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A piezoelectric drop-on-demand generator for accurate samples in capillary electrophoresis

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ABSTRACT

In this work, we propose a piezoelectric droplet generator for injection of well-defined amounts of sample in capillary electrophoresis. We demonstrate stable, precise and drop-on-demand droplet formation for various solutions, with precise control of waveform driving piezoelectric crystal inside the ink-jet head. By tuning the waveform, we can also manipulate the droplet size and delivery frequency. This injector was used in sampling for capillary electrophoresis. As a state-of-the-art application, the analysis of theobromine, caffeine and theophiline using micellar electrokinetic chromatography was developed. The volume of sample (single droplet) analyzed in this experiment was 179 pL (RSD = 1.2%, $n = 10$). The detection limits for caffeine, theobromine, and theophiline are 0.02, 0.08 and 0.06 mM L^{-1}, respectively. Compared with conventional methods, the combination of picoliter droplet dispenser with capillary electrophoresis allows precise and accurate sampling, as well as for reduced sample consumption, which will prove to be an efficient tool in quantitative separation and analysis.

1. Introduction

In the past decade, microdroplet techniques have been of great interest in research due to their rapid mass/heat transfer, reduced sample consumption and ultra-high throughputs [1–4]. Microdroplets have been widely applied in various areas, such as synthesis microreactors [5], sample injection in analytical methods [6,7], and microarray-based dispensing technique [8]. Moreover, precision-controllable nanoliter-droplets are recognized as an excellent pathway for biological studies [9,10], especially in single-cell analysis and drug screening [11,12]. For these reasons, numerous strategies have been developed for droplet formation and manipulation. Microfluidic-created shear field on integrated microchip is extensively utilized for high-throughput droplet formation [13–18]. Alternatively, electrowetting-based digital microfluidics allow the formation of sub-microliter droplets and controllable manipulation [19–21]. Other mechanisms, including electrospray [22] and surface tension [23], are also used for droplet generation, all of which provide new possibility for the wide application of droplet-based systems.

Ink-jet printing is a novel and powerful technology that can produce precisely controllable droplet with specified volume and velocity, potentially expanding in drug screening [24], tissue engineering [25] and electronics manufacturing [26]. Compared to other methods, the ink-jet-based droplet generation is especially attractive because the droplet contents can be easily analyzed by various methods since it can be compatibly connected with analytical techniques, such as nanoliter microarray based chemiluminescence detection [27], capillary electrophoresis (CE) [28], and mass spectrometry (MS) [29]. The mechanism of the ink-jet process has been well studied [30]. Factors such as the properties of the solution (viscosity, density and surface tension), the characteristic of driving waveform and the ink-jet head structure have been found to affect the ink-jet process seriously [31–34].

Capillary electrophoresis is a powerful method for both qualitatively and quantitatively analyzing the sample rapidly and precisely. Coupling the ink-jet droplet generation with capillary electrophoresis not only provides an approach to chemically analyze the contents of droplet, but also provides a novel method to sample. The ink-jet printing droplet has been previously coupled with capillary elecphoresis [35], where an acoustic levitator is used to achieve analyte enrichment. This work is pioneering; however, a detailed study about the control of droplet volume to sample in electrophoresis; the separation performance

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of droplet contents and the quantitative relationship is still in great demand. Our group previously reported the application of ink-jet-printing as an accurate sampling method for capillary electrophoresis [28].

In this work, a systematic characterization of this system, especially the droplet generation control and the quantitative relationship of ink-jet-based sampling, was performed. A home-made circuit and software to drive the piezoelectric actuator are described. The waveform (the driving voltage and the pulse width) was precisely controlled for stable, drop-on-demand droplet formation. Various solutions (methanol/water, caffeine/water, protein/water, etc.) were dispensed as single on-demand droplet by adjusting the driving waveform within appropriate ranges. The relationship between the voltage, width of pulse and volume of droplets was also investigated. Droplets containing theobromine, caffeine and theophiline were separated by capillary electrophoresis using sodium dodecyl sulfate (SDS) as the micellar phase. Quantitative relationship between the injection volumes and signal responses was obtained for these three substances.

2. Materials and methods

2.1. Apparatus

The ink-jet microchip was provided by Fuji Electric Co., Ltd. (Tokyo, Japan). A VW-9000 high-speed microscope (camera units: high-speed monochrome VW-600M, macrozoom units: long-distance macrozoom unit VW-Z2 with 4× optical zoom) was from Kyence Corporation (Tokyo, Osaka). A balance BP2111D was provided by Sartorius (Goettingen, Germany). The UV detector (Model: CE-971UV) for capillary electrophoresis was from JASCO (Tokyo, Japan). All aqueous solutions were prepared by ultrapure water which was purified by a Millipore-Q device (Millipore Japan Co., Tokyo, Japan).

2.2. Reagents

Ethanol, glycerol, methanol, theobromine, caffeine, and theophiline were purchased from Wako Pure Chemical Industries Ltd. (Tokyo, Japan). Extran MA 01 was purchased from Merck (Darmstadt, Germany) and NaOH and HCl from Kanto Kagaku (Tokyo, Japan). All aqueous solutions were prepared with ultrapure water which was purified by the Millipore-Q device (Millipore Japan Co., Tokyo, Japan). The carboxylate-modified polystyrene microspheres (i.d.: 40 nm, 4%) were purchased from Duke Scientific Corporation (Pala Alto, CA, USA). All buffers were filtered through a 0.45 μm membrane filter before use.

2.3. Pretreatment and assembly of ink-jet chip

The pretreatment of ink-jet chip was performed according to the instructions provided by the supplier, and was described previously [27]. Basically, the ink-jet microchip (see Fig. 1) microchannel was filled with 20% (w/w) Extran MA 01 solution for 30 min to clean the channel and make the channel hydrophilic. Then the channels were washed with ultrapure water. After that, sample solutions were introduced into the channels of the ink-jet microchip through capillary tubes (Drummond, 75 mm hematocrit tube, 0.1 mL). The piezoelectric ceramic on the ink-jet was connected with the control circuit.

2.4. Image capturing

The high-speed microscope VW-9000 machine is employed to observe the droplet formation of ink-jet chip. As shown in Fig. 1, the microscope was placed on the holder, whose position and direction can be regulated. The nozzle part of the ink-jet was set as the focus of the microscope to monitor the process of droplet formation. The frame rate of the camera was 35,000 fps and the resolution was 256 × 128 pixels.

2.5. Measurement of volume/mass of droplet

It should be noted that for measurement of small-volume droplet, special consideration of evaporation should be taken to obtain accurate mass/volume data. In the experiment, the measurement of volume/mass of droplet was performed according to a method reported previously [36]. Basically, the mass of 10,000 droplets was monitored on an accurate balance automatically at a time interval of 10 s. Then another 10,000 droplets

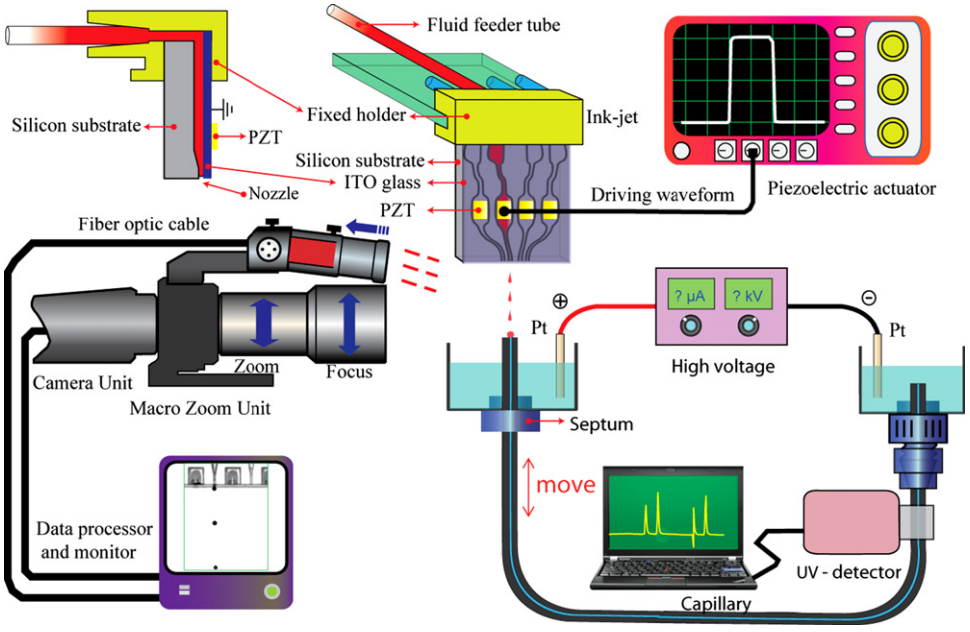

Fig. 1. Schematic illustration of the whole experimental setup. Ink-jet printing of droplet generation, high-speed microobservation system, and capillary electrophoresis system are presented in the figure.

were ejected and the mass was recorded. The accurate mass of the droplet was calculated from the mass increase which incorporated the consideration of the loss caused by evaporation.

2.6. Ink-jet-based droplet formation for sample injection in capillary electrophoresis

The ink-jet printing of droplet formation is used for sample injection of capillary electrophoresis. The capillary inlet was placed upward, and the nozzle of ink-jet is aligned with the inlet of capillary tube under the monitor of microscope as shown in Fig. 1. The ink-jet is fixed on an *XY*-stage with frames. The position precision of *XY*-stage used in our experiment is less than 0.5 μm. Therefore by adjusting the *XY*-stage manually, the nozzle of ink-jet is moved just on top of the capillary tube so that the droplet generated can fall directly into the capillary tube. Fig. 1 shows the whole experimental setup which includes the ink-jet printing system, the observation system and the capillary electrophoresis system. For each electrophoresis sample injection, the inlet of capillary was moved up out of the buffer reservoir, 2 cm higher than the outlet of capillary. The ink-jet nozzle is just on top of the inlet of capillary with a distance of 0.1 cm. The droplets generated directly fall into the capillary inlet. When all the droplets entered the capillary, the capillary was moved down about 2 cm into the buffer reservoir. Then high voltage is applied for capillary separation.

Capillary separation was performed at room temperature 20 ± 0.5 °C and relative humidity 39 ± 1% RH. The buffer solution was 50 mM glycine–NaOH buffer, pH 9.5; samples of caffeine, theobromine, and theophilline were dissolved in the buffer solution; high voltage was 10 kV, capillary ID:50 μm, effective length 43 cm and absorbance wave length 254 nm, driving waveform pulse width was 27 μs, driving voltage 44 V, and frequency 1 kHz.

3. Results and discussion

3.1. Structure of ink-jet chip and principle of piezoelectric actuator circuit

The structure of the ink-jet device used in our experiments is shown in Fig. 2a. A piece of piezoelectric ceramic was fixed on the top of solution chamber. When an electric pulse is applied, the piezoelectric ceramic will change shape in response (inverse piezoelectric effect). The press on the solution chamber, which is generated from the change in shape of piezoelectric ceramic, ejects the solution through the nozzle, forming a droplet. In ink-jet printing droplet formation, the piezoelectric ceramic actuator (driving voltage, driving pulse width and frequency) was crucial to generate uniform and stable droplets. In our experiment, a home-made circuit and software are used to drive the piezoelectric ceramic (Fig. 2b). Basically, the waveform can be designed on the computer and the signal is passed to the circuit via a USB port. Then the signal is handled on the circuit (RAM chip, FPGA chip) and then amplified through amplification circuit (Q1, Q2 for voltage amplification; Q3, Q4 for current amplification). The amplified signal is then applied and actuates the piezoelectric ceramic. Thus, with this experimental setup, the parameters such as driving voltage, pulse width, and frequency can be easily manipulated and tuned (Fig. 2c).

3.2. Ink-jet printing droplet formation

Ink-jet-based droplet formation has been widely used for a variety of applications. In conventional, commercialized ink-jet printing instruments, actuator parameters are always fixed because only certain solutions can be ejected. Under this condition, the inverse (Z) of the Ohnesorge number (Oh), which is defined as the ratio of the Reynolds number and to the square

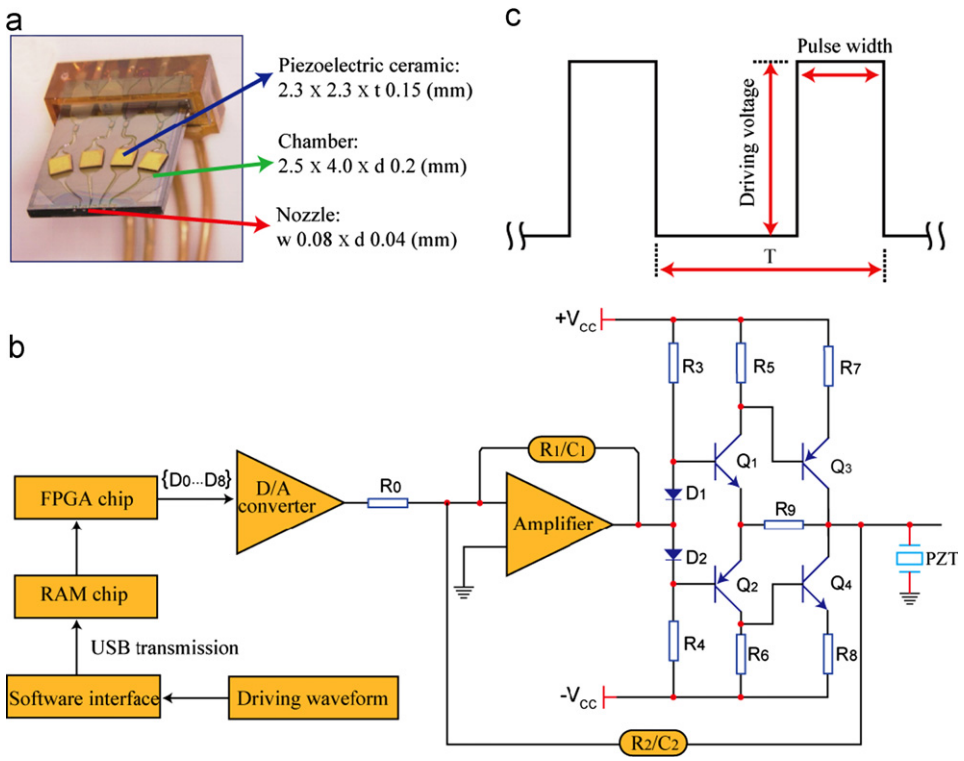

Fig. 2. Structure of ink-jet chip and principle of piezoelectric actuator circuit. (a) Picture of real ink-jet chip (four channel) used in our experiment. Ink-jet channel containing piezoelectric ceramic, solution chamber, and nozzle with their respective dimensions is shown in the picture. b) Piezoelectric actuator circuit. Software for waveform design. (c) Typical driving waveforms (square shape) characterized by driving voltage, pulse width and frequency are used in our experiments.

root of the Weber number, is utilized to consider whether a solution can be ejected or not. However, this limitation constrains the applicability of ink-jet printing for various purposes. In our experiments, a home-made driving circuit combined with a software to control the piezoelectric actuator was employed to control the ejection of droplets. With this experimental setup, the

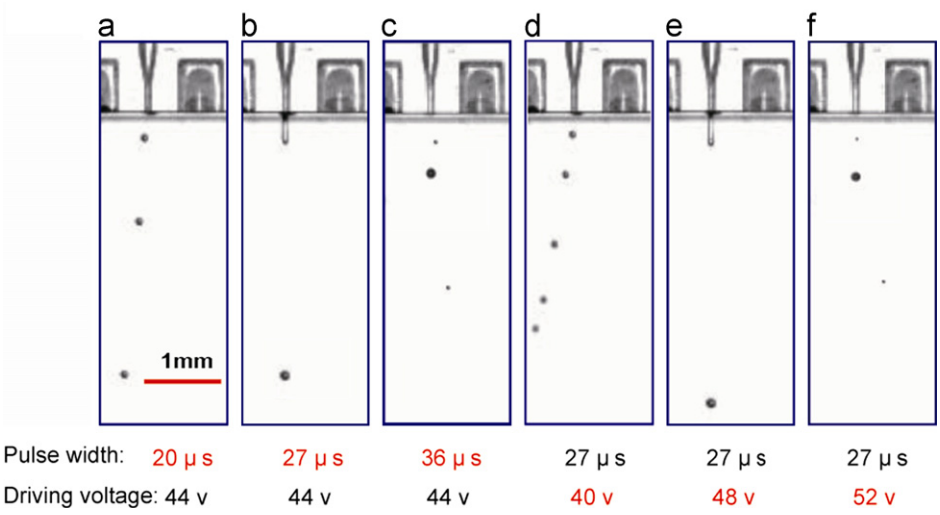

Fig. 3. Droplet generation under different driving waveforms of ink-jet. (a)–(c) Driving voltage is kept constant and the pulse width is changed; (d)–(f) Pulse width is unchanged and the driving voltage is increased. (a) and (d) Droplet generated cannot fall in straight line; (b) and (e) drop-on-demand droplet is generated; (c) and (f) satellite droplets are observed. Solution: water. Ink-jet driving frequency: 1 kHz.

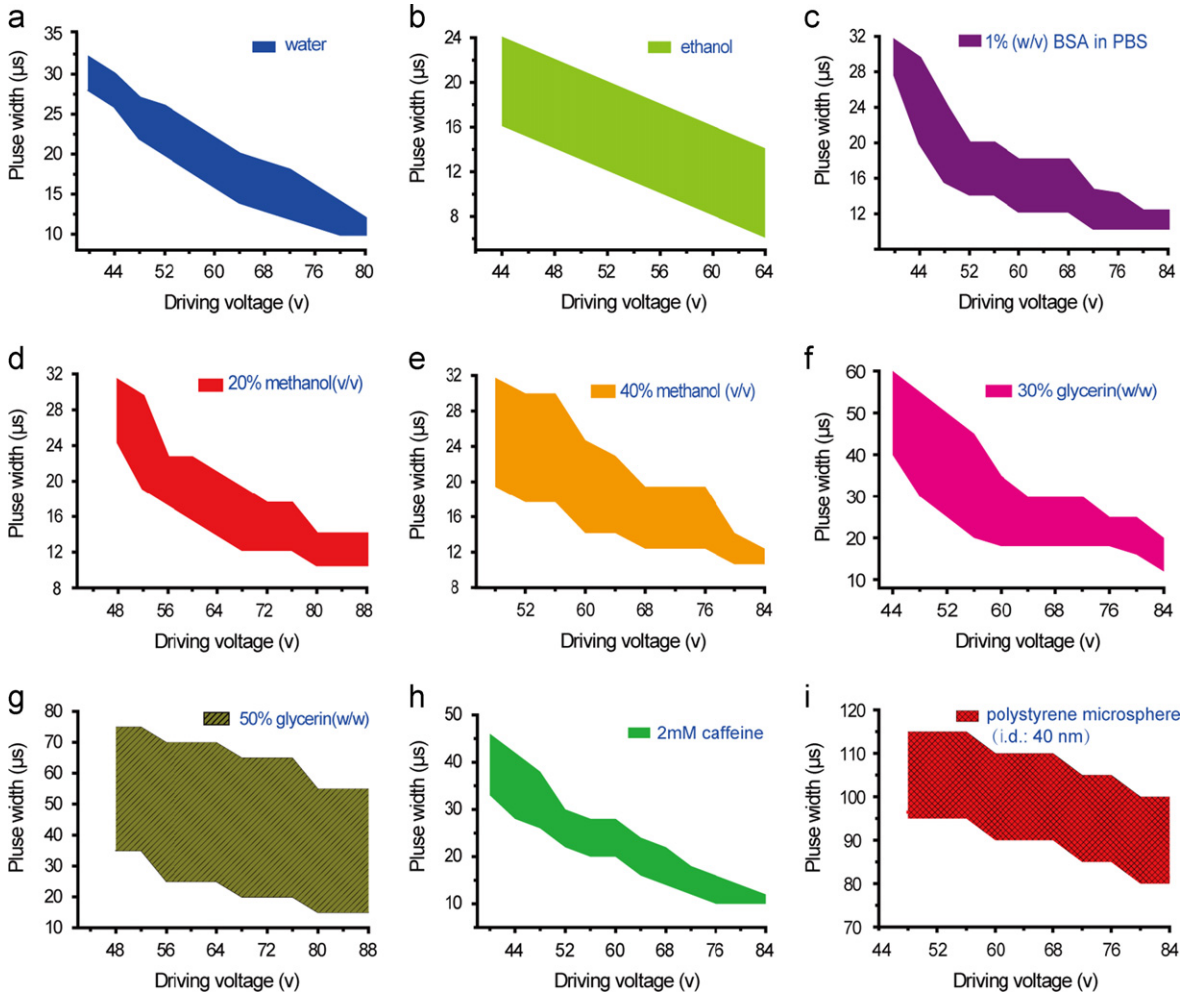

Fig. 4. Generation of stable, uniform and drop-on-demand droplet for different kinds of solutions under different driving voltages and pulse widths. The colored area in each figure represents the proper ranges of driving voltage and pulse width for respective solutions. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

parameters of actuator can be easily manipulated and tuned, which will facilitate the control of droplet formation.

In the experiments, three different conditions of droplet generation by ink-jet printing were observed. As shown in Fig. 3a, in which the driving voltage is set as 44 V and pulse width 20 μs, the droplet generation is not stable and the droplets cannot fall in a straight line. With the increase of pulse width to 27 μs, stable droplet generation can be formed and single droplet-on-demand droplet can be obtained (Fig. 3b). With the further increase of pulse width (36 μs), droplets will split after generation and satellite droplets are formed (Fig. 3c). Under the same experimental setup, if the pulse width was kept unchanged and the driving voltage was tuned, similar results were also observed (Fig. 3d and e). From those results, we can conclude that when the driving voltage or the pulse width is too low, the droplets can neither be formed nor be stable, probably due to inadequate energy provided by the piezoelectric actuator to overcome the surface tension to form droplets. When these two parameters are in proper ranges, drop-on-demand droplet generation can be obtained. When the driving voltage and the pulse width are too large, the droplet will split up because of high energy. Thus, the droplet formation could be well-controlled by adjusting the driving voltage and pulse width.

The above results also indicated that it is possible to generate the stable and drop-on-demand droplets via manipulation of the driving voltage and pulse width into appropriate scopes from solutions of different compositions that have different physical properties. Stable, single, drop-on-demand droplet generation is desirable in a variety of applications for its advantages of uniformity, ease of operation and definite mass and volume. In the experiments, we examined nine different solutions with our method and a proper range of driving voltage and pulse width was identified for respective solutions (see Fig. 4). As shown in Fig. 4, the colored areas indicate the ranges in which stable, drop-on-demand droplets can be generated. By using our home-made circuit and software, the driving voltage and pulse width can be easily tuned so that proper conditions of ink-jet printing can be identified to generate stable droplets from different solutions. Compared to conventional methodology, which can use only certain solutions, our approach has made it possible to use various solutions for stable, single, drop-on-demand ink-jet droplet formation. These results indicate that our technique is very promising because the wide scopes of solutions used for ink-jet printing can enlarge their application for various purposes.

3.3. Manipulation of droplet volume

With our designed system, the volume of droplet can also be easily controlled by manipulating the waveforms of driving actuator. As shown in Fig. 5a, the volume/mass of the droplets had a good linear relationship with different driving voltages when the droplets were generated by ink-jet printing. The linear relationship between the volume of droplet and the rise of driving voltage is as follows:

$$y = 6.83x - 166.07 \quad (1)$$

where y is the volume of one droplet, and x represents the driving voltage, with $R^2 = 0.9971$. On the other hand, when the driving voltage is fixed, the volume of droplet will increase with the addition of pulse width (Fig. 5b) through the linear relationship

$$y = 7.58x - 1.11 \quad (2)$$

with $R^2 = 0.9989$. Therefore, by manipulating the waveform of ink-jet piezoelectric actuator, changing the driving voltage and pulse width through our home-made circuit and software, we can easily, accurately control the volume/mass of droplet, which will further facilitate ink-jet printing of droplet generation for practical application.

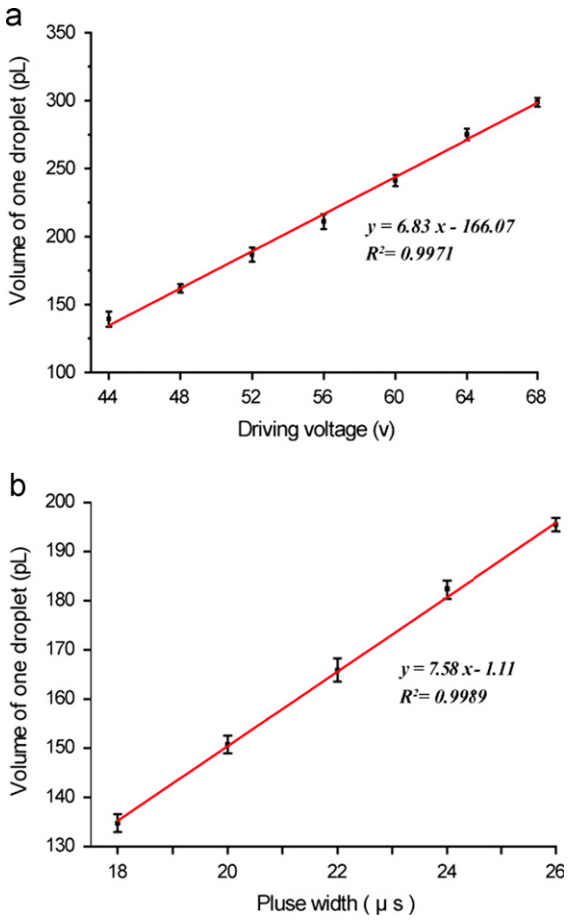

Fig. 5. Linear relationship between droplet volume and driving waveform: (a) droplet volume versus the driving voltage and (b) droplet versus the pulse width. For both conditions, very good linear relationship as obtained. Solution: 10% methanol (v/v), pulse width: 18 μs, and frequency: 1 kHz. Each data point in the graph was measured 10 repeated times).

3.4. Application as sample injector for capillary electrophoresis

Traditional capillary electrophoresis injection modes such as siphon injection, pressure injection, vacuum injection and electrokinetic injection suffered from the injection discrimination effect and the deviation of sample volume between each injection. Besides, these methods cannot give out the absolute, accurate injection volume [37–39]. Our laboratory previously developed a capillary electrophoresis system using ink-jet-printing as the sampling method. Ink-jet printing can generate highly stable and controllable nanoliter drop-on-demand droplet; thus it is ideal for precise and accurate sample injection in electrophoresis. In a previous study, the injection process was thoroughly investigated and the analytical performance of this new electrophoresis system was compared with those of traditional systems.

In this work, a systematic characterization of quantitative relationship of ink-jet-based sampling for electrophoresis was performed. With our designed ink-jet system, the microdroplet can be easily, precisely generated and controlled from various solutions. This serves as an essential quality control for the ink-jet sampling method. As shown in Fig. 1 the inlet of capillary tube was aligned with the nozzle of ink-jet under microscope through adjustment of the *XY*-stage. The droplets generated by ink-jet

printing were then directly infused into the capillary tube and finished the process of sample injection was completed. As a model scheme, solutions composed of theobromine, caffeine, and theophiline are used for droplet generation and separated by micellary capillary using sodium dodecyl sulfate (SDS) as the micellar phase.

With the utilization of ink-jet for sampling in electrophoresis, the injection volume can also be manipulated by changing the driving waveform or the number of pulses. In the experiments, we investigated the electrophoresis performance of different injection volumes by controlling the number of droplets for each injection. Fig. 6a shows the electrophoresis graphs of samples composed of different numbers of droplets (2, 5, 10, 20, and 40) injected into the capillary for electrophoresis. Fig. 6b shows the linear fitting of peak area of different substances corresponding to the number of droplets injected. As shown in Fig. 6a and b, these three substances were successfully separated under our conditions. And the intensity of respective substance increases linearly with the addition of injection volume. In the experiment, we also control the injection volume to be constant with fixed number of droplets (40) and with the increased concentration of analytes, the respective signals also increase linearly as shown in Table 1.

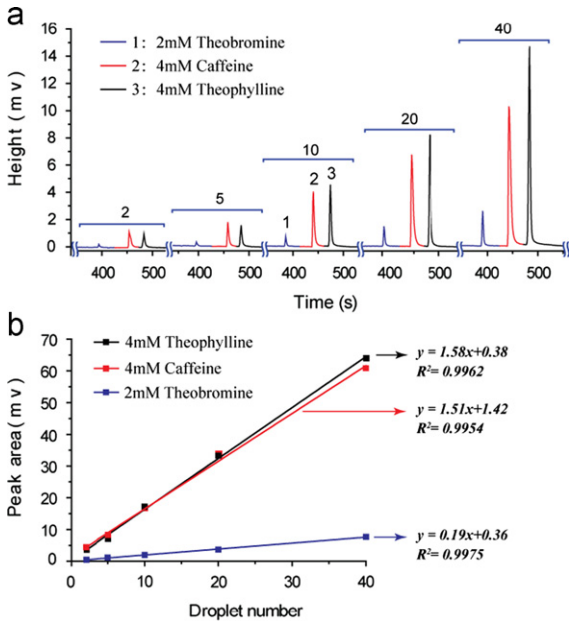

Fig. 6. Correspondence of droplets number to the signal intensity of capillary electrophoresis: (a) electrophoresis graph of samples composed of different numbers of droplets (2, 5, 10, 20 and 40) and (b) linear fitting of peak area versus the number of droplets. (For each data point, 10 times repeated experiments were measured).

Table 1
Performance of capillary electrophoresis for different concentrations of solutions injected by ink-jet printing. Samples composed of different concentrations of solutions with fixed volume (40 droplets).

Analyte	t^r min	RSD of t^r, $n=10$ (%)	RSD of peak area, $n=10$ (%)	Linear dose curve	Detection limit/ (mM L^{-1})
Theobromine	6.55	0.2	0.83	$y=3.93x=0.11$ $R^2=0.9983$	0.08
Caffeine	7.55	1.2	1.22	$y=17.12x=2.88$ $R^2=0.9993$	0.02
Theophilline	8.38	2.1	0.78	$y=33.91x=2.81$ $R^2=0.9985$	0.06

These results indicate the high reliability and accuracy of the ink-jet based electrophoresis method.

Such high accuracy and reliability were reasonable because the droplet generated by ink-jet printing under our experimental condition was uniform and stable. All the contents in the droplet were accurately loaded into the capillary tube; thus the signal response should be consistent with the quantity of injection volumes. These results indicated that the ink-jet-based droplet generation can be used for sample injection in practical electrophoresis application. Besides, the volume of the droplet used in this experiment can be calculated to be 179 pL (RSD = 1.2%, $n=10$) with methods described before. Considering that the concentration of the solution is known (4 mM caffeine, 2 mM theobromine, and 4 mM theophiline), absolute quantity of sample can be obtained. Based on these results, we propose that with the ink-jet printing of droplet generation for electrophoresis injection, a lot of parameters, including droplet volume, the concentration of the solution, and the instrumental responding factor for certain substances can be determined. The separation and analysis of some biological and environmental samples are continuously being studied in our two laboratories.

4. Conclusion

In this work, ink-jet printing for uniform, stable drop-on-demand droplet formation was developed and investigated. The utility of home-made circuit board and software enables us to tune the driving waveform of ink-jet chip conveniently. The solutions that can be ejected are enlarged extensively and the formed droplets can be manipulated easily and precisely. Finally, this highly precise picoliter droplet generator is employed in sampling for capillary electrophoresis which is advantageous over conventional injection methods in that the actual volume of sampling can be obtained. We propose that the combination of picoliter droplet generator with capillary electrophoresis will be applicable for real sample separation and analysis. Besides, the ink-jet printing platform developed can be applied for a variety of other practical purposes.

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