

Miniature Liquid Flow Sensor and Feedback Control of Electroosmotic and Pneumatic Flows for a Micro Gas Analysis System

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Accurate liquid flow control is important in most chemical analyses. In this work, the measurement of liquid flow in microliters per minute was performed, and feedback control of the flow rate was examined. The flow sensor was arranged on a channel made in a polydimethylsiloxane (PDMS) block. The center of the channel was cooled by a miniature Peltier device, and the change in temperature balance along the channel formed by the flow was measured by two temperature sensors. Using this flow sensor, feedback flow control was examined with two pumping methods. One was the electroosmotic flow method, made by applying a high voltage (HV) between the reagent and waste reservoirs; the other was the piezo valve method, in which a micro-valve-seat was fabricated in a PDMS cavity with a silicone diaphragm. The latter was adopted for a micro gas analysis system (μ GAS) for measuring atmospheric H_2S and SO_2 . The obtained baselines were stable, and better limits of detection were obtained.

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Introduction

Liquid flow is required in many instrumental analyses, such as flow injection analysis (FIA), liquid chromatography, and biochemical analytical procedures. In all of these methods, liquid flow affects the repeatability, accuracy, and sensitivity of the analysis. Recently, analytical instruments have been drastically downsized, and required flow rates are becoming lower and lower. Usually, bulky pumps, such as plunger, peristaltic, or syringe pumps, are used in flow analyses. However, with the first two of these pumps, it is difficult to maintain control in the $\mu\text{l min}^{-1}$ range, while the latter pump can not drive the solution flow continuously for a long time.

Recently, we developed a micro gas analysis system (μ GAS) that uses the flow of the absorbing/reagent solution. The prototype¹ requires $2 \mu\text{l min}^{-1}$ of the flow rate in a zigzag-shape microchannel scrubber. The required flow is very small, and handling of the solution is practically difficult. An improved system, utilizing a honeycomb structure microchannel scrubber, achieves the best collection-preconcentration efficiency of the results reported thus far.² This system requires a flow rate of $15 \mu\text{l min}^{-1}$. The absorbing solution is made to flow with micropumps driven with bimetal actuators. The solution passing time through the scrubber is a function of the liquid flow rate. Therefore, the sensitivity is changed by the varying flow rate. To overcome this problem, it is therefore necessary to control the flow rate accurately. Here, we demonstrate a method for sensing and feedback control of the liquid flow in a channel. This method has been applied to μ GAS for measuring atmospheric H_2S and SO_2 .

Experimental

PDMS channel flow sensor

A cooling thermal flow sensor was made on a channel block, as shown in Fig. 1. Either a channel or a microchannel was then

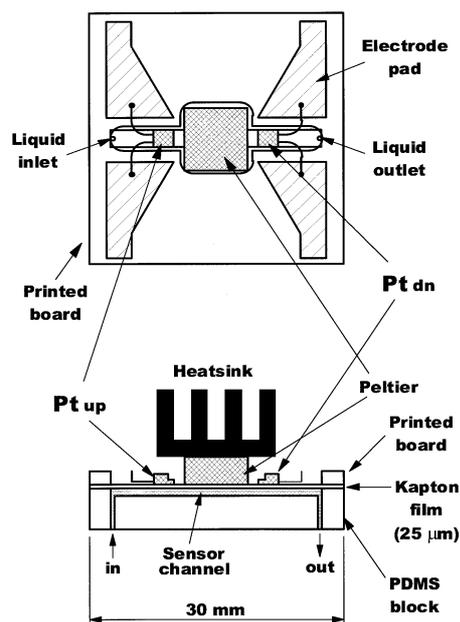


Fig. 1 Top view and cross-sectional view of the thermal flow sensor. A thin Kapton film was pasted onto a channel block made of PDMS. A miniature Peltier device and Pt sensors (Pt up and Pt dn) were placed on the channel, and Pt sensors were electrically connected to electrode pads of a printed board.

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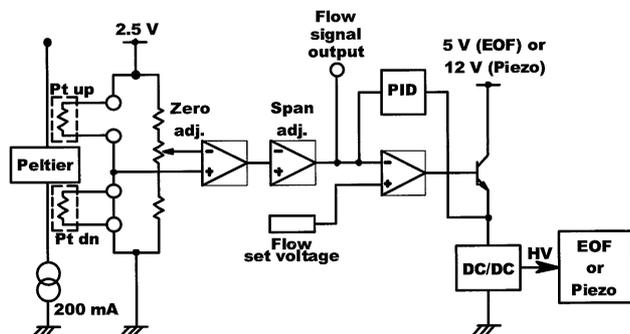


Fig. 2 Electric circuit diagram for the flow sensor and feedback flow control. Pt up and Pt dn are Pt sensors placed upstream and downstream of the Peltier device, respectively.

prepared on a polydimethylsiloxane (PDMS) block made from SILPOT[®] 184 W/C, Dow Corning. The channel was prepared by the molding of PDMS on a polypropylene (PP) sheet (w 2.0 mm \times t 1.0 mm \times l 18 mm) pasted on a 30 mm \times 30 mm glass plate. The PP sheet/glass acted as a channel master. A polyimide film (Kapton[®] 25 μ m t) was pasted on the channel with an adhesive (Cemedine PPX, Cemedine). Electric connection pads were prepared on a printed board (13K, Sunhayato) where the Cu pattern was formed by photolithography and Cu etching was performed with a mixture of FeCl₃·6H₂O 10 g, HCl 30 ml, and water 120 ml at 40°C. The middle of the printed board was hollowed out by a 3D modeling machine (Modela MDX-15, Roland DG) for placing a miniature Peltier device and platinum temperature sensors. The Peltier device was CP1.0-7-06L from Melcor (purchased from RS components, 229-9549), which was 8 mm \times 8 mm in size with a maximum power of 1.4 W. The platinum temperature sensor was Pt 100 Ω , 2 mm \times 2.3 mm \times t 1.5 mm, obtained from RS components (362-9840). These devices were pasted on Kapton[®] film with thermal conductive silicone (SCH20, Sunhayato) and electrically connected onto the electrode pads of the printed board. The channel-side of the Peltier device was cooled by applying 200 mA (0.03 W) using a homemade constant-current controller. The two Pt sensors were incorporated in a bridge circuit, as shown in Fig. 2, and any change in the amplified bridge balance was treated as a flow signal. The actual flow rate was determined by measuring the moving speed of the liquid front in a small Teflon tube (0.3 mm i.d.). Thus, calibration of the flow sensor was performed.

Electroosmotic flow generation through a scrubber

An electroosmotic flow was generated by applying a high voltage (HV) to platinum electrodes placed in solution reservoirs, as shown in Fig. 3(a). Before use, the scrubber for gas collection was successively treated with 0.1 M HCl and 0.1 M NaOH for surface conditioning, and then washed with water. HV (0–5 kV) was applied by a miniature DC/DC converter, Q50-5 (EMCO), with a control input voltage of 0–5 V.

Piezo valve fabricated on a PDMS cavity

A piezo valve was constructed on a PDMS block. The structure is shown in Fig. 4. The control cavity, which was 9 μ m deep and 6.5 mm in diameter, was prepared in the PDMS block using PDMS molding in the same way as in the flow sensor channel. The original master was prepared on a glass plate (30 mm \times 30 mm) by photolithography and glass etching with a buffered HF solution.¹ A silicone rubber membrane (t 25

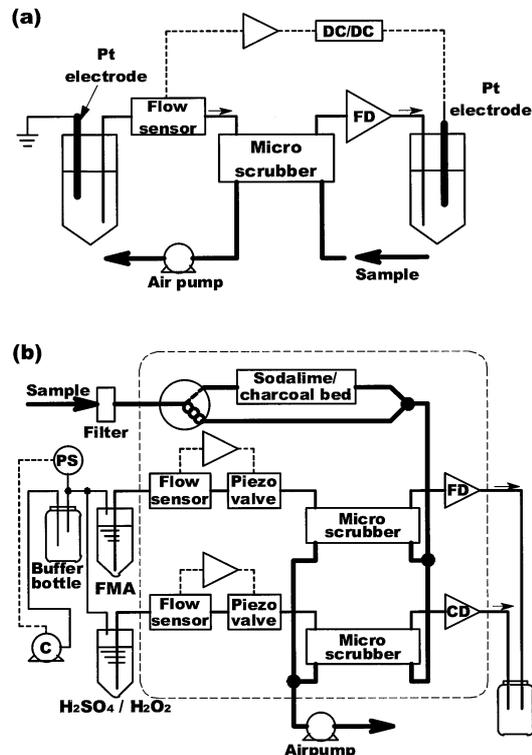


Fig. 3 H₂S analysis system with EOF control (a) and H₂S/SO₂ analysis system with piezo valve flow control (b). C, miniature compressor; PS, pressure sensor; FD, fluorescence detector; CD, conductivity detector.

μ m) was fixed on the PDMS block to be pushed by a piezo actuator *via* a 2.0 mm glass bead. The piezo stack actuator, AE0203D16, obtained from NEC Tokin (3.5 mm \times 4.5 mm \times 20 mm), was fixed on a glass plate with epoxy and settled in a copper tube. The copper tube (L 16.5 mm) was originally o.d. 3/8", and the outside was screw threaded (M10). The piezo actuator z -position was adjusted with the top block made of acrylonitrile-butadiene-styrene (ABS) and the screwed copper tube, and then the copper tube was fixed tightly with a nut. The piezo actuator was driven by applying a DC voltage (0–100 V) using a DC/DC converter, BYH12-100S02, obtained from Bellnix (Saitama, Japan)

Feedback flow control

In this work, feedback flow control was first examined for both electroosmotic flow and microfabricated valve flow control. The flow set signal was compared with the actual flow signal, and a high voltage was applied so that the flow signal became the same as the set signal. This was performed with the circuit shown in Fig. 2. A PID constant was examined, and the optimum condition was obtained with a 1 M Ω resistor and 10 μ F capacitor.

Micro gas analysis system combined with feedback flow control

The flow control system with the flow sensor was incorporated in a gas measurement system, as shown in Fig. 3(b), to measure H₂S and SO₂ simultaneously. A 5 μ M or 1 μ M fluorescein mercuric acetate (FMA) alkaline solution and a 5 μ M H₂SO₄/0.006% H₂O₂ solution were, respectively, introduced to the microchannel scrubbers, and each flow was controlled at 15 μ l min⁻¹ while monitoring the flow rate. See Ref. 2 for details concerning of the scrubber. Collected sulfide and sulfate

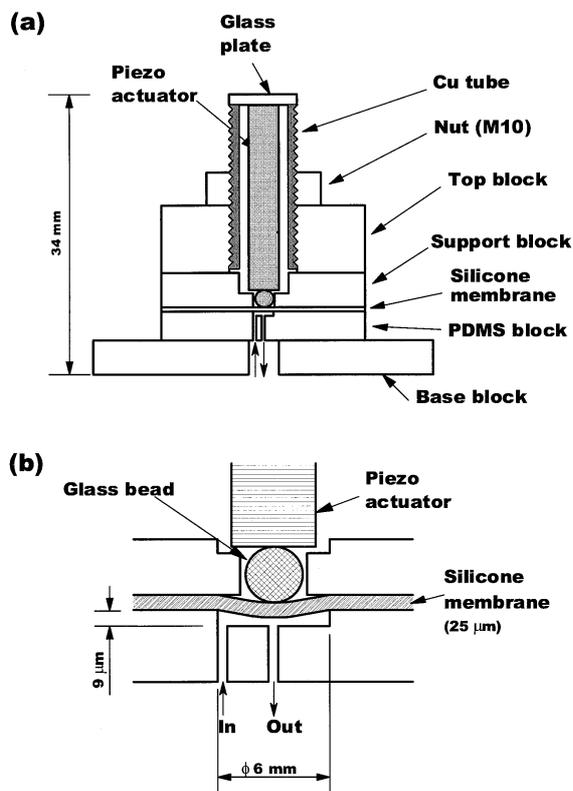


Fig. 4 Structure of the piezo valve; whole structure (a) and close up of the valve (b). The liquid outlet clearance in the PDMS block cavity with a silicone diaphragm was controlled by a piezo actuator. The support block and the top block were made of ABS, and the piezo actuator was supported in a copper tube, of which the outside was screwed.

were determined from the fluorescence and conductivity signals, respectively.³

Results and Discussion

Flow sensor

In this work, flow sensors were made using channels prepared on PDMS blocks. Recently, PDMS has become the representative material for micro chemical analysis devices.⁴ This flow sensor is generally expected to be compatible with all PDMS-based micro devices. There are two temperature sensors both upstream and downstream of the miniature Peltier device. The sensor principle can be explained as linear thermal conduction along the channel, as has been previously discussed for a heated thermal gas flow sensor.⁵ However, different from the previous gas flow sensor, the fluid was cooled in the present sensor to avoid bubble formation. The thermal conductivity of water ($0.597 \text{ W m}^{-1} \text{ deg}^{-1}$) is 3.3-times higher than that of PDMS ($0.18 \text{ W m}^{-1} \text{ deg}^{-1}$), and the cooling is supposed to conduct mostly to water *via* a thin Kapton film ($0.15 \text{ W m}^{-1} \text{ deg}^{-1}$). When the flow is stopped, both temperatures at the two Pt sensors are the same. Whereas the downstream is cooled more, the upstream cooling is relieved when the fluid is moving through the channel, as shown in the upper panel of Fig. 5. As a result, the difference in the temperatures increases with the increase in the liquid flow rate. The lower panel of Fig. 5 shows the sensor characteristics, with different channel sizes, of the current study. In the beginning, the smallest microchannel

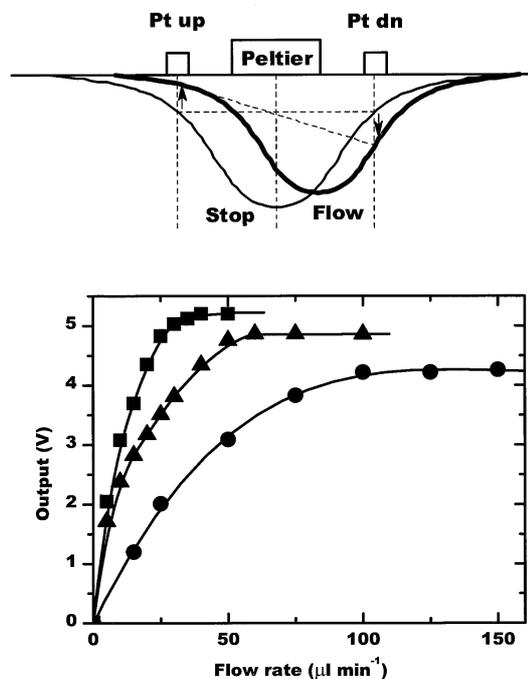


Fig. 5 Temperature profile along the flow sensor channel (upper) and flow sensor outputs with different channel sizes (lower). Channel size: ■, $w 2.0 \text{ mm} \times d 0.5 \text{ mm}$; ▲, $w 2.0 \text{ mm} \times d 1.0 \text{ mm}$; ●, $w 3.0 \text{ mm} \times d 2.0 \text{ mm}$, all lengths were 18 mm.

was made for the flow sensor, but in such a case the sensitivity was high and the dynamic range was too small. Therefore, the adopted channel size was relatively big ($2 \text{ mm } w \times 1 \text{ mm } d$), although the target flow range was below $50 \mu\text{l min}^{-1}$.

Some liquid flow sensors have been reported for analytical use. Time-of-flight types⁶⁻⁸ are reliable for flow rate monitoring, but it was necessary to have a continuous signal for feedback control. Also, a small and inexpensive sensor with low-power consumption is a necessary condition for incorporating it into μGAS . Thermal sensors made using silicon chip technologies for continuous measurement have been previously reported.⁹⁻¹¹ However, their measurable ranges are milliliters per minute and therefore are not suitable for micro chemical analysis devices. Also, further the heating sensor may induce the generation of bubbles, which would seriously interfere with the analytical signals. Here, the miniature flow sensor that we developed was on a channel of the PDMS block, and provided a flow signal continuously for microliters per minute without bubble generation.

Electroosmotic flow in the scrubber

Electroosmotic flow (EOF) and magnetohydrodynamic flow (MHF) were expected to be ideal flows as both noise-free and mechanical-free methods.¹²⁻¹⁸ EOF could be generated through a microchannel scrubber made with the PDMS block and a porous PTFE membrane. The scrubber acted as an EOF generator as well as a gas collector. When a strong alkaline solution was used as the absorbing/reaction reagent, because bubbles were generated at the Pt electrode and in the channel, a stable EOF was not obtained. The FMA fluorescence intensity was constant in the NaOH range from 0.1 mM to 0.1 M. However, the NaOH concentration had to be kept below 0.5 mM to prevent bubble generation (Fig. 6(a)). Hence, 0.1 mM was adopted for the NaOH concentration in the EOF system.

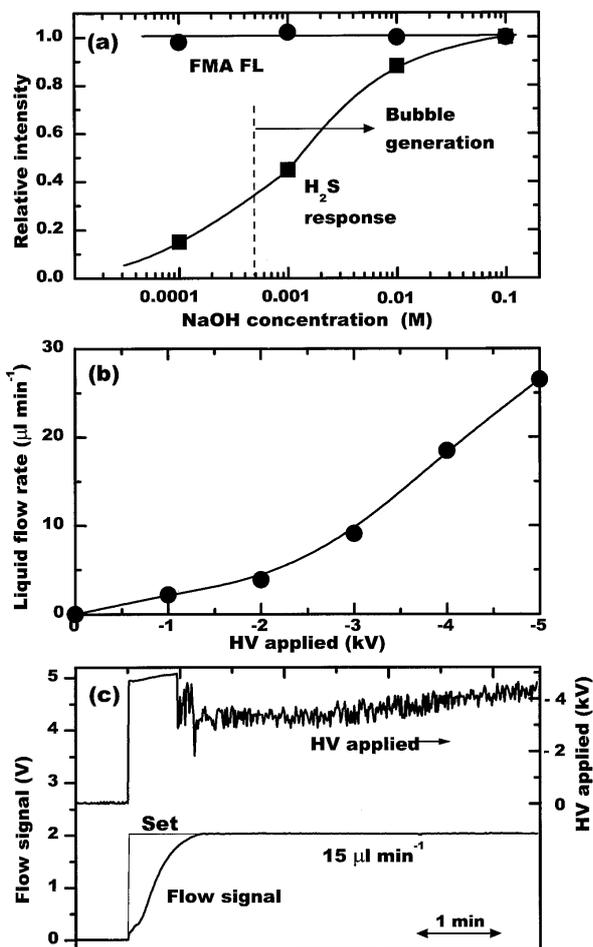


Fig. 6 EOF characteristics in the H₂S measurement system. (a) Effect of NaOH concentration on FMA fluorescence, ●, and H₂S response intensity, ■, obtained for 5 ppbv H₂S with 5 μM FMA solution. A bubble was made when NaOH was above 0.5 mM (vertical dashed line). (b) Liquid flow rate generated by applying HV to a 0.1 mM NaOH solution. (c) EOF control. Flow set signal changed from 0 V to 2.1 V (15 μl min⁻¹).

The obtained liquid flow rate with this absorbing solution is shown in Fig. 6(b) as a function of the applied HV. In this study, a relatively high flow rate was obtained by a small HV power source. The EOF could be controlled by feedback of the flow sensor signal, as shown in Fig. 6(c). When the set point was changed from 0 to 2.1 V (corresponding to 0 and 15 μl min⁻¹, respectively), the maximum HV power was applied until the actual flow signal reached the set signal. After that, stable and constant flow was obtained. It can be seen that the applied voltage was fed back well to make the flow signal constant. This is the first study to demonstrate a way to control the EOF rate. The EOF rate is affected by the surface condition of the capillary or channel, even if a constant voltage is applied. In other words, ideally this kind of feedback control is needed for steady flow. Unfortunately, the H₂S collection in this study was poor when 0.1 mM NaOH was used, as in Fig. 6(a), and hence we also examined another method, namely the piezo valve control method.

Flow control by piezo valve

The solution reservoir was pressurized by a miniature compression system at constant pressure,¹⁹ and the out-coming solution was regulated by a diaphragm valve. We tested a

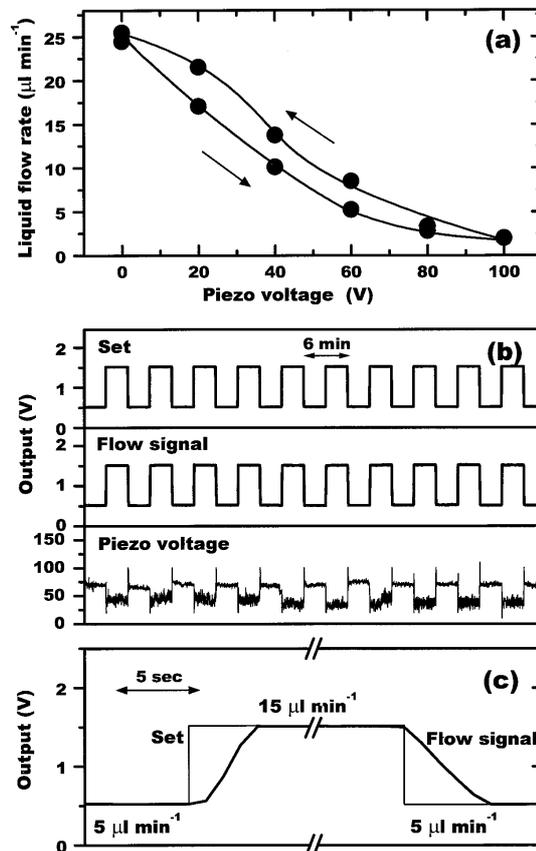


Fig. 7 Piezo valve flow control. (a) Liquid flow rate as a function of piezo voltage. (b)(c) Feedback flow control performance obtained by changing the set voltage at 0.5 V (5 μl min⁻¹) and 1.5 V (15 μl min⁻¹) alternatively in a 6 min cycle. The water in the reservoir was pressurized at 12 kPa.

solenoid actuator and a piezo actuator for valve driving. The solenoid, which was tested first, had a big stroke, but it was difficult to control the position stably and precisely. Next, the piezo actuator was examined. The piezo stroke was much smaller (max 16 μm at 150 V) and the DC voltage required was higher compared to the solenoid, but precious control of the stroke was achieved with small power consumption. The piezo valve was fabricated with a PDMS block and a silicone diaphragm. These materials are resistant to most chemicals, and the present piezo valve is suitable for a chemical analysis system. Furthermore, the PDMS block was relatively soft compared to such materials as stainless steel, which is commonly used for fluid control devices, so that the shut off of the valve could occur easily without any valve gasket.

The liquid flow rate was obtained as a function of the applied voltage to the piezo stack. This valve was of a normally open type, and the flow rate decreased according to the increase in the voltage with some hysteresis, as shown in Fig. 7(a). Because of the presence of hysteresis, flow rate control could not be achieved by simply adjusting the voltage. In this system, the flow signal was fed back to the applied voltage in order to maintain a constant flow rate. This feedback control was demonstrated as shown in Figs. 7(b) and (c). The set point was set at 0.5 V and 1.5 V alternatively for 3 min each. These set voltages corresponded to 5 and 15 μl min⁻¹. When the set point was decreased to 5 μl min⁻¹, the applied voltage to the piezo valve first increased rapidly and then repeated small fluctuations. As a result, the flow rate was controlled as shown

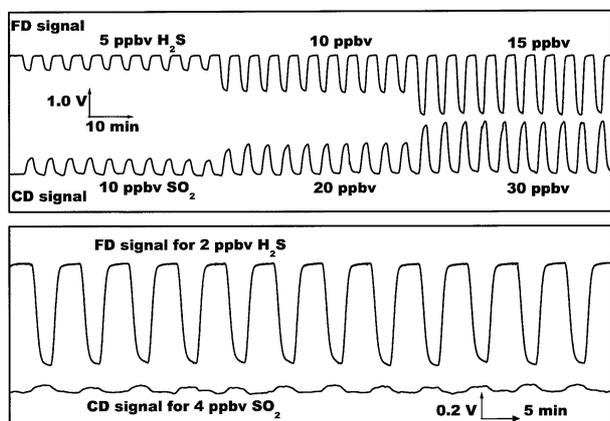


Fig. 8 Responses obtained with a microchannel scrubber-based micro gas analysis system. A mixture of H₂S and SO₂ was prepared and introduced into the system. The 3-way solenoid valve in the gas line was operated to have a 3 min zero signal and 2 min sampling. The lower panel shows the responses to low-level gases. The FMA concentrations used in the upper and lower panels were 5 μ M and 1 μ M, respectively.

in the middle panel of Fig. 7. The flow rate signal became quite the same as the set signal. The 90% response time was 3.4 s in the increase and 5.1 s in the decrease.

The present control method is a bit more complicated than the micropumps based on driving a diaphragm pneumatically²⁰ or with a solenoid actuator.²¹ The former device was fabricated by photolithographic technology. Though the PDMS membrane diaphragm was several mm in diameter, the obtained flow rate was a few microliters per minute. Another concern of this kind of diaphragm pump is pumping noise, because the fluid is pushed out periodically. Our system achieved a stable flow at a range of several and several-tens microliters per minute.

The flow control systems were applied to H₂S and SO₂ measurements. In a previous study,² micropumps driven by bimetal actuators were used in the H₂S/SO₂ measurement system, in which small noises were observed in the baseline. The responses obtained with the piezo valve flow control are shown in Fig. 8. The upper panel data were obtained for 5, 10, and 15 ppbv H₂S and 10, 20, and 30 ppbv SO₂. The lower panel consists of data for very low levels of the gases. In this case, the FMA concentration was one fifth of that of the upper panel in order to obtain a high sensitivity for H₂S. Further, the limits of detections were improved by utilizing the flow control to be 0.01 ppbv for H₂S and 0.4 ppbv for SO₂. These were obtained from three-times of the noise intensity. The relative standard deviation were 1.3% for 2 ppbv H₂S and 2.6% for 4 ppbv SO₂ in the 12 response measurements. The better sensitivities were due to the better baseline noises with the feedback flow controls. Furthermore, the signal intensity is basically inversely proportional to the liquid flow rate because the collection time is a function of the flow rate. Flow control while monitoring of the actual flow rate prevents errors due to a change in the flow rate. A precious measurement of a continuous gas measurement should utilize such feedback liquid flow control.

Conclusions

Feedback flow control for microliters per minute was performed

with a cooling thermal flow sensor and a piezo valve, both made in molded PDMS blocks. This flow control allows the handling of small flows, and is expected to be applied to micro flow injection analysis systems.

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