Journal of Chromatography A, 1216 (2009) 3337–3342

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Accurate nano-injection system for capillary gas chromatography

Hu-Lie Zeng*, Nobuko Seino, Tatsuro Nakagama, Yubun Kikuchi, Hazumu Nagano, Katsumi Uchiyama

Department of Applied Chemistry, Urban Environmental Sciences, Tokyo Metropolitan University, 1-1 Minamiohsawa, Hachioji, Tokyo 192-0397, Japan

ARTICLE INFO

Article history:
Received 4 July 2008
Received in revised form 31 January 2009
Accepted 16 February 2009
Available online 21 February 2009

Keywords:
Nano-injector
Inkjet microchip
cGC
Sample introduction

ABSTRACT

The first version of nano-injection device for capillary gas chromatography (cGC) based on inkjet microchip was developed. The nano-injector could accurately control the injection volume in nano-liter, even pico-liter range. Its configuration and mechanism were discussed in detail. Adopting photolithography and plasma etching technology, we firstly fabricated the inkjet microchip and stuck to a piezoelectric device to eject droplets. Then, a special feedback tube was added to make it function as a nano-injector for cGC, which was an important design to compensate pressure difference between the evaporation chamber of cGC and the sample extrusion chamber of inkjet microchip. The injected volume can be precisely controlled by the number of injected droplets. Excellent precision (RSDs were below 10.0%, $n = 5$) was observed for the injection of ethanol at elevated pressure. Minimum injection volume was about 1.25 nL at present. Additionally, good repeatability of the calibration curves for the hydrocarbons ethanolic solution (the RSDs of all components were below 5.30%, $n = 5$) confirmed its feasibility in quantitative analysis regardless of concentration. These results suggested that it can be an accurate nano-injector for cGC.

1. Introduction

Precise sample dispensation, introduction and delivery in nano-liter scale are the most frequent tasks in contemporary chemistry and biotechnology. This is because minimizing the volume of sample or reagents consumed is an effective means for precious samples as well as for reducing the analytical cost. The research on the accurate manipulation of liquid below nano-liter range has been increasing attentions in recent years. For instance, the solenoid micro-pump based nano-injector had been constructed to create a transient pressure to push the liquid through a micro-aperture in microanalysis system [1]. The nano-liter sample introduction method for capillary electrophoresis adopting rotary valve had been presented, which determined the injection volume by a mini-hole made by drill [2]. The nano-pipette to load and dispense nano-liter volume of liquid by electroosmotic mechanism had been proposed by a research group in Texas Tech [3]. Furthermore, an injection system at molecular level had been devised through attaching carbon nanotube to the atomic force microscope (AFM) system, which injected protein-coated quantum dots into living-human cells [4]. Besides, most well-known and frequently used nano-dispensing devices employ pressure [5–9] or piezoelectric [10–13] device. The former drives liquid by decentralizing pressure, and the latter gives a subtle displacement to push the liquid through the transfiguration of piezoelectric device. Viewing the injection volume of them, the piezoelectric device can inject smaller volume of liquid more easily in several nano-liter even pico-liter. In our research group, an injector based on inkjet mechanism had been developed for chemical analysis [12,13], which could eject several tens of pico-liter droplets at atmospheric pressure. It could be the effective ultra-micro injector with high precision and accuracy in nano-liter even pico-liter range.

In this paper, we have applied the inkjet microchip as an accurate nano-injector for cGC and micro-GC, whereby the micro-GC has been a strong analytical tool in miniaturization of instruments [14]. Heretofore, there are two ways to introduce samples by a syringe: the split and splitless injection in cGC or micro-GC. Split mode, which is the most important and popular way, was used to avoid overloading of sample in conventional cGC, but the discrimination of samples of high boiling point is unavoidable in some degree. Splitless injection is also limited by the uncertainty for the introduction of the sample volume below nano-liter [15]. On the other hand, the introduction of sample by valve and headspace mode had been imported in cGC as special introduction methods. However, all methods mentioned above could not accurately introduce the liquid sample below nano-liter. Therefore, we have developed an accurate nano-liter sample introduction system based on inkjet microchip for cGC. The method could be a basic research in handling the nano-liter even pico-liter sample introduction in contemporary analytical chemistry.

* Corresponding author. Tel.: +81 426771111; fax: +81 426772821.
E-mail address: zhluse@gmail.com (H.-L. Zeng).

0021-9673/$ – see front matter.
doi:10.1016/j.chroma.2009.02.051

2. Experimental

2.1. Instrumentation

The gas chromatograph system used in this study was Micro-GC (the new version of cGC which is not listed yet, Shimadzu, Kyoto, Japan), equipped with a flame ionization detection (FID). The capillary column used was the capillary column of UltraAlloy$^+$-5 (10 m × 0.25 mm I.D., 1.0 μm d.f.). Helium gas was used as the carrier gas and its flow rate was 0.7 mL/min. Split mode was applied for syringe injection at the split ratio of 380:1. A pulse power supply (new product assembled by Fuji Electric System, Tokyo, Japan) was used to drive the piezoelectric device of inkjet microchip. The on–off valve settled between the nano-injector and the evaporation chamber was supplied by GL Sciences (Tokyo, Japan). All liquid samples were filtered through 0.45 μm membrane filter (JHWP02500, Nihon Milipore, Tokyo, Japan).

2.2. Chemicals

Ethanol was purchased from Woko Pure Chemical Industries, Ltd. (Tokyo, Japan). Decane, undecane, dodecane, tridecane and tetradecane were from Kanto Chemical Co. Inc. (Tokyo, Japan). Analytical reagent grade chemicals were used unless otherwise indicated.

2.3. Fabrication of nano-injector

To adapt to cGC injection port, a single-channel narrow inkjet microchip was devised as shown in Fig. 1A. It was prepared via photolithography, dry plasma etching and anodic bonding. In the procedures, the pattern was etched on silicon substrate using plasma beam after photolithography. Then silicon plate with pattern was bonded with a thin pyrex glass cover by anodic bonding. Using epoxy glue, a square shaped piezoelectric device was placed just over the extrusion chamber, and adhered on the pyrex glass cover which was pre-coated with indium tin oxide (ITO) film. As shown in Fig. 1B, the back side of the piezoelectric device was covered by thin film of gold, and its front side was fixed tightly with a flexible wiring, so that the piezoelectric device could press the thin pyrex glass cover (Thin pyrex glass plate of 0.35 mm is elastic to some degree.). Finally, a hollow cubic holder and a polyethylene tube were installed at the sample inlet of the single-channel inkjet microchip as shown in Fig. 1C. The constructed nano-injector could be driven by the pulse power that supplied to the gold layer (anode) and ITO layer (cathode).

2.4. Inkjet microchip ejection

The droplets were generated by pressing the extrusion chamber by the piezoelectric device, which was driven by the pulsed power voltage. The number of ejected droplets could be controlled by the number of applied pulses between 1 and 6400. Furthermore, some parameters of pulse power could be adjusted when required: the voltage from 0 to 200 V, the frequency of pulses in 0.1, 1, 2 and 4 kHz, the pulse duration of two successive pulses (see Fig. 1D) from 2 to 100 μs (pulse duration I) and from 10 to 60 μs (pulse duration II). For cGC injection, we selected the pulse frequency of 2 kHz, the pulse duration of two successive pulses of 80 and 20 μs [12,13], and applied voltage of 60 V for piezoelectric device considering stability of pulse (see Fig. 4). Then the injection volume could be easily manipulated through changing the number of pulses. The injected volume of decane, undecane, dodecane, tridecane and tetradecane ethanolic solution were determined by the comparison of the recorded peak areas in chromatograms with those obtained by the split injection of sample by a micro-syringe.

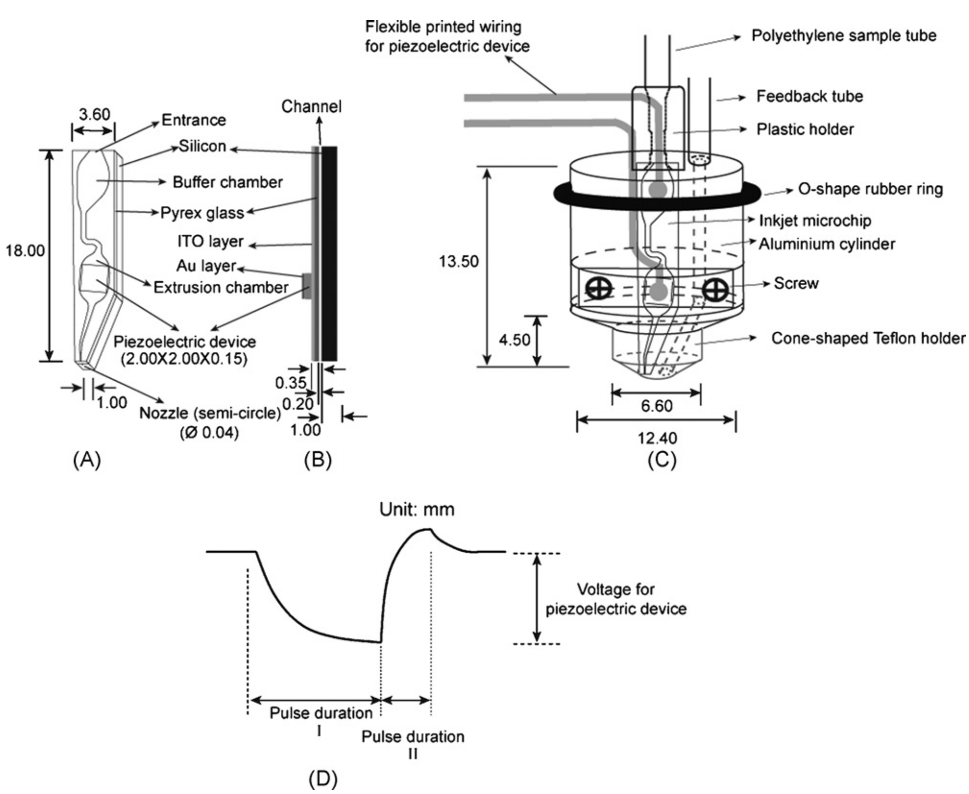

Fig. 1. The schematic diagram of the signal-channel inkjet microchip (A), schematic diagram of side section view of the inkjet microchip (B), the structure of nano-injector based on the inkjet microchip (C) and the pulse shape of two successive pulses for driving piezoelectric device (D).