A Parallel Plate Wet Denuder for Acidic Gas Measurement

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A parallel plate wet denuder (PPWD) was designed and tested for acidic gas absorption in this study. The PPWD is composed of two frosted glass plates coated with nano-TiO2 particles. The gap of the plates is 4 mm, the active surface is 7.5 cm in width and 15 cm in height. The DI water is flowing downward along the surfaces to form a uniform water film to absorb the gas flowing upward along the gap. The gas absorption efficiency and memory effect were tested using test gases of HF (3.57–3.80 ppb), HCl (0.48–15.63 ppb), and HNO3 (8.43–20.92 ppb) generated from permeation tubes at the flow rate of 5–10 L/min, scrubbing DI water flow rate of 1.0 mL/min/plate, and pH = 6.8 ± 0.3. The experiment was also conducted for HF and HCl with scrubbing water pH value of 3.08 and 4.10 to examine the effect of pH on the absorption efficiency. The experimental data at different flow rates match with the theoretical values very well assuming perfect absorption condition at the water film when the scrubbing water pH = 6.8 ± 0.3. The absorption efficiency of the three gases at the sampling flow rate of 5 L/min was nearly 100% when the scrubbing water pH value was 6.8 ± 0.3, but was found to decrease slightly when the pH value of scrubbing water was reduced from 6.8 to 3.08, which indicates slight modification of perfect absorption condition at the water film. The memory effect test showed that the rise time was 15 to 25 min and the fall time was 10 to 25 min for the three gases. Good uniformity of the water film was observed during the 9-day ambient air sampling for HF, HCl, and HNO3, which indicates the applicability of the present PPWD for ambient air sampling. © 2008 American Institute of Chemical Engineers AIChE J, 54: 2198–2205, 2008

Keywords: wet denuder, air sampling, air pollution control, acidic aerosols

Introduction

The diffusion denuders are widely used to separate trace atmospheric gases and particle pollutants for accurate sampling of both species. Several kinds of dry diffusion denuder were developed in the past 20 years.1 For example, Sioutas et al.2 developed a glass honeycomb denuder and Tsai et al.3,4 developed a porous metal denuder for ambient air measurement. The major limitation of the dry denuder is that the coating and extraction procedures are time consuming, and it can not be used as a continuous sampler for long time ambient air monitoring.5

The wet diffusion denuder was developed to enable real-time and automatic sampling of both particulate pollutants and gaseous species. Simon et al.6 described four wet tubular denuders including: (a) internal threaded glass-filled PTFE denuder, (b) porous-wall denuder, (c) wettable membrane-line denuder, and (d) silica-coated denuder. They found that the wettability of the active surface of denuder (a)–(c) was not good when pure water was used as scrubbing liquid. The uniform flowing liquid for gas absorption can be achieved by using nonionic fluorocarbon surfactant. However, the surfactant will result in the base line drift and the increase in the
Table 1. Operation Parameters and Gas Absorption Efficiency in Previous Researches

<table>
<thead>
<tr>
<th>Type of PPWD</th>
<th>Test Gas</th>
<th>Gas Flow Rate (L/min)</th>
<th>Scrubbing Water</th>
<th>Liquid Flow Rate (µL/min/plate)</th>
<th>Absorption Efficiency</th>
<th>Memory Effect</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica-coated</td>
<td>SO₂</td>
<td>15–2.0</td>
<td>0.5 H₂O₂</td>
<td>265</td>
<td>80–100%</td>
<td>No discussion</td>
<td>7</td>
</tr>
<tr>
<td>Silica-coated</td>
<td>HONO, HNO₃</td>
<td>15–1.0</td>
<td>0.5 mM H₂O₂</td>
<td>265</td>
<td>90–100%</td>
<td>No discussion</td>
<td>8</td>
</tr>
<tr>
<td>Silica-coated</td>
<td>SO₂</td>
<td>1.6–0.2</td>
<td>0.5 mM H₂O₂</td>
<td>15</td>
<td>85–100%</td>
<td>No discussion</td>
<td>9</td>
</tr>
<tr>
<td>Polyester sheet</td>
<td>SO₂, HNO₃</td>
<td>5.0</td>
<td>1.0 mM H₂O₂</td>
<td>0.25</td>
<td>100%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Membrane-based</td>
<td>SO₂</td>
<td>2–1</td>
<td>5 mM H₂O₂ + 5 Mn NaOH</td>
<td>500</td>
<td>94–100%</td>
<td></td>
<td>10</td>
</tr>
</tbody>
</table>

The present parallel plate wet denuder

The PPWD was designed based on the gas penetration theory of Gormley and Kennedy for a rectangular channel flow. The gas penetration efficiency \( P \) can be calculated by the following equations:

\[
P = \frac{c_{\text{out}}}{c_{\text{in}}} = 1 - 2.96\mu^{2/3} + 0.4\mu, \quad \text{for } \mu < 0.005
\]

\[
P = \frac{c_{\text{out}}}{c_{\text{in}}} = 0.91\exp(-7.54\mu) + 0.053\exp(-85.7\mu), \quad \text{for } \mu \geq 0.005
\]

where \( c_{\text{out}} \) is pollutant outlet concentration, \( c_{\text{in}} \) is pollutant inlet concentration, the dimensionless parameter \( \mu = \frac{D_g h}{W^2} \), \( D_g \) is the diffusion coefficient of the gas, \( L \) is the length of the parallel channel, \( W \) is the width of the channel, \( Q \) is the air flow rate, and \( h \) is the gap between the two parallel plates. The diffusion coefficient of HF, HCl, and HNO₃ are 0.2072, 0.1665, and 0.118 cm²/s, respectively, calculated by Chapman-Enskog kinetic theory.

The structure of the PPWD is shown in Figure 1, which is constructed by two plexiglass plates (M). A frosted glass plate coated with nano-TiO₂ particles (P25, Degussa, Germany) (FP) of 150 mm in length and 75 mm in width is glued onto the inner surface of each plate. The gap between the two glass plates is 4 mm. Two small liquid reservoirs at the top and bottom of the plates (M) are used as overflowing and collecting reservoirs for scrubbing water, respectively. The glass plates were sand blasted with the average depth of 81.17 µm to enhance the uniformity of downward overflowing scrubbing water. To enhance the hydrophilicity further, the sand-blasted frosted glass plates were coated with TiO₂ nanoparticles. First the frosted plates were sonicated with...
ultra-pure water for 20 min and then purged with high pressure air for 1 min. The 0.5 g nanoparticles were mixed with 50 mL ultra-pure water and then stirred with a magnetic stone for 10 min. The solution was subsequently poured onto glass surfaces laid horizontally at room temperature. After half an hour and with excess solution removed from the surfaces, the glass plates were heated to 300°C at a rate of 9°C/min and kept for 90 min. The calcination procedure removed the organic pollutants and facilitated bonding of TiO2 nanoparticles onto the glass surfaces.

The laboratory mass-transfer equipment which involves a flowing gas absorbed by liquid is used to measure the diffusivity, the solubility, and the reaction rate constants of gases in solution, and can be used to obtain information to design the gas absorption equipments. The physical-chemical parameters of the laboratory equipments such as laminar jet, cylindrical, conic, spherical wetted wall, rotating drum,14 and the present PPWD are shown in Table 2. As compared with the other laboratory equipments, the liquid phase mass transfer coefficient $k_l$ calculated based on James et al. for the present PPWD is found to be larger, and the contact time of the present PPWD is long enough to ensure a high gas absorption efficiency.

The texture of the active surfaces may influence the uniformity of the water film and gas absorption efficiency. The water contact angle on different plates was measured by using the Contact Angle System (FTA125, First Ten Angstroms, VA). As will be discussed later, the frosted glass plates coated with nano-TiO2 particles are found to have very small contact angle and uniform water film. Therefore, they are used in the present PPWD design.

Gas absorption efficiency test

The gas absorption efficiency experiment was carried out by using two PPWD (PPWD1 and PPWD2) in series to sample the acidic gases at different sampling air flow rates. The experimental results of the absorption efficiency were calculated as the ratio of the concentration determined by PPWD1 to the total concentrations determined by both PPWD1 and PPWD2. The experimental set up is shown in Figure 2. All gas tubing and valves were made of Teflon to prevent the interaction between the gases and the tube and the fittings. Pure nitrogen gas was used as the carrier gas, and dilution air was used to prevent the contamination from the gas species we tested. Nitrogen gas was introduced into two different routes by a three-way valve (V1). The carrier gas flow ($Q_c$) through the oven and the permeation tube was controlled by a mass flow controller (MKS). The standard gas was generated by the permeation tube (VICI Metronics) with a known concentration at a certain temperature. The dilution air flow ($Q_d$) was controlled by the other mass flow controller and mixed with the carrier gas flow to obtain a desired test gas concentration. A porous metal denuder3,4 was used to test the concentration of the standard gas, which was sampled by both PPWD1 and PPWD2 to measure the absorption efficiency. The sampling air flow rate was 5–10 L/min.

The scrubbing solution is the ultra-pure water with the pH of 6.80 ± 0.3 and the resistivity of greater than 18.2 MΩ cm. A high pressure bottle was used to store the scrubbing water to prevent ultra pure water from contamination, into which the nitrogen gas was introduced to push the scrubbing water into the overflowing reservoir of the PPWD. The liquid flow rate was controlled by a needle valve with the flow rate of 1 mL/min per plate. After sampling for 15-min, the liquid sample in the collecting reservoirs was aspirated by a peri-

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**Table 2. Physicochemical Parameters for the Laboratory Mass-Transfer Equipments**

<table>
<thead>
<tr>
<th>Type</th>
<th>Laminar Jet</th>
<th>Cylindrical Wetted Wall</th>
<th>Conic Wetted Wall</th>
<th>Spherical Wetted Wall</th>
<th>String of Discs</th>
<th>Rotating Drum</th>
<th>Stirred Vessel</th>
<th>Stirred Vessel</th>
<th>Present PPWD</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_l$ (cm/s)</td>
<td>0.016</td>
<td>3.6 x 10^{-3}</td>
<td>5 x 10^{-5}</td>
<td>5 x 10^{-5}</td>
<td>3.6 x 10^{-3}</td>
<td>0.016</td>
<td>1.6 x 10^{-3}</td>
<td>2 x 10^{-3}</td>
<td>HF: 2.80 x 10^{-2}</td>
</tr>
<tr>
<td>Contact time (s)</td>
<td>10^{-4}</td>
<td>10^{-1} x 2</td>
<td>0.2</td>
<td>0.1</td>
<td>10^{-3} x 2</td>
<td>2.10^{-4} x 10</td>
<td>0.6</td>
<td>0.8</td>
<td>17.99</td>
</tr>
<tr>
<td>Interfacial area (cm²)</td>
<td>3</td>
<td>1000</td>
<td>80</td>
<td>400</td>
<td>10,800</td>
<td>Diameter: 10 cm, Length: 12 cm</td>
<td>80</td>
<td>Diameter: 10 cm, Length: 15 cm</td>
<td>225</td>
</tr>
</tbody>
</table>
staltic pump and then analyzed by IC (Model 120, Dionex Corp.) with a concentrator column (IonPac TAC-2) and an anion column (IonPac AS12A). The standard solution of 999.62 mg/L (Merk Taiwan) was used to calibrate the concentration of F, Cl, and NO₃. The R-squared of F, Cl, and NO₃ were all higher than 0.995 which is required for IC analysis. The method detection limit (MDL) based on 15-min sampling at 5 L/min were 0.04 ppbv for HF, 0.07 ppbv for HCl, and 0.02 ppbv for HNO₃, respectively.

The test for gas absorption efficiency with different pH values of the scrubbing water was conducted for HCl and HNO₃ in this study. H₂SO₄ solution (12 N) was used to lower the pH value from 6.80 to 3.08, and 4.10 for the scrubbing water. The sampling flow rate was 5 L/min. Ambient air measurement on NCTU campus (National Chiao Tung University, Hsinchu, Taiwan) was conducted continuously for 9 days for HF, HCl, and HNO₃ gases from November 7 to 16, 2007. Two to three 15-min samples were taken and analyzed every day. The wettability of the present frosted glass surfaces was also observed.

**Memory effect test**

The memory effect test was carried out in this study to determine the rise time and fall time of the PPWD for HF, HCl, and HNO₃ with pure nitrogen gas (RH = 0%) at 5 L/min. The rise time means the time needed for the concentration to respond to 90% of the test gas concentration from the moment when the standard gas starts to be introduced into the PPWD. The fall time means the time needed for the concentration to drop from 100 to 10% of the test gas concentration after the standard gas stops introducing into the PPWD. The experimental set up is the same as Figure 2. The PPWD was first rinsed by ultra-pure water until the background value is zero. After that the standard gas was introduced into the PPWD to measure the rise time. After reaching 100% of the test gas concentration, the standard gas flow was stopped and the fall time was measured.

**Results and Discussion**

**Uniformity, thickness, and evaporation of the water film**

Glass surface texture and liquid flow rate were both found to be important to the uniformity of the liquid film. The water contact angle of the smooth plate was measured to be 46.5° ± 2.05°, the hydrophilicity was observed to be poor, and the water film was nonuniform on the smooth glass surfaces. This is because that the gravitational force of the water film overwhelmed the hydrophilic force between the glass surfaces and the water film. Dry channels were generated which affected the gas absorption efficiency to be shown later. The contact angle for the frosted glass plate, 82.3° ± 1.8°, was found to be larger than that of the smooth plate, and the water film was shown not to be uniform either. By coating the frosted glass plate with nano-TiO₂ particles, the water contact angle was measured to be as small as 4° ± 3.58° without UV light irradiation, and the water film was found to be very uniform for at least 9 days, in the 9-day continuous air sampling experiment in this study. This finding is similar to Yu et al. who found that the contact angle for water of porous TiO₂ film could be as small as 3° without UV light irradiation. Similarly, low water contact angle (9.5°) on the TiO₂-coated substrates without UV light irradiation was also found in the previous research. Therefore, the gas absorption efficiency and the memory effect were both tested by using the frosted glass plates coated with nano-TiO₂ particles.

In this study, we found the liquid flow rate per plate, Qₐ, should be higher than 1 mL/min to obtain a uniform water film and thus this flow rate was used to conduct the gas absorption experiment. At this flow rate, the retention time

![Figure 2. Experimental set up for gas absorption efficiency and memory effect tests.](image)

*Nitrogen gas (NG), MKS four channels readout (MKS RD), mass flow controller (MC), permeation tube and oven (P and O), heated tube (HT), three-way valve (V₁, V₂, V₃), parallel plate wet denuder (PPWD), porous metal denuder (PMD), peristaltic pump (PP), scrubbing water container (SC), needle valve (NV), rotometer (R), air pump (AP).*

![Figure 3. Scrubbing water evaporation at the sampling flow rate of 2 to 10 L/min.](image)
of the water film, $t$, was measured by direct observation to be $27 \pm 2$ s. The average downward velocity of the flowing water film was $0.56$ cm/s, obtained by dividing the length of active surface, 15 cm, by the retention time of the water film. The thickness of the water film, $w$, was calculated to be $40.0 \pm 3.56$ mm by using the following equation:

$$w = \frac{Q_L \times t(s) \times (\frac{1}{cm})}{7.5(cm) \times 15(cm)} \tag{3}$$

Theoretically, the thickness of the water film with a known average downward velocity, $u_{av}$, can be calculated by the following equation:

$$w = \sqrt{\frac{u_{av} \times 3\mu_L}{\rho_L g}} \tag{4}$$

where $\rho_L$ is the density of water, $g$ is the gravitational acceleration, and $\mu_L$ is the viscosity of water. The theoretical thickness is calculated to be $41.1$ mm, which is very close to $40.0 \pm 3.56$ mm obtained from the experimental observation.

Pure nitrogen gas (RH = 0%) was further used to test the evaporation loss of the scrubbing water film. As shown in Figure 3, the evaporation loss of the scrubbing water is seen to increase with the nitrogen flow rate and is 0.03, 0.35, 0.6, 0.67, and 0.73 cm$^3$ for the nitrogen flow rate of 2, 4, 6, 8, and 10 L/min, respectively. At 10 L/min, the evaporation loss is only 2.4% of the total liquid sample (30 cm$^3$) after 15-min sampling. At 5 L/min, the evaporation loss is less than 1% of the liquid samples. That is, overestimation of gas concentration due to water evaporation was negligible at ambient sampling condition at ambient air sampling condition.

**Gas absorption efficiency**

When the smooth glass surface was used, dry channels were formed. The gas absorption efficiency for HF at the sampling flow rate of 5 L/min is only about 25%.

With the frosted glass surfaces as the active surfaces, the gas absorption experiment was carried out for HF of 3.57–3.80 ppb, HCl of 0.48–15.63 ppb, and HNO$_3$ of 8.43–20.92 ppb.
respectively. The pH value of scrubbing water was 6.8 ± 0.3 and the gas retention time was 0.54–0.27 s at the sampling flow rate of 5–10 L/min. Results of gas absorption efficiency are shown in Figures 4a–c. As can be seen in Figure 4a for HF, the gas absorption efficiency is high, which is 99.05% ± 0.34%, 96.76% ± 1.57%, and 94.53% ± 1.11% at the sampling flow rate of 5, 7, and 10 L/min, respectively. Similarly for HCl and HNO₃, the gas absorption efficiency was also very high and it decreased slightly from 99.75% ± 0.67% (5 L/min) to 93.80% ± 2.25% (10 L/min) and from 99.80% ± 0.44% (5 L/min) to 96.23% ± 0.74% (10 L/min) for HCl and HNO₃ respectively (Figures 4b, c). Theoretical gas absorption efficiency can be calculated by Eqs. 1 and 2 and shown in Figures 4a–c as solid lines. Good agreement with the experimental data indicates that the assumption of the perfect absorption conditions at the water film was valid.

The gas absorption efficiency for HCl decreased slightly from 99.75% ± 0.67% to 98.9% ± 0.09% and 93.41% ± 1.61% when the scrubbing water pH was changed from 6.80 to 4.10 and 3.08, respectively, as shown in Figure 5. Similarly decrease of gas absorption efficiency with decreasing pH is found for HF. The effect of the pH value was not significant and was caused by slight modification of perfect absorption conditions at the water film.

Figure 5. Effect of pH values of scrubbing water on gas absorption efficiency.

Figure 6. Test results of memory effect for (a) HF, (b) HCl, and (c) HNO₃.
absorption condition at the water film as the pH value was decreased, which needs to be investigated further.

Memory effect test

As can be seen in Figures 6a–c, the rise time and fall time for HF, HCl, and HNO₃ are 20 and 25 min, 15 and 10 min, and 25 and 10 min, respectively. The fall time for HF was much longer than HCl and HNO₃ due to interaction between HF and glass surfaces. Low et al.²² indicated that HF will react with glass surface. The fluoride ions will attack the Si—OH bond or B—OH bond on glass surface and replace OH groups to generate H₂O molecules. The reversible reaction will regenerate the HF molecules. Long fall time was due to residual F⁻ on the glass surface which was washed out by the next incoming fresh scrubbing water.

Although the clean and dry standard gases were used, the rise time for HNO₃ was longer than both HF and HCl due to the direct interaction of HNO₃ with part of the dry exposed plexiglass surfaces near the entrance and exit of the sampler.²² In Figure 6c, experimental results of memory effect for HNO₃ are also compared with the results of Rosman et al.⁵ It is obvious that the memory effect of the present PPWD is less significant than the previous denuder under dry air sampling condition.

Continuous ambient air measurement

The daily observation of the active surfaces of the present PPWD during the 9-day ambient air sampling in the NCTU campus shows a good wettability condition. The sampled concentrations for HF, HCl, and HNO₃ are shown in Figure 7. Results show that the highest concentration of the acidic gas in the NCTU campus is HCl. The concentrations were lower than the method’s detection limit to 0.25 ppbv, 0.21–1.48 ppbv, and 0.08–0.47 ppbv for HF, HCl, and HNO₃, respectively. After the 9-day sampling, pure nitrogen gas was introduced into the PPWD for 30-min to test if the sampler can return back to background condition. The concentrations were found to be lower than the method’s detection limit to 0.06 ppbv for the three gases, respectively, which were all lower than the MDLs of these gases. This test indicates the applicability of the present PPWD for the long-term ambient air sampling.

Conclusions

A novel PPWD was designed and developed in this research. Hydrophilicity for scrubbing water can be achieved by using the frosted glass plates as active surfaces. The gas absorption efficiency for HF, HCl, and HNO₃ were 99.05% ± 0.34% to 94.53% ± 1.11%, 99.75% ± 0.67% to 93.80% ± 2.25%, and 99.80% ± 0.44% to 96.23% ± 0.74% when the sampling flow rate was 5–10 L/min, respectively. Good agreement with the experimental data indicates that the assumption of the perfect absorption conditions at the water film was valid. Besides, gas absorption efficiency for HCl decreased slightly from 99.75% ± 0.67% to 98.9% ± 0.09% and 93.41% ± 1.61% when the scrubbing water pH was changed from 6.80 to 4.10 and 3.08, respectively.

The result of the continuous ambient air measurement showed that the present PPWD is applicable for the long-term ambient air sampling. Furthermore, the rise time and fall time for HF, HCl, and HNO₃ were all shorter than 30 min, which implied the system can be used in monitoring the ambient acidic gases with high concentration variation.

Acknowledgments

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Literature Cited


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