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A gravity driven micro flow injection wetting film extraction system on a polycarbonate chip

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Abstract

A micro flow injection wetting film liquid–liquid extraction system has been developed for trace analyte concentration and on-chip detection. A hydrophobic channel fabricated on a polycarbonate chip was used to support the wetting film, and hydrostatic pressure generated by the difference in liquid levels was employed to drive the fluids. Sequential injection of segments of aqueous sample solution and organic solvent was conducted by switching the sample- or solvent-containing vials to an on-chip sampling probe, and detection was performed by a co-focused, laser induced fluorescence detector. Using butyl rhodamine B as a model analyte and butanol as the solvent for both film-coating and elution, various experimental conditions such as hydrostatic pressure, coating time, channel length, sampling volume, and sample acidity were investigated. Under optimized conditions, a 24-fold enrichment factor was obtained with the consumption of about 3 μL sample solution, and a detection limit (3σ) of 6.0×10^{-9} M butyl rhodamine B was achieved at the sampling rate of 19 h^{-1}. Eleven consecutive runs of a 1.0×10^{-5} M butyl rhodamine B solution produced a relative standard deviation of 1.5% for the detected fluorescence signals.
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1. Introduction

Microfluidic chips for chemical and biochemical analyses have been extensively developed since the introduction of the concept of micro total analysis by Manz et al. [1]. Although most studies on microfluidic chips dealt with the separation and detection of biochemical and chemical species by chip-based electrophoresis [2–4], microfluidic devices concerning sample pretreatment techniques, such as analyte derivation, matrix isolation and analyte concentration, have recently attracted much attention from analytical scientists [5]. Pressure driven microfluidic liquid–liquid extraction is one of the rapidly developed techniques. The first report on microfluidic extraction was made by Kitamori's group [6]. In this work, a Y-shaped microchannel was fabricated in a glass chip. When an aqueous solution of Fe-bathophenanthrolinedisulfonic acid complex and a chloroform solution of tri-*n*-octylmethylammonium chloride were introduced separately by two syringe pumps from the side introduction channels into the central extraction channel, a parallel two-phase laminar flow was formed in the extraction channel. The Fe complex was extracted into the chloroform flow by phase transfer through the interface of the organic and aqueous phases based on molecular diffusion. Since then, a number of works on chip-based extraction with parallel two-phase laminar flow [7], parallel three-phase laminar flow [8], two-phase cross flow [9] and two-phase countercurrent flow [10] have been reported by several groups. In general, the microfluidic extraction based on laminar flow possesses distinguished advantages. First, it may provide high extraction efficiency owing to the enhanced ratio of the interfacial area to phase volume as well as the significantly reduced diffusion distance inside the microchannels. Second, it consumes an extremely low quantity of sample and reagent that is most beneficial for bio-applications where samples are extremely

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valuable and reagents are expensive, and beneficial for environmental protection due to the reduction of organic waste discharge. Third, it does not require a special phase separator integrated onto chips. Nevertheless, the laminar flow-based microfluidic extraction has a troublesome problem, this being instability of the aqueous/organic interface. Thus, various channel structures, such as guided channel [8], axis-shifted channel [7], hydrophobic/hydrophilic hybrid channel [9,10], and intermittent partition walls [11] have been developed to stabilize the interface. These structures increased the difficulties in the chip fabrication. Besides the laminar flow-based micro extraction systems, a segmented flow-based microfluidic extraction system [12], a micro-porous membrane-based microfluidic extraction system [13] and a stagnant droplet-based microfluidic extraction system [14] have also been reported. The extraction efficiency of the segmented flow model could be significantly enhanced by the increase of the interface area for the two phases. However, a phase separation device was required to be integrated on the chip [12]. For the micro-porous membrane extraction, no such problems like emulsion formation, phase separation and interface instability existed. But its extraction efficiency was restricted by the relative low mass transfer rate across the membrane. Although an enrichment factor of 1000-fold was obtained by the microfluidic extraction model of stagnant droplet [14], its non-continuous operation model made it difficult to be coupled to other flow analytical systems.

Sequential injection wetting film extraction, a novel flow extraction technique introduced by Ruzicka and Christian's group [15] in 1996, is based on the film-forming characteristics of organic solvent on Teflon tubing walls. The organic solvent, aqueous sample solution and eluting solution were sequentially aspirated into an extraction coil made of Teflon tubing. When the organic solvent band passed the coil, a uniform organic film was formed on the inner wall of the extraction coil due to the wettability of the tubing wall towards the solvent. The extractable analytes in the aqueous sample band were extracted into the organic wetting film when the sample band passed the coil. The extracted analyte was then eluted by microliters of eluting solution. Without need for phase segmentor and phase separator, an enrichment factor as high as 150 was achieved at a sampling rate 10 h^{-1}, and both the consumption of organic solvents and discharge of laboratory waste were significantly reduced. Since then various sequential or flow injection wetting film extraction systems have been coupled with spectrophotometry for determination of trace molybdenum [16], vanadium(IV) and vanadium(V) [17], chromium(VI) and chromium(III) [18] and nitrophenols [19], with flame atomic absorption spectrometry for determination of trace copper [20], and with β-activity detection for determination of trace strontium-90 [21]. To the best of our knowledge, up to now, no microchip-based flow injection wetting film extraction systems have been reported.

In this work, the hydrophobic property of the microfluidic channels fabricated on polycarbonate chips was exploited to develop a novel micro flow injection wetting film extraction (MFWE) system. Gravity force was used for driving fluids and a laser induced fluorescence detector (LIF) was employed for on-channel detection. With butyl rhodamine B (BRB) as a model analyte, various experimental parameters affecting the performances of the MWFE system were investigated.

2. Experimental

2.1. Chemicals

Aqueous stock solution of 1.00×10^{-3} M butyl rhodamine B (Tianjin Chemical Reagent Co., Tianjin, China) was prepared by dissolving 0.0535 g of BRB in 100 mL of water. The BRB working solutions in the range of 1.00×10^{-5} to 1.00×10^{-8} M were prepared by step-wise dilution of the stock solution with water. Butanol (Shanghai Chemical Reagent Co., Shanghai, China) was used without further purification. All chemicals used were analytical grade or better and Millipore simplicity pure water was used throughout the work.

2.2. Apparatus

A home-made confocal microscope laser induced fluorescence (LIF) system [22], equipped with an argon ion laser (Sanle Instrument Co., Nanjing, China), was used for detection. The laser beam was isolated by a dichroscope (488 nm/520 nm) and focused to a 20-μm spot on the channel from below the chip. The emitted light was collected by the same focusing system, and detected by a PMT (Hamamatsu, Beijing). The signal output of the PMT was recorded with a model XWTD-164 chart recorder (Dahua Instruments. Shanghai).

2.3. Fabrication of the microchip device

A hot wire imprinting method was used to fabricate the microchannel onto PC plates of 2 mm thickness (a product of Ketelong Co., Taiwan, China). A piece of straight copper wire (200 μm in diameter × 7 cm) was placed over a 2 cm × 6 cm PC plate all the way across the length of the plate. The PC plate and the wire were sandwiched by two glass plates, and the sandwich assembly was placed between two electrically heated stainless steel blocks. When the temperature was heated to 142 °C and maintained at the level, a pressure of 1.0 MPa was applied to the blocks for 5 min. The pressure was released after the temperature was cooled down to 60 °C with running water, the sandwich assembly was withdrawn from the heating blocks, and the PC plate was removed. Then the wire was carefully pulled away from the PC plate to reveal the channel across the length of the plate. The channel-imprinted plate and another flat PC plate of the same type and size as the imprinted one were thoroughly cleaned in isopronol and dried under a N_2 stream. The two plates were face-to-face contacted and then sandwiched by the glass plates and placed again between the heating blocks that were kept at 144 °C. A

pressure of 1.0 MPa was applied to the heating blocks for 2 min to bond the two PC plates together. After the bonded chip was removed from the heating blocks, both the left and right edges of the bonded chip were ground with emery paper. Using the method described in Reference [23], two holes were drilled, with a 0.35 mm o.d. flat-tipped drill bit, along the channel to a depth of 4 mm from each terminal of the channel. Two pieces of fused-silica capillary (200-μm i.d. and 375-μm o.d., product of Refine Chromatography Ltd., Yongnian, China), one 1 cm long that was used as a sampling probe to introduce sample and solvent and the other 40 cm long that was used to hold the liquid segments and generate hydrostatic pressure, were, respectively, inserted into the holes. Care must be taken to eliminate the dead volume between the bottom of the holes and the terminals of the capillaries. Epoxy glue was used to seal the connection joints. To avoid blocking of the channel by epoxy, an epoxy-freezing approach [24] was employed. Briefly, a freshly mixed and fluidic epoxy was applied to the gap between the hole and the capillary. The fluidic epoxy spread in the gap due to capillary action until the epoxy almost reached the terminal of the capillary, observed with the help of a microscope. The chip was immediately put into a refrigerator and maintained at −4 °C for 5 h to freeze the epoxy. The epoxy was partially cured during this operation. The chip was then removed from the refrigerator and the epoxy was fully cured at room temperature for 6 h.

2.4. Experimental set-up of the MFWE system

The experimental set-up of the gravity driven micro flow injection system for wetting film extraction is illustrated in Fig. 1. The microchip device for MFWE, positioned in a plastic holder, was put on the working platform of the confocal microscope LIF system. The laser beam was focused onto the downstream of the channel, 2 mm away from the capillary-to-channel connection joint. The sample dispensing system for micro flow injection analysis developed by Du et al. [25] was modified to perform sequential injection of sample and solvent into the MFWE system. Briefly, six cap-removed and bottom slotted 0.2 mL microtubes (a 1.5-mm wide × 2-mm deep slot was sawed on the conical bottom of each microtube) were used as the reservoirs for organic solvent, water, and four sample solutions, respectively. The slotted vials were horizontally fixed on a plastic platform in an array, with the slot of each vial being positioned horizontally to allow free passage of the sampling probe through all the vial slots sequentially by linearly moving the platform along the direction of the array. The gravity driven system was composed of a 40 cm long fused-silica capillary and a 25 mL beaker for waste collection.

2.5. Procedures.

2.5.1. Liquid–liquid extraction

Prior to use, the micro extraction unit was sequentially flushed with ethanol and water. The vial for water (the blank) was manually shifted to the sampling probe. By adjusting the length of the vertical section of pressure inducing capillary, a suitable level difference between the sampling probe and the liquid surface in the waste beaker was produced, resulting in a desired flow rate. After a stable base line was established, the extraction procedure began. The coating/eluting solvent, aqueous sample solution and water (used to wash-out the sampling probe after it was withdrawn from the sample vial) were sequentially aspirated into the extraction unit, each for a specified time (typically, 120 s for coating/eluting solvent, 60 s for sample solution and 2 s for water), by sequentially

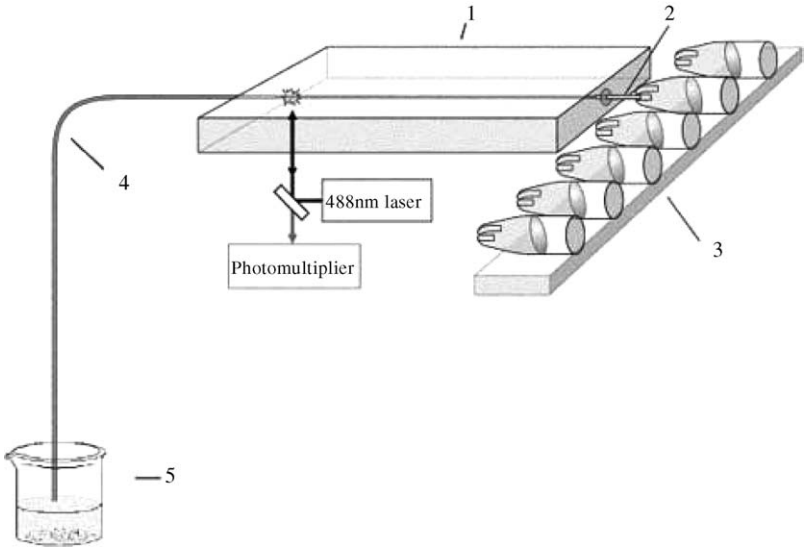

Fig. 1. The experimental set-up for the chip-based micro flow injection wetting film extraction. (1) Microfluidic chip made of polycarbonate; (2) fused-silica capillary sampling probe; (3) array of bottom-slotted vials for organic solvent, blank and sample solutions; (4) fused-silica capillary for inducing hydrostatic pressure; (5) beaker for wastes. This figure was not drawn to scale.

switching the corresponding vial into sampling position so that the sampling probe was inserted into the solution through the slot. LIF signal trace was recorded with a chart recorder. Owing to the solvent for elution being the same as that for the coating, the elution for the current run was accompanied by the coating for the next run.

2.5.2. Measurements of enrichment factor

Two BRB working solutions were prepared. The first (solution A), whose concentration C_A was in the 10^{-6} M level, was prepared in water (or 0.01 M NaOH solution). The second (solution O), whose concentration (C_O) was about 20-fold of C_A, was prepared in butanol. Solution A was subjected to the MFWE under optimized conditions, resulting in a transient fluorescence signal with peak height of I_A. Then, solution O was continuously aspirated to pass the channel, producing a steady state signal I_O. Thus, the enrichment factor F was estimated with the equation $F = I_A C_O / C_A I_O$.

3. Results and discussion

3.1. Method development for MWFE

In conventional wetting film extraction systems, hydrophobic Teflon tubing is used as the supporter of organic wetting film. For the proposed MFWE system, a microchannel with hydrophobic surface is required to support the organic film. Glass chips have been widely used in various microfluidic analytical systems, mainly due to their excellent optical and electroosmotic properties. However, they are not very much suitable for the MFWE unless the hydrophilic surface of the native glass channel is modified to be hydrophobic. Polymer-based microchips have recently attracted much attention [26] because they are much less expensive than glass, are not as fragile as glass, and are capable of being mass-produced by either embossing or molding technology outside a clean-room environment. The hydrophobic property of the native polymer surface, although troublesome for the chips to be used for chip-based electrophoresis, is an advantage worthwhile being exploited to fabricate microfluidic chips for MFWE. Thus, PC plates were used for fabrication of the MFWE chip as described in Section 2.

Another requirement to establish a wetting film extraction system is a suitable fluid driving and sample/solvent injection system. In previously reported works on sequential/flow injection wetting film extraction [17–21], either syringe pumps or peristaltic pumps, in combination with various switch valves, were employed to perform these tasks. However, neither of them is suitable to be coupled to the MFWE because the large dead volume (usually several decades to hundreds of microliters) involved in the valve and the connection tubing of conventional sequential/flow injection system does not match the microliter volume of the microfluidic channel. Electroosmitic driving that has been widely applied in chip-based electrophoresis is also not applicable to the MFWE system due to non-conductive organic solvent being involved. Hydrostatic pressure driving [25,27], also known as a gravity pump, is another alternative for pumping fluids in microfluidic systems. It possesses such advantages as non-pulse pumping and simplicity in equipment. Using the gravity pump in combination of a microvial array for liquid dispensation, Du et al. [25] developed a novel chip-based micro flow injection spectrophotometry system. This driving and sample injection model seems to be suitable to the proposed MFWE system. Nevertheless, the gravity pump generates a constant flow rate only under the condition of both the hydrostatic pressure (the driving force) and the back-pressure (the resistant force consisting of friction and surface tension) being kept constant. This may be satisfied provided that one phase of liquid is driven by its own gravity. However, if two phases of immiscible liquids with different densities and viscosities are involved to form a two-phase segmented flow, both the driving force and the resisting force, accordingly the flow rate, may no longer be constant. Tests confirmed this expectation. Thus, if the polymer channel and fused-silica capillaries of the MFWE systems were wholly filled with water, the flow rate for the single-phase water flow induced by a 27 cm difference in water levels was 8.0 μL/min. When butanol was gradually introduced into the flow system to substitute the water while the difference in liquid levels was kept 27 cm high, the flow rate for the two-phase segmented flow (water followed by butanol) was gradually decreased. When all of the channel and capillaries were filled by butanol, the flow rate for single-phase butanol flow was 2.5 μL/min. The ratio of the flow rate of water to the flow rate of butanol was 3.2. When the difference in liquid-levels was step-wisely decreased from 27 to 10 cm, the observed rates of single-phase flows for either water or butanol were steadily decreased but the ratio of water-flow-rate to butanol-flow-rate was increased from 3.2 to 4.8 (Table 1). The table also lists the fluorescence signals and the relative standard deviations (R.S.D.s) of the signals produced by the MFWE system working at various liquid-level differences (note: these data were obtained with a volume-based sampling technique so that the injected sample volumes were kept constant regardless of the flow-rate changes). With the decrease in the difference of liquid-levels, the fluorescence signals were steadily increased while the R.S.D.s were tendentiously deteriorated. The higher signals obtained at smaller liquid-level differences can be ascribed to the slower moving velocity of the sample segment and, consequently, the long contact time between the sample segment and the wetting film, while the poorer R.S.D.s of the signals can be attributed to the greater fluctuating flow rates being generated by the smaller liquid-level differences. Thus, a 25 cm difference in liquid levels was applied in the following studies in order to obtain a less fluctuating flow rate for the two-phase segmented flow. Under this condition, quite satisfactory precision of the determinations could be obtained, provided that sampling time and elution/coating time were strictly controlled.

Table 1
Effect of the difference in liquid levels on the flow rates of single-phase water and single-phase butanol and on the fluorescence signals of MFWE[a]

Difference in liquid levels (cm)	Flow rates (μL/min)		Ratio of F_w/F_b	Relative peak height	S.D. for peak height ($n = 3$)
	Water	Butanol			
27	8.0	2.5	3.2	100	0.6
20	5.2	1.55	3.4	116	2.0
15	3.0	0.75	4.0	156	6.3
10	1.7	0.35	4.8	201	6.9

[a] MFWE was performed with 10^{-5} M BRB at flow rates generated by the specified liquid-level differences. A 1.0 μL of sample solution was injected with a volume-based sampling technique. The time duration for elution/coating was 120 s.

The inner diameter of the capillary used to induce hydrostatic pressure was found to have dramatic influence on the flow rates: relative rates of water flow generated by a 25 cm high water column inside capillaries with the diameter of 200, 100 and 50 μm were 100, 6.0 and 0.57, respectively. This was mainly because the thinner the capillary the greater the surface tension that resisted the hydrostatic force of the water column. This observation clearly shows the gravity driven model is very sensitive to the change of the resistant forces. The flow rates generated by the later two capillaries were too slow (less than 1 μL/min) to meet the requirement of the present MFWE system. Thus, the capillary with 200 μm inner diameter was used.

In most conventional wetting film extraction systems, air bubbles were applied to prevent the direct contact of coating solvent, sample solution and eluting solution. Hence, the axial mass transfer of analyte between the organic coating solvent and the aqueous sample solution was avoided owing to the presence of air barrier. The wetting film-based extraction is the only possible way for mass transfer of analytes from sample solution to eluting solution to occur. In the present system, however, when air bubbles were introduced to prevent direct contact of the sample solution and the elution/coating solvent, the analytical signals were almost the same as without air bubbles but the signal reproducibility severely deteriorated. In worst case, the fluids even stopped flowing due to the presence of the air segments. This indicated that the axial transfer of analyte between segments in the present MFWE system was negligible, most possibly due to the small ratio of diameter-to-length for the segments. The poor reproducibility may be attributed to the flow instability caused by the air bubbles. Thus, air segment was avoided.

3.2. Influences of various experimental conditions

3.2.1. Coating solvent and the time duration for the coating

In a wetting film extraction system, the type of organic solvent may significantly affect the thickness and stability of wetting film formed on the inner wall of channels. It may also influence the partition coefficient of the analyte between the solvent and the aqueous solution. As mentioned in the previous sections, the organic solvent used for coating was also used for elution in the present system. In such a circumstance, it may also impact the elution process. Although the elution step of the current run was accompanied by the coating step of the next run and the two steps could not be isolated from each other, we use the term "coating" for the combined process in this section.

Although various organic solvents such as benzene, chloroform, methyl-isobutyl-ketone have been used in the previous reported wetting film extraction systems, only water-immiscible alcohols, including butanol, isobutanol, isopentanol and hexanol, were examined in the proposed MFWE extraction system because benzene, ketones and chloro-substituted methane attack the microfluidic chips made of PC. Using these alcohols for coating, the fluorescence signals of a BRB standard solution, produced by MFWE, were observed and compared. Tests revealed that the relative sensitivities, expressed by normalized peak heights, of 110, 100, 46 and 48 were observed for isobutanol, butanol, isopentanol and hexanol, respectively. Butanol was finally chosen because its viscosity was lower that of isobutanol.

The time duration for coating might affect the thickness of the wetting film and consequently the sensitivity of the extraction system. Using butanol as the coating and elution solvent, the influence of coating time on the fluorescence signal was investigated. Since the variation of coating time would result in changes of the flow rate, and consequently the sampling volume if a time-based sampling technique was employed, a volume-based sampling technique was used in this investigation to ensure a constant volume of sample solution being subjected to the MFWE. Thus, the sampling probe and the extraction channel themselves were also served as the sampling loop. As shown in Fig. 2, if no butanol was coated onto the channel wall, a moderate peak height of fluorescence signal, about 60 % of the maximum signals observed under the coating condition, was obtained. The signal produced without coating can be attributed to adsorption of the analyte by the hydrophobic surface of the channel (note: BRB is apt to be absorbed on both hydrophobic and hydrophilic surfaces). A similar observation has been reported by Luo et al. for their conventional wetting film extraction of bromothymol blue [15]. When the channel surface was coated with butanol, constant and maximum fluorescence signals were obtained in the coating time ranging 30–180 s. This might be ascribed to the limited surface area of the micro-channel (about 20 mm^2) that was quickly saturated by the coating solvent within 30 s—the shortest tested coating time. In the present MFWE system, a quite long period of 120 s was used

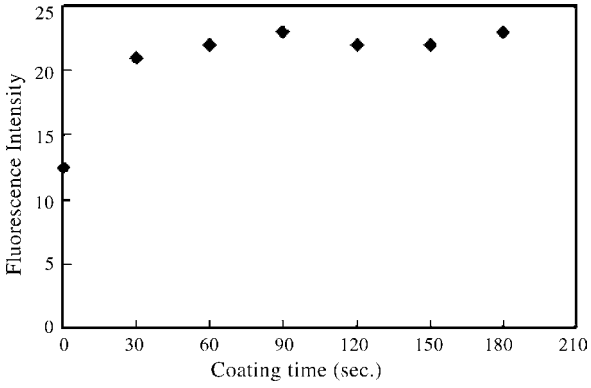

Fig. 2. Effect of coating time on the peak height signals. Gravity driving, 25 cm level difference; length of extraction channel, 5.6 cm; BRB concentration, 1.0×10^{-6} M; sampled volume, 1.0 μL (volume-based sampling).

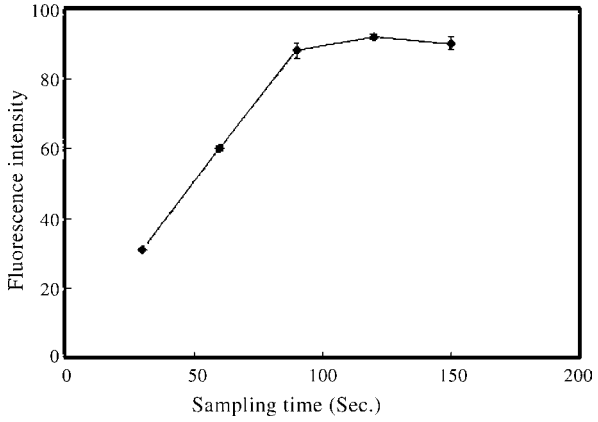

Fig. 3. Effect of sampling time on the peak height signals. Elution/coating time 120 s; other experimental conditions were the same as described in Fig. 2 except for the sampling parameter. The error bars indicate one standard deviation of three measurements.

for coating and elution in order to eliminate carry-over effect of different samples.

3.2.2. The length of hydrophobic channel

To examine the influence of channel length on extraction efficiency, the laser spot was shifted to the locations of 1/4, 1/2, 3/4 and full length of the channel then MFWE was performed. It was found that the fluorescence signals of MFWE were linearly increased with the increase of channel length, the regression equation being $F = 10L + 5$ (F, fluorescence signals in arbitrary unit; L, the channel lengths in centimeter; $R^2 = 0.9999$). This observation indicates that the extraction efficiency and accordingly the sensitivity of the proposed MFWE may be further improved if a longer channel, for instance a serpentine or spiral channel imprinted on a plastic chip with a small footprint, is used.

3.2.3. Sampling time

In the proposed system, a time-based sampling model was used if not specified. As discussed in Section 3.1, the flow rate of the two-phase segmented flow driven by a gravity pump was not constant in the entire extraction process. Thus, the relationship between the sampled volume and the sampling time was investigated first. It was observed that the sampled volume almost linearly increased with the increase of sampling time within 100 s. With a further increase of the sampling time, the sampled volume increased more quickly, leading to positive deviation from the linearity. As to the detected signals, shown in Fig. 3, they were linearly enhanced with the increase of sampling time from 30 up to 90 s. Since the sampled volume was more quickly increased with the increase of the sampling time after the sampling time was over 100 s, the detected signal would be further enhanced after 90 s if the extraction capacity of the wetting film had not been saturated. Unfortunately, the observed signals for the sampling times longer than 90 s were leveled off. These experimental results indicated that the maximum extraction capacity of the present wetting film was reached at the sampling time of 90 s for a 1.0×10^{-6} mol/L BRB standard solution. In the following studies, a sampling time of 60 s (corresponding to about 3 μL sample) was applied.

3.2.4. Acidity of the sample medium

The influence of sample acidity on the detected fluorescence signal was investigated by adjusting the sample medium to pH 1.0, 6.9 and 13.0 with hydrochloric acid, phosphate buffer and sodium hydroxide solutions, respectively. Then the samples with different acidities were subjected to MFWE. It was found that relative peak heights of 71, 100 and 165 were obtained for the acidic, neutral and basic samples, respectively. It was also observed that the samples prepared with either pure water or phosphate buffer (pH 6.9) produced the same fluorescence signals.

3.3. Analytical performances

Eleven determinations of a 1.00×10^{-5} M BRB standard solution with the proposed method produced a relative standard deviation of 1.5% for the detected signals. Fig. 4 shows a recorded trace for a series of BRB standard solutions (prepared in water, pH 7.0) in the concentration range of 1.00×10^{-6} to 10.0×10^{-6} M BRB, the correlation coefficient of their linear regression equation ($F = 55.2C + 16.7$, F represents fluorescence signals in arbitrary unit, C represents BRB concentrations in μM) being 0.9997. Tests also showed that the linear dynamic range could be expanded down to 5.00×10^{-8} M and up to 1.00×10^{-5} M. Compared to the signal produced by continuous aspiration of a BRB standard solution prepared in butanol into the channel, an enrichment factor of 16 was obtained at the sample throughput rate of $19\,h^{-1}$. When the sample was prepared in a dilute NaOH medium (pH 13.0) an enrichment factor of 24 was obtained. The detection limit (based on three times of the baseline noise) was 6.0×10^{-9} M BRB.

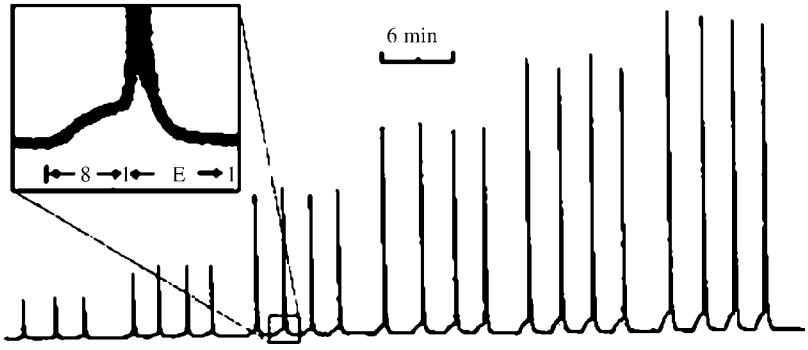

Fig. 4. Recording trace of the signals produced by the micro flow injection wetting film extraction system with a series of standard BRB solutions. Elution/coating time, 120 s; Sampling time, 60 s. Other experimental conditions were the same as described in Fig. 2. BRB concentrations from left to right ($\times 10^{-6}$ M): 1.0, 2.0, 4.0, 6.0, 8.0 and 10.0. In the insert, the signal detected in the time duration *S* was for aqueous sample segment while the signal detected in the time duration *E* was for the eluant.

4. Conclusion

Since the native surface of the micro channels fabricated on a polymeric chip is an excellent supporter for organic wetting films, microfluidic polymer chips, in conjunction with a gravity pump and a vial array for sample and solvent distribution, can be used to perform on-chip micro flow injection wetting film extraction for trace analytes. For the two-phase segmented flow, a gravity pump cannot generate steady flows. However, this does not deteriorate the reproducibility of the analytical signals produced by the micro flow injection wetting film extraction system, provided that reasonable liquid level difference is applied and regular sample and solvent aspiration is conducted. Although a 24-fold enrichment factor has been achieved in the developed micro flow injection wetting film extraction system with a 5.2 cm long hydrophobic extraction channel, higher enrichment factor may be expected if longer polymeric channels are used.

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