Talanta 116 (2013) 527–534

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

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

Shin-Ichi Ohira*, Minako Heima, Takayuki Yamasaki, Toshinori Tanaka, Tomoko Koga, Kei Toda

Department of Chemistry, Kumamoto University, 2-39-1 Kurokami, Kumamoto 860-8555, Japan

ARTICLE INFO

Article history:
Received 1 April 2013
Received in revised form
15 July 2013
Accepted 16 July 2013
Available online 24 July 2013

Keywords:
Open channel scrubber
Indoor environment
Ammonia
Flow injection analysis

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.

1. Introduction

Ammonia (NH_3) 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_3 [4] and human skin also releases NH_3 at a rate of a few ng cm^{-2} in 5 min [5].The body surface area is approximately 1.9 and 1.6 m^2 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_3 at an Indian museum [2] and 6–30 ppbv NH_3 at Danish churches [3]. Indoor ammonia level monitoring requires a limit of detection (LOD) of sub-ppbv NH_3. 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_3 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_2, 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

* Corresponding author. Tel./fax: +81 96 342 3384.
E-mail address: ohira@sci.kumamoto-u.ac.jp (S.-I. Ohira).

0039-9140/$ - see front matter
http://dx.doi.org/10.1016/j.talanta.2013.07.037

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 $\mu L\,min^{-1}$ of absorbing solution was evaporated by the sample air flow of hundreds of $mL\,min^{-1}$ [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 $\mu L\,min^{-1}$. 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 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 (~800 mL), and then its pH was adjusted to 11 with 2 M sodium hydroxide solution. Sodium sulfite (0.378 g, 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) in ultrapure water (~100 mL) by warming to ~65 °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). The permeation tube was kept at 10.0 °C in a water bath with a carrier gas flow of $0.1\,L\,min^{-1}$. The permeation rate was $512\,ng\,min^{-1}$. Purified nitrogen gas (99.9% purity, 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.

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*.

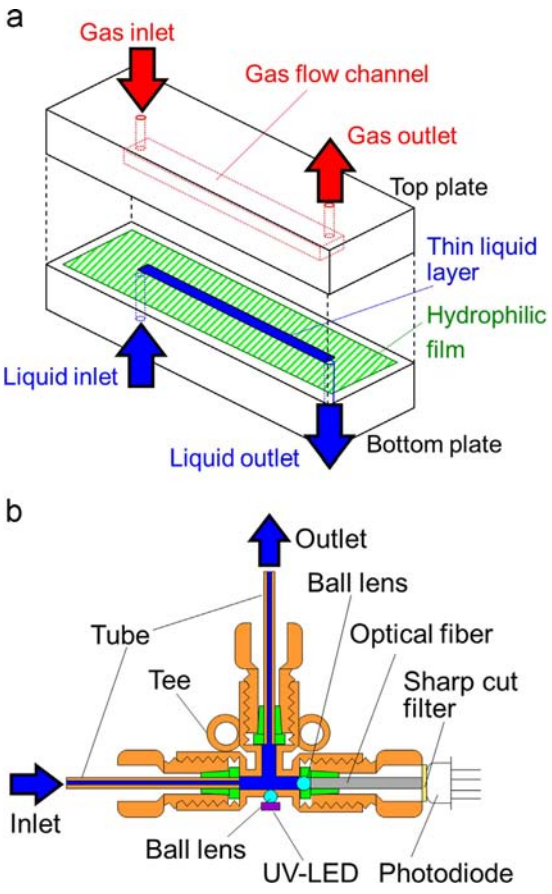

Fig. 1. Schematic diagrams of (a) OCS and (b) fluorescence detector.

The OCS in this study consisted of two polyvinylchloride (PVC) plates. A gas flow channel was prepared in the top plate by machining. The channel was 75 mm long, 5 mm wide and 2 mm deep. The ends of the gas flow channel were connected to fluoropolymer tubes *via* miniature tube fittings (M-5AN-6, www.smcworld.com). The bottom plate contained two M6 screw holes for flangeless fittings (P-207, http://webstore.idex-hs.com).

The absorbing solution was flowed into the bottom of the channel as a thin layer. A hydrophilic surface on the channel bottom was obtained using a regenerated cellulose dialysis membrane (Spectra/Por Biotech membrane, 129020, www.spectrumlabs.com). The dialysis membrane was soaked in warm deionized water for an hour to wet it and remove adsorbed compounds such as glycerin. Then, two of the holes with a diameter of 1.0 mm were punched in the membrane to allow the solution to pass through it. The dialysis membrane was placed on the bottom plate, and the holes were aligned with the solution inlet and outlet. The top and bottom plates were tightened with eight M3 screws.

2.3. Flow-through fluorescence detector

A simple, highly sensitive fluorescence detector was assembled using a commercial tee connector (P-712, webstore.idex-hs.com), ball lenses, and solid state optical devices. A schematic diagram of the fluorescence detector is presented in Fig. 1b. A surface-mounted ultraviolet light-emitting diode chip (UV-LED, λ_{max} 365 nm, 3 mW@20 mA, NSSU100A, www.nichia.co.jp) and an amplifier-integrated photodiode (OPT301, www.ti.com) with a 100 MΩ feedback resistor were used as an excitation light source and emission light transducer, respectively. The junction of a tee connector was used as a flow-through fluorescence cell. Excitation light was introduced into the junction *via* a sapphire ball lens (ϕ2.0 mm, NT43-642) that was inserted into a hole drilled through the tee connector. The emitted light was collected and transferred using a plastic fiber optic (ϕ2 mm, Eska® CK80, www.mrc.co.jp) *via* a sapphire ball lens (ϕ2.5 mm, NT43-819, both from www.edmundoptics.com), which were fixed with ferrule and nut for the 1/16 tube (holes were enlarged to ϕ2.0 mm). The transferred emission light was detected with a photodiode *via* a sharp-cut optical filter (SC420, 50% cut off at 420 nm, fujifilm.jp) that prevented scattered excitation light. The photodiode output signal was amplified 100 × and recorded with a data logger (midi logger GL220, www.graphtec.co.jp). The data were acquired with 5 Hz frequency then averaged for 1 s using spreadsheet software.

2.4. Flow system and operation

A schematic diagram of the flow-based ammonia gas monitoring system with the OCS is depicted in Fig. 2. Absorbing solution consisting of 5 mM H_2SO_4 was pumped by a miniature peristaltic pump (Pump1, WPX1-1.6S4WM4-R, www.welco-web.co.jp) at a rate of 450 μL min^{-1}. The solution flow rate was monitored with a mass flow meter (LF-310, Stec, Japan) and recorded. The pump tubing used was Pharmed® tube (0.5 mm i.d. × 3.7 mm o.d., www.tygon.com). Tube compression force and rotation speed of the miniature peristaltic pump were adjusted by placing polytetrafluoroethylene (PTFE) sheets (1.0 and/or 0.3 mm thick) in the rotor assembly basement and changing driving voltage, respectively. The outlet of the pump was connected to a pumping dumper, mass flow meter and a resin column. The pumping dumper consisted of a silicone tube (2 mm i.d. × 3 mm o.d. × 100 mm long) and polyetheretherketone (PEEK) tube (0.25 mm i.d. × 1.6 mm o.d. × 100 mm long). A cation exchange resin (Dowex Monosphere 650C in H^+-form, www.sial.com)-packed column (3-mL capacity solid phase extraction cartridge shells and adapters, 5010-60121 and 5010-60000, www.glsciences.com) was connected before the OCS to remove ammonium ions in the absorbing solution. The OCS was angled 7° from ground level so that the inlet was positioned higher than the outlet. A part of the OCS effluent was introduced into a sample loop (26.4 μL, 0.5 mm i.d., PEEK tubing) by suction with a peristaltic pump (Pump 2) at a rate of 220 μL min^{-1}. A three-way solenoid valve (MTV-3-1/4UFH-3, www.takasago-elec.co.jp) was introduced to periodically switch between the OCS effluent and ammonium standard solution. The rest of the OCS effluent was overflowed into the gas aspiration line and then kept in a water/mist trap. Derivatization reagent was flowed into the system by Pump 3 at a rate of 460 μL min^{-1}. The injected solution was mixed and reacted as it flowed into the fluorescence detector *via* a heated reactor. The heated reactor was prepared using a wirewound resistor (47 Ω, 12 W, W24-47RJI, www.welwyn-tt.com) as a heater and a stainless steel tube (0.5 mm i.d. × 1/16 o.d., 168 cm long, 0.33 mL in volume) that was coiled around the resistor. The reactor was covered by polystyrene foam as a heat insulator. The temperature was kept at 65.0 ± 0.1 °C with a digital temperature controller (E5CN-RT, www.omron.co.jp). The dc driving voltage of the heater was 12 V.

Sample gas was continuously aspirated by a miniature air pump at a rate of 0.1 standard liter per min (SLPM). The sample gas flow rate was adjusted with a flow sensor (PFMV505-1,

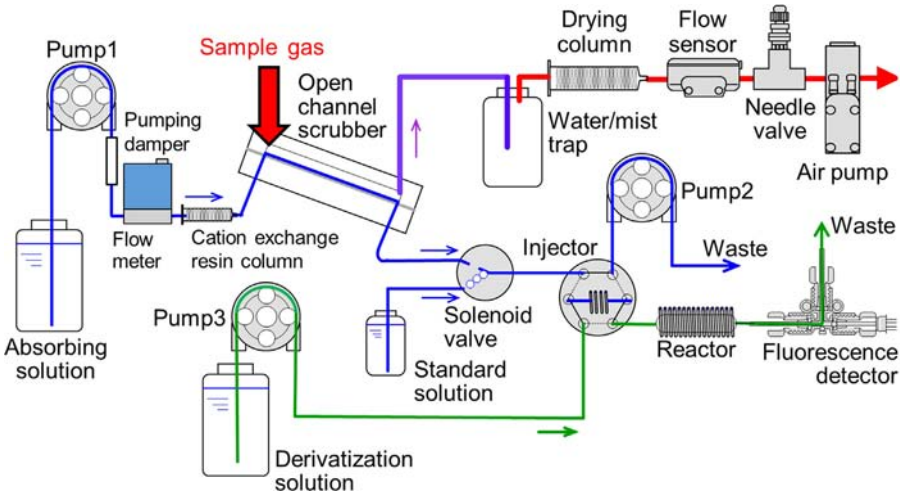

Fig. 2. Schematic flow diagram of ammonia gas analysis system with OCS. Blue, red, purple and green lines show absorbing solution, sample gas, mixture of absorbing solution and sample gas and derivatization solution flows, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

www.smcworld.com) and a needle valve (LN-6, www.as-1.co.jp). A drying column (10 mL capacity) filled with common silica gel was connected with an adapter just before the flow sensor to protect it from moisture.

3. Results and discussion

3.1. Flow-based ammonia solute analysis system

When ammonia gas is collected into a suitable absorbing solution, it can be analyzed as ammonia solute. In this study, a flow-based ammonia solute analyzer using OPA-sulfite chemistry was developed. A solution containing OPA, sulfite, and pH phosphate buffer was used for the derivatization. OPA-sulfite chemistry is a highly sensitive and cost-effective reaction for ammonia, and suited our purposes in this study because it could be coupled with a home-made fluorescence detector. The reagent concentrations were preliminary optimized by batch reaction; we used 10, 3, and 190 mM concentrations of OPA, sulfite and phosphate buffer (pH 11), respectively. It has been recommended that OPA and buffer solutions are prepared separately to avoid decreasing reagent lifetime [11]. However, the reagent mixture in this study was sufficiently stable for at least 3 days in an amber glass bottle at a room temperature (~27 °C). The fluorescence spectra of the OPA-sulfite-ammonia product, 1-sulfonateisoindole, with different ammonium ion concentrations are shown in Fig. 3. The excitation and emission maxima of 1-sulfonateisoindole are 362 and 422 nm, respectively.

The home-made flow-through fluorescence detector used in this study is depicted schematically in Fig. 1b. Suitable light source and long-pass optical filter were selected based on the spectra in Fig. 3. The excitation light was generated by a UV-LED and introduced *via* a sapphire ball lens. A surface-mounted UV-LED light with poor directivity (~110°) was effectively focused on a tee junction. The radially emitted fluorescence was collected by a ball lens and then detected by a photodiode *via* a fiber optic and long-pass (sharp-cut) optical filter to remove scattered excitation light. The ball lens has been reported as a light coupler for fluorescence detection in capillary electrophoresis. Light sources such as a UV-pulsed laser [21], LED [22] and small-diameter capillary have been coupled using ball lens. The ball lens was also easy to use as an interface between light and liquid; it was positioned simply by inserting it into a hole drilled in the tee junction.

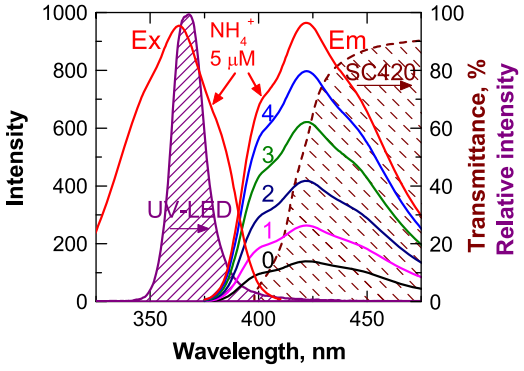

Fig. 3. Fluorescence spectra of the products of ammonium ions and OPA. The derivatization solution was 10 mM OPA/3 mM Na_2SO_3/0.1 M phosphate buffer (pH 11). Small aliquots of ammonium chloride solution were added to fluorescence-developing reagents and then heated at 65 °C for 10 min. Fluorescence spectra were obtained with a F-2500 spectrometer (www.hitachi-hitec.com) with the following settings: λ_{Em} for Ex: 422.0 nm/λ_{Ex} for Em: 362.0 nm, Ex slit: 5.0 nm/Em slit: 2.5 nm, scan speed: 60 nm/min, PMT applied voltage: 400 V. UV-LED (λ_{max} 365 nm, NSSU100A, www.nichia.co.jp) and sharp-cut filter (SC420, 50% cut off at 420 nm, fujifilm.jp) spectra were obtained with a miniature fiber optic spectrometer (S2000) and light source (DT1000A, both from www.oceanoptics.com).

OPA chemistry is highly sensitive to ammonia, but the reaction is known to be slow [23,24], especially with a weak nucleophile such as sulfite. The rate of the reaction of ammonia with OPA-sulfite reagent was investigated at different temperatures. The derivatization reagent was kept in a plastic bottle (150 mL), placed in a water bath at room temperature (27 °C) or 65 °C and stirred at 300 rpm. Small aliquots of standard solutions were added so the reagent solutions contained 10 μM ammonium or 10 mM methylamine. The solution in the bottle was sucked up with a peristaltic pump via a sample loop placed on an injector. The solution was injected into the water carrier and then introduced into the fluorescence detector every 1.5 min. The obtained results are plotted as relative peak height to highest ammonia response in Fig. 4a. The ammonia with OPA-sulfite required ~35 min at room temperature to achieve maximum fluorescence intensity. In contrast, the fluorescence response at 65 °C quickly increased and reached its maximum within 2.5 min. The maximum intensity at 65 °C was higher than that at room temperature. The intensity of fluorescence then gradually decreased. A high reaction temperature (65 °C) was therefore required to accelerate the reaction to increase sample throughput. The temperature was increased using a heated reactor consisting of a stainless steel (SS) tube coiled around an enameled wirewound resistor. SS (heat capacity 0.5 J g^{-1} °C^{-1}) was used because it is a better thermal transducer than polytetrafluoroethylene (PTFE, heat capacity 1.2–1.4 J g^{-1} °C^{-1}), which is frequently used as a reaction tube in flow injection analysis systems. The effects of temperature on the relative response using different tube materials and solution flow rates are shown in Fig. 4b. The reactor

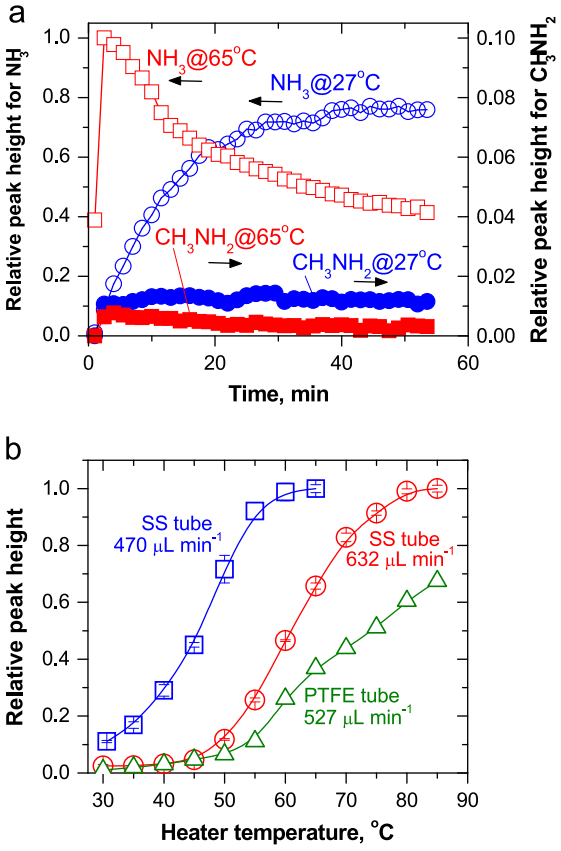

Fig. 4. Effects of reaction temperature. (a) The effect of reaction temperature on response time. (b) The effects of reactor temperature and material on fluorescent response. Reactor volume was 330 μL for both SS and PTFE tubes. Test ammonium solution (1 μM) was injected into derivatization solution flow with an injector (injection volume: 26.4 μL).

made with a SS tube was more effective than the PTFE reactor with the same tube volume (330 μL). The optimum reactor tube material, flow rate and reactor temperature were determined to be the SS tube, 470 μL min^{-1} and 65 °C, respectively. These conditions were selected taking into account response intensity, baseline stability, solution consumption, and sample throughput.

The calibration behavior of ammonium ions was studied under the optimized conditions. The LOD based on three times the noise level was 10 nM or 264 fmol (measured injection volume: 26.4 μL). The obtained LOD was better that or similar to those of other systems for ammonia solute detection with OPA–sulfite chemistry and home-made fluorescence detectors containing a photomultiplier tube as a phototransducer [25,26]. The sensitivity of the present system was high despite using a cost-effective photodiode as a phototransducer. This might be caused by the highly effective thermal transfer of the stainless steel tube reactor and the structure of the fluorescence detector, which focused the light with a ball lens, had a short distance between light in and out, and exhibited effective light transfer. The dynamic range of the system was up to ~75 μM, and it could handle a sample throughput of 40 h^{-1}. The effluent from the OCS containing absorbed ammonia gas was analyzed by introducing it into a sample loop for flow injection analysis.

3.2. Hydrophilic channel surface preparation for stable in-line gas collection

In the OCS, sample gas was in direct contact with an absorbing solution. Absorbing solution was flowed as a thin layer on the bottom of the channel surface. A stable hydrophilic surface was required to keep the solution as a thin layer. In our previous OCS, a hydrophilic surface was prepared with a cotton mesh and absorbing solution was flowed at a low flow rate of 50 μL min^{-1}, and the OCS was used in an off-line manner [19]. Here, the OCS needed to be used in an in-line manner for continuous ammonia monitoring. In addition, a highly stable thin solution layer and excellent gas collection performance were required. A higher relative absorbing solution flow rate was also required for a fast response time and to eliminate relative humidity effects, *vide infra*. To address these requirements, we used a hydrophilic surface on the channel bottom.The solution flow on hydrophilic (covered with regenerated cellulose membrane) and hydrophobic (bare PVC) surfaces on the channel bottom is shown in Fig. 5. A thin solution layer readily formed with the hydrophilic surface. In contrast, the channel fulfilled with solution when its surface was hydrophobic. High solution flow rate with cotton mesh, which was previously used [19], could not make a stable thin solution layer. To improve the stability of the gas collection performance of OCS with relatively higher solution flow rate, three kinds of materials, electrically polished stainless steel plate (ESS), regenerated cellulose dialysis membrane (RC), and treated glass plate (GP) were tested as hydrophilic surfaces. The reported water contact angles of ESS, RC and GP are 5.4° [27], 12° [28] and $<8°$ [29], respectively. However, the ESS and GP did not have sufficient lifetimes as hydrophilic surfaces. Surface oxidation by water and contaminants reduced the hydrophilicity of ESS and GP, respectively. Fortunately, the RC membrane maintained a hydrophilicity for a long period. However, when purified water was flowed as an absorbing solution on the RC membrane-covered surface, the 90% response times for rising and falling with 50 ppbv NH_3 were ~360 and ~270 s, respectively. This slow response time was expected to be caused by the negative ζ-potential of regenerated cellulose membranes over a wide pH range [30] Ammonium ions from the collected ammonia gas were absorbed onto the negatively charged membrane surface. This memory effect improved considerably when 5 mM sulfuric acid was used as the absorbing solution. Sulfuric acid was chosen because of its lower volatility compared with other mineral acids, and the concentration was decided based on the isoelectric point of the surface potential for the RC membrane to avoid memory effects [30]. The 90% response time for both rising and falling with sulfuric acid as the absorbing solution decreased to less than <90 s, which was chosen as the cycle time for the flow injection analysis system. In addition, the acid solution showed good collection efficiency for ammonia gas, *vide infra*.

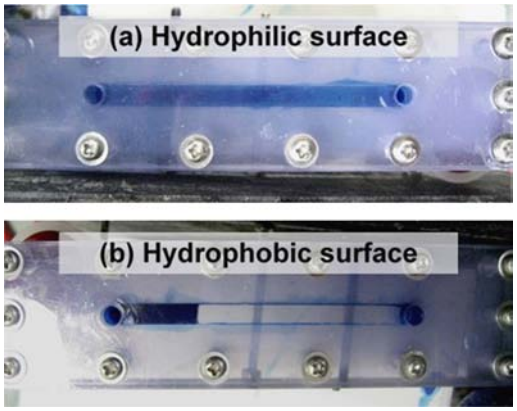

Fig. 5. Top view of OCS with flow of an aqueous dye solution over a (a) hydrophilic and (b) hydrophobic channel bottom surface. Dye solution was introduced from the left side of channel bottom with a flow rate of 0.2 mL min^{-1}. The OCS was angled 7° with respect to the ground so that the inlet was higher than the outlet.

3.3. Collection efficiencies for ammonia

The ammonia gas collection efficiency, *f*, of the OCS was simulated theoretically to determine suitable channel dimensions for ammonia gas collection. Calculations were based on the theory for gas diffusion in a sample gas channel. The gas concentration at the interface between an absorbing solution and sample gas is ideally zero if the absorbing solution functions as a perfect sink. This causes a gas concentration gradient to develop in the channel. Analyte gas molecules diffuse from the top of the channel to the bottom, which is covered by absorbing solution. A spreadsheet that simulates *f* for planer geometry is available online [19]. *f* for ammonia gas were theoretically simulated on the spreadsheet using different OCS dimensions and sample gas flow rates with an ammonia diffusion coefficient of 0.24×10^{-4} m^2 s^{-1} (Fig. 6a). Simulated *f* decreased exponentially with increasing gas flow rate. A longer, wider channel increases residence time, which corresponds to a longer absorbing time. Also, a narrower channel decreases diffusion distance. Considering both the *f* simulation results and empirical solution flow behavior, we chose channel dimensions of 75 mm long, 5 mm wide, and 2 mm deep. The Reynolds number of an air sample with these channel dimensions was between 22.3 and 112 with sample gas flow rates from 0.10 to 0.50 L min^{-1} at 20 °C. This indicates that under these conditions, sample gas flowing in the channel can be considered fully developed laminar flow.

The *f* values of the OCS for ammonia gas collection were evaluated using 112 ppbv NH_3 standard gas. The ammonia in the OCS effluent was analyzed using the developped flow injection analysis system. In this study, *f* was obtained by determining the mole ratio of ammonia in the absorbing solution to that in the introduced sample gas. Obtained and simulated *f* for different absorbing solutions, 5 mM H_2SO_4 and derivatization reagents are presented in Fig. 6b. Purified water was not tested as an absorbing solution because of the observed memory effects described above. The value of *f* obtained using 5 mM H_2SO_4 as an absorbing solution agreed well with simulated values. However, *f* obtained using OPA

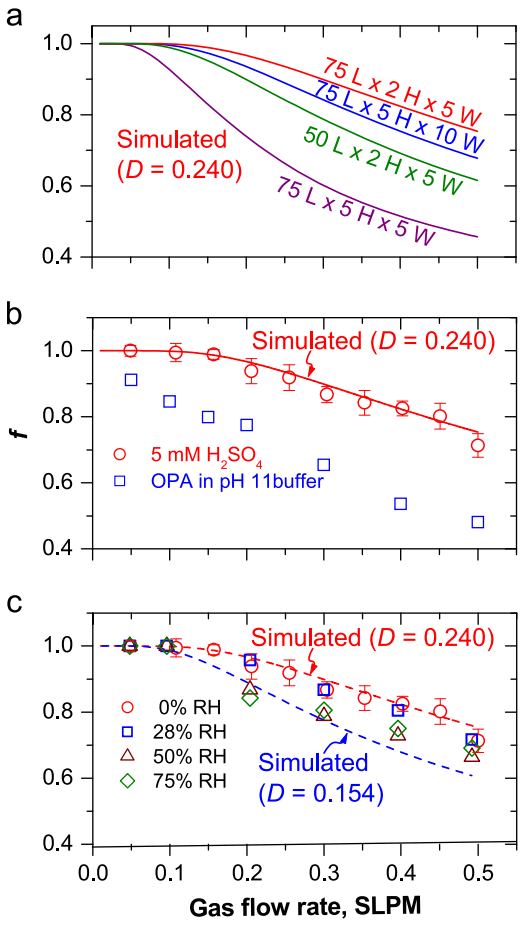

Fig. 6. Simulated and experimental collection efficiencies, *f*. The diffusion coefficients, *D*, shown in panels were used for simulations. (a) Simulated *f* with different channel dimensions. (b) Comparison of different absorbing solutions. (c) Effect of sample humidity on *f*. The tested concentration was 112 ppbv NH_3. Experiments were performed at 25 °C.

in buffer solution at pH 11 was less than the simulated value. At high pH, the protonation of ammonia (pKa 9.27) was not promoted enough to allow effective gas collection. Also, the low reaction rate of OPA with ammonia at high pH could not accelerate dissolution of ammonia. Based on *f* and memory effects, 5 mM H_2SO_4 was selected as the absorbing solution. A sample gas flow rate of 0.1 SLPM was chosen for use in a further experiment. Under these conditions, ammonia in the sample gas could be collected quantitatively.

3.4. Humidity effects

The humidity of a gas sample may affect the response of a gas analysis system. In the present system, low humidity may cause evaporation of absorbing solution, concentrating ammonium solutes and increase the response. The microchip based membrane free gas collector obtained the effluent of 50–83% less than influent which was flowed at several μL min^{-1} because of solution evaporation [18]. Conversely, high humidity may hydrate ammonia molecules, decreasing both diffusion coefficient and *f*. First, the evaporation during solution flow in the OCS was measured. Absorbing solution was introduced at a rate of 465 μL min^{-1} and dry nitrogen gas was flowed at a rate of 0.1 SLPM. The total OCS effluent flow rate was 460 μL min^{-1}. These liquid flow rates were obtained gravimetrically. Only a small amount of water was evaporated under these conditions because the solution flow rate was relatively high and the gas flow rate was relatively low. A small change in flow rate (only 1.1%) will not cause a significant signal increase. This relatively larger solution flow rate decreased solution evaporation in highly transferable membraneless OCS. However, diffusion coefficient was strongly affected by humidity, which then influenced *f*. The gas diffusion coefficients reported for dry and wet ammonia gas are 0.240 and 0.154 cm^2 s^{-1}, respectively [31]. *f* simulated using these diffusion coefficients are depicted in Fig. 6c. *f* for humid standard gas was less than that of dry gas, especially at higher gas flow rates. The effect of humidity on *f* was also determined experimentally. *f* for humid gas (RH > 50%) were close to simulated values with a diffusion coefficient of 0.154 cm^2 s^{-1}. The reason why experimental *f* was slightly higher than simulated values at higher flow rates is unclear at present. However, *f* at 0.1 SLPM was not affected by humidity and remained almost constant at ~1. The effect of humidity on the present system was examined up to 90% RH, as shown in Fig. 7. Humidity had no significant effects on the response of the system.

3.5. Solution-based calibration for gas analysis system

Gas analysis systems are generally calibrated with standard gases. However, standard gases are difficult to store and prepare, especially out of the laboratory or for trace and sticky gases such as ammonia. As previously described, the present OCS can collect ammonia gas into solution quantitatively under the optimized conditions. It is expected that *f* will be stable because the maximum value of *f* obtained by directly contacts between the phases in the OCS. System calibration with periodic solution injection is suited for on-site analysis. However, it was pointed out that the SO_2 concentration was underestimated by a gas analyzer with solution-based calibration, which was improved by adjusting injection volumes [32]. Thus, the present gas analysis system was calibrated with both standard ammonium chloride solution and ammonia gas to minimize error. The relationship between gas concentration, $C_{gas.}$(ppbv), and solution concentration, C_{sol} (μM), can easily be calculated based on moles by the following equation:

$$C_{gas} = \frac{RT/P}{GFR} C_{sol} LFR = kC_{sol} \quad (1)$$

where *R* is the gas constant (8.314 J mol^{-1} K^{-1}), *T* is temperature (K), *P* is ambient pressure (N m^{-2}), *GFR* is sampling gas flow rate (SLPM), and *LFR* is absorbing solution flow rate (L min^{-1}). Under

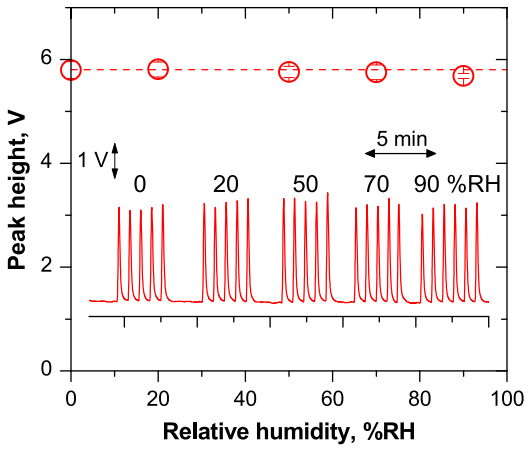

Fig. 7. Effect of relative humidity on system response. Experiments were performed at 25 °C. Inset shows response chart obtained with 119 ppbv NH_3 and various degrees of relative humidity. Peak height is plotted against relative humidity.

the experimental conditions, $GFR = 0.10$ SLPM, $LFR = 421 \times 10^{-6}$ L min^{-1}, and the constant k was 92.29. Calibration curves were obtained experimentally using both liquid and gas standards, and are presented along with a response chart in Fig. 8. Experimentally obtained calibration equations for gas and liquid standards were:

$$\text{Peak height}, V = (0.0949 \pm 0.0025) \times C_{gas}, \quad \text{ppbv} + (0.308 \pm 0.104) \quad r^2 = 0.9949 \tag{2}$$

$$\text{Peak height}, V = (8.94 \pm 0.32) \times C_{sol}, \quad \mu M + (0.308 \pm 0.102) \quad r^2 = 0.9974 \tag{3}$$

The constant k corresponds to the ratio of the slopes in these equations. The experimentally obtained k was 94.20 ± 4.19, which is close to the theoretical value, 92.29. This demonstrates that solution-based calibration is appropriate for the present system.

The solution and sample gas flow rates are the variables in Eq. (1). These flow rates may be changed by variation of the motor rotation or damage to the pump tubing, especially during long-term monitoring. These flow rates were monitored with thermal flow meters in the present system. The flow rates during our one week of monitoring with the present system were 441 ± 12 μL min^{-1} and 101 ± 0.5 mL min^{-1} for solution and gas, respectively. Less than 3% of flow rates were validated. The flow rates monitored with flow meters can be directly fed back to the pump rotation speed to regulate them [33] It is also possible to consider these flow rates using software calculations if required.

The LOD for the analyzer based on three times the noise level was estimated to be 10 nM and 0.9 ppbv for liquid phase ammonium ions and gas phase ammonia, respectively. The dynamic range for ammonium ions was ~75 μM, which corresponds to 7500 ppbv. The relative standard deviation for 53 ppbv NH_3 gas determination was 3.2% ($n = 960$), which was obtained over

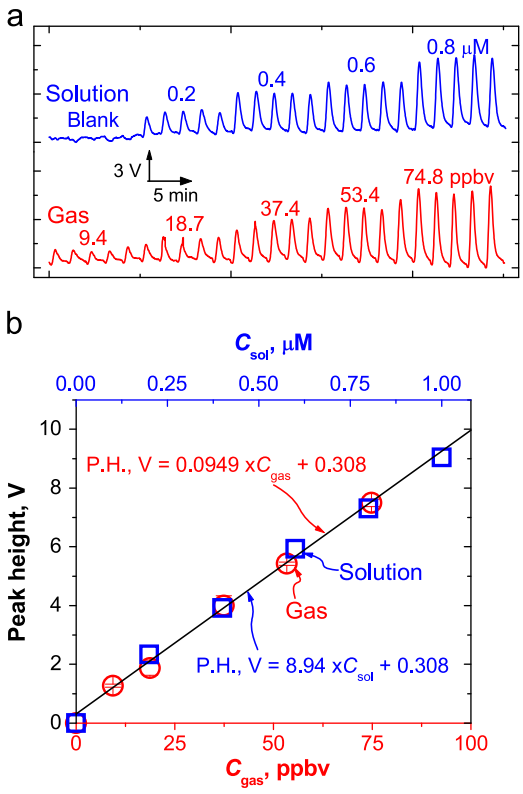

Fig. 8. System calibration with NH_4Cl solution and NH_3 standard gas. (a) Response chart and (b) calibration curves are shown with square marks for aqueous and circles for gaseous standards. X-axis was scaled to place position of $C_{gas} = 94.2 \times C_{sol}$.

continuous measurement for 24 h. The system can analyze the level of ammonia in a gas sample 40 times per hour.

3.6. Interference from amines

Relatively high concentrations of amines have been detected in indoor environments [34]. For example, ~90 ppm of methylamine and ~9 ppm of ethylamine were detected at a city market near a fish display and pharmaceutical plant, respectively [34]. The interference of these amines with detection of ammonia using the developed system was examined by simulating collection efficiencies and solution-based responses.

Collection efficiencies were simulated using the present OCS dimensions, diffusion coefficients calculated using the method of Fujita [35] and a gas flow rate of 100 mL min^{-1}. The absorbing solution, 5 mM H_2SO_4, was expected to act as a perfect sink for these amine compounds, which have higher pKa values than ammonia. The f values for the amines were lower than those for ammonia because of their smaller diffusion coefficients. However, the calculated f values were still greater than 0.8. Therefore, most of the amines can be collected into the absorbing solution.

The responses of several kinds of volatile amine solutions were also studied. There was no significant response from 10 mM solutions of ethyl-, dimethyl-, trimethyl-, diethyl-, and triethylamines. Only a 10 mM solution of methylamine showed a response, although it was just 0.1% that of 5 μM ammonium chloride. The reaction rate of methylamine with OPA-sulfite was also determined (Fig. 4a). Methylamine with OPA-sulfite generated a weakly fluorescent product and the intensity of the signal decreased over time at higher temperature. Overall, the 10 mM solution of methylamine induced a positive error of 0.5 ppbv onto the ammonia response, which corresponded to an amine gas concentration of >900 ppmv. Therefore, the ammonia in most indoor environments can be analyzed with the present system without any significant interference from amines.

3.7. Monitoring of indoor air and validation

The developed system was used to monitor the level of ammonia in a laboratory as an example of an indoor environment. Results were compared with those determined using the impinger method, in which room air was simultaneously collected into 5 mM H_2SO_4 using a traditional impinger. Impinger collection was performed during the day time, typically from 8 AM to 8 PM. Sample gas was passed through 20 mL of 5 mM H_2SO_4 at a flow rate of 1.0 SLPM for 60 min. The absorbing solution was then analyzed by ion chromatography. The ion chromatograph (ICS-1100) consisted of cation exchange columns (CG-12A and CS-12A, 4 × 50 mm, 250 mm, respectively), an electrodialytic membrane suppressor (CSRS-300, all from www.dionex.com) and a conductivity detector. Ammonium ions were eluted at 3.9 min using 20 mM methanesulfonic acid eluent flowing at a rate of 1.2 mL min^{-1}. The concentration of ammonia gas was calculated from the concentration of ammonium ions in the absorbing solution and the collection efficiency with an impinger for ammonia (~99%).

The results obtained with both methods are depicted in Fig. 9. The OCS system can analyze with a time resolution of 1.5 min. A large change in the concentration of ammonia for a short time caused by the use of ammonia solution in the laboratory at 3 PM on Oct. 12 was effectively detected by the OCS system (Fig. 9b). The concentration of ammonia in the air during the monitoring term ranged from 12.3–739 ppbv with an average of 28.2 ppbv. The regression plot between impinger-IC and the OCS system is shown in Fig. 9c. The relationship between impinger-IC and the OCS

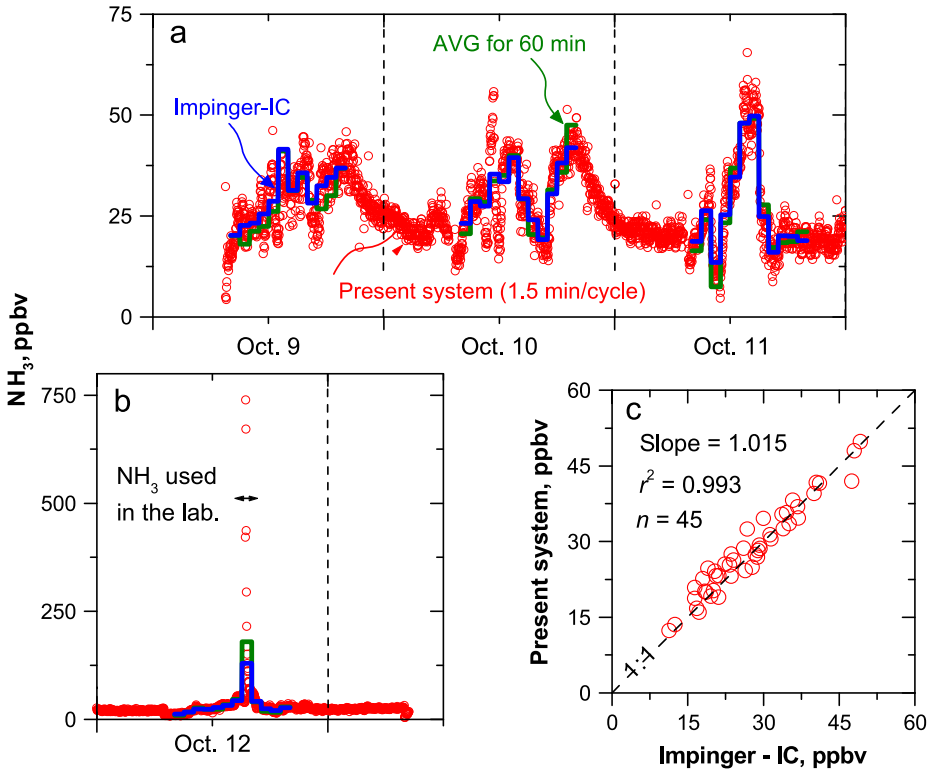

Fig. 9. Measurement of ammonia concentration in a laboratory. Red circles, green line and blue line show the results obtained with the OCS system, OCS system averaged for 60 min during impinge collection and impinger-IC system. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

system is:

$$[\text{OCS method, ppbv}] = (1.015 \pm 0.13) \times [\text{Impinger}-\text{IC, ppbv}] \quad r^2 = 0.993\ (n = 45)$$

This equation indicates that the results obtained by the two methods are consistent, demonstrating the effectiveness of the developed system to analyze ammonia in indoor air samples.

4. Conclusion

A robust, sensitive analysis system that can rapidly detect ammonia gas was developed for indoor ammonia monitoring. This system can easily be calibrated on-site with an aqueous standard. Relative humidity had no significant effect on the operation of the system. The results achieved using the developed system agreed well with those obtained using a traditional gas analysis method. The developed system is readily applicable to other kinds of water-soluble gas analysis with suitable derivatization chemistry.

Acknowledgments

This project was supported by JSPS Grants-in-Aid for Scientific research (C), Grant no. 21550087.

References

[1] US Department of Health and Human Services, Toxicological profile for ammonia, ⟨http://www.atsdr.cdc.gov/toxprofiles/tp126.pdf⟩, 2004.
[2] M.K. Reddy, M. Suneela, M. Sumathi, R.C. Reddy, Environ. Monit. Assess. 105 (2005) 359–367.
[3] L. Skytte, K.L. Rasmusen, M.R.- Svendsen, B. Svensmark, P. Brimblecombe, Sci. Total Environ. 417–418 (2012) 13–20.
[4] K. Toda, J. Li, P.K. Dasgupta, Anal. Chem. 78 (2006) 7284–7291.
[5] K. Nose, T. Mizuno, N. Yamane, T. Kondo, H. Ohtani, S. Araki, T. Tsuda, Anal. Sci. 21 (2005) 1471–1474.
[6] T. Lindgren, Build. Environ. 45 (2010) 596–600.
[7] Z. Bai, Y. Dong, Z. Wang, T. Zhu, Environ. Internship 32 (2006) 303–311.
[8] B. Lee, C.K. Lee, D.S. Lee, Bull. Korean Chem. Soc. 32 (2011) 2039–2044.
[9] B. Timmer, W. Olthusis, A.V.D. Berg, Lab. Chip 4 (2004) 252–255.
[10] E. Asadi, M.C.G. da Silva, J.J. Costa, Environ. Monit. Assess. 185 (2013) 865–875.
[11] Z. Genfa, P.K. Dasgupta, Anal. Chem. 61 (1989) 408–412.
[12] N. Amornthammarong, J. Jakmunee, J. Li, P.K. Dasgupta, Anal. Chem. 78 (2006) 1890–1896.
[13] B. Horstkotte, C.M. Duarte, V. Cerdà, Talanta 85 (2011) 380–385.
[14] N. Amornthammarong, J.-Z. Zhang, Anal. Chem. 80 (2008) 1019–1026.
[15] S. Xue, K. Uchiyama, H. Li, J. Environ. Sci. 24 (2012) 564–570.
[16] Z. Genfa, P.K. Dasgupta, S. Dong, Environ. Sci. Technol. 23 (1989) 1467–1474.
[17] K. Toda, Anal. Sci. 20 (2004) 19–27.
[18] S. Hiki, K. Mawatari, M. Saito, T. Kitamori, Anal. Chem. 83 (2011) 5017–5022.
[19] K. Toda, T. Koga, T. Tanaka, S. Ohira, J.M. Berg, P.K. Dasgupta, Talanta 82 (2010) 1870–1875.
[20] S. Ohira, K. Goto, K. Toda, P.K. Dasgupta, Anal. Chem. 84 (2012) 8891–8897.
[21] C. Bayle, N. Siri, V. Poinsot, M. Treilhou, E. Causse, F. Couderc, J. Chromatogr. A 1013 (2003) 123–130.
[22] S. Wang, X. Huang, Z. Fang, P.K. Dasgupta, Anal. Chem. 73 (2001) 4545–4549.
[23] E. Kulla, P. Zuman, Org. Biomol. Chem. 6 (2008) 3771–3780.
[24] G. Huang, J. Hou, X. Zhou, Environ. Sci. Technol. 43 (2009) 5851–5856.
[25] B. Horstkotte, C.M. Duarte, V. Cerdà, Talanta 85 (2011) 380–385.
[26] S. Xue, K. Uchiyama, H. Li, J. Environ. Sci. 24 (2012) 564–570.
[27] D.J. Trevoy, H. Johnson, J. Phys. Chem. 58 (1958) 833–837.
[28] C. Yamane, T. Aoyagi, M. Ago, K. Sato, K. Okajima, T. Takahashi, Polymer J. 38 (2006) 819–826.
[29] J.J. Cras, C.A. Rowe-Taitt, D.A. Nivens, F.S. Ligler, Biosens. Bioelectron. 14 (1999) 683–688.
[30] N. Park, Y. Yoon, S. Moon, J. Cho, Desalination 164 (2004) 53–62.
[31] D.J. Eatough, V.F. White, L.D. Hansen, N.L. Eatough, E.C. Ellis, Anal. Chem 57 (1985) 743–748.
[32] X. Yao, K. Shairsingh, P.H. Lam, G.J. Evans, J. Environ. Monit. 11 (2009) 1292–1297.
[33] S. Ohira, K. Toda, Anal. Sci. 22 (2006) 61–65.
[34] J. Namieśnik, A. Jastrzębska, B. Zygmunt, J. Chromatogr. A 1016 (2003) 1–9.
[35] S. Fujita, Kagaku Kogaku 28 (1964) 215–254.