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In situ gas generation for micro gas analysis system

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Abstract

This manuscript describes an easy, simple and small system for gas generation. The aim of this work was to establish gas generation for on-site checking or on-site calibration of a micro gas analysis system, μGAS. The new technology, μGAS, achieves real-time measurement of trace level gases in the field. To make the measurement more reliable and convenient, a small gas generation system has been developed. Source reagent solution and generator solution are made to flow by micropumps, mixed in a miniature coil, and then introduced into a microchannel gas desorber. The gas desorber is comprised of a honeycomb-shaped microchannel covered with a thin porous polytetrafluoroethylene membrane. A good generation factor is obtained due to the wide vaporization area and thin solution layer of the microchannel desorber. Generation of H_2S, SO_2, CH_3SH and NH_3 gases were examined. Concentrations of the gases are easily controlled by the source reagent concentration and the solution flow rates. At 100 μL min^{-1} flow rates for both the source and generator solutions, 30 ppbv to 2 ppmv concentrations are formed with a gas flow rate of 200 mL min^{-1}. The gas concentration is proportional to the source concentration. The gas generation can be performed only when needed. The gas generation system is combined with μGAS for on-site calibration.

Keywords: Standard gas in situ generation; On-site calibration; Micro gas analysis system; Microchannel gas desorber; Hydrogen sulfide; Sulfur dioxide; Methyl mercaptan; Ammonia; Micro flow analysis

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1. Introduction

Miniature analysis instruments that are capable of measuring trace levels of gases in areas where there are no power lines are attractive for environmental analysis [1], safe management in industries and medical diagnostics [2,3]. These kinds of devices can be used anywhere and anytime. For field measurement, a micro gas analysis system (μGAS) has recently been developed [4]. This is comprised of a membrane-based wet scrubber and a micro-detector. In comparison to conventional wet scrubbers, an effective concentration factor is obtained by the microchannel scrubber. The concentration factor, which is directly related to the sensitivity, is inversely proportional to the thickness of the absorbing solution layer [5]. Especially, a honeycomb-shaped microchannel covered with porous polytetrafluoroethylene (pPTFE) membrane achieved excellent performance [6]. The feature of μGAS is that not only is the device itself small, but the whole system is also small, for use in the field – including the detector and pumping devices. Therefore, μGAS is a powerful tool for outdoor gas analysis. However, μGAS should be calibrated in the laboratory before being taken out to the field. As opposed to aqueous species, preparation of test gases in the field is difficult and needs a bulky gas dilution system and heavy standard gas cylinders. The stability of a standard gas in its cylinder is also a concern due to adsorption onto the inner wall of the cylinder and reactions with contaminants, etc. [7,8]. A gas permeation device is convenient and is sometimes incorporated into an analysis instrument [9]. A permeation device was first reported by O'Keeffe and Ortman four decades ago [10]. The gas generation rate is determined by weighing the permeation device periodically, and the device should be kept in a thermally controlled bath or box. The weighing process takes a long time; usually the weight measurement needs to be continued for weeks or months. To overcome this problem, special monitoring processes such as thermogravimetry [11] and UV optical absorption instruments [12] are coupled to permeation devices.

Some acid or base species can be vaporized from aqueous solution by making it strongly acidic or basic. The generated

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gases are extracted into the air phase at a membrane-based gas desorber. Tarver and Dasgupta introduced H_2S and CH_3SH, collected in an alkaline absorbing solution, into a gas chromatograph by mixing the solution with acid and transferring it to a gas desorber comprised of a porous polypropylene (pPP) membrane tube [13]. Similarly, Kanda and Taira determined nitrous acid by vaporization as NO and successive monitoring of ozone-induced chemiluminescence [14,15]. They used porous polytetrafluoroethylene membrane tube (pPTFE, 1 mm i.d. × 2 mm o.d.) for the desorber [16]. The estimated passing time of the reagent solution through the desorber is ∼2 min. In this paper, we propose a small and effective gas generation method for on-site gas analysis. The honeycomb microchannel is used for the desorber. As for the gas collection, the honeycomb microchannel achieves excellent performance for gas desorption. This micro gas generation system has been integrated with μGAS.

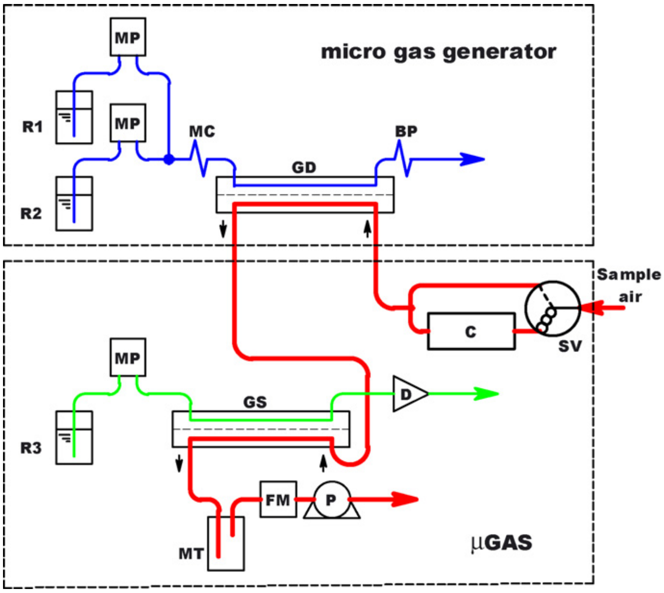

Fig. 1. Flow diagram of micro gas generator and micro gas analysis system. R1, R2: source and desorbing solutions, MP: micropump, MC: mixing coil (0.97 mm i.d. × 50 cm), GD: microchannel gas desorber, BP: back pressure tube (0.3 mm i.d. × 100 cm), SV: three-way solenoid valve, C: air purification column, R3: absorbing/reaction solution for gas determination, GS: microchannel gas scrubber, D: micro-detector (fluorescence for H_2S and CH_3SH; conductivity for SO_2 and NH_3), MT: mist trap, FM: flow meter, P: airpump.

2. Experimental

2.1. Reagents

The source reagents for generation of SO_2, H_2S and CH_3SH were $NaHSO_3$ (Nacalai), Na_2S anhydrous (Aldrich) and CH_3SNa (Fluka). They were all of reagent grade. Stock solutions were prepared to be 10 mM in 0.1 M NaOH (0.3 M NaOH for CH_3SH), and working solution was prepared by dilution of the stock solution with the same NaOH solution. Alkaline concentrations for CH_3SH were three times those of the others. Distilled deionized water was used for the solutions after degassing by aspiration with ultrasonication to avoid reaction with dissolved oxygen [17]. The desorbing solutions for these acid gases were 0.1 M H_3PO_4 (0.3 M for CH_3SH). For NH_3 generation, the source was NH_4Cl in 0.01 M H_3PO_4 and it was mixed with 0.3 M NaOH solution.

Continuous monitoring of the generated H_2S and CH_3SH was performed by μGAS and reaction with fluorescein mercuric acetate (FMA). The absorbing/reaction solution was 10 μM FMA with 0.1 M NaOH. Monitoring of NH_3 was performed by conductometric μGAS with 20 μM H_2SO_4 solution.

2.2. Gas desorbers

For the gas generation, two types of gas desorbers were examined. One was an annular type with pPP tube (Accurel® PP from Membrana, 0.6 mm i.d. × 0.2 mm thickness, pore size 0.2 μm) or pPTFE tube (Poreflon® from Sumitomo Electric Fine Polymer, 1 mm i.d. × 2 mm o.d.). These membrane tubes (length: 2.3–100 cm) were jacketed with 3 mm i.d. Teflon tube. The configuration was the same as that used for gas collection with pPTFE [18] and with pPP [19,20]. See these references for details of the construction. The other type of gas desorber was a honeycomb-shaped microchannel desorber. This was also the same as that developed for gas collection [6]. A microchannel (70 μm deep and 200 μm wide) was arranged in a honeycomb structure (hexagon size: 0.5 mm each side) over an area of 11.4 mm × 51.6 mm on a PDMS plate. A thin pPTFE membrane (Poreflon®, thickness 30 μm, pore size 0.45 μm) was pasted on the microchannel halfway through PDMS curing.

2.3. Gas generation system and μGAS

A flow diagram of the gas generation system is shown in Fig. 1 together with μGAS. Also the gas generation system with the honeycomb-shaped desorber is shown in Fig. 2 with pictures of real devices. The source reagent was mixed with the desorbing solution and reacted in the mixing coil, then introduced into a microchannel gas generator. Generated vapor

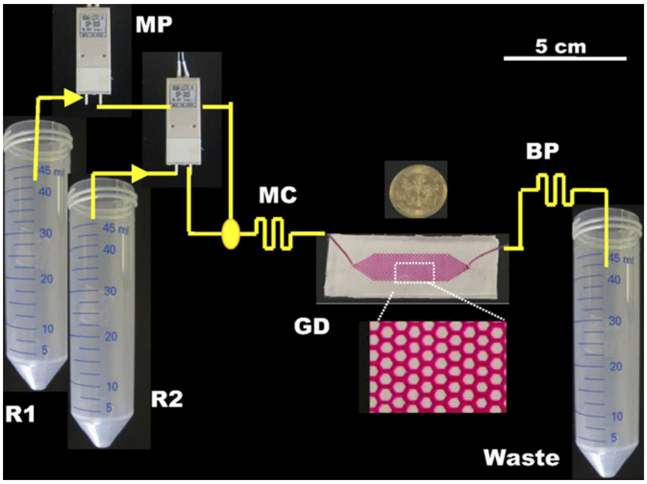

Fig. 2. Liquid flow system for gas generation with microchannel gas desorber. All pictures of the parts are at the same scale. The coin shown above the GD is a 500 JPY coin.