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Capillary electrophoresis with contactless conductivity detection coupled to a sequential injection analysis manifold for extended automated monitoring applications

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ABSTRACT

A capillary electrophoresis (CE) instrument with capacitively coupled contactless conductivity detection (C^4D) based on a sequential injection analysis (SIA) manifold was refined. Hydrodynamic injection was implemented to avoid a sampling bias by using a split-injection device based on a needle valve for precise adjustment. For safety and reliability, the integrity of the high voltage compartment at the detection end was fully maintained by implementing flushing of the high voltage interface through the capillary. With this set-up, extended fully automated monitoring applications are possible. The system was successfully tested in the field for the determination of the concentration levels of major inorganic cations and anions in a creek over a period of 5 days.

1. Introduction

Instrumentation for capillary electrophoresis (CE) is much more simple than for column chromatography as the separation is achieved by the relatively straightforward application of voltages. High pressure pumps and eluents are not needed and the consumption of chemicals is very low. A significant further simplification was also brought about by the introduction of contactless conductivity detection (C^4D), which, with the exception of a simple measuring cell based on a pair of short tubular electrodes, is fully electronic and thus less demanding in construction and power consumption than the common optical detection methods employing UV-radiation. For reviews see for example [1,2]. Field portable CE-instruments employing C^4D have therefore been developed in our research group [3,4] and Hutchinson et al. [5] have demonstrated that a portable instrument may be employed for the identification of post-blast residues of IEDs (improvised explosive devices).

Capillary electrophoresis furthermore has potential for extended on-site measurement applications, such as in environmental monitoring or in process control. The coupling of conventional CE-instruments with flow-injection analysis (FIA) manifolds for sample handling ahead of the separation step has indeed been reported for such applications. Arce et al. [6] have reported a system with analyte preconcentration for use in a water purification plant using a commercial CE-Instrument and indirect optical detection, and Sirén et al. [7] have reported an assembly for monitoring use in a paper mill.

Nevertheless, commercial CE-instruments designed for the laboratory are not well suited for on-site deployment and coupling to external sample handling manifolds. It is, on the other hand, relatively easy to construct a CE-separation unit as part of an extended FIA-manifold and such systems have been constructed by several researchers (see the recent review by Kubáň and Karlberg [8]). The use of C^4D is also attractive for such a set-up and FIA-CE-C^4D instruments have been reported [9–11]. Sprung et al. [10] detailed the construction of a system for on-line measurements, and Kubáň et al. [11] have demonstrated the on-line field monitoring of the drainage of a pasture for some inorganic anions and cations. The use of a sequential injection analysis (SIA) system, based on a syringe pump and a multi-position valve, instead of an FIA-manifold typically using a peristaltic pump, has several advantages, such as allowing sample pretreatment and automated flushing of the separation capillary. This combination was introduced by Růžička and coworkers in 2002 [12,13] who used UV-detection. Kulka et al. [14] reported a similar system in 2006 and Horstkotte et al. [15,16] demonstrated the determination of nitrophenols. Zacharis et al. [17] designed an SIA-CE-instrument employing laser-induced fluorescence for detection. Wuersig et al. [18] used an SIA set-up to

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achieve fast injections into capillaries of only a few centimeters in length and could thus demonstrate the separation of inorganic cations and anions in approximately 10 s. C^4D was employed in the latter case for detection.

In this contribution we present an SI–CE-C^4D system designed for monitoring applications over extended unattended periods and demonstrate its functionality in several days of on-site monitoring of the concentrations of inorganic anions and cations in a creek. The new set-up incorporates a number of improvements compared to previous designs in order to achieve high reliability and specific adaptations to allow autonomous operation.

2. Experimental

2.1. Chemicals and materials

All chemicals were of reagent grade. Deionised water (Millipore, Bedford, MA, USA) was used throughout the experiments. Stock solutions (5 mmol L^{-1}) of chloride, nitrate, sulfate, nitrite, fluoride and phosphate were prepared from their potassium or sodium salts. Stock solutions (5 mmol L^{-1}) of ammonium, potassium, calcium, sodium, magnesium and lithium ions were prepared from their chloride salts. All chemicals were purchased from Fluka (Buchs, Switzerland) or Merck (Darmstadt, Germany). All multi-ion standards were prepared from these stock solutions. The separation buffer consisted of 12 mM L-histidine and 2 mM 18-crown-6 adjusted to pH 4 with acetic acid. The capillary was preconditioned with 1 M NaOH for 10 min and deionised water for 10 min prior to flushing with electrolyte solution (for 1 h). The capillary was then used continuously for successive analyses.

2.2. Instrumentation

The SIA manifold is based on a syringe pump (Cavro XLP 6000) and a 6-port channel selection valve (Cavro Smart Valve) (both purchased from Tecan, Crailsheim, Germany). The SIA-CE interface consists essentially of two consecutive T-junctions for connecting the capillary and electrophoretic ground electrode to the liquid channel. It was machined in a perspex block (2 cm × 2 cm × 3 cm); details have been given previously [19]). The micro-graduated splitting valve was obtained from Upchurch Scientific (P-470, Oak Harbor, WA, USA) and the isolation valves for pressurization from NResearch (HP225T021, Gümligen, Switzerland). All fluid connections to the selector valve were made with 0.02 in. inner diameter (id) and 1/16 in. outer diameter (od) Teflon PFA tubing (Upchurch Scientific) with the exception of the connection between the selector valve and the SIA-CE interface where 0.01 in. id and 1/16 in. od PEEK tubing (4 cm) was used in order to minimize dispersion.

The electrophoresis section is based on a dual polarity high voltage power supply (Spellman CZE2000, Pulborough, UK) with ±30 kV maximum output. Polyimide coated fused silica capillaries of 50 μm id and 363 μm od from (Polymicro, Phoenix, AZ, USA) were used for separation. The detection end of the capillary was connected with a fitting to a perspex block, which contains a channel of 0.4 mm id and 2 cm length at the end of which the high voltage electrode is placed. This assembly was isolated in a safety cage made from perspex, which was equipped with a microswitch to interrupt the high voltage on opening. Detection was carried out with a C^4D-cell built in-house, and is based on two tubular electrodes of 4 mm length, which are separated by a gap of 1 mm and a Faradaic shield. Details on this detector can be found elsewhere [20]. The resulting signal was recorded with an e-corder 201 data acquisition system (eDAQ, Denistone East, NSW, Australia) connected to the USB-port of a personal computer.

For the field test the instrument was set up in a pumping station located next to the creek Kleine Aa, a tributary to Lake Sempach, Switzerland. A submersible pump conveyed a constant stream of water from the creek (~2 L s^{-1}) into an overflowing bucket, from where a small part was diverted with a peristaltic pump to a beaker of 20 mL which was also overflowing (the excess was collected with a funnel underneath and led to a drain). Samples were aspirated into the SI-manifold from this beaker through an inlet filter (10 μm pore size, Supelco, Buchs, Switzerland) in order to remove suspended matter. Occasional water samples were collected, filtered with 0.45 μm membrane filters, and inorganic anions and cations analyzed later in the laboratory by ion-chromatography (IC, Metrohm, Switzerland) within 2 days.

2.3. System control

The system was controlled with the personal computer using an RS232-serial connection to the syringe pump. The multi-position valve is daisy-chained to the syringe pump. Auxiliary TTL-output ports on the two units allow switching of the stop-valves, of the high voltage, the polarity of the high voltage and triggering of the recording of electropherograms with the help of a purpose built electronic interface. The two solenoid operated isolation valves were controlled via a special driver board obtained from the supplier of the valves (CoolDriver, 225D5X12, NResearch). The programming package LabVIEW (version 8.0 for Windows XP, from National Instruments, Austin, TX, USA) was used to write the control code for the SIA-CE system. Different modules were written to independently carry out tasks such as injection, flushing, separation etc. All modules were then assembled together to produce the instruction protocol for the entire analytical method. The program can be modified easily during the optimization steps or during setting up of the system.

3. Results and discussion

3.1. System design

A schematic drawing of the system is depicted in Fig. 1. The SI-manifold consists of the standard arrangement based on a two-way syringe pump and a multiport valve with a holding coil between the two units. This is used for the initial conditioning of the capillary by flushing with sodium hydroxide solution, rinsing the system with the separation buffer, and aspiration of a plug of the sample solution and passing this volume to the capillary inlet. Injection proper is carried out hydrodynamically. The volumes injected in capillary electrophoresis are in the nanoliter range and too small for direct handling with the SI-manifold. Thus only part of the dispensed sample plug is injected into the separation tubing by pressurization of the interface while pushing the sample plug past the capillary inlet. This is more difficult to implement than electrokinetic injection, but a sampling bias, which would arise with the latter mode, is avoided. Separation is carried out by applying the high voltage from the detection end, the second electrode in the SI–CE interface is grounded.

Two modifications have been made to the set-up compared to earlier designs [15,16,18]. The first of these concerns the method used for pressurization of the SI–CE interface for injection and flushing of the capillary. Previously, a length of flexible tubing was connected to the outlet of the interface, the end of which was closed with a valve for injection. Solution would thus be pumped into the expanding piece of tubing leading to a gradually increasing pressure. The performance of this set-up would depend on the length and the condition of the tubing. However, predictability and reproducibility are poor, and only one setting is possible which has to be