A MICROFLUIDIC-BASED THERMAL DIGESTION CHIP FOR DISSOLVED ORGANIC NITROGEN DETECTION

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ABSTRACT

This paper presents a micro thermal digestion chip, and its application to the detection of dissolved organic nitrogen (DON) in natural waters. After injecting water sample and digest reagent ($K_2S_2O_8$) into the chip, the mixed sample was heated by the micro heater, and the temperature is detected by the Pt film micro sensor integrated on the chip. After keeping 120°C for 30 minutes, the DON converts into nitrate. Urea and glutamic acid were used as the typical DON in this paper. The spectrophotometry was employed to measure the optical absorption value of digested DON solution at 220nm and 275nm.

KEYWORDS

Digestion, chip, microfluidics, dissolved organic nitrogen (DON)

INTRODUCTION

Dissolved organic nitrogen (DON) is the mixture of compounds ranging from simple amino acids to complex humic substances, and it plays an important role in plant nutrition in ecosystems [1]. More and more attention is paid for its concentration, bioavailability and ecological environmental effect [2]. Before the detection of DON, a digestion pretreatment procedure must be proceeded to convert the organic nitrogen into nitrate. Subsequently, electrochemical or optical inspection methods could be employed to complete the nitrate detection. The traditional high temperature oxidation (HTO) digestion method [3] using high pressure sterilizer for DON determination is high power consuming, and it is not suitable for portable detection. Especially, with the development of MEMS-based microsensors (e.g. micro ion sensitive electrodes), small-sized, low power consumption, and portable detection systems are required.

In this paper, a micro thermal digestion chip based on microfluidic technique is designed and fabricated, and it is used for the detection of dissolved organic nitrogen in natural waters. $K_2S_2O_8$ was used as the oxidizing agent, and only 5μL mixed sample was heated up to 120°C in the reaction tank each time. After the conversion of DON to nitrate, the corrected absorption value was detected by spectrophotometry. This digestion chip could be also used for the digestion of total nitrogen, total phosphorus, and some other parameters in water quality monitoring.

DESIGN AND FABRICATION

This micro digestion chip is composed of a sampling section, a mixing section, and a reaction section, as shown in Figure 1. Various forms of dissolved organic nitrogen (e.g., urea, amino acids, proteins …) could be converted to nitrate under the temperature more than 100°C with the participation of oxidizing agent (e.g., $K_2S_2O_8$). Since the reaction product is acidic (pH~2), silicon is used as the substrate material. The water sample and oxidizing agent are injected and mixed through the inlets and microchannels, and then the mixed solution flow into the reaction tank. A micro heater is attached on the backside of the chip, and a micro Pt film temperature sensor is fabricated on the backside of the chip by MEMS technique. Several thermal isolating channels are designed on the backside of the chip to decrease the heat loss. Only 5μL mixed solution was heated, and the power consumption is less than 2 watts. During the heating process, the inlets and outlets are all shut off using pinch valves. In order to minimize the interference of the sample in the mixing channel, a gas inlet is designed in this chip. The digested sample could be sucked out when the gas inlet is open. The mixed sample at the interface of microfluidic channels and connectors may not be digested completely, which may bring some errors of absorption measurement. To eliminate the dead volume, a micro needle tip, which has almost the same diameter to the inner diameter of the connector, was used to decrease the volume as much as possible in this experiment.

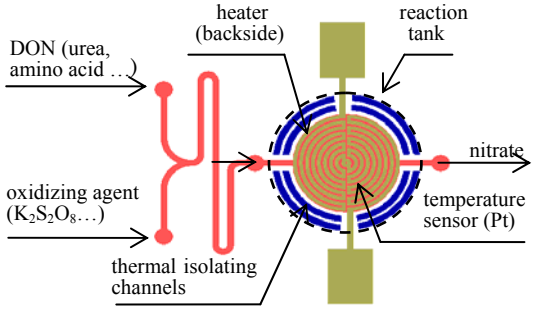

Figure 1. Working principle of the thermal digestion chip

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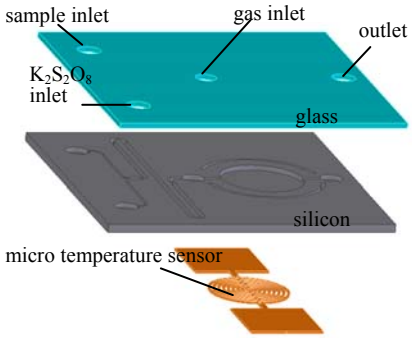

Figure 2. Schematic structure of the thermal digestion chip

The micro digestion chip is fabricated by MEMS technology. The schematic structure of this thermal digestion chip is shown in Figure 2. Firstly, a Pt-based micro temperature sensor is fabricated on the back side of silicon substrate by lift-off process, and then the micro-channels, micro reaction tank and thermal-insulation channels are etched by using deep reactive-ion etching,. After drilling holes for fluidic interconnection using ultrasonic, a glass wafer is bonded to silicon substrate to finish the fabrication of the digestion chip. A micro heater is attached by thermally conductive adhesive on the back side of the reaction tank. The fabricated digestion chip is shown in Figure 3(a) and 3(b).

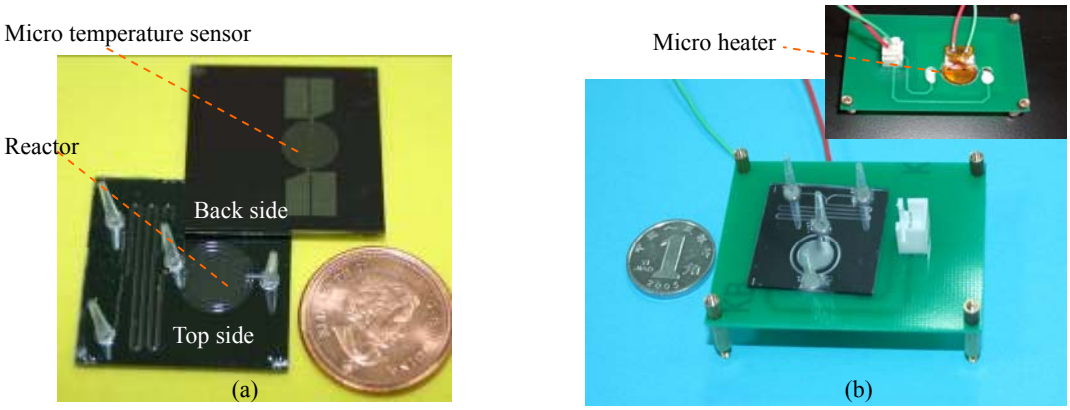

Figure 3. Picture of the fabricated thermal digestion chips (a) and packages (b)

DIGESTION EXPERIMENT

Water sample and digest reagent ($K_2S_2O_8$, 40g/L, company) were injected to the micro digestion chip through the inlet channels, and then the solution flew into the digestion tank after mixed thoroughly. The volume ration of water sample and digest reagent is 2:1 by controlling the flow rate of each solution. After shutting off the inlets and the outlet using pinch valves and micro needle tips, the mixed solution in the digestion tank was heated by the micro heater, and the temperature was detected by the Pt film micro sensor integrated on the chip. A 5.1V DC voltage was applied on the micro heater, and the resistance of the calibrated micro temperature sensor was monitored using Keithley 2001 multimeter. At the temperature of 120°C, $K_2S_2O_8$ decomposes as sodium bisulfate and atomic oxygen which can oxidize the nitrogen compound into nitrate. After keeping this temperature for 30 minutes, the dissolved organic nitrogen converted into nitrate completely. DI water and $K_2S_2O_8$ were mixed and digested to act the blank sample for the absorption value measurement. After each digestion process, a washing step was performed using DI water to clean the reaction tank and the channels. Urea and glutamic acid were used as the typical DON in this paper. The calibrated spectrophotometry(Biospec-Nano, Shimadzu Inc.) is employed to measure the optical absorption value of digested DON solution at 220nm and 275nm. Measurement of UV absorption at 220nm enables the determination of nitrate. Since dissolved organic matter also may absorb at 220nm and nitrate doesn't absorb at 275nm, a second measurement at 275nm was used to correct the nitrate value. The absorption value of nitrate was corrected as follow:

$$Abs(nitrate) = Abs_{220} - 2 \cdot Abs_{275} \tag{1}$$

Experimental date on urea and glutamic acid digestion is shown in Figure 4(a) and 4(b). In order to compare the digest efficiency, the concentrations of urea and glutamic were all converted to the concentration of nitrogen. The corrected absorption values of urea and glutamic acid increase with the increasing of the concentration, and it performs a good linear relationship between the absorption value and the concentration. The micro digestion chip proposed in this paper could also be integrated with the existing MEMS-based microelectrode system to realize the

fully-integrated micro sensor system which can be employed to the detection of total nitrogen, total phosphorus, and some other parameters in water quality monitoring.

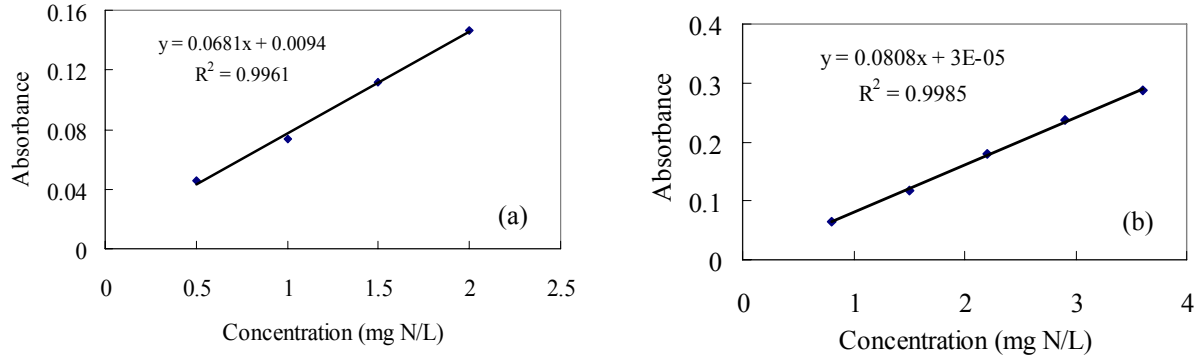

Figure 4. Calibration curve of urea (a) and glutamic (b) after thermal digestion: 120°C for 30min, the oxidizing agent is 40g/L $K_2S_2O_8$.

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