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# A real-time monitoring system for soluble gas pollutants and it's application for determining the control efficiency of packed towers

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ABSTRACT

This study used a parallel-plate wet denuder coupled with an ion chromatograph (PPWD-IC) to monitor soluble gas pollutants in the exhaust stack and investigate the removal efficiency of packed towers. Gas pollutant concentrations measured by the PPWD-IC system were first validated with those obtained by a manual porous metal denuder sampler (PDS) as the reference sampler. The measured concentrations of the PPWD-IC system are in good agreement with those of the PDS with the coefficient of determination ($R^2$) greater than 0.93. The PPWD-IC system was then used to determine the removal efficiency of packed towers in high-tech factories. Results show that the PPWD-IC system is able to monitor multiple high-concentration gas pollutants semi-continuously, such as HF, HCl, $HNO_2$, $HNO_3$, $CH_3COOH$, and $NH_3$, in the exhaust stack with a temporal resolution of 20 min. The PPWD-IC system was employed to test the gas removal efficiency of a new honeycomb wet scrubber in an optoelectronic factory. The removal efficiency of the wet scrubber equipped with the honeycomb module at the liquid-to-gas ratio of 18.5 L/m$^3$ is shown to be close to 100% for HF (112.4–448.4 ppbv) and $CH_3COOH$ (696.3–6537.0 ppbv) and 99% for HCl (3394.9–10794.5 ppbv), respectively.



## 1. Introduction

In semiconductor and optoelectronic industries, acid HF, HCl, $HNO_3$, $H_2SO_4$ and basic $NH_3$ gases are emitted during wafer cleaning and wet-etching processes where large amount of these chemicals are used [1–6]. Packed towers with radom packing materials are widely used to control the emission of these soluble gas pollutants in the industries [7]. To control emissions, the Taiwan EPA promulgated strict emission standards which require greater than 95% control efficiency for either HF, HCl or $HNO_3$ for packed towers in the semiconductor factory; 85% or 75% control efficiency for HF and HCl when the inlet concentration is greater than 3 ppmv or less than 3 ppmv, respectively, for packed towers in the optoelectronic factory [8,9]. However, these traditional packed towers were shown to have poor removal efficiency for acid (HF and HCl) and basic ($NH_3$) gases when the inlet concentration is less than 1 ppmv and 3 ppmv, respectively [6], which can't meet the emission standards. In addition, the high-tech industries do not need to report the continuous emission data to the authorities because of lack of suitable monitoring instruments for the exhaust gases with high and time-varying concentration. Furthermore, the emission was found to influence the air quality in clean room through the intake of make-up air, which may lead to airborne molecular contamination and loss of product yield [10]. Therefore, real-time monitoring of exhaust gases from the same factory itself is essential to ensure a good clean room air quality and high product yield. An automatic monitoring instrument with sufficient time resolution and high sensitivity for exhaust gas monitoring is thus in critical demand.

A denuder sampler is a manual device consisting of coated denuders and a filter pack to sample gas and particulate pollutants simultaneously [11]. Various dry diffusion denuders have been developed in the past, including annular, coiled, honeycomb, and porous metal types [11–14]. A porous metal denuder sampler (PDS) made of porous metal discs (2.54 cm in diameter, 100 μm in pore size and 0.317 cm in thickness, P/N 1000, Mott Inc., Farmington, Connecticut, USA) was developed for sampling in ambient and workplace environments [14,15]. The measured acid and basic gas concentrations of the PDS were compared with those obtained by the other samplers, including silica gel tube, impinger, and honeycomb denuder system, and results showed excellent agreement [16]. The PDS was also used to determine the emission characteristics and removal efficiency of packed towers in semiconductor and optoelectronic industries [4,6]. The sampling method using the

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PDS was adopted as a standard reference method by the Taiwan EPA for sampling inorganic acid gases in the exhaust duct [17]. However, this manual sampler can't be used for long-term ambient air and stack emission monitoring because of laborious, time-consuming, and contamination-prone coating, drying, and extraction procedures.

Wet denuders coupled with an ion chromatograph (IC) have been developed to enable semi-continuous monitoring of gas species in ambient environments [18–26]. Recently, a parallel-plate wet denuder (PPWD) was designed and tested at low concentration of HF (3.57–3.80 ppbv), HCl (0.48–15.63 ppbv), and $HNO_3$ (8.43–20.92 ppbv) [27]. The PPWD is composed of two sand-blasted glass plates coated with nano-$TiO_2$ particles to enhance the hydrophilicity to form uniform liquid film. The gas absorption efficiency of the PPWD for HF, HCl, and $HNO_3$ was found to be nearly 100% at the sampling flow rate of 5 L/min. In addition, the PPWD coupled with an ion chromatograph (model 861, Metrohm AG, Herisau, Switzerland) (PPWD-IC) was studied for online monitoring of $CH_3COOH$ at 0.9–698 ppbv [28]. So far, the study of the PPWD is limited to the laboratory test at low concentration (less than 21 ppbv) except acetic acid gas, and the applicability of the PPWD-IC system to measure gas pollutants emitted from the packed towers has not been investigated yet.

In our recent study, to improve the removal efficiency of wet scrubbers, a new wet scrubber with a very low pressure drop was developed to control low-concentration soluble acid gases using a multi-parallel-plate module (MPPM) to replace typical tower packings based on the design concept of the PPWD [29]. The parallel plates of the MPPM were made of polypropylene coated with nano-$TiO_2$ particles to enhance hydrophilicity for scrubbing liquid to form uniform liquid film. The removal efficiency of the MPPM scrubber for HCl, $HNO_3$, and $CH_3COOH$ of 20–2000 ppbv was 99.0–99.9%, 98.3–100%, and 98.7–99.6%, respectively, at the retention time of 0.5 s. The MPPM was shown to be able to effectively enhance the absorption of low-concentration acid gases as compared to the typical tower packing materials. However, surface preparation work, including sand-blasting and coating, for the plates of the MPPM is a time-consuming and meticulous procedure. To control the gas retention time, the gap between the plates has to be also adjusted to a desired value in mm, leading to increasing difficulty in assembling the MPPM. Therefore, it is necessary to change the relatively complicated design of the MPPM for practical applications.

In this study, a honeycomb module made of water-absorbing polypropylene fabric (Techlon Fibre Co., Ltd., Changhua County, Tawian) of 1 mm in thickness was used in the new honeycomb wet scrubber to replace the MPPM to eliminate the need for sand-blasting and coating while maintaining the high removal efficiency. Fig. 1 shows the schematic diagram of the present honeycomb module which is a modification of the MPPM. A polypropylene (PP) fabric of 0.875 kg/m in weight separated by 0.1-mm-thick corrugated PP forming a 3-mm gap is scrolled in a cylindrical steel casing (300 mm in diameter and 300 mm in height). The fabric is 500 denier/60 filament in warp and 1000 denier/120 filament in weft. The warp and weft densities of the fabric are 140 and 33 threads/in., respectively. The specific surface area of the honeycomb module is as large as 483.2 $m^2/m^3$, which is much higher than 90 $m^2/m^3$ specified by the Taiwan EPA as the design criteria of packing materials for packed towers unable to meet the efficiency-based emission standards for acid gases.

The objectives of this study is to first assess the applicability of the PPWD-IC system to measure high-concentration soluble gas pollutants and then use this system to investigate the removal efficiency of packed towers. Measured concentrations of HF, HCl, and $CH_3COOH$ were first compared with those obtained by the PDS reference sampler to validate the accuracy of the PPWD-IC system. The PPWD-IC system was then applied to determine the removal efficiency of traditional packed towers and a new honeycomb wet scrubber for soluble gases in high-tech industry in Taiwan.

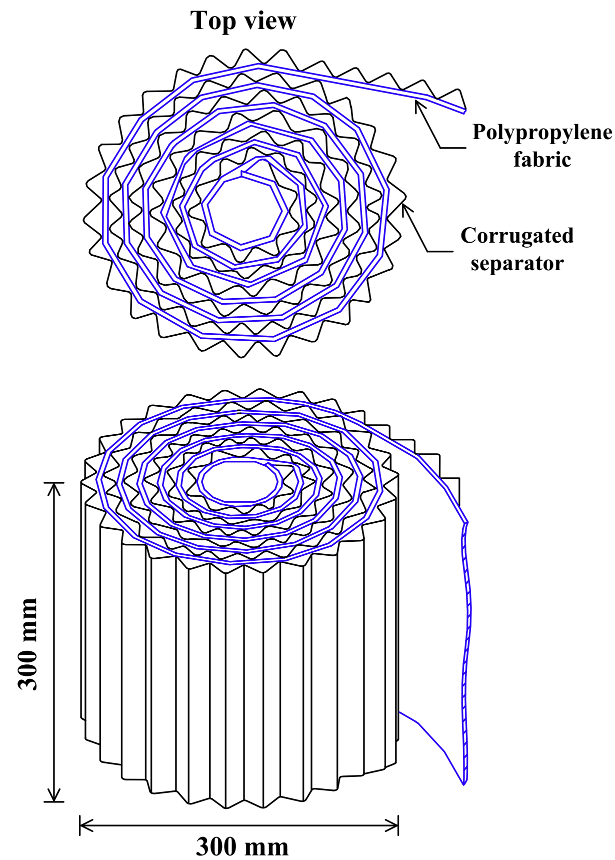


**Fig. 1.** Schematic diagram of the present honeycomb module (partially unfolded to show the details).

## 2. Experimental method

### *2.1. Design of parallel-plate wet denuder*

The detailed description and preparation procedure of the PPWD can be found elsewhere [27,28] and is described briefly in the following. As shown in Fig. 2, the PPWD consists of two plexiglass plates as the main body (M) of 310 mm in height on which a sand-blasted glass plate (GS) of 170 mm in height, 75 mm in width and 3 mm in thickness coated with nano-$TiO_2$ particles (AEROXITE $TiO_2$ P25, Evonik Degussa GmbH, Hanau, Germany) to enhance the hydrophilicity. The gap between the plates is maintained at 4 mm. At the top of sand-blasted glass plate, a small reservoir (OR) and a porous metal plate (PM) are used to disperse scrubbing liquid and form downward uniform liquid film, respectively. Gas pollutant is introduced from the upstream of the PPWD through the gas passage (GP) at 5 L/min and ultra-pure deionized water is used to absorb soluble gas on the wetted surfaces. The denuder effluent was collected in the reservoir at the bottom of the PPWD and continuously pumped either into the IC for sample analysis or a drain. The theoretical gas collection efficiency of the PPWD can be predicted by calculating the analytical solutions for the gas penetration theory of Gormley and Kennedy for a rectangular channel flow [30–32] with the diffusion coefficients of $2.07 \times 10^{-5}$, $1.67 \times 10^{-5}$, and $1.33 \times 10^{-5}$ $m^2/s$ for HF, HCl and $CH_3COOH$,