A MICROFLUIDIC CHIP BASED ELECTROS-PRAY INTERFACE FOR MASS SPECTROMETRY WITH A LOW-TEMPERATURE ALLOY MICRO-ELECTRODE

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ABSTRACT
In this study, a novel approach for interfacing microfluidic glass chip with electrospray ionization mass spectrometry (ESI-MS) without dead volume was developed using monolithic ESI tip and low-temperature alloy microelectrode. A novel and simple fabrication approach for the microelectrode of the ESI interface was developed based on low-temperature-alloy microelectrode molding technique [1]. A monolithic ESI tip was fabricated on the glass chip to minimize the size of the Taylor cone. The new interface is characterized by ease of fabrication, low cost, zero dead volume and long lifetime. The performance of the novel interface was evaluated in the analysis of reserpine, with results comparable to those of commercial nanospray tips.

KEYWORDS: Electrospray ionization mass spectrometry, monolithic ESI tip, low temperature alloy, glass chip

INTRODUCTION
The combination of microchip with mass spectrometry provides a promising platform for the analysis of complex biological samples. Currently, glass still is the ideal material for fabrication of chip-based ESI-MS interface owing to its high resistance to organic solvent used in ESI-MS, low MS background level and optical transparency. However, fabrication of a dead-volume-free monolithic spray tip with a microelectrode is still a challenge. In this work, we produced a monolithic ESI interface on a glass chip using low-temperature alloy microelectrode molding technique [1] and fabrication technique for monolithic tip of glass chip [2].

EXPERIMENTAL
Standard photolithographic and wet chemical etching techniques were used for fabricating microchannels on glass plates. As shown in Figure 1(a-b), a V-shaped electrode channel was fabricated with the tip end connected to the central channel.
after the wet etching process.

The fabrication process for the microelectrode is shown in Figure 1(c-d). A commercial low-temperature alloy, solder (52Bi-32Pb-16Sn) with a melting point of 97°C, was used to fabricate the microelectrode. The molten solder was perfused the whole electrode channel under 120°C, forming a stable phase interface at the neck region between the electrode and central channels due to surface tension, and then allowed to solidify at room temperature. A monolithic ESI tip with a tip diameter below 100 μm (see Figure 2B) was produced by using an emery drill to grind the glass chip as described elsewhere [2].

All of the mass spectrometry experiments were carried out on a LCQ DECA ion-trap mass spectrometer. The sample solution was delivered by a Harvard syringe pump with a flow rate of 500 nL/min. The emitter tip was positioned at a distance of 2 mm from the heated transfer capillary. The electrospray voltage varied from 2000-2500 V to optimize the spray performance.

**RESULTS AND DISCUSSION**

The performance of the chip-based ESI interface was evaluated using reserpine and horse myoglobin as model samples in direct infusion experiments. Figure 3(A) shows the result obtained from a 10 nM reserpine solution in 60% methanol with a sampling frequency of 0.12 spectra/s, corresponding to a sample consumption of 9.96 amol. Figure 3(B) shows the result obtained from a 5.88 μM horse myoglobin.
solution in 60% methanol containing 0.5% acetic acid. The long-term stability of the present system was 4.4% RSD in a period of 30 minutes (see Figure 3(C)).

Figure 3. Ion trap mass spectra. (A) Single spectrum obtained during 0.12 s by infusing 10 nM reserpine in 60% methanol corresponding to 9.96 amol sample. (B) Single spectrum obtained during 1.44 s by infusing 5.88 μM myoglobin corresponding to 70.8 fmol sample. (C) Total ion current by infusing 5.88 μM myoglobin in 30 minutes.

CONCLUSIONS

In summary, the present chip-based ESI interface offers several advantages, including ease of fabrication, low cost, good stability, long lifetime and comparable sensitivity to commercial nanospray tips. Studies on coupling this system with capillary electrophoresis are being undertaken in the author’s group.

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REFERENCES
