amplifiers on the pick-up side (OPA602 and OPA2227) were obtained from Texas Instruments (Austin, TX, USA), and the synchronous detectors (AD630) from Analog Devices (Norwood, MA, USA). The resulting signals were recorded with an e-corder 401 data acquisition system (eDAQ, Denistone East, NSW, Australia) connected to the USB-port of a personal computer.

2.3. System control

The system was controlled with a personal computer *via* its parallel port. A purpose-built electronic interface allowed switching of the stop-valves, of the 3-port valves and of the high voltage, as well as triggering of the recording of electropherograms. The solenoid valves were controlled *via* a special driver board obtained from the supplier of the valves (CoolDrive, 116D5X12, NResearch). The Forth programming package ProForth for Windows (Micro-Processor Engineering Limited, Southampton, UK) was used to write the control code. Different modules were written to independently carry out tasks including flushing of the interface and capillaries, sample delivery, hydrodynamic injection and electrophoretic separations. All modules were then assembled together to produce the instruction protocol for the entire analytical method.

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