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Talanta 67 (2005) 646–650
Talanta
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On-line determination of trace sulfur dioxide in air by integrated microchip coupled with fluorescence detection

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Received 30 December 2004; received in revised form 14 March 2005; accepted 15 March 2005
Available online 15 April 2005

Abstract

A microchip-based method was developed for on-line determination of trace sulfur dioxide (SO_2) in air. Gaseous SO_2, which diffused through the porous glass materials on the microchip, was absorbed into an absorption solution of triethanolamine (TEA) as sulfite ions and reacted with *N*-(9-acridinyl)maleimide (NAM), which was used as a fluorescent reagent. The fluorescence of NAM-sulfite in micro-fluidic channel was detected. The calibration curve of sulfite ions in the range of 1.5–30 μmol/L (SO_2 3–60 ppbv) showed a linear relation $R^2 = 0.995$, and the relative standard deviation (R.S.D.) was 1.9% for 10 μmol/L sulfite ions in five measurements. The entire measurement procedure was achieved by the integrated microchip, and the consumption of reagents was drastically reduced. It was satisfactory to apply this method to determine on-line the SO_2 level in the air.

Keywords: Microchip; Sulfur dioxide; Fluorescence detection; On-line monitoring device

1. Introduction

Sulfur dioxide (SO_2) is a major air pollutant in many parts of the world. The combustion of sulfur-containing fossil fuels for domestic heating and for power generation is the main contributor to environmental levels of sulfur dioxide. Sulfur dioxide has a serious effect not only on the ecology but also on human health. There are many analytical techniques available for the detection of sulfur dioxide, including spectrophotometry [1,2], chemiluminescence method [3–5], ion chromatography [6–8], spectrofluorometry [9], potentiometry [10], etc. However, owing to the size and complexity of the instruments, the measurements are often off-site. Compared to natural water and soil analyzers, atmospheric trace gas analyses mostly require on-site determination because of fluctuations in the concentration levels and difficulties with sample storage and the stability of stored samples. Several methods have been reported for on-line determination of SO_2 in the air by on-site collection of SO_2 with a chromatomembrane cell [11] or a gas permeation denuder [12,13] and spectrophotometry determination by flow injection analysis. In these methods, the gas is collected by active sampling, that is to say, a pump is needed. Compared to active sampling, passive sampling is simpler because it does not need a pump, and the gas is absorbed by its diffusion. A passive sampler was successfully used in a personal/environmental exposure study and in indoor/outdoor air pollution monitoring [7]. However, a tedious elution procedure was needed.

In addition, as the demand for environmental analysis has grown in recent years, the amount of chemicals has increased considerably as a side effect, and these chemicals are highly diversified and often very toxic or corrosive. Accordingly, simplification and miniaturization of the experimental equipment in the field of environmental analysis have received great attention. Especially, the micro-total analysis system (μ-TAS), based on a micro-fluidic channel chip, has been expected to realize entire chemical measurement on a device of a few square centimeters. The attractive features associated with these devices are the potential for system integration in which various processing steps of the assay are included in the fluidic platform, the rapid analysis of highly multi-

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doi:10.1016/j.talanta.2005.03.017

plexed systems, the ability to dramatically reduce reagent consumption, the high throughout analysis, and on-site monitoring.

In this study, a microchip-based method was developed to make an on-line determination of the SO_2 in the air. The entire determination procedure could be completed with one microchip, including gas absorption, chemical reaction, and fluorescence detection. Gaseous SO_2, which diffused through the porous glass materials on the microchip, was absorbed into an absorption solution of triethanolamine (TEA) and reacted with *N*-(9-acridinyl)maleimide (NAM) [14,15] as a fluorescent reagent in a micro-fluidic channel. Then the fluorescence was detected (Ex. 360 nm, Em. 432 nm). The fluorescence derivation scheme utilizing NAM was investigated. It was satisfactory to apply this method to make an on-line determination of the SO_2 level in the air.

2. Experimental

2.1. Reagents

Stock standard sulfite solution was prepared by dissolving sodium sulfite in milli-Q water and was standardized by idoimetric titration when needed. NAM was dissolved in acetone and mixed with borate buffer solution at a ratio of 1:5. A solution of 3 g/L triethanolamine (TEA) was freshly prepared by dissolving 1.5 g TEA in 500 mL milli-Q water.

Borate buffer was prepared as follows: boric acid (1.55 g) and potassium chloride (1.85 g) were made up to 250 mL with mill-Q water (A). Sodium carbonate (2.65 g) was made up to 250 mL with milli-Q water (B). The pH values of buffers were adjusted by the addition of solution A–B.

TEA and NAM were purchased from Wako Pure Chemical Industries Ltd. (Japan). Na_2SO_3 was obtained from Kanto Chemical Industries Ltd. (Tokyo, Japan). All reagents were of special grade, and all the solutions were prepared by using de-ionized water purified with the milli-Q Plus Water System (Millipore).

2.2. Fabrication of gas absorption microchip

The diagram of the base plate and cover plate of the microchip is shown in Fig. 1. On the base plate (Fig. 1a), the micro-channels of the hexagonal gas absorption sector were 250 μm wide and 100 μm deep, and the other micro-channels were designed to be 500 μm in width and 100 μm in depth. Besides inlets and outlet holes (0.7 mm in diameter), a circular opening with an 11 mm diameter was designed on the cover plate (Fig. 1b). A porous glass of the same size (Vycor 7930; Corning International, Tokyo, Japan) with a pore size of 4.0–7.0 nm and a specific surface area of 200 m^2/g was adhered onto the circular opening where gas dispersed through the porous glass into the gas absorption solution in the micro-channels.

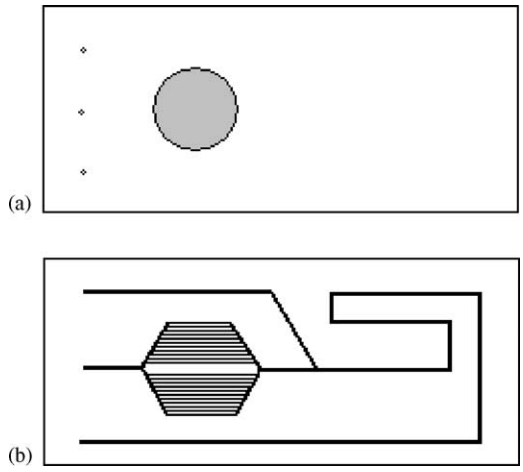

Fig. 1. Schematic image of the integrated analytical microchip: (a) cover plate and (b) base plate.

Micro-channels were fabricated using ordinary photolithography and the wet etching method. The quartz glass, obtained as 26 mm × 50 mm plates, with one approximately 1.0 mm thick (base plate) and another approximately 0.5 mm thick (cover plate), was used to make the microchip. The main chemical chip fabrication steps are illustrated in Fig. 1. First, silicon was deposited on the base plate (Fig. 2a). The silicon was used to protect the substrate plate during glass etching and minimize the diffused light when NAM-sulfite was detected in the micro-channel by the fluorometer. Therefore,

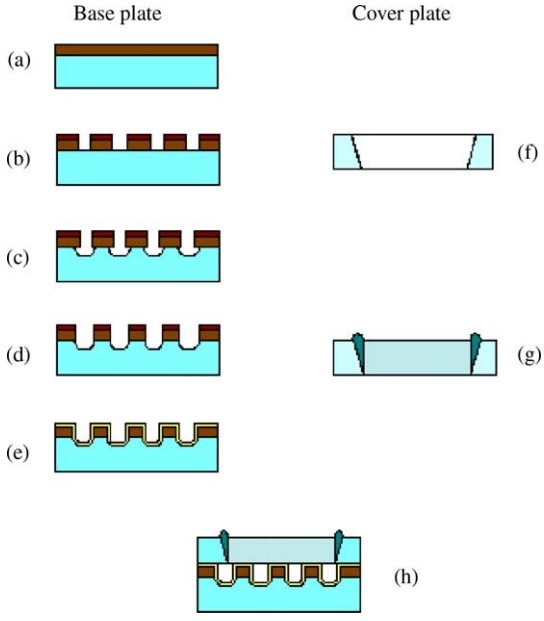

Fig. 2. Schematic diagram of fabrication procedure of the gas absorption microchip: (a) Si deposition, (b) patterning, photolithograph and etching the silicon (RIE), (c) trench etching of quartz plate by BHF, (d) silicon removing by RIE, (e) removing photoresist and SiO_2 deposition, (f) circular opening drilled by ultrasonic, (g) porous glass bonding, and (h) bonding of base plate and cover plate.

the microchip is chocolate brown except for the part of the micro-channels. A 2 μm-thick positive photoresist was spin-coated on the silicon. UV light was exposed through a photomask by using a mask aligner to transfer the micro-channel pattern onto the photoresist. The photoresist was developed and a micro-fluidic channel pattern was obtained. The unprotected silicon layer was removed by reactive ion etching (RIE) (Fig. 2b). The bare glass surface with the micro-channel pattern was etched with BHF (HF:NH_4F, 1:10 Fig. 2c). The silicon on the micro-fluidic channel was removed by reactive ion etching (Fig. 2d). Before bonding with the cover plate, the photoresist was removed, and SiO_2 was sputtered on the surface of the base plate (Fig. 2e). Reagent inlet, outlet holes, and the circular opening on the cover plate were drilled by ultrasonic (Fig. 2f). In order to prevent the blockage of the adhesive in the micro-channels on the base plate, the porous glass was adhered to the circular opening before the bonding of the base plate and the cover plate (Fig. 2g). Finally, the base and cover plates were laminated in a furnace at 60 °C for 6 h after being washed in H_2SO_4:H_2O (3:1), de-ionized water, and 1% HF (Fig. 2h).

2.3. Apparatus

The on-line determination device consisted of a syringe pump (KD Scientific, USA), the developed microchip, a computer control system, and the ultraviolet LED miniature fluorometer (NSHU590E; Nichia Corp., Tokushima, Japan). The miniature fluorometer (320 mm × 230 mm × 177 mm) was designed for microchip use. The reagents were introduced to the micro-channel by a 0.5 mm i.d polytetrafluoroethylene (PTFE) tube. The sulfur dioxide absorption by the porous glass on the microchip was investigated in a wind tunnel, which was used to maintain the concentration of SO_2 standard gas generated by a permeater (Gastec Co., Japan). The volume of the wind tunnel was 252 L, and the SO_2 concentration in the wind tunnel was checked by a SO_2 analyzer (FLAD 1000, Shimadzu, Japan).

2.4. On-line absorption for determination of sulfur dioxide in the air by the integrated microchip

For on-line determination, the microchip was inserted into the miniature fluorometer where the fluorescence could be detected on-line. The schematic diagram used in this study is shown in Fig. 3. In order to improve the efficiency of the gas absorption, a fan with a wind velocity of 1 m/s on the back of the miniature fluorometer was used [16]. The absorption solution, 3 g/L TEA, and fluorescence derivation reagent, 100 μmol/L NAM, were delivered into the micro-channel by a syringe pump. Gaseous SO_2, which diffused through the porous glass materials on the microchip, was absorbed into the absorption solution and reacted with NAM in the micro-fluidic channel, and the fluorescence was detected.

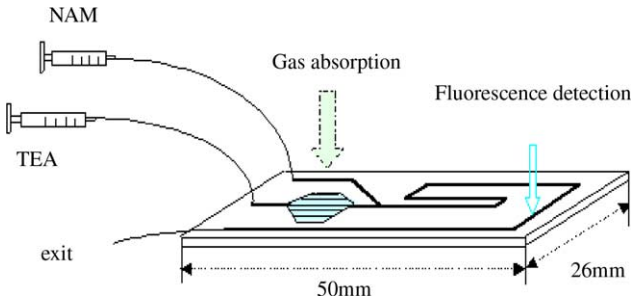

Fig. 3. Schematic diagram of the detection system.

3. Results and discussion

3.1. The integrated microchip

The gas absorption, chemical reaction, and fluorescence detection were integrated on one single microchip. The gas absorption sector was developed based on the study of Korenaga et al. [16]. In previous research, the gas absorption sector was designed as a hexagon-shaped area. Although it provided a larger gas–liquid contact area, it was found that the gas absorption solution stayed in some part of the area. In order to prevent retention of the gas absorption solution, several micro-channels were designed. Thus, the gas absorption solution was divided into several branches when it passed the hexagon-like gas absorption sector. Not only did it provide a larger gas–liquid contact area, but also the retention of the gas absorption solution could be effectively avoided. The porous glass plate was designed to be circular because of the limitation of fabrication techniques.

TEA was used as a gas absorption solution in this study. Furthermore, TEA could act as a buffer solution. Therefore, a simpler determination method was expected using 3 g/L TEA with pH 9.6 as a gas absorption solution and buffer solution for NAM and a sulfite derivation reaction. This was investigated in the wind tunnel by introducing the mixture solution of NAM and TEA into the micro-channel. However, the pH decreased with the increase of the SO_2 concentration. The derivation reaction using NAM could not be fulfilled with an unsuitable pH. Therefore, the other inlet and micro-channel were adopted for the mixture of NAM and borate buffer solution introduction. TEA, only as a gas absorption solution, was introduced from the other micro-channel for SO_2 absorption. The micro-channel's length was designed to be about 120 mm long for the chemical reaction based on the derivation of NAM and sulfite. The fluorescence intensity was detected in the micro-channel by the miniature fluorometer.

3.2. Fluorescence derivation of NAM in micro-channel

The fluorescence reaction of NAM and sulfite was reported in a previous paper [14,15]. It is a highly sensitive, selective, and simple fluorometric method for sulfite determination in solution. In this study, the fluorometric method was applied to determine the absorbed SO_2 in the air as sulfite ions. The

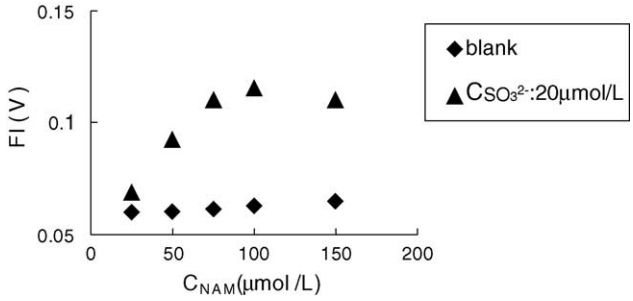

Fig. 4. The effect of NAM concentration on fluorescence intensity: pH 9.3 and flow rate: 1 μL/min.

derivation reaction of NAM and sulfite was investigated using the integrated microchip. Standard sulfite solution was used in the study. The gas absorption sector was sealed by scotch tape during the experiment.

The effect of the concentration of NAM in the range of 25–150 μmol/L was investigated. The result is shown in Fig. 4. The fluorescence intensity increased with an increase of NAM concentration within a certain range. When the concentration of NAM was higher than 100 μmol/L, the fluorescence intensity had almost no change, but the background signal increased. In consideration of the two effects, a NAM concentration of 100 μmol/L was chosen for the following experiments.

The effect of pH values in the range of 6.4–10.5 was investigated. The result showed there was a stronger fluorescence intensity when the pH was in the range of 8.6–9.5. In the following study, the pH of 9.3 was selected.

The effect of the flow rate of TEA and NAM in the range of 1–5 μL/min was examined. The result showed that the fluorescence intensity was maximum when the flow rate was 1 μL/min according to Fig. 5. The fluorescence intensity decreased with the increase of the flow rate, which suggests that the complex formation was time-dependent. However, in the gas absorption experiment, it was found that the gas absorption solution vaporized through the pores on the porous glass

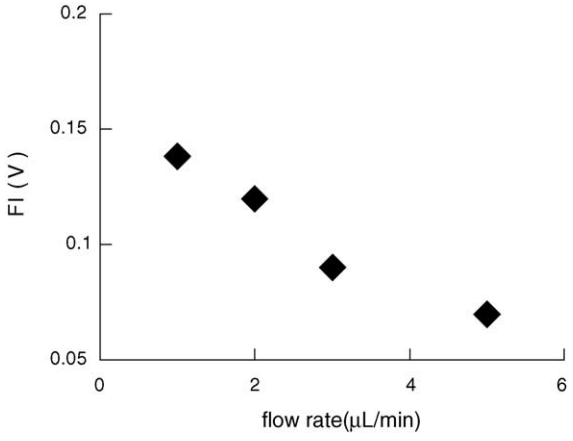

Fig. 5. The effect of flow rate on fluorescence intensity: C_{NAM}: 100 μmol/L, C_{TEA}: 3 g/L, $C_{SO_3^{2-}}$: 30 μmol/L, and pH 9.3.

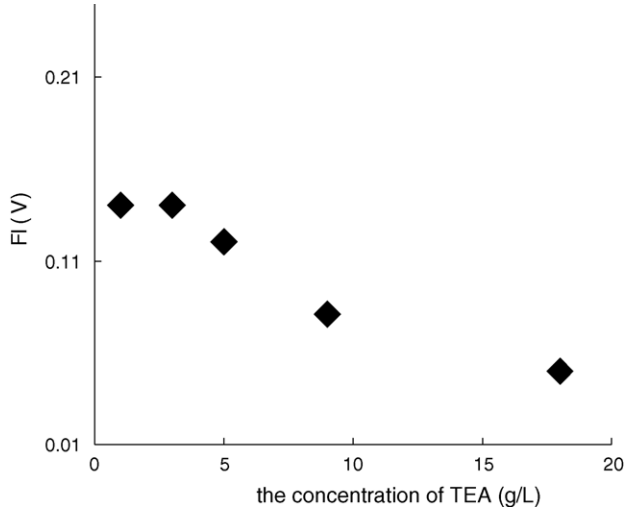

Fig. 6. The effect of TEA concentration on fluorescence intensity. C_{NAM}: 100 μmol/L, flow rate:1 μL/min, $C_{SO_3^{2-}}$: 30 μmol/L, and pH 9.3.

when it passed the gas absorption sector on the microchip at a flow rate of 1 μL/min. The gas absorption experiment indicated the quicker the flow rate of the gas absorption solution, the lower the gas absorption efficiency [16]. As a result, the 2 μL/min flow rate was selected for the study.

The effect of various TEA concentrations on the fluorescence intensity is shown in Fig. 6. A TEA solution with a higher concentration reduced the fluorescence intensity of NAM-sulfite. According to the effect of TEA concentration on fluorescence intensity and the gas absorption efficiency, 3 g/L TEA was selected as an absorbing solution.

3.3. Interference of coexisting substances

As reported in a previous paper [15], 100-fold NO_3^-, Cl^-, SO_4^{2-}, NO_2^-, CO_3^{2+}, NH_4^+, and 10-fold S^{2-} did not interfere with the determination of sulfite. In addition, TEA was selected as the absorption solution because it provided high absorption efficiency for SO_2. However, the other gases, such as NO_2, CO_2, etc., also can be absorbed by TEA. Compared with NO_2, CO_2, etc., SO_2 not only is by far the most strongly acidic gas, but it also has the highest Henry's law solubility [17]. Usually, NO_2 has a lower concentration in the air. The concentration of CO_2 is high, but it does not consume TEA irreversibly [18]. Considering the gas absorption efficiency and interference with the fluorescence intensity of NAM-sulfite, the concentration of TEA was kept at 3 g/L in the study. It showed that the interference species with common concentrations did not interfere with the determination of SO_2.

3.4. Calibration curve and reproducibility

The calibration curve of sulfite in solution was acquired under an optimized condition. The linearity was in the range of 1.5–30 μmol/L with a correlation coefficient of 0.995. The equation was $y = 0.0024x + 0.056$, where y was the fluores-

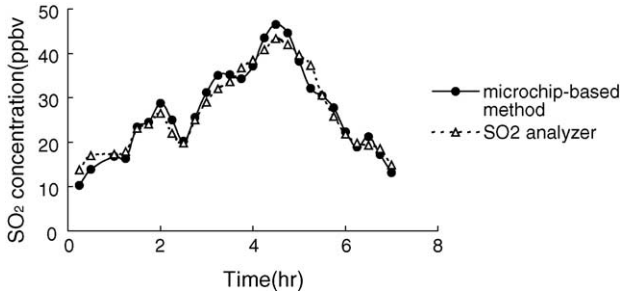

Fig. 7. The results for SO_2 concentration determination in a room. The SO_2 concentration from SO_2 analyzer are shown for comparison.

cence intensity, and *x* the concentration of sulfite in the solution (μmol/L). The linearity of SO_2 was obtained in the range of 3.0–60 ppbv (7.86–157 μg/m^3) by the experiment in the wind tunnel using SO_2 standard gas. The detection limit was 1.4 μmol/L of the sulfite ion (S.N.R. = 3), which is equal to 2.8 ppbv of sulfur dioxide in the air. The relative standard deviation was 1.9% for 10 μmol/L sulfite in five measurements.

3.5. Application

The microchip-based determination method was applied to the determination of the SO_2 level in ambient air in Minami-Ohsawa, Tokyo, Japan. The on-site monitoring result (outdoors) showed a very low SO_2 level (approximately <2.8 ppbv) in this area during the period of the study. Therefore, a great variety of pollutants must not have been present. In order to check the performance of the developed microchip-based determination method, a further on-line monitoring of SO_2 was carried out in a room where the SO_2 level could be changed by using the SO_2 permeation tube. The SO_2 concentration was monitored continuously for 7 h in the room. The results are shown in Fig. 7. The method was compared with the UV-fluorescence method. It showed a good agreement between the two methods.

4. Conclusions

This work describes a microchip-based method for on-line determination of SO_2 in ambient air. Due to the fact that the entire measurement procedure can be achieved with a microchip, the method is simpler, and the measurement rate is rapidly improved. It is environmentally friendly because the consumption of reagents and waste production are drastically reduced. The developed device is portable and suitable for on-site continuous monitoring. With these advantages, the proposed method was suitable for on-line determination of the SO_2 level in ambient air in the district where the consumption of sulfur-containing fuels is much higher, and desulfurization equipment is non-existent or non-functional. If a continuous liquid-conveying pump is available, the method is expected to achieve continuous data acquisition and analysis.

Acknowledgement

One of the author (Wei Chang) thanks XIAN University of Engineering Science and Technology, China, for the financial support.

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