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A sheath flow gating interface for the on-line coupling of solid-phase extraction with capillary electrophoresis

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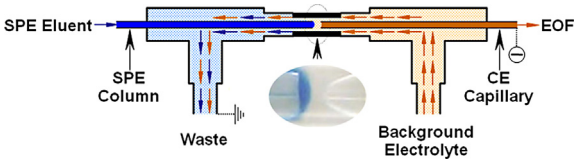
HIGHLIGHTS

- First use of the sheath flow design, and thus achievement of the heretofore smallest void volume.
- Nearly no dilution of the SPE eluate.
- No degradation of the CE efficiency.
- Automation of the injection process, and thus simplification of the operation and improvement of the reproducibility.
- Feasibility for the coupling of LC or FIA with CE.

GRAPHICAL ABSTRACT



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ABSTRACT

A sheath flow gating interface (SFGI) is presented for the on-line coupling of solid-phase extraction (SPE) with capillary electrophoresis (CE). The design, construction and operation of the SFGI are described in detail. After operating conditions were investigated and selected, the SFGI was evaluated on a SPE–CE–UV setup using hydroxylated poly(glycidyl methacrylate-co-ethylene dimethacrylate) monolith as the absorbent and using three phenols as the test analytes. The preconcentration factors obtained with the SPE–CE–UV system and the SPE–UV part are 530 and 550, respectively. The plate numbers obtained using the SPE–CE–UV system are slightly better than or comparable to those with the CE–UV part. The precisions (RSDs) of 100 consecutive injections are 2.43%, 3.86%, and 4.25% for peak height, peak area and migration time, respectively. The measured recoveries for the river water samples spiked at three different levels are in the range of 93.6–102.8% with the interday RSD values ranging from 2.0 to 4.5% ($n = 3$). These data collectively demonstrate that the SFGI has the ability to exactly and reproducibly transfer nanoliters of fractions from SPE onto CE with no degradation of the efficiencies of SPE and CE, suggesting a great potential to be routinely used for the coupling of SPE, microcolumn LC or FIA with CE.

1. Introduction

Capillary electrophoresis (CE) has gained increasing importance because of its excellent separation efficiency, short analysis time, minimal needs of samples, and high versatility of separation modes. Most commonly, ultraviolet (UV) detection is applied in CE because of its simplicity and wide applicability. The UV detection method, however, suffers from low concentration sensitivity due to the intrinsically small injection volumes (1–10 nL) and the short

Abbreviations: ACN, acetonitrile; AIBN, azobisisobutyronitrile; BGE, background electrolyte; EDMA, ethylene dimethacrylate; GMA, glycidyl methacrylate; γ-MAPS, γ-methacryloxypropyltrimethoxysilane; PTFE, polytetrafluoroethylene; SFGI, sheath flow gating interface; TFGI, transverse flow gating interface.

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optical path-length as a result of the small inner diameter (25–75 μm) of the capillary [1].

An effective way to enhance the sensitivity is preconcentration of samples by solid-phase extraction (SPE) prior to separations. In order to combine SPE with CE, off- line, at-line, in-line and on-line methods have been used. From these modes, the on-line approach is preferred as it offers shorter total analysis times, minimum of sample handling, limited risk of sample losses, and possibility of automation. Additionally, as the SPE column is physically separated from the CE capillary in the on-line system, independent operation and optimization of the SPE and the CE are allowed [2–4].

On-line coupling of SPE with CE requires a special interface. In addition to implementation of electric connection for CE, the interface should have the ability to exactly transfer nanoliters of fractions from SPE onto CE with a minimized degradation of the efficiencies of SPE and CE. For such a purpose, varieties of interfaces have been designed, including the types of valve-loop [5–7], T-split [8–10], valve-loop-vial or T-piece [11–16], two-leveled two cross [17,18], flow-gating [13,19–21], and the interfaces with integrated SPE [22,23]. With the first three types of interfaces, success of the coupling has been achieved to some extent, but some limitations have been recognized. Because of the large void volume resulting from the loop and the eluate flow path between the two capillaries, serious dilution and dispersion of the eluate have occurred, thus leading to a loss of SPE efficiency, especially when a small eluent volume is used [7–9,13,16]. Degradation of CE efficiency has also been found due to the use of in-line valve injection [5,7,13] or the backpressure caused in the tee [5,9]. Additionally, it seems to be critical and a little difficult to exactly time each step of the SPE–CE operation [6–8,10]. The two-leveled two cross interface eliminates the need of valves and, thus the shortages associated with the valves. However, the position of the SPE outlet relative to the CE capillary is critical to the performance of the SPE–CE system, and the contamination of the CE capillary from the SPE effluent has been observed [17,18]. For the interface with integrated SPE, as the SPE column is part of the CE system, some deleterious influences of the SPE sorbent may occur on the CE system during analysis [22]. Most of the aforementioned interfaces require relatively complicated switching procedures that may result in poor reproducibilities [6–8,10].

The transverse flow gating interface (TFGI) is a cross-like interface, having the SPE column and CE capillary positioned on opposite sides of the cross with a proper gap. A transverse flow of background electrolyte (BGE) through the gap is used to control the SPE eluate collection and injection. As the SPE eluate is directly collected in the gap, the valves and loops used commonly in other previous interfaces are not needed in this interface. Therefore, a quite small void volume can be achieved, resulting in a reduced dilution and dispersion of the collected SPE eluate [13,20]. In spite of this, some extent of the dilution and dispersion has still been reported [19,20].

This paper reports a sheath flow gating interface (SFGI) for the on-line coupling of SPE with CE. By adopting the sheath flow design, the void volume of the SFGI was minimized to ten nanoliters, and thus the problems resulting from the void volume have been circumvented. By selecting suitable operating conditions, such as the BGE flowrate, the adverse effects of some previous interfaces on CE have been overcome. By automatically controlling the injection progress, the operation of the SFGI has been simplified and the injection repeatability has been improved. The above merits of the SFGI were demonstrated on a SPE–CE–UV setup using phenols as the test analytes.

2. Experimental

2.1. Chemicals and materials

Acetonitrile (ACN), methanol, toluene, dodecanol, azobisisobutyronitrile (AIBN) and γ-methacryloxypropyltrimethoxysilane (γ-MAPS) were obtained from Shanghai Chemicals (Shanghai, China). Glycidyl methacrylate (GMA) and ethylene dimethacrylate (EDMA) were produced by Acros (Sweden). Other reagents were from Kaibo (Wuhan, China). All of the above reagents were of analytical reagent grade. All solutions were prepared with water from a GW-UN Milli-Q system from Persee General (Beijing, China), filtered through 0.45 μm filters, and sonicated for 15 min prior to use. Fused silica capillaries were polyimide-coated, of 370 μm o.d. and 50 or 250 μm i.d., and from Yongnian (Handan, China). Polytetrafluoroethylene (PTFE) tubing was from Elite Instruments (Dalian, China). Acrylic boards were transparent, 5 mm thick, and from Longyu (Weishan, China).

2.2. Apparatus

Fig. 1 shows the schematic of the entire instrumental setup for evaluation of the SFGI. SPE was performed on a 2 cm long 250 μm i.d. hydroxylated poly(GMA- *co*-EDMA) monolithic column. Samples and the rinse buffer were filled in two micro- syringes separately, and forced through the SPE column by pressurized nitrogen gas. The gas sources were conveniently connected or disconnected to the syringes with the aid of a homemade adapter. Eluent was driven through the SPE column by a Lab Alliance LC pump (Model 500) equipped with a homemade T-splitter. Liquid flow path switching was achieved by connecting either of the liquid flow paths to the SPE column through a section of 1/16 in. o. d. and 250 μm i.d. PTFE tubing. CE capillary was 50 μm i.d., 30 cm long with 13 cm to the detection window. Two Binda high-voltage power supplies (Model 2003, Beijing, China) were used in parallel way in the negative voltage mode. One was set at a low voltage for injection, and the other at a high voltage for separation. Detection was performed on-capillary by using a UV absorbance detector (Model 500, Lab Alliance). The original flow cell part of the detector was replaced with a homemade counterpart for the on-capillary detection. A Longer syringe pump (LSP01-1A, Baoding, China) was used to drive BGE through the SFGI to control the injection for CE. A Phoenix microscope (XSP-02, Jiangxi, China), coupled with an Aoni digital video camera (184DF, Shenzhen, China) using a homemade coupler, was focused on the central portion of the SFGI for direct

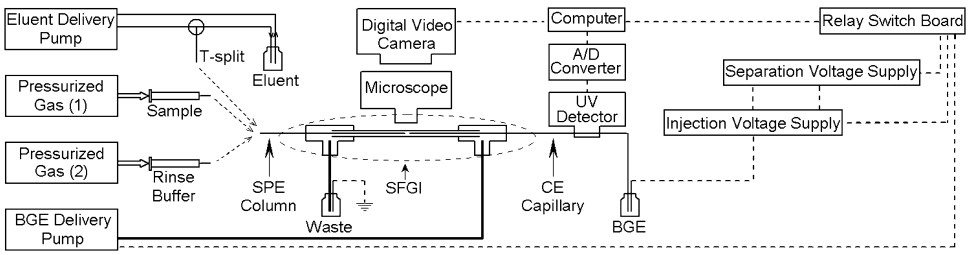

Fig. 1. Schematic of the SPE–CE–UV set-up for evaluation of the SFGI.