MICROFLUIDIC THERMAL DIGESTION OF AQUEOUS SAMPLE AT TEMPERATURE HIGHER THAN 100^{O}C

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ABSTRACT

This work reported a microfluidic solution for aqueous sample pretreatment at temperature up to 150 ^{o}C without boiling. The preliminary experimental results showed that temperature over 145 ^{o}C along with pressure higher than 1000 kPa was successfully realized in this continuous-flow chip. The absorbance of the samples after chip digestion at 700 nm had a linear correlation coefficient of 0.996 with total phosphorus concentrations varied from 1 mg/L to 5 mg/L.

KEYWORDS

Microfluidic thermal digestion, aqueous sample, high temperature, high pressure.

INTRODUCTION

With the development of wireless water environment monitoring, on-site total phosphorus measurement is in great demands, where thermal digestion is an important sample pretreatment [1]. In conventional thermal digestion, aqueous sample along with digestion agent, such as $K_2S_2O_8$ solution, are heated to 120 ^{o}C in a pressurized container for organic phosphorus compound decomposition. However, digestion in a pressurized container faces difficulties in on-site measurement. Meanwhile, microfluidic solutions for this aqueous sample operation at temperature high than 100 ^{o}C have been rarely reported [2].

In this work, a microfluidic thermal digestion chip for water treatment at temperature over 100 ^{o}C without boiling is presented. The principle to get high temperature in chip is discussed in details and the fabrication process is also given out. The high temperature and high pressure experiments show that this microfluidic chip can provide pressure over 1000 kPa and temperature over 150 ^{o}C without boiling. Linear correlation coefficient of 0.996 of the absorbance of the digested sample at 700 nm is obtained in the total phosphorus digestion experiment, when the total phosphorus concentration varies from 1 mg/L to 5 mg/L.

PRINCIPLE AND FABRICATION

The working principle of the chip is shown in Fig. 1. According to the Hagen–Poiseuille equation, the pressure drop in a fluid flowing through a channel is decided by the channel size (fourth power relation) and the flow rate (linear relation). The smaller channel (pressure increasing zone) will dramatically increase the pressure in the upstream channel. The wider channel (heating zone) will provide a long heating time and reduce the unnecessary pressure increasing at certain flow rate. According to the Antoine equation, when P_1 is higher than 500 kPa, the boiling point of water in the heating zone can be raised to 150 ^{o}C, which may guarantee a workable thermal digestion in chip.

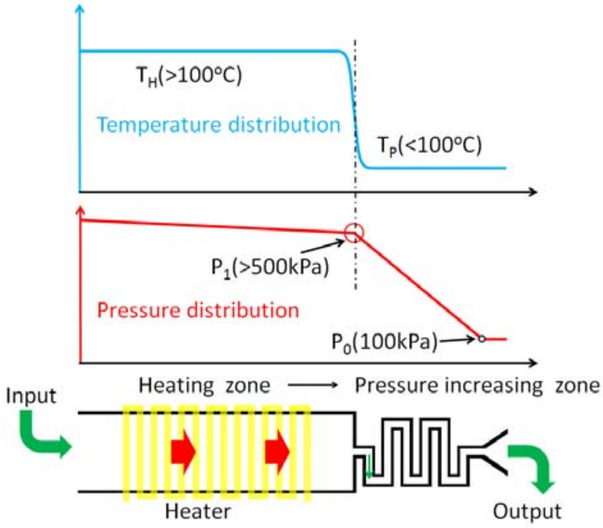

Figure 1. Working principle of the present chip with pressure and temperature distributions along the microchannel.

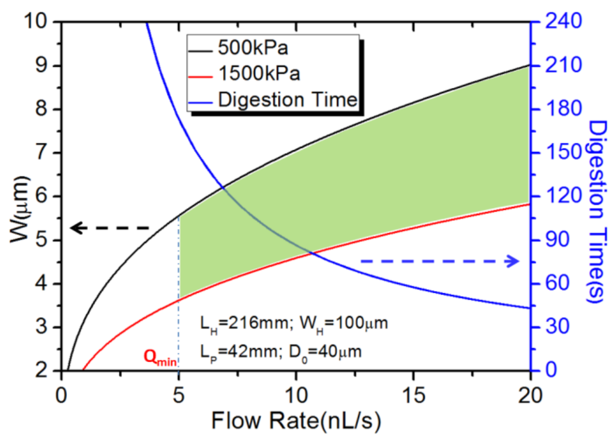

Figure 2. Phase chart of the present microfluidic thermal digestion chip. The green region refers to the acceptable chip design.

Except for the heating zone and the pressure increasing zone in Fig. 1, another mixing zone was needed to mix the sample and digestion agent, and the mixing was realized by a pure diffusion. In order to get a good mixing result, the diffusion length in the mixing zone should be large enough. The final sizes of the channel in the mixing zone were L_M = 270 mm and W_M = 40 μm. The channel depth (D_0) was set to 40 μm at first to optimize the other more critical dimensions. The channel sizes in the heating zone were designed to be L_H = 208 mm and W_H = 100 μm based on the allowable area. Sizes of the microchannel in the pressure increasing zone (L_P, W_P) would have a great impact on the high pressure performance, and should be designed carefully. L_p is set as 42 mm and W_p was designed based on the phase chart, as shown in Fig. 2, in which the temperature of the pressure increasing zone was set at 50 ^{o}C. In order to keep the time for collecting 50 μL sample (minimum volume for test) in three hours, the minimum flow rate (Q_{min}) was set at 5 nL/s. The minimum pressure 500 kPa was to make sure the boiling point being higher than 150 ^{o}C, and the maximum pressure of 1500 kPa for the safety consideration. Therefore, the acceptable design window was shown as the green area in Fig. 2, and W_p was finally set to 5 μm.

The fabrication process of this chip was shown in Fig. 3, and the depth (D_0) was set as 20 μm and 40 μm in this experiment. Microchannels and part of the isolation trench were etched by deep reactive ion etching (DRIE) after a photolighography, and the etched wafer was then bonded with glass to form the closed channels. After that, KOH solution was used to thin the silicon wafer and SiO_2 was deposited on the silicon by a pressure enhanced chemical vapor deposition (CVD) before Pt heating/sensing resistances were patterned by a traditional lift-off process. At last, the silicon was etched through to make the in/outlet and the isolation trench.

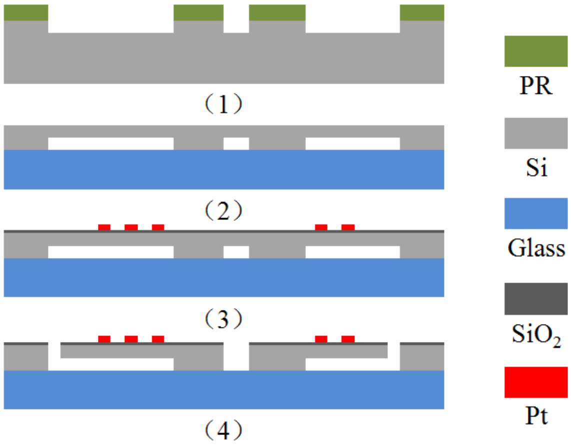

Figure 3. Fabrication process of this chip.

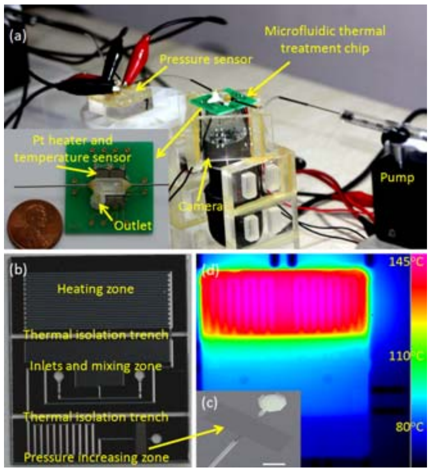

Figure 4. Experiment setup (a), photo of the chip (b), SEM of the channel in the pressure increasing zone (c) with scale bar of 500 μm, and infrared photo (d) of an un-packaged chip with the heating zone of 145 ^{o}C.

EXPERIMENTAL RESULTS

Experiment setup for both high pressure performance measurement and digestion of total phosphorus is shown in Fig. 4a. The chip has three zones separated by thermal isolation trenches (Fig. 4b-c). Fig. 4d shows an infrared photo of the chip before package. When T_H was 145 ^{o}C, T_P was about 80 ^{o}C, which decreased the water viscosity dramatically and made the pressure increasing function degraded considerably [3].

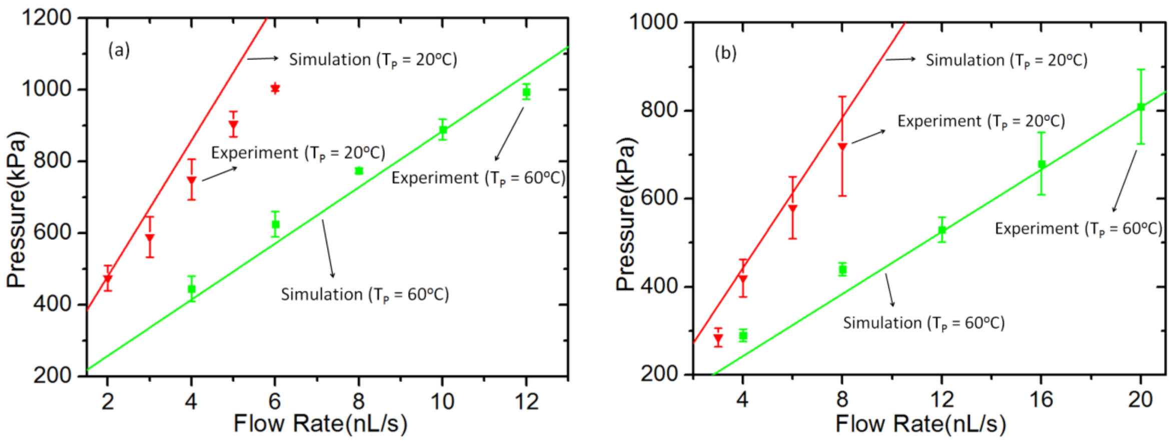

Figure 5. Effect of T_p on the pressure in the heating zone (a) D_0=20 μm; (b) D_0=40μm.

The high pressure performance was firstly measured, and the results are shown in Fig.5, each for depth of 20 µm and 40 µm. As shown in Fig.5(b), at the flow rate of 8 nL/s, the pressure in the heating zone dropped from 720 kPa to 440 kPa when T_P increased from 20 °C to 60 °C. In order to reduce the influence of viscosity decreasing, cooling was added onto the pressure increasing zone to stabilize the temperature in the following experiments. The result also shows the experiment result matches the simulation well.

Total phosphorus samples were digested by the present chip, and the absorbance value at 700 nm of the collected sample was then measured by spectrophotometer (Biospec-nano, Shimadzu Corp., Japan). The heating temperature was set at 145 °C in the following experiment. At first, the influence of the ration of $K_2S_2O_8$ solution was studied. The flow rate of total phosphorus sample was 16 nL/s, and the flow rate of $K_2S_2O_8$ solution was set each at 2 nL/s, 4 nL/s and 8 nL/s, which resulted in ratio of 8:1, 4:1 and 2:1. The preliminary experimental result indicated that the 4:1 had the highest digestion efficiency, so it was fixed in the following experiments.

Samples with different total phosphorus concentrations were then digested by the present chip and compared with conventional methods (5b-1 COD Analyzer, Lianhua Tech., China) along with non-digestion control. The flow rate of total phosphorus sample was 16 nL/s, which generated a digestion time of 40 s and a pressure of 690 kPa at the inlets. The results were shown in Fig. 7. The absorbance values of chip digestion provided a good linear relationship between total phosphorus concentrations (1 mg/L - 5 mg/L), while the linear correlation coefficient reached 0.996. The absorbance values of conventional digestion were bigger than the chip digestion, but with a bad linearity, which may be caused by the large concentration.

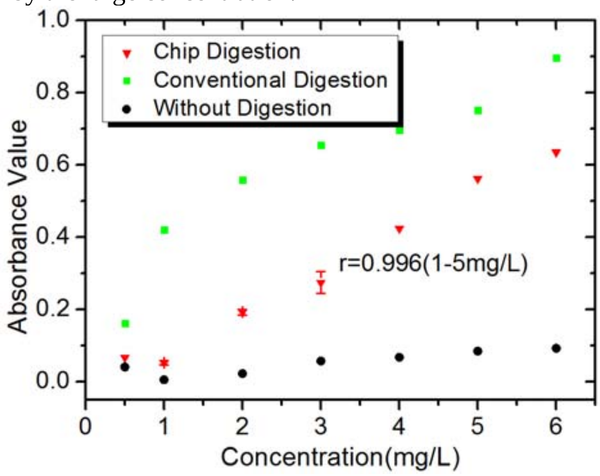

Figure 6. Preliminary digestion performance of the present chip.

CONCLUSIONS

This work reported a microfluidic reactor for thermal digestion of aqueous sample. The presented chip can provide a reaction environment with high pressure over 500 kPa and high temperature over 145 °C without boiling. Total phosphorus sample was digested by this chip, and the result showed a good linearity with the varried concentrations.

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