Short communication

Electrically floating conductivity detection system for capillary electrophoresis

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Abstract

A conductivity detector is designed for capillary electrophoresis in which the detection electronics are isolated and float with the separation voltage applied to the capillary. This design minimizes the detrimental effect of the high voltage to the detection system and is powered using a battery. A simple arrangement is fabricated for the conductivity measurement electrodes. The electrical signal generated at these electrodes is carried through the floating electronics and then transmitted to a data-acquisition computer through a optical (infrared) serial link. As a preliminary demonstration, a sample solution containing three alkali metal ions is analyzed. The detection limits for the ions are about $2 \cdot 10^{-6}$ M.   © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

Although capillary electrophoresis (CE) as a separation method has the virtues of rapid separation and high resolution, one of its limitations is thought to be its detection capabilities [1,2]. Optical detection is most commonly used, with absorbance being the most prevalent. The short path length inherent in the capillary, however, limits the detection sensitivity that is achieved with absorbance detection. Fluorescence (particularly, laser-induced fluorescence) detection can be used to provide higher sensitivity, but is applicable only to species that are either natively fluorescent or those that can be derivatized with a fluorophore.

Non-optical modes of detection provide alternative means for measuring analytes in CE. Of these modes, electrochemical detection [3–24] offers certain advantages. These advantages include applicability to analytes that do not contain chromophores, universality (e.g., using conductivity [3–9]), selectivity and high sensitivity (e.g., using amperometry [10–24]), and the potential for low cost. But this form of detection suffers from two main drawbacks: (1) the interference caused by the high separation voltage to the measurement electronics resulting in lower sensitivities than that can be achieved otherwise and (2) the manually intensive construction of the measurement electrodes and the complicated alignment of the electrodes with the capillary. Several approaches have been taken in the past to address the first drawback. These include the use of a porous glass joint [10], nafion joint [12], a palladium decoupler [13] and performing detection

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in an end-column mode [6,7]. These approaches, however, have not been able to completely decouple the separation voltage from the detection electronics. For example, narrow inside diameter capillaries or low conductivity buffers have been required in some cases to minimize the current in the separation capillary and reduce its detrimental effect on detection performance [7]. Various electrode designs have also been implemented with CE for electrochemical detection. These designs typically require precise alignment of the capillary with the microelectrode(s) used for the detection measurement, and create the burden of maintaining consistent alignment between runs to obtain reproducible results. Integration of the measurement electrodes with the separation capillary has been used to address this second drawback. For example, Dadoo et al. [14] and Zhong and Lunte [21] have demonstrated the use of permanently attached (glued) metal electrodes to the capillary and Voegel et al. [24] have used thin metal films deposited on the outlet tip of the capillary for detection purposes.

In this communication, we describe a conductivity detector for CE in which the detection system is isolated and electrically floats with the separation voltage in order to minimize the effect of the high separation voltage on the detection measurement. The conductance (electrical) signal is transmitted from the isolated detector to a data-acquisition computer without a physical connection in between by optical means using an infrared serial link. A simplified electrode design [14] that attaches the electrodes to the separation capillary is also constructed. This design provides a fixed alignment of the measurement electrodes with the capillary and, hence, alleviates the need to actively maintain consistent alignment from run to run. A sample containing three alkali metal ions is analyzed with the system as a preliminary demonstration.

2. Experimental

2.1. Capillary electrophoresis system

A CE system similar to that described previously [7] was used for the experiments. In brief, a 0–30 kV power supply (Spellman High Voltage Electronics,

Bronx, NY, USA) provided the separation voltage. The capillaries (Polymicro Technologies, Phoenix, AZ, USA) used for the runs ranged between 50 μm and 100 μm I.D. (375 μm O.D.) and 30 cm and 50 cm in length. They were flushed with 10 mM sodium hydroxide and water for 10 min each before use. The system was enclosed in a Plexiglass box for safety purposes.

2.2. Conductivity measurement electrodes

The electrode system is similar to one we have demonstrated in the past for amperometric measurements [14]. A schematic diagram of the system is shown in Fig. 1. An insulated platinum wire (25–50 μm in diameter, California Fine Wire Company, CA, USA) is initially attached along the outlet end of the capillary and aligned with the channel opening at the end bore of the capillary. Epoxy is used to hold the wire in place. Once the epoxy has dried, the wire is cut carefully at the end bore of the capillary with a scalpel to expose two disc-shaped non-insulated electrode tips for the conductance measurement. These two exposed tips of the resulting wires are aligned with the channel opening at the end of the capillary under a microscope and the other two ends of the wires are connected to the detection electronics. This section of the capillary is placed into the outlet reservoir during the analyses. Care was taken to prevent the tip of the capillary with the electrodes attached from touching the walls of the reservoir in order to preserve the alignment.

2.3. Conductivity detection system
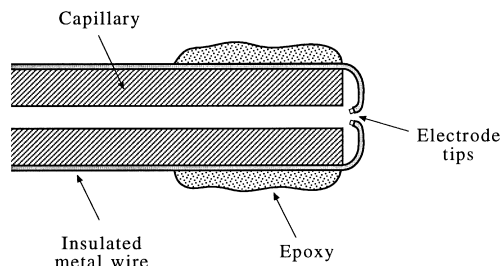
A schematic diagram of the electrically floating

Fig. 1. Schematic of the conductivity measurement electrode system.
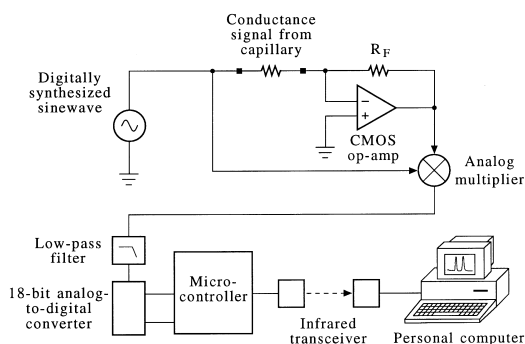
Fig. 2. Schematic of the electrically floating conductivity detector and data-acquisition system.

detection system is shown in Fig. 2. The system is similar to that presented before [9]. In brief, a precision battery-powered (using a 5-V battery) circuit was built for the measurements. An analog lock-in amplifier with an 18-bit analog-to-digital converter was designed to measure a.c. conductivity (operating at 1 kHz). A microcontroller chip controlled the parameters for the analyses and transmitted the resulting data over an infrared serial link to a computer used for data acquisition. Laboratory-written software was written to collect the data and display the electropherograms.

2.4. Reagents

The chemicals used to prepare the separation electrolyte [2-(*N*-morpholino)ethanesulfonic acid (MES) and histidine] were purchased from Sigma. Stock solutions (10 m*M*) of the samples (chloride salts of potassium, sodium and lithium) were diluted in the separation buffer prior to injection. Water was purified using an Ultra-Pure purification system from Millipore and all solutions were filtered before use.

3. Results and discussion

3.1. Electrode system

The electrodes constructed as described in Section 2.2 were found to be robust and reliable. Once fabricated, no further change in alignment was required because of the permanent nature of the

attachment of the electrodes to the capillary. The same electrodes were used to perform more than 100 runs without any significant change in performance. The primary reason for electrode failure was misalignment or breakage caused by accidental contact of the capillary outlet end with a surface. A protective sheath around the vulnerable section of the capillary should eliminate this problem in the future. It is important to note that this design for manufacturing electrodes can only be used for malleable materials such as metals, and cannot be applied to materials such as carbon fiber. Although platinum wire electrodes were used in this study, we have also utilized copper-, nickel- and gold-based electrodes successfully.

3.2. Detection electronics

To test the efficacy of the floating electronics, resistances up to 10 MΩ were placed in series between the outlet reservoir and ground (thereby placing the outlet detection end of the capillary at a high potential). Applying the high voltage to the CE system did not significantly affect the noise in the conductance baseline, suggesting that the isolated floating electronics help to decouple the interference from the separation voltage on the detection measurement.

3.3. Analysis of alkali metal ions

Fig. 3 depicts an electropherogram of a sample containing potassium, sodium and lithium ions. All three components are resolved under the conditions used in the separation and further optimization of the conditions was not performed for this initial study. The concentration detection limits were observed to be $2 \cdot 10^{-6}$ *M* for the ions which are in par with those that have been obtained in the past. We expect further optimization of the running conditions (e.g., buffer ionic strength, etc.) [7] to improve these limits. The detector response was tested for linearity. The response was found to be linear within two-orders of magnitude with $r^2 = 0.98$. The reproducibility of the migration times for the analytes were better than 2% R.S.D. and in the detector response (as measured by the peak heights) better than 5% R.S.D.
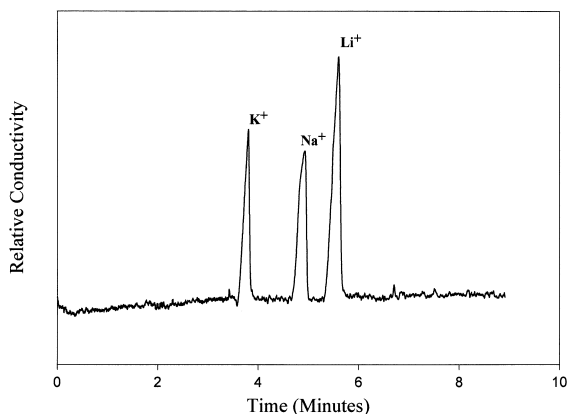
Fig. 3. Electropherogram of a sample containing potassium (1), sodium (2) and lithium (3) ions (injected at $5 \cdot 10^{-5}$ M). The separation capillary is 50 cm×75 μm I.D. containing 10 mM MES–histidine (pH 6.0) as the electrolyte. The separation voltage is 10 kV. The electrodes consisted of 37 μm diameter platinum wire.

Acknowledgements

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