

Trends in Atmospheric Trace Gas Measurement Instruments with Membrane-based Gas Diffusion Scrubbers

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A diffusion scrubber (DS) is an excellent tool for gas analysis, and there are many types of DS devices, varying both in structure and construction. In this paper, recent work on atmospheric trace gas measurements by means of DS devices are reviewed. Theoretical considerations on representative DSs are summarized first. Then, the characteristics of the key material, a gas-diffusion membrane, are discussed, and recent improvements and novel scrubbers for highly effective collection are outlined. A chromatograph is a suitable tool for the multi-gas analysis of collected species. On the other hand, solid-state fluorescence/absorbance detectors have been developed for the continuous measurement of target gases. The methods based on DS collection and subsequent detection have high sensitivities, and the detection limits can be in the low-pptv levels. Accordingly, they are capable of measuring background levels, and detecting very low levels of contaminants in a cleanroom. Miniaturized advanced DS units, perhaps the next generation of DS devices, are introduced at the end of this review. DS systems have contributed significantly to our knowledge of the atmospheric dynamics and atmospheric chemistry.

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1 Introduction

In contrast to natural water and soil analyses, atmospheric trace-gas analyses mostly require on-site and continuous measurements because of fluctuations in the concentration levels and difficulties with sample storage and/or the stability of stored samples. Classically, gas analysis has been conducted by bubbling an air sample through a solution, followed by chemical analysis. Recently, dry methods for specific gas analyses (*e.g.* UV-fluorescence, UV-absorbance, chemiluminescence and infrared absorption methods for SO₂, O₃, NO_x and organic gases, respectively) have been used. FTIR, NDIR and electrochemical sensors are capable of measuring gases continuously, but usually lack the sensitivity required for the environmental monitoring of trace gases. Recently developed tunable diode laser absorption spectrometers (TDLAS)¹ and laser-induced fluorescence² instruments can measure ppb levels

of pollutants. However, these are large, expensive and complex instruments. A commercially available differential optical absorption spectrometer (DOAS) is highly sensitive, but the distance between the light source and the detector is very long, (*typ.* > 100 m to several km); hence, the light path must be aligned precisely. Moreover, the elimination of interferences by complicated compensation procedures is required.³⁻⁶ Gas chromatography (GC) is also used in standard analysis methods for odorous components,⁷⁻⁹ but it requires troublesome, complicated and time-wasting procedures, which involve sampling into a Tedlar bag or a canister in the field, bringing the sample back to the laboratory, preconcentration and GC analysis. For all of these situations, the classical methods, based on sampling and chemical analysis, have recently changed in their style of deployment. Instead of bubbling into a solution, gas collection is carried out on the inner wall of a tube coated with an absorbing material. This is called a denuder. Theoretical considerations on mass transfer to the walls of a cylindrical tube, where the tube wall acts as a sink, were first presented by Gormley and Kennedy.¹⁰ For a denuder of length

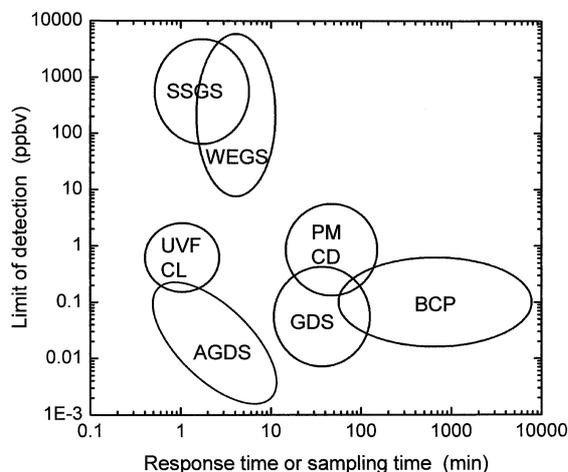


Fig. 1 Performances of gas-analysis methods. The circles represent the typical characteristics of each gas measurement method. SSGS, solid state gas sensor; WEGS, wet electrochemical gas sensor; UVF and CL, UV-fluorescence and chemiluminescence; PM, paper meter (ribbon paper is impregnated with reagent); CD, solution conductivity detection; BCP, bubbling and chemical procedure; GDS, gas diffusion scrubber; AGDS, advanced gas-diffusion scrubber. Note that this scheme shows the representative performance, and specially improved instruments are not reported.

L (m), where the wall surface is a perfect sink for the analyte gas of diffusion coefficient D ($\text{m}^2 \text{s}^{-1}$), being sampled at a volumetric flow rate of F ($\text{m}^3 \text{s}^{-1}$), the collection efficiency (f) is generally expressed as follows with dimensionless constants A and B (true for situations where more than $\sim 20\%$ of the gas is collected):

$$f = 1 - A \exp(-BLD/F). \quad (1)$$

This equation is based on a perpendicular gas-diffusion model with laminar flow during transportation along the tube. After collection, the tube is washed with a suitable liquid and the collected analyte is eluted. Such a denuder, originally developed by Ferm,¹¹ obviously needs discrete sampling/elution sequences. Subsequently, another type of collector was developed in the 1980s. Instead of the absorber being coated on the tube wall, an aqueous solution placed behind a gas-permeable membrane is used as the analyte sink.^{12,13} We simply call this a gas diffusion scrubber (DS) here, to distinguish it from the denuder. The significant difference from the denuder is that gas can flow over the absorbing layer continuously, making it capable of continuous measurement. Recently, many types of DS devices have been developed and coupled with selective reactions and novel detectors, so that the sensitivity, time resolution, portability and multi-gas measurement ability have been dramatically improved over conventional commercial instruments, as shown in Fig. 1. Dasgupta, the original inventor of the DS and of Asian descent, himself, has reported a variety of DS-based instrumentation.¹⁴⁻¹⁸ In East Asia, DS devices and their applications have caught the scientific imagination. Many novel and interesting DS devices and their applications have been reported. In this review, recent developments of instruments coupled to gas diffusion scrubbers, with special focus on those developed in East Asia, are discussed.

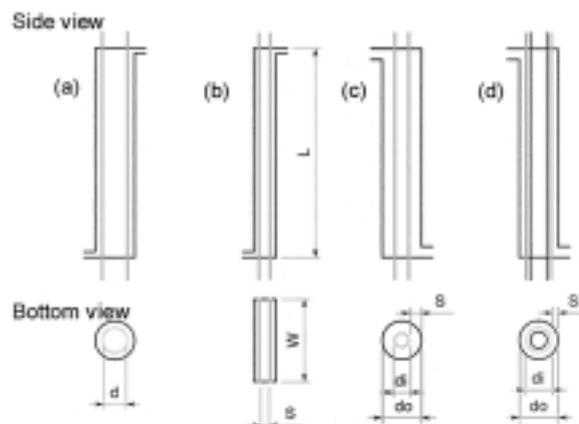


Fig. 2 Schematics of gas diffusion scrubbers. (a) Cylindrical DS, (b) parallel plate DS, (c) annular DS, (d) annular DS with a core.

2 Theoretical

2.1 Representative DS devices and their collection efficiencies

The simplest DS structure consists of a cylindrical porous membrane tube in which a sample gas flows through as shown in Fig. 2 (a). If the flow velocity and the tube diameter are small, the Reynolds number, (Re , Eq. (2)) is small (< 2300) and the air stream is considered to have laminar flow.

$$Re = \frac{Ud}{\nu} = \frac{4\rho F}{\eta\pi d}, \quad (2)$$

where U is the flow speed, d is "the equivalent diameter" (the inner diameter of the tube in this case), ν is the kinematic viscosity of air ($1.51 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$ at 20°C 1 atm), ρ is the density of the fluid (1.205 kg/m^3 at 20°C 1 atm), and η is the viscosity of air ($1.82 \times 10^{-5} \text{ Pa s}$ at 20°C 1 atm). If the laminar-flow profile fully develops before the collection membrane is encountered, the collection efficiency f is expressed by Gormley and Kennedy's equation, and more specifically as in Eqs. (3) and (4).

$$f = 1 - 0.81905 \exp(-3.6568\mu) - 0.09753 \exp(-22.305\mu) - 0.0325 \exp(-56.961\mu) - 0.01544 \exp(-107.62\mu) \quad (3)$$

where

$$\mu = \pi DL/F, \quad (4)$$

with the proviso that the wall acts as a perfect sink, and $f > \sim 0.2$ (at low collection efficiencies a different equation must be used). If the sink efficiency at the wall is very poor, μ in Eq. (3) must be replaced by μ^* ,

where

$$\mu^* = \varepsilon\mu, \quad (5)$$

and ε is a factor related to the sink efficiency, < 1 . At significant collection efficiencies, the terms after the 2nd one in Eq. (3) are small and do not contribute significantly to the total; thus, a two-term approximation of Eq. (3) is often used,

$$f = 1 - 0.819 \exp(-3.657\mu). \quad (6)$$

There are other types of denuders, *e.g.* parallel plate (rectangular), planar or annular. The equations for the collection efficiencies for each of these collectors have been discussed.^{19,20} For rectangular or parallel plates with a channel width (W) and a separation between the plates (S ; $S \ll W$) as Fig. 2 (b):

$$f = 1 - 0.914\exp(-7.5408\varphi) - 0.0531\exp(-83.06\varphi) - 0.01528\exp(-249.27\varphi) - 0.00681\exp(-498.15\varphi) \quad \text{for } \varphi > 0.13 \quad (7)$$

$$\varphi = DLW/FS. \quad (8)$$

This equation was originally developed by Gormley.²¹ Note that the two-term approximation of Eq. (7) can be written as

$$f = 1 - 0.914\exp(-3.77A_T D/FS), \quad (9)$$

where A_T is the total collection area of the parallel-plate denuder.

For an annular denuder in which both the outer wall of the inner tube (d_i) and the inner wall of the outer tube (d_o) are truly effective sinks, Ali *et al.*²² have argued that the relevant equation will be simply obtained by substituting the applicable value of the total collector surface area and the separation between the plates, *i.e.*, since

$$A_T = \pi(d_o + d_i)L \quad (10)$$

and

$$S = (d_o - d_i)/2. \quad (11)$$

The equation for an annular denuder should be as follows:²³

$$f = 1 - 0.914\exp(-7.54\theta DL/F), \quad (12)$$

where

$$\theta = \pi(d_o + d_i)/(d_o - d_i). \quad (13)$$

Possanzini *et al.*,²⁴ however, were the original inventors of the annular denuder, and advanced an entirely empirical equation for the collection of SO₂ with a tetrachloromercurate-coated annular denuder,

$$f = -0.82\exp(-5.63\theta DL/F). \quad (14)$$

While efforts have been made to use the denuder equations for membrane-based DS devices,²⁵⁻²⁷ in the case of the typical annular geometry DS, however, only the outer wall of the inner tube is effective in collecting the gas, as shown in Fig. 2 (c), while gas is collected on both tube walls in the annular denuder. The imperfect sink efficiency of the membrane and/or the sink chemistry causes even more complications. None of the above equations are generally applicable, hold only for specific chemistries and specific dimensions, and are not generally useful in predicting actual collection efficiencies. From Eq. (12) for an annular denuder, the equation for annular DS can be introduced by a compensation of the surface area, as Tanner²⁵ did. Equation (12) is multiplied by the surface area ratio of inner tube, $d_i/(d_o + d_i)$ to obtain Eq. (15):

$$f = 1 - 0.914\exp\left(-7.54 \frac{\pi d_i}{d_o + d_i} \frac{DL}{F}\right). \quad (15)$$

This assumption simply gives the fraction, but it is effective only for the case where the outer tube also acts as a sink as well as the inner tube. Therefore, this equation should give a smaller value. Though numerical solutions were developed by Lundberg *et al.*,²⁸ a general discussion of how to use this has been given by Dasgupta,^{20,29} but is also subject to a modification by the wall uptake efficiency.

The configurations for both the cylindrical and the annular DS devices are the same. In both types of scrubbers, a membrane tube is centered in a larger bore jacket tube as in Fig. 2 (a) and (c). The only difference is that the arrangement of liquid and gas flows are reversed. Thus, the respective DS devices may be conveniently referred to as gas-inside scrubbers (GIS) and gas-outside scrubbers (GOS) for the cylindrical DS and the annular DS.³⁰

Membrane tubes do not act as ideal sinks. The analyte gas molecules need to permeate through the membrane to reach the absorbing solution. Corsi *et al.*³¹ assumed that a linear concentration gradient was formed through the membrane wall, and the performance was theoretically assessed by combining the gradient and Gormley-Kennedy's concept.

2.2 Collected analyte quantity and concentration in the solution

The collected analyte gas in volume V_g (m³) is the product of f , F , the collection time t (s) and the gas concentration C_g (*e.g.*: C_g is 1×10^{-9} when the gas concentration is 1 ppbv):

$$V_g = fFtC_g. \quad (16)$$

The collected amount Q in mol is obtained from Eq. (16) and the equation of state with the gas temperature T (K), atmospheric pressure P (Pa) and the gas constant R (8.31 J K⁻¹ mol⁻¹).

$$Q = \frac{PfFtC_g}{RT}. \quad (17)$$

Here, f is a function of F as in Eqs. (3) - (15). Therefore, Q is almost proportional to F in the low flow rate region, and constant at a high flow rate, as shown in Fig. 3. In these experiments, the maximum Re is *ca.* 500, and all the air flow is considered to be laminar. The supply of gas molecules to the membrane surface and gas permeation through the membrane are the rate-determining steps in the low and high air flow ranges, respectively. The sampling rate effect depends on the membrane tube material, as shown in Fig. 3. In order to obtain a larger amount of analyte, the gas flow rate needs to be sufficiently high, but note that a high F causes much water evaporation, which can affect the final concentration in the solution if the solution is pumped rather than aspirated. Generally, it is the concentration of the analyte collected into the absorbing solution (C_s) that is measured after collection. C_s (M) can be expressed as the quotient of Q divided by the solution volume V_s (dm³),

$$C_s = Q/V_s. \quad (18)$$

Accordingly, it can be easily understood that small volume DS is profitable for efficient collection.

3 Discussion

3.1 Scrubber material

The most important part of the scrubber-based instrument is the gas-permeable membrane. A gas-collection method without

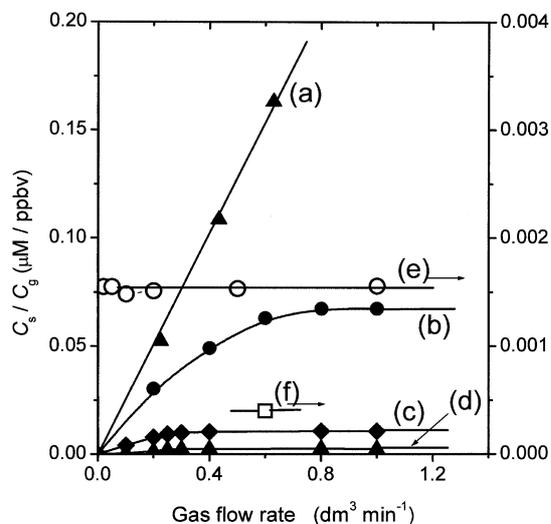


Fig. 3 Effect of the air sampling rate. The ordinate is the ratio of the analyte concentration collected in an absorbing solution (in μM per ppbv gas). The details of DSs, the test gas concentrations and the liquid flow rates were as follows: (a) ePTFE DS filament filled, 1.016 mm i.d. \times 60 cm, 5.5 ppbv H_2S , liquid flow rate $200 \mu\text{l min}^{-1}$; (b) Nafion DS, 0.41 mm i.d. \times 70 cm, 11 ppbv H_2S , liquid flow $120 \mu\text{l min}^{-1}$; (c) pPTFE DS, 2 mm i.d. \times 10 cm, 80 ppbv NO_2 , 300 ml min^{-1} ; (d) stopped flow 3 min, with the other conditions the same as in (c); (e) silicone DS, 0.41 mm i.d. \times 87 cm, 82 ppbv H_2S , liquid flow $100 \mu\text{l min}^{-1}$; and (f) Teflon AF DS, 1.07 mm i.d. \times 1.6 cm, 256 ppbv H_2S , stopped flow 30 min. The ordinate scale on the right applies to (e) and (f).

a membrane, namely into a liquid droplet or a liquid film, was developed by Dasgupta's group.³²⁻³⁸ Several Japanese groups have described novel gas collection and analysis approaches using this technique.³⁹⁻⁴¹ We have electrochemically measured SO_2 in a droplet *in situ* using a microring electrode arranged in a droplet at the chip of a capillary.⁴² However, a complicated sequence is usually needed for droplet collection and the subsequent measurement. On the contrary, in the membrane-based DS, a continuous supply of an absorbing solution is available and the measurement procedure is relatively easy. Furthermore, basically only gases are selectively collected in the scrubber because the diffusion coefficients of particles are much smaller than those of gases.^{11,28,43-45} The membrane-based diffusion scrubber was first developed by Dasgupta almost two decades ago, and a Nafion membrane was used as the tube material in that work.¹² The analyte gas, NH_3 , is collected as NH_4^+ on the outer surface of the polymer, which then diffuses through the ion-exchange lattice of the polymer. On the other hand, in the case of porous membranes, gas molecules diffuse through the pores or spaces among the fibers. Generally, this gas phase diffusion rate is much larger than the transport rate in the condensed phase. However, the permeation rates of some gases through certain membranes can also be high, as shown in Table 1. Porous polytetrafluoroethylene (pPTFE) and porous polypropylene (pPP) membranes are preferred as gas-diffusive materials. Simultaneous measurements can be made if the gas-permeation rates of two different gases in two kinds of membranes are significantly different. For example, H_2S and CH_3SH both fluoresce after a reaction with fluorescence mercuric acetate (FMA) and diffuse well through the pPTFE membrane, but only H_2S permeates through the Nafion membrane.³⁰ Not only the permeation rate, but also the memory effect is affected by the membrane material,⁴⁶ and all these

things should be considered when the membrane is chosen. If a larger permeation rate is needed for the non-porous membrane, the rate can be improved by expanding,^{47,48} surface treatment⁴⁹ or making the film thinner.⁵⁰⁻⁵²

3.2 Highly effective collection

In general, the collection efficiency f for DS use is supposed to be near 100%. The typical DS, namely the cylindrical type, is good for achieving high f values. However, the cylindrical DS does not always give perfect collection. An important factor required to obtain both high sensitivity and good time resolution is the amount of concentration achieved in the absorbing solution. In other words, it is better that air is sampled at a high flow rate through a DS with a high surface-to-volume ratio of solution. Accordingly, the annular DS is the recently preferred method. De Serves and Ross showed the advantage of an annular DS equipped with a small-bore PP tube over a glass coil-type gas collector.⁵³ For more effective collection using an annular DS, a monofilament is inserted into a small-bore membrane tube.^{15,47,54,55} Lee's group developed thin-layered annular DS by winding a channel around a large-bore tube.²⁷ This DS attains a 4 pptv limit of detection (LOD) with a sampling time of 10 min. These improved annular DS devices are schematically shown in Fig. 2 (d). Lee's group also succeeded in minimizing the solution volume for the cylindrical DS.^{56,57} Instead of supplying a solution, the sample air is humidified with a Nafion device, and the water vapor is condensed at the cooled DS with the accompanying water-soluble gases. The condensed water is then sampled from the bottom of the DS and introduced into the detection system. Miniaturization of the DS is also superior for highly effective collection, which is discussed later.

3.3 New functional DS

Komazaki *et al.* developed a novel DS for a NO_x measurement.⁵⁸ It has an annular configuration and does not have a gas-permeable membrane. The inside wall of the outer tube is coated with a mixture of TiO_2 and hydroxyapatite. In the center of the DS, black light is settled, and UV light is irradiated on the TiO_2 catalyst. There, NO_x is oxidized and adsorbed as NO_2 or HNO_3 . After this oxidation/adsorption, water is fed into the annular gap, and eluted nitrite and nitrate are then measured by an ion chromatograph (IC). Thus, the total NO_x is measured.

3.4 Detection methods for collected species I: chromatography

Diffusion scrubbers are capable of only gas collection. The collected analytes need to be measured subsequently. An ion chromatograph (IC) is often used for this purpose. The absorbing solution is generally passed through a concentration column, eluted, and then introduced into an IC system composed of a separation column, a suppressor and a conductivity detector.^{16,17,59-61} This analysis is favorable for acidic and basic gases. Although the limit of detection (LOD) depends on the IC performance, it has been reported that LODs of 20 to 50 pptv were achieved when gas was sampled for 60 min at a gas flow rate of $1 \text{ dm}^3 \text{ min}^{-1}$ with a normal DS. With the advanced DS, LODs of several pptv can be achieved.²⁷ A high-performance liquid chromatograph (HPLC) is used for aldehyde measurement after collection into a 2,4-dinitrophenylhydrazine (DNPH) solution^{26,62} in which the chemistry is the same as that in the standard method.⁶³ A gas chromatograph can also be used in combination with a gas desorber.^{64,65} Interestingly, the desorber has almost the same construction as the absorber, and the alkaline absorbing solution is mixed with acid before the desorber.

Table 1 Gas permeation rates of various kinds of membrane tubes and flat membranes

Membrane	Material	i.d./mm	Thickness/ μm	Nominal pore size/ μm	Permeation rate/fmol s ⁻¹ cm ⁻² ppbv ⁻¹ *		
					SO ₂	H ₂ S	CH ₃ SH
Membrane tube							
Teflon AF2400 ^a	Amorphous Teflon	1.07	12.7	—		0.016	
St. Gobain Performance Plastic ^a	Silicone	0.41**	102**	—		0.2	
Nafion, Perma-Pure ^a	Cation-exchange membrane	0.41**	83**	—		9.3	0
ePTFE, Zeus ^{a,b}	Expanded PTFE	1.016	127	30-50	669	784	230
Poreflone, Sumitomo E. F. P. ^b	Porous PTFE	1.0	500	0.1	542	501	120
Flat membrane							
Floropore ^c	Porous PTFE		60	0.22	10		
			100	1.0	7.5		
			100	2.0	8.4		
Millipore ^c	Porous PTFE		125	10	5.6		
Advantec, Toyo Roshi ^d	Porous PTFE		75	0.8	19		
			75	3.0	32	38	
			89	0.1	105	74	
Gelman Metrical, Pall ^d	Porous PP		89	0.1	105	74	
SSP-M100, Specialty Silicone	Silicone		25	—		0.52	
Sylgard 184, Dow Corning ^e	PDMS		7-70	—		1.8-0.42	

* Permeation rates were obtained at the gas flow rate of *ca.* 1 dm³ min⁻¹. At this flow rate, the permeation rates of expanded PTFE and porous PTFE are proportional to the flow rate, and those of other materials are not affected by the gas flow rate. ** Estimated scale after expansion. a. From Ref. 46. b. Ref. 29. c. Ref. 50. d. Ref. 51. e. Ref. 49.

3-5 Detection methods for collected species II: miniature absorbance/fluorescence detector

Recently, miniature detectors for continuous gas measurements have been developed, based on chemical reactions for color or fluorescence formation. They are attractive for field measurements, and make continuous measurements possible. These miniature detectors are comprised of a solid-state light source, *e.g.* a LED or laser, and a solid-state detector, like a photodiode or a miniature photomultiplier. A color filter is attached in front of the light detector, if desired. Simple fluorescence and absorbance detectors were developed for sulfide⁴⁷ and formaldehyde⁶⁶ measurements. If a very high sensitivity is required, a long detector cell made of Teflon AF is used to form a liquid core waveguide (LCW). The fluorescence generated in the long region is collected at the end of the AF tube into an optical fiber. This detector has been used for fluorometry^{67,68} and chemiluminescence measurements⁶⁹ of H₂O₂ and hydroxymethyl hydroperoxide, and fluorometry of HCHO.^{70,71} LODs of 10–30 pptv have been obtained for continuous or near real-time measurements.

3-6 Applications for atmospheric trace gas analysis

In the United States, the Environmental Protection Agency (EPA) organizes an atmospheric analysis field campaign at a different super-site every year,^{72,73} and the DS instrument is one of the useful tools for field campaigns.⁷¹ In Japan, there are similar projects. Background levels of acidic atmospheric gases were measured at Oki and Rishiri islands, and daily fluctuations of sub-ppbv levels were obtained.^{61,74} The trajectories of the obtained data were analyzed, and it was found that the acidic gas concentrations were high when the westerly flow was passing through a lower boundary layer over the Yellow Sea and the South Korea Peninsula.

In addition to its use in atmospheric analysis, the DS device has been used for monitoring cleanroom air in semiconductor industries.^{75,76} It has recently been reported that very low levels of basic and acidic gases affect the accuracy of the photoresist

pattern, especially in chemically amplified resistor systems. The development of photoresist patterns is based on decomposition by proton catalysis, but the protons are neutralized if basic gases are present. Semiconductor patterns and wafer sizes are becoming finer and larger, respectively. Consequently, the measurement of sub-part-per-billion levels of NH₃ and amines has come to be required. Some patents for the purpose of cleanroom monitoring have been filed.⁷⁷⁻⁷⁹ The instrument in question is packaged in a box integrated with a touch-panel or a computer-operated system.^{80,81}

3-7 Field capability

Many chemical analysis systems have expensive and heavy liquid pumps, which mean that they are for laboratory use only. Flow control is important in continuous measurement, because the collection time is directly related to the flow rate, and the sensitivity is inversely proportional to the liquid flow rate. In order to control the liquid flow in a device that can be used in the field, a simple pressurizing method using a homemade circuit, pressure sensor and a miniature compressor has been developed.⁴⁷ This pressurization makes the instrument capable of not only working in the field, but also obtaining a smooth baseline and a better signal-to-noise ratio because a mechanical pumping noise is not generated. When precise flow control is not needed, *i.e.* when the stopped-flow mode is adopted, the solution can be made to flow by gravity by simply setting the solution reservoir a bit higher than the DS.^{52,61}

Compact detectors comprising a solid-state light source and a solid-state light detector are also of great utility in field analysis. Recently, instruments coupled with these pumping systems and detectors that are capable of use in the field and can be driven by a 12-V battery have been developed. SO₂ and H₂S gas levels were measured around a volcano crater of Mt. Aso, Nakadake. The instrument, with a data logger and a battery, was carried along a mountain trail that included a highly inclined and rocky area.³⁰ A mapping example of the gas levels obtained is shown in Fig. 4.

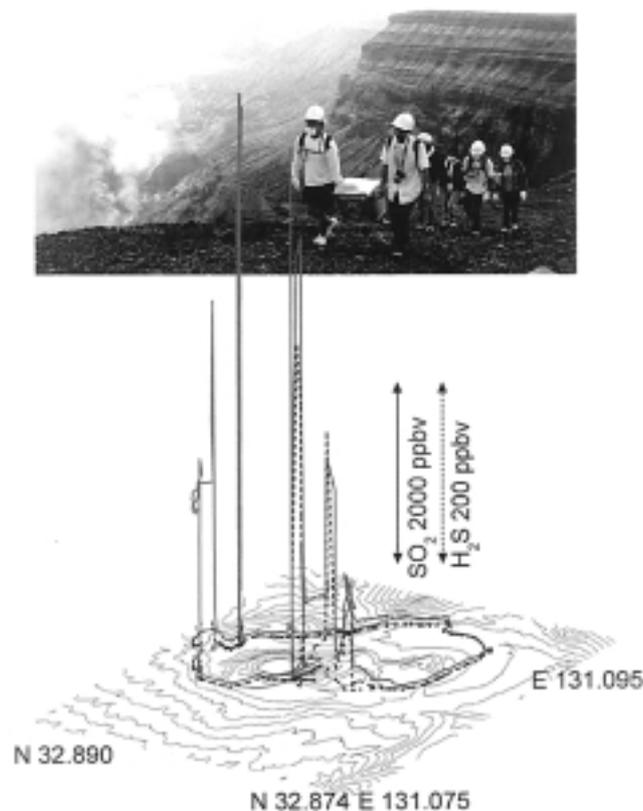


Fig. 4 Monitoring of H_2S and SO_2 carried out by walking around Mt. Aso on August 22, 2003. The gas levels from 2 ppb to 7 ppm were obtained and are drawn on a map. The dotted line indicates the route instrument was brought, and the solid and dashed lines show SO_2 and H_2S concentrations, respectively. The picture shows the measurement party walking by the crater with the instrument.

3.8 Microscrubber

The miniaturization of gas-analysis systems is desirable not only to attain field capability, but also for multipoint analysis, the popularization of pollution monitoring/control and the mapping of gas levels. Moreover, a small amount of reagent consumption is an advantage for an environmentally-friendly instrument. These merits have been discussed previously.⁸²⁻⁸⁴ Miniaturization of wet DS is a topic in which much interest is now being shown, whereas there are few reports on dry collectors/desorbers that use micro structures and silica powders.^{85,86}

Miniature scrubbers have the advantages of fast responses and high sensitivities. Initial attempts on miniaturization have been made for annular DSs.^{54,55} Solution volumes of small bore-porous membrane tubes have been minimized by inserting a fishing line. Although the collection efficiency of this DS is half that of a cylindrical DS, the analyte concentration in the absorbing solution is 8-times greater than that in the cylindrical DS.³⁰ The conventional planar DS is more appropriate for miniaturization. The planar DS was previously constructed with a relatively thick gasket,^{51,87,88} and a miniature scrubber has recently been studied. Ohira made a cross-flow microchannel scrubber in 1999,⁸⁹ which is shown in Fig. 5 (a). The air-flow-channel array and the liquid-flow-channel array were both fabricated on separate glass plates, crossed with each other, and a PTFE membrane was sandwiched between these channel plates. The array comprised 25 sets of channels, which were 50 μm deep and 150 μm wide. SO_2 was collected into the liquid

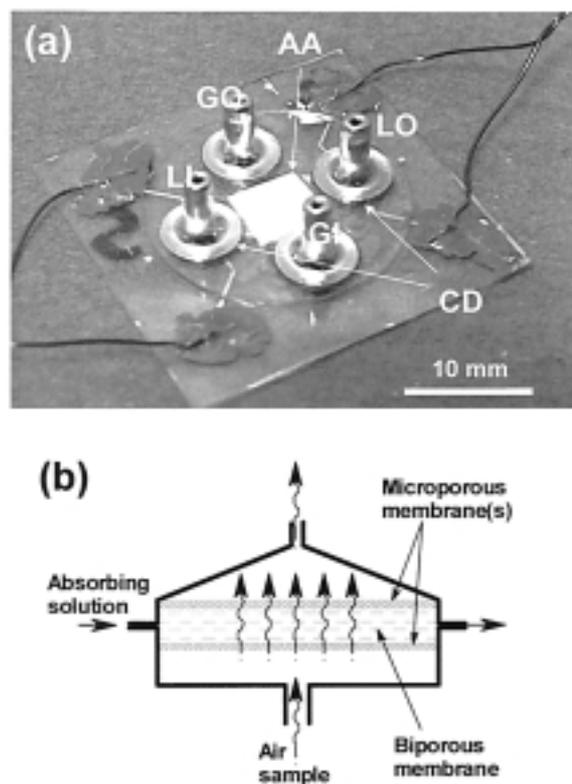


Fig. 5 Miniature gas collectors. (a) The first microscrubber. Conductivity electrodes and air flow channels (150 μm wide \times 25 units) are fabricated on a 30 mm \times 30 mm glass plate, and liquid flow channels and membrane holding pad are fabricated on 18-mm-diameter glass plate. A gas permeable membrane was sandwiched by these substrates. CD, conductivity detection electrode (under the eyelets); AA, gas absorbing area; LI, liquid inlet; LO, liquid outlet; GI, gas inlet; GO, gas outlet. (b) Schematic of chromatomembrane cell.

phase in the crossed area, and the conductivities before and after the collection area were measured. A fluorometric NO_2 determination system⁹⁰ with a porous glass plate scrubber⁹¹ and a Y-shaped microchannel reactor⁹² has been developed by Korenaga's group. In the Y-shaped channel reactor, the analyte reacts with the reagent under acidic conditions and the product diffuses into the alkaline region to emit fluorescence. The pH gradient formed in the channel is wisely used as the key to success in this device. Miniaturization of the scrubber is also important. The sensitivity is inversely proportional to the thickness of the liquid layer.⁵² In order to make a very thin solution layer, a microchannel scrubber was developed and coupled with a miniature fluorescence detector.^{50,93} The reagent consumption is only 2 $\mu\text{l min}^{-1}$, namely 1 ml for 8 h of operation, or 86 ml per a month. Even though the device is such minimized, ppbv level of H_2S can be measured continuously.

3.9 Chromatomembrane cell

During the last half decade, a new type of gas collector has been investigated.⁹⁴⁻¹⁰⁴ It was proposed by Moskvin and Simon, and is called a chromatomembrane cell (CMC). The CMC does have a membrane, and the gas is collected into a very small amount of the solution as same as the microchannel scrubber. However, two things are completely different from the DS. First, the absorbing solution is held within a main membrane itself. Second, the gas sample is forced to flow across through

the membrane. The main membrane used in the CMC has two types of pores, namely micropores (*e.g.* 0.1–0.5 μm) and macropores (*e.g.* 200–500 μm). The biporous membrane is sandwiched, or supported, by microporous membrane(s) to hold the aqueous solution in the macropores as shown in Fig. 5 (b). The gas goes through the micropores and soluble gases are trapped into the solution held in the macropores. The gas sampling rate is limited at only several ml min^{-1} . However, the collection efficiency is almost perfect and the system with the CMC gives high sensitivity. A stopped-flow sequence is required for the CMC system, especially in the case where only one side of the biporous membrane is supported with the microporous membrane, and there is only one common outlet for the gas and liquid.

3-10 *In-situ* measurement in the scrubber

In the continuous measurement system, the liquid flow rate affects the signal and must be accurately controlled. In contrast, the stopped-flow method does not need such an accurate liquid flow control. If the chemical signal is monitored *in-situ* through the DS, gas analysis can be conducted in the stopped-flow mode. Furthermore, real-time monitoring by monitoring the rate of change in the signal is possible. The magnitude of the signal increases linearly with the collection time, and the slope is proportional to the gas concentration. The SO_2 level is measured by monitoring the change in the conductivity of the H_2O_2 -added sulfuric acid solution in a 80-nl DS.⁵² NO_2 and O_3 are also measured by monitoring the *in situ* change in the absorbance, where a porous membrane tube filled with water acts as a long absorbance cell.^{105,106} The refractive index of the porous membrane (RI) is small and almost identical to that of water. Consequently, light travels relatively well through the membrane tube. Water captured at pores also assists light conductance. As mentioned above, the porous membrane tube acts both as an effective collector and a good absorbance cell. The AF tube can, of course, be used for the same purpose, utilizing its superior light conductance.^{107,108} However, better overall performance is generally obtained with the porous tube cell, because the gas permeability of the porous tube is much higher than that of the AF tube. A cartridge-type device based on a similar principle will be available on the market as a simple detector.¹⁰⁹

4 Conclusions

As described above, the diffusion scrubber (DS) is an excellent tool for atmospheric trace gas measurements. Many new DSs have been developed in the last decade, and the sensitivity, long-term stability, field capability and reagent consumption have been dramatically improved. There are many fields of DS application using combinations with suitable detection systems for each purpose. It is believed that the DS-based instruments will become increasingly popular for use in atmospheric analysis.

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