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## Flow-based ammonia gas analyzer with an open channel scrubber for indoor environments



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### ABSTRACT

A robust and fully automated indoor ammonia gas monitoring system with an open channel scrubber (OCS) was developed. The sample gas channel dimensions, hydrophilic surface treatment to produce a thin absorbing solution layer, and solution flow rate of the OCS were optimized to connect the OCS as in-line gas collector and avoid sample humidity effects. The OCS effluent containing absorbed ammonia in sample gas was injected into a derivatization solution flow. Derivatization was achieved with *o*-phthalaldehyde and sulfite in pH 11 buffer solution. The product, 1-sulfonateisoindole, is detected with a home-made fluorescence detector. The limit of detection of the analyzer based on three times the standard deviation of baseline noise was 0.9 ppbv. Sample gas could be analyzed 40 times per hour. Furthermore, relative humidity of up to 90% did not interfere considerably with the analyzer. Interference from amines was not observed. The developed gas analysis system was calibrated using a solution-based method. The system was used to analyze ammonia in an indoor environment along with an off-site method, traditional impinger gas collection followed by ion chromatographic analysis, for comparison. The results obtained using both methods agreed well. Therefore, the developed system can perform on-site monitoring of ammonia in indoor environments with improved time resolution compared with that of other methods.

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### 1. Introduction

Ammonia (NH<sub>3</sub>) is an abundant basic gas that presents a risk in indoor environments. The US Department of Health and Human Services reported the hazardous nature of ammonia [1]. Historical pictures and murals in museums [2] and churches [3] can be damaged by ammonia gas. Ammonia enters indoor environments through a variety of sources such as human bodies, flowers, cleaning agents, and construction materials. Human bodies generate ammonia by metabolism of urea and protein, and then release it *via* urine, breath and skin. Human breath typically contains sub-ppmv NH<sub>3</sub> [4] and human skin also releases NH<sub>3</sub> at a rate of a few ng cm<sup>-2</sup> in 5 min [5]. The body surface area is approximately 1.9 and 1.6 m<sup>2</sup> for an adult man and woman, respectively. If ammonia was equally released from the body surface, several mg of ammonia would be released from a person each day. Concrete walls that contain urea-based anti-freezing materials are also considered to be a source of ammonia in indoor environments [6,7]. Overall, ammonia gas released indoors from

many sources affects not only human health but also industrial products and historical materials. Indoor ammonia levels are relatively higher than outdoor ones because of these alternate sources and the closed environment. Reported indoor ammonia levels were 20–200 ppbv NH<sub>3</sub> at an Indian museum [2] and 6–30 ppbv NH<sub>3</sub> at Danish churches [3]. Indoor ammonia level monitoring requires a limit of detection (LOD) of sub-ppbv NH<sub>3</sub>. Ammonia levels should be frequently or continuously monitored to protect human health and historical items.

Many wet chemical methods have been used for gaseous NH<sub>3</sub> determination. Wet chemical methods involve absorption of gas by a solution followed by chemical treatment and detection. A simple method based on solution conductivity has been used with an acid as an absorbing solution [4,8,9]. Solution conductivity is decreased by dissolved ammonia. However, high levels of acidic gas such as CO<sub>2</sub>, which is typically high concentration in indoor environments (thousands of parts per million by volume, ppmv) [10], interfered to the results without an elimination. Highly sensitive and selective fluorometric methods have also been used for ammonia gas analysis [11,12]. Dissolved ammonia reacts with *o*-phthalaldehyde (OPA) and a reducing reagent to generate an isoindole derivative that exhibits strong fluorescence. This reaction has traditionally been used for amino acid analysis with

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mercaptoethanol as a reducing reagent. Modified reaction using sulfite as a reducing reagent that was more selective for ammonia than with mercaptoethanol has also been reported [11]. This reaction was widely used for ammonium ions in sea water [13,14], rain and river water determination with microchip flow analyzer [15]. Reagent lifetime was furthermore improved by using hydroxymethanesulfonate as an *in-situ* source of sulfite in solution [12]. These reactions were also adapted to flow analysis systems and successfully used to detect atmospheric trace ammonia (sub- to single digit ppbv) by gas collection with a diffusion scrubber and sampling periods of 5–8 min [11,12,16]. The sample gas was collected with a membrane-based diffusion scrubber [17] in these systems. Sample gas and absorbing solution flows were separated by a gas-permeable membrane. The configuration of the diffusion scrubber allowed it to connect directly to a flow analysis system. The enrichment factor, which corresponds to the flow rate ratio of sample gas to absorbing solution, can also be large. However, the membrane governed the mass transfer efficiency, which might be changed by internal or external factors during long term sampling. Periodic calibration with standard gas was recommended to compensate the performance of the diffusion scrubber.

Membrane-free gas collectors are an effective way to address the mass transfer limitation of membranes. Gas collectors in which sample gas and absorbing solution are in direct contact using a microchannel platform have been reported for ammonia [9,18]. In these systems, sample gas and absorbing solution were introduced into a microchannel [9] as segments or laminar parallel flow [18]. Target molecules in sample gas were quantitatively transferred into directly contacting absorbing solution. The sample gas and absorbing solution were separated with a hydrophobic membrane, the properties of which needs to be considered for long-term monitoring. Relative humidity caused slight negative interference because a few  $\mu\text{L min}^{-1}$  of absorbing solution was evaporated by the sample air flow of hundreds of  $\text{mL min}^{-1}$  [18]. Recently, our group reported the first open channel scrubber (OCS), which is a miniaturized membrane-free gas collector [19]. Sample air was flowed on a thin layer of absorbing solution in a channel. Target gas molecules were directly collected by the absorbing solution moving at a flow rate of  $50 \mu\text{L min}^{-1}$ . The bottom of the channel was covered with a thin cotton mesh to keep the solution as a layer. The OCS was used as an off-line gas collector. The OCS effluent was collected into small vials for 10 min, which were then made up to 10 mL and subjected to ion chromatography or flow injection analysis. Evaluation of the gas collection performance of the OCS was the purpose of our previous study. The effects of gas collection channel dimensions, gas diffusion coefficient, sample gas flow rates were investigated with the respect to collection efficiency. The OCS was successfully used to detect ppmv levels of volcanic  $\text{SO}_2$ .

In this work, a robust and fully-automated flow injection analysis system containing an OCS is developed to detect ammonia gas in indoor environments. The OCS is arranged for on-line connection, and sample humidity effects are eliminated. System calibration is performed with standard solutions. The results obtained by the developed system are compared with those from a conventional method, impinger collection followed by ion chromatographic analysis.

## 2. Experimental

### 2.1. Reagents and standard gas

The working gas absorbing solution and derivatization reagent solution were 5 mM sulfuric acid and 10 mM OPA/3 mM sodium

sulfite in 0.19 M phosphate buffer (pH 11), respectively. The derivatization reagent solution was prepared as follows. Phosphate buffer solution was first prepared by dissolving anhydrous disodium hydrogen orthophosphate (26.8 g) in ultrapure water ( $\sim 800 \text{ mL}$ ), and then its pH was adjusted to 11 with 2 M sodium hydroxide solution. Sodium sulfite (0.378 g, [www.nacalai.co.jp](http://www.nacalai.co.jp)) was dissolved in the phosphate buffer. This solution was mixed with OPA solution, which was prepared by dissolving OPA (1.34 g, [www.tcichemicals.com](http://www.tcichemicals.com)) in ultrapure water ( $\sim 100 \text{ mL}$ ) by warming to  $\sim 65^\circ\text{C}$ . The mixture was diluted to 1 L in a volumetric flask.

System performance was tested with ammonia standard gas of known concentration, which was prepared with a permeation tube (P-3, [www.gastec.co.jp](http://www.gastec.co.jp)). The permeation tube was kept at  $10.0^\circ\text{C}$  in a water bath with a carrier gas flow of  $0.1 \text{ L min}^{-1}$ . The permeation rate was  $512 \text{ ng min}^{-1}$ . Purified nitrogen gas (99.9% purity, [www.kumasan.co.jp](http://www.kumasan.co.jp)) was used as a carrier and diluent gas. The ammonia standard gas concentration was adjusted by changing total nitrogen flow rate. The test gas humidity was adjusted by changing the mixing ratio of water-saturated and dry gases [20].

Ammonium chloride and amine compounds used as standard or for interference studies were obtained all from [www.nacalai.com](http://www.nacalai.com).

### 2.2. Open channel scrubber

A schematic diagram of the OCS used in this study is shown in Fig. 1a. Basic device structure was the same as previously reported [17]. In this study, the dimensions of the gas flow channel were arranged to facilitate liquid handling to connect directly a flow-based gas analysis system. The channel dimensions were decided based on a theoretical simulation of gas collection efficiency, *vide infra*.

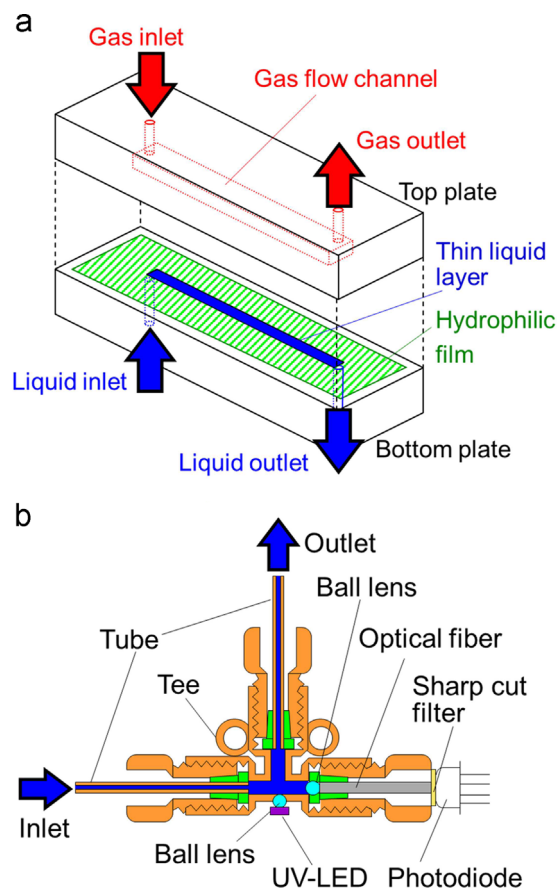


Fig. 1. Schematic diagrams of (a) OCS and (b) fluorescence detector.

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