Ink-jet Microchip Interface between Liquid Flow and Flame-ionization Detector

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An ink-jet microchip interface between the continuous liquid flow and flame-ionization detector (FID) for gas chromatography (GC) has been developed. An ink-jet microchip for a conventional recorder was modified for the interface. When the interface was used for a flow-injection analysis (FIA) system with FID, 3.3 ng of the detection limit (S/N = 3) of ethanol in water was performed.

A popular direction in research today is to miniaturize chemical analysis methods. Miniaturization involves reducing the overall size of the analysis device, generating less waste and providing for the analysis of small samples.[1] Particularly, an ink-jet device is very attractive in various fields from the point of view of dispensing nano- and picolevel small droplets of liquid with good control of the volume and velocity.[2] Typical applications are high-throughput screening, genomics,[3] and combinatorial chemistry.[4–7] Some ink-jet dispensing techniques have also been used in many areas of chemistry and science including the fabrication of biosensors, sample introduction for mass spectrometers,[8,9] and sample introduction for capillary electrophoresis (CE).[10,11] In our previous works, an ink-jet microchip was applied for the introduction of nanodroplet samples in thermal conductivity detector (TCD)[12] and a laboratory-made atomic emission detector (AED).[13]

Meanwhile, on-line coupled chromatographic techniques are sensitive and selective techniques available for environmental and food sample. The on-line coupling of liquid chromatography (LC)–gas chromatography (GC) combines the effectiveness of sample preparation in the LC step with the high efficiency and sensitivity of GC. In the past, many attempts have been made to couple LC and FID[14] which is widely used for the universal and sensitive detection of organic compounds. Most of them were based on interfaces,[15,16] conveyed volatile analytes from eluent to the FID, or generated a jet of droplets by inducing a sharp temperature gradient at the tip of the introduction capillary. Such a system had two major disadvantages, namely, the complexity of the design and the very high probability of vaporizing the sample with solvent.[17]

Some advantages of small-sized ink-jet microchips as the injection device of analytical instruments are considered to be easy to set up, easy to control the number and the volume of the injection by changing the electric parameters (piezoelectric driven voltage, frequency, pulse wavelength, etc.), also it easily evaporates the liquid sample. If continuous liquid flow can be evaporated by continuously ejecting pico- or nanoliter droplets using an ink-jet microchip, it would become a powerful interface between the FID and liquid chromatographic systems, LC and flow injection analysis (FIA), etc.

In this study, the nanodroplet introduction technique was used for the interface between liquid flow and FID. An FIA–FID system was constructed using an ink-jet microchip and was evaluated for the detection of ethanol in water.

A picture and schematic diagram of the ink-jet microchip we used are shown in Figure 1. The microchip (Fuji Electric, Tokyo, Japan) is used for an industrial recorder and was employed in this study. A microchannel of the microchip was formed by dry plasma etching on the surface of the silicon substrate and was covered with a Pyrex glass plate by anodic bonding. Indium tin oxide (ITO) was deposited on the Pyrex glass surface and was connected to ground. A piezoelectric element (0.15-mm thickness, 2-mm square) was fixed on the ITO surface over the microchannel. The nozzle is designed for about 300 pL of the ejected droplet volume when a water-soluble ink (viscosity: about 5 mPa·s) was used for the droplet solution. Actually, the width and height of the rectangular ink-jet nozzle are 78 and 38 μm, respectively (Figure 1). Before using the microchip, in order to prevent the formation of bubbles in the microchannel, the microchannel was filled with a 20% (v/v) Extran MA 01 alkaline (Merck, Ltd., Tokyo, Japan) aqueous solution for 15 min and then washed with water. A polyethylene tube (0.55 mm i.d., 1.25 mm o.d., 10 mm of length) was connected to the microchip holder (Figure 1) for the introduction of the liquid flow.

The microchip was placed on the sample injection port of a GC-14A gas chromatograph with FID (Shimadzu, Kyoto, Japan).[12] A glass insert (3.0 mm i.d., 4.4 mm o.d., 186 mm of length) was placed in the heating chamber of the injection port.

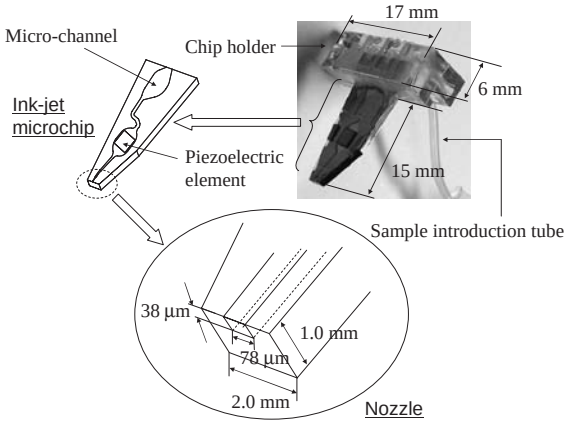

Figure 1. A picture and schematic diagram of the ink-jet microchip.

The injection port and the FID were directly connected using an empty glass column (3.2 mm i.d., 5.0 mm o.d., 600 mm of length, GL Sciences, Tokyo, Japan).

The set-up procedure is as follows: 1) A rectangular penetration hole (7 × 2 mm) was made at the center of a round glass plate (diameter: 50 mm, thickness: 3.2 mm). 2) The tip of the microchip was inserted into the hole and fixed with an epoxy adhesive. 3) A round penetration hole (diameter: 10 mm) was made at the center of a round stainless steel plate (diameter: 45 mm, thickness: 2 mm). 4) The round plate was welded to a stainless steel nut on the top of the sample injection port. 5) A silicone rubber O-ring (diameter: 24.5 mm, hole diameter: 19.5 mm, thickness: 2.5 mm) was put on the round steel plate, and then the round glass plate equipped with the microchip was mounted on the top of them. They were then fixed with binder clips. The distance between the nozzle of the microchip and the top of the glass insert were 1 mm.

A Rheodyne 7520 injector with a 0.2 μL-sample rotor (Supelco, Bellefonete PA, U.S.A.) was connected to the polyethylene tube attached to the microchip through PEEK tubing (1/16 inch i.d., 0.25 mm o.d., 114 mm of length), and then at the upstream side, it was connected to a LC-10ADvp (Shimazu, Kyoto, Japan) HPLC pump. Water was used as the carrier. In order to monitor the pressure in the sample-heating chamber of the injection port, a digital differential pressure gauge GC-62 (Nagano Keiki, Tokyo, Japan) was connected to the chamber. A personal computer with CDS plus (ver5.0) software (LAsoft, Chiba, Japan) was used for processing the chromatographic data. The water used in this study was purified using a Milli-Q system (Nihon Millipore, Tokyo, Japan). All solutions were degassed Wako Pure Chemical Industries (Osaka, Japan).

When the HPLC pump was operated, sample droplets were continuously ejected from the microchip by driving the piezoelectric element on the microchip using a DC power supply GMS200-02 (Metronix, Japan) through a laboratory-made driver and then were introduced into the heating chamber of the GC system. As a result, when the carrier flow rate was set at 4 μL/min, the optimum driving conditions for the microchip were 90 V (for the applied voltage), 100 μs (for the applied pulse width) and 100 Hz (for the applied frequency).

It was confirmed that the FID signals of ethanol in water were obtained at various sample concentrations by the continuous introduction of the sample droplets using the microchip interface as shown in Figure 2. The FID signals were also found by only the introduction of water presumably because of the change in the background noise by changing the total gas flow rate for vaporizing water at injection. The range of RSD values of the peak area shown in Figure 2 was from 2.4 to 6.1% ($n = 3$). Good linear relationships between the sample introduction volume in FID (ng) (x) and the peak area (y) or peak height (y') of the FID signal were found $\{y = 2.3623x + 275.67$ ($R^2 = 0.9978$), $y' = 0.0353x + 3.9115$ ($R^2 = 0.9885$), $n = 3\}$. From these data, the detection limit of ethanol was estimated to be 3.3 ng defined as three times the standard deviation of the blank, which would be improved by reducing the diffusion of the sample in the injection port, the connecting tube, etc.

In conclusion, the utility of an ink-jet microchip as the interface between an FID and a flow-injection system was demonstrated. A microchip would be useful for the interface of many unified chromatographic systems (LC–GC, LC–AED, etc.), as well as the injection device for miniaturized and integrated separation systems.

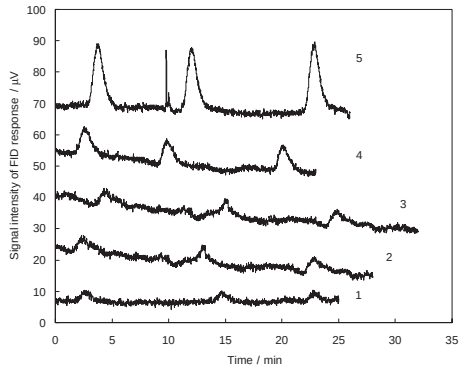

Figure 2. FID signal response of ethanol solution. Ethanol concentration (v/v): (1) Blank; (2) 100 ppm; (3) 500 ppm; (4) 1000 ppm; (5) 3000 ppm; Ink-jet microchip conditions: applied piezoelectric element driving voltage, 90 V; pulse length wave, 100 μs; applied frequency, 100 Hz; FID conditions: injector temperature, 200 °C; column temperature, 200 °C; detector temperature, 350 °C; air flow rate, 200 mL/min; hydrogen gas flow rate, 83 mL/min; carrier gas (Helium gas) flow rate, 20 mL/min; measurement range, 10^3; continuous flow conditions: sample injection volume, 0.2 μL; eluent solution, water at 4 μL/min.

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