



The development of a hydrodynamic flow assisted double junction interface for signal improvement in capillary electrophoresis–mass spectrometry using positively charged nonvolatile additives



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ABSTRACT

To alleviate signal suppression resulting from nonvolatile positive ion additives, a hydrodynamic flow assisted double junction capillary electrophoresis–mass spectrometry (CE–MS) interface was proposed. The double junction interface which could alleviate the ion suppression due to nonvolatile negative ion additives was modified so that a hydrodynamic flow could be introduced to the interface. Using this setup, the apparent velocity of the ions was determined based on its electrophoretic mobility, electroosmotic flow in the transfer capillary, and hydrodynamic flow introduced by the syringe pump. CE–MS analysis of positively charged triazines was performed to demonstrate the practical value of this approach by using cetyltrimethylammonium ion (CTA⁺) as an additive. Because the separation column was dynamically coated with CTA⁺, the EOF was reversed and the separation was performed under counter EOF mode. Under an appropriate hydrodynamic flow, the analytes (triazines) could be propagated toward the MS, whereas the additive (CTA⁺) ion was retained in the interface. Consequently, the problem of signal suppression by CTA⁺ was alleviated, and the signals were enhanced more than 20-fold.

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1. Introduction

Because of its high separation resolution, low sample consumption and extremely selective MS detection, CE–ESI–MS is a powerful analytical technique that has been widely used [1,2]. CE often involves adding nonvolatile additives or salts to improve the separation [3,4]. However, nonvolatile additives are not suitable for ES–MS, primarily because of its effect on ion suppression [5–8]. To resolve the problems resulting from using nonvolatile additives, many different approaches have been proposed [5,6,9–15]. The most widely used approach involves using alternative volatile buffers, such as ammonium acetate [10]. Unfortunately, the resolution can be inferior to that obtained when nonvolatile additives are used. The partial filling technique is another widely used approach [11,12], which prevents ion-suppression because no additive is introduced into the ESI source. However, the resolution is often degraded because of the short effective separation length.

In a previous study [16], we developed a double junction interface to address the ion suppression problem while maintaining separation integrity. In the interface, a short transfer column

was connected between the separation column and ESI sprayer. Controlling the electroosmotic flow (EOF) of the transfer column allowed the nonvolatile additives to be retained in the junction reservoir, whereas the analytes flowed toward the ESI source. The interface has demonstrated its practical value in overcoming ion suppression resulting from nonvolatile anions, such as borate ion [17], phosphate ion [16], and dodecyl sulfate ion [18].

Although the double junction interface can prevent anionic additives from entering the ESI source, it is unsuitable for handling positively charged additives because the additive, analyte, and EOF exhibit an identical flow direction. To solve this problem, this paper proposes a hydrodynamic flow assisted double junction interface. A side channel was created on the double junction design for hydrodynamic flow to be applied to the junction. With the assistance of the appropriate hydrodynamic flow, the flow direction of the analytes and the nonvolatile cationic additives can be tuned to flow in opposite directions. Consequently, ion suppression resulting from nonvolatile cationic additives can be alleviated.

This study analyzed the triazines in positive ion mode using positively charged CTA⁺ ion as the additive to demonstrate the practical value of the hydrodynamic flow assisted double junction interface. During the CE–MS operation, a reversed electric field was applied to the transfer column. When the reversed electric field was applied, both the triazines and CTA⁺ ion were flowed in the opposite

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direction of the ESI source. To move the triazines flow to the ESI source while retaining the additive in the junction reservoir, an appropriate forward hydrodynamic flow was applied to ensure that only the triazines exhibited a net velocity toward the ESI source. Consequently, ion-suppression resulting from nonvolatile CTAB could be alleviated.

2. Materials and methods

2.1. Chemical reagents

Methanol (MeOH) (HPLC grade), acetone (HPLC grade), ammonium acetate and acetic acid were purchased from J.T. Baker (Phillipsburg, NJ, USA). Formic acid (FA) was purchased from Fluka Chemical Co. (Milwaukee, WI, USA). Deionized water (Milli-Q water system, Millipore Inc., Bedford, MA, USA) was used for preparation of the buffer solution and sample solutions. The triazine standards (simazine, atrazine, propazine, ametryn, terbuthyrene, simetryn and prometon) were obtained from Supelco (Bellefonte, PA, USA). A stock standard solution of triazine mixture was prepared in methanol and stored in a refrigerator. Cetyltrimethylammonium bromide (CTAB) was purchased from Sigma–Aldrich Chemical Co. (St. Louis, MO, USA). Poly(dimethylsiloxane) (PDMS) monomer and crosslinker (Sylgard® 184) were obtained from Dow Corning (Midland, MI, USA). The poly(methyl methacrylate) (PMMA) plates were obtained from Chi Mei Corp. (Tainan, Taiwan). Fused-silica capillaries (375 μm o.d. \times 50 μm i.d., 375 μm o.d. \times 75 μm i.d., 700 μm i.d. \times 850 μm o.d.) were purchased from Polymicro Technologies (Phoenix, AZ, USA). PEEK tubing was obtained from Upchurch Scientific (Oak Harbor, WA, USA). Oasis HLB 1 cc (30 mg) extraction cartridge was purchased from Waters (Milford, MA, USA).

2.2. Fabricating the hydrodynamic flow assisted double junction interface

The hydrodynamic flow assisted double junction interface comprised a poly(dimethylsilane) (PDMS) based microdevice, a transfer capillary, an ESI emitter, and a side channel capillary (Fig. 1a). To fabricate the PDMS based microdevice, a poly(methyl methacrylate) (PMMA) mold (Fig. 1b) was assembled on a PMMA plate (100 mm \times 80 mm \times 5 mm), and fixed using scotch tape (3M, Taipei, Taiwan). The mold was composed of four 25 mm \times 10 mm \times 3 mm PMMA plates, one PMMA rod, and one poly(ethylene ketone) (PEEK) tube. A hole for inserting a side channel capillary (375 μm o.d.) was drilled on the PMMA front plate by using a 400 μm (o.d.) drill. Another hole for inserting a PEEK sealing tube was drilled on the PMMA back plate by using an 800 μm (o.d.) drill. Two holes were drilled on the left and right plates by using a 400 μm (o.d.) drill. Two 400 μm diameter channels were drilled near the terminus of the PEEK tube and near the bottom of the PMMA rod using a 400 μm (o.d.) drill. After the drilling, a 375 μm (o.d.) capillary was inserted into the hole in the left PMMA plate, passing through the channels of the PEEK tubing, PMMA rod, and hole in the right PMMA plate. Another capillary was inserted into the PEEK tubing through the hole in the front PMMA plate. The distance between the PEEK tubing and the PMMA rod was approximately 1 cm.

A PDMS monomer and cross-linker were mixed vigorously and degassed. The mixture was poured slowly onto the PMMA mold and cured at 80 °C in an oven for 72 h. After curing, the rods and capillary were carefully withdrawn from the mold. Subsequently, the microdevice (Fig. 1c) could be detached from the PMMA mold, and it was ready for use. A 1 cm capillary (375 μm o.d., 75 μm i.d.) was inserted into the channel of the microdevice as the transfer column (Fig. 1d). In addition, a 2 cm tapered capillary with a 10 μm

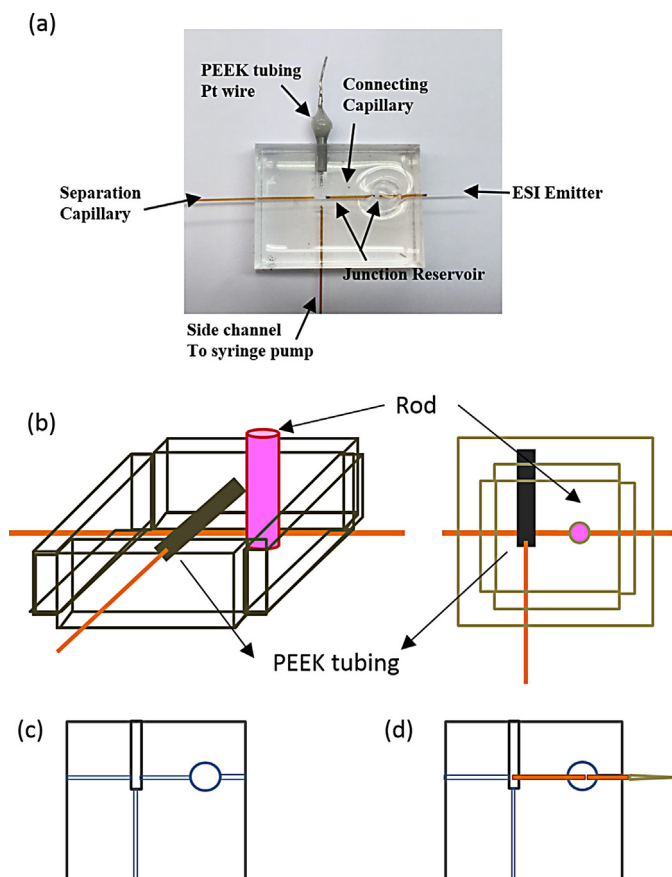


Fig. 1. The hydrodynamic flow assisted double junction interface. (a) Setup of the interface. (b) The PMMA mold for fabrication of the PDMS based double junction interface. (c) PDMS based double junction micro device. (d) PDMS based double junction interface with a 1 cm transfer capillary and an ESI emitter.

orifice was inserted into the PDMS microdevice as the ESI emitter (Fig. 1d). The sheath liquid reservoir (i.e., the vertical liquid reservoir) connecting the ESI emitter and transfer capillary was filled with make-up liquid. A liquid junction reservoir (i.e., the horizontal liquid reservoir) was created by inserting a PEEK sealing tube approximately 5 mm into the end of the PEEK channel. The ESI voltage was applied to the sheath liquid reservoir. The voltage of the terminus of the CE was applied using a Pt wire inserted through the PEEK tubing. The electric field of the connecting capillary was established by the voltages applied to the two liquid reservoirs.

2.3. Low sheath flow interface

The low flow interface consisting of a PMMA base liquid reservoir and an ESI sprayer was fabricated based on the published method [19]. A 1.5 cm \times 700 μm i.d. \times 850 μm o.d. fused silica capillary was tapered to produce a 10 μm orifice as the ESI sprayer. To reduce the dead volume, one end of the separation capillary was tapered to 40 μm before its insertion to the low flow interface. To taper the capillary, a small weight (about 50 g) was attached to the capillary, and the capillary was drawn to a taper tip using a propane-butane/oxygen microtorch. For the separation column, the tapered capillary tip was cut to about 1.5 cm to produce a 40 μm tapered tip. To make an ESI sprayer, the tapered tip was etched with 48% aqueous hydrogen fluoride solution for about 3 min to produce a 10 μm orifice sprayer.

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