

Technical note

# Emission characteristics and control efficiency of acidic and basic gases and aerosols from packed towers

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## Abstract

Large amount of acidic liquids, such as H<sub>2</sub>SO<sub>4</sub>, HF, HCl and HNO<sub>3</sub>, and basic NH<sub>3</sub> liquid are used in high-tech industries in cleaning and etching processes in the Hsinchu Science-Based Industrial Park in Taiwan. The industries use packed towers (or scrubbers) to control emission of these inorganic pollutants, in which acidic gases but not particles are regulated by the Taiwan EPA's strict emission standard for semiconductor industry. To understand whether the emission standard is met and to investigate the emission rates, emission profiles, emission factors, and control efficiencies of various gaseous/aerosol species, measurement of pollutants before and after the packed towers was conducted using a sensitive porous metal sampler during January 2001 to February 2003. Results show that the pollutants are mainly in the gaseous phase, and the control efficiency of pollutants is low and variable when the inlet concentration is low. In addition to the control efficiency data, emission factors before the control device for various gas and particle species have also been developed for estimating the emission rates.

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## 1. Introduction

The Hsinchu Science-based Industrial Park is located in the Hsinchu area in the northwestern Taiwan. Two major industries: semiconductors and optoelectronics use acidic chemicals extensively (i.e. H<sub>2</sub>SO<sub>4</sub>, HF, HCl, HNO<sub>3</sub> and HPO<sub>3</sub>) during cleaning and etching processes, as listed in Table 1. In the table, HF and HCl are considered as hazardous air pollutants (HAPs), among total of 188 HAPs listed by the US EPA (2003a). As shown in the table, H<sub>2</sub>SO<sub>4</sub> is the most consumed acid in both industries, followed by HF and HCl in semiconductor industry, and HCl and HNO<sub>3</sub> in optoelectronic

industry. Also listed in the table are the yearly emissions for various species before and after control device obtained in this study. Because it is in the particulate form, H<sub>2</sub>SO<sub>4</sub> is shown not to be the predominant species in the emission. HF and HCl are the predominant species in the emission in both industries.

The industries use traditional packed towers to control the emissions. However, the emission rates, control efficiencies, emission profiles, and emission factors of various gaseous and aerosol species are largely unknown. To protect the environment and human health, Taiwan EPA (Taiwan EPA, 1999) promulgated a strict emission standard for the semiconductor manufacturing Industry in April 1999, which specifies that the removal efficiency of acidic gases be more than 95%, or the total emission rate in each factory (after control devices) for each individual species be <0.6 kg/h

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Table 1  
Yearly consumption of acidic liquids and their emissions in HSIP in 2001

	Semiconductor industry <sup>a</sup> (unit: 1000l)	Optoelectronics industry <sup>b</sup> (unit: 1000l)	Total emission <sup>c</sup> , before control (unit: 1000 kg)	Total emission <sup>c</sup> , after control (unit: 1000 kg)
HF	2120	5.5	14.6	10.9
HCl	1260	27.0	43.4	10.3
HNO <sub>3</sub>	410	17.0	8.0	0.3
H <sub>3</sub> PO <sub>4</sub>	1120	2.8	N/A <sup>d</sup>	N/A <sup>d</sup>
H <sub>2</sub> SO <sub>4</sub>	7090	46.0	12.4 <sup>e</sup>	7.8 <sup>e</sup>
Other mixed acid	1360	3.9	N/A	N/A

<sup>a</sup> 48 plants.

<sup>b</sup> 16 plants.

<sup>c</sup> Including both industries; obtained in this study.

<sup>d</sup> N/A—not available. The number of samples is not enough to estimate total emission of phosphoric acid.

<sup>e</sup> Based on SO<sub>4</sub><sup>2-</sup>.

(HNO<sub>3</sub>, HCl, H<sub>3</sub>PO<sub>4</sub> and HF) or 0.1 kg/h (H<sub>2</sub>SO<sub>4</sub>). If the above standard cannot be achieved, specific design criteria and operating conditions of the packed tower must be met. However, it is still not known whether this strict standard can be met in semiconductor industry because of lack of sensitive methods to determine the low concentration in high-flow exhaust stream. Similar standard was promulgated by the US EPA (2003b) which requires process vents (stacks) of all major sources to achieve a 95% control efficiency or 0.42 ppmv concentration limit for inorganic HAPs (primarily HCl and HF).

## 2. Methods

Currently, the standard methods of the Taiwan EPA use an impinger to absorb a gas pollutant and the detection limits are not low enough for most emissions where the concentrations are usually <1 ppmv. The standard methods can be used only in some rare cases when inlet concentrations are high enough. Since exhaust gas in high-tech industry is at normal temperature and pressure, therefore it is possible to use an adsorption method for gas species and a filtration method for particulate species.

The sampler used in the present study consists of a Teflon filter (Gelman Science, 2 μm pore size) to collect particles followed by two coated porous metal discs (diameter: 4.7 cm, thickness: 0.23 cm and pore size: 100 μm) for basic and acidic gas sampling. The flow rate of the porous metal denuder was maintained at 2l/min and sampling time was 30 min. The porous metal discs were tested for adsorption efficiency and capacity of various inorganic gases (Tsai et al., 2001a, b). After sampling, the samplers were sealed with parafilm and brought back to the laboratory for subsequent analysis by an ion chromatograph (model 4500i, Dionex Corp.)

within 24 h. Details were described in the earlier work (Tsai et al., 2000).

In this study, the monthly emission before the control device is plotted versus monthly consumption of liquid chemicals, and the emission factor is obtained from the linear regression of the data points. After knowing the emission factor, the monthly emission (kg/month) after the control device per unit time,  $E$ , can be calculated as

$$E = AE_F \left( 1 - \frac{\eta}{100} \right), \quad (1)$$

where  $E_F$  is the emission factor, and  $\eta$  is the removal efficiency (%) of the control equipment, which was also obtained in this study.

## 3. Results and discussions

In this study, the emission data obtained were categorized into different types of scrubbers and industries. The predominant pollutants were found to be in the gas phase in the stack inlet for both acidic and basic scrubbers. The fraction of gas pollutant is 72.7% and 94.3% for the inlet of acidic and basic scrubbers, respectively. However, the fraction of gaseous pollutants decreases and the particulate fraction increases in the stack outlet due to lower removal efficiency of fine particles compared to gas pollutants and possible re-entrainment of scrubbing liquid droplets into the scrubber outlet. The particles are formed in the duct due to the interaction of ammonia gas with co-existing acidic gases in both acidic and basic scrubbers. In the acidic gas scrubbers, it is found that significant NH<sub>3</sub> gas co-exists with acidic gases. According to the industry, NH<sub>3</sub> is generated in reaction chambers not from wet chemical stations. The removal efficiency of NH<sub>3</sub> is low and it becomes the predominant gas in the stack outlet followed by HF and HCl. The predominant species are

$F^-$ ,  $Cl^-$ ,  $NH_4^+$ , and  $SO_4^{2-}$ , and the profile at the inlet remains nearly the same as that at the outlet. For basic gas scrubbers, the predominant gas pollutant is  $NH_3$ , only a very small fraction of acidic gases exists. For particulate species, the outlet mass concentration is higher than the inlet, and the predominant particulate species are  $SO_4^{2-}$  and  $NH_4^+$  at the inlet and outlet with existence of certain fractions of  $F^-$  and  $Cl^-$ .

For optoelectronics industry, the emission profile is similar with the exception that the fraction of HF in the outlet of basic gas scrubber is higher than that in semiconductor industry.

Although there are many parameters and operation conditions that could influence the control efficiency of a packed tower, this study has found that the inlet concentration is the most important parameter. The experimental data show that the control efficiency for most gas pollutants is low and quite variable at low inlet concentrations. For example, for the removal efficiency of HF shown in Fig. 1, when the inlet concentration is less than about  $650 \mu\text{g}/\text{m}^3$ , the efficiency increases with the increasing inlet concentration. When the inlet concentration is higher than  $650 \mu\text{g}/\text{m}^3$ , the efficiency is found to be higher and becomes more or less a constant. Similar trend also occurs for HCl,  $F^-$ , and  $Cl^-$ . For  $NH_3$ , and  $SO_4^{2-}$ , the control efficiency is more variable. The control efficiency of  $HNO_3$  is close to 100% due to its extremely high solubility to water. At  $25^\circ\text{C}$ , the Henry's law co-efficient for  $HNO_3$  is  $210,000 \text{ M}/\text{atm}$ , which is several orders of magnitude higher than for  $NH_3$  ( $62 \text{ M}/\text{atm}$ ), and HCl ( $727 \text{ M}/\text{atm}$ ) (Seinfeld and Pandis, 1998).

Best fitted equations or average values of control efficiencies of all gaseous and particulate species were obtained in this study. For species that have a clear trend of control efficiency versus inlet concentration, the best fitted equations are given. For species with variable

control efficiency with respect to inlet concentration, only the average efficiency with standard deviation is given.

The control efficiencies were used to compute the yearly emission rate for each species after the control device, and the results are shown in Table 1, in which the emission rate before the control device is calculated based on actual measured concentrations. The table shows that HF and HCl are the most predominant species followed by  $H_2SO_4$  in the stack.

The emission factor before the control device is obtained by linear regression of the monthly emission of a pollutant species versus monthly consumption of its corresponding liquid chemical. Because the emission profile for both industries under investigation is not very different, the emission factor was calculated for all scrubbers of both industries. For example, Fig. 2 shows the emission factor for HF, or the slope of the line, is  $0.0064 \text{ kg}/\text{l}$ , with  $R^2$  value of 0.84 ( $R$  is the co-efficient of correlation). The data are somewhat scattered especially when the emission rate is low, but most data points are bounded within  $-40\%$  to  $+40\%$  of the regression line. Similar plots can be obtained for other species. There is no emission factor for  $NH_3$  since there are no monthly consumption data available as Taiwan EPA does not require the report of these data. Table 2 is the summary of the emission factor before control device, range, and  $R^2$  of the linear regression for various species obtained in this study. It is found that the emission factor for HCl ( $0.0191 \text{ kg}/\text{l}$ ) is the highest, followed by  $HNO_3$  ( $0.0168 \text{ kg}/\text{l}$ ) and HF ( $0.0064 \text{ kg}/\text{l}$ ). In comparison, the emission factors for particulate pollutants (such as  $SO_4^{2-}$ :  $0.0017 \text{ kg}/\text{l}$ ,  $NO_3^-$ :  $0.0033 \text{ kg}/\text{l}$  and  $F^-$ :  $0.0023 \text{ kg}/\text{l}$ ) are much lower than those of gaseous pollutants. The low emission factor for  $H_2SO_4$ , together with the fact that  $HNO_3$  removal efficiency is very high, and HF and HCl are the second and third most used liquid chemicals

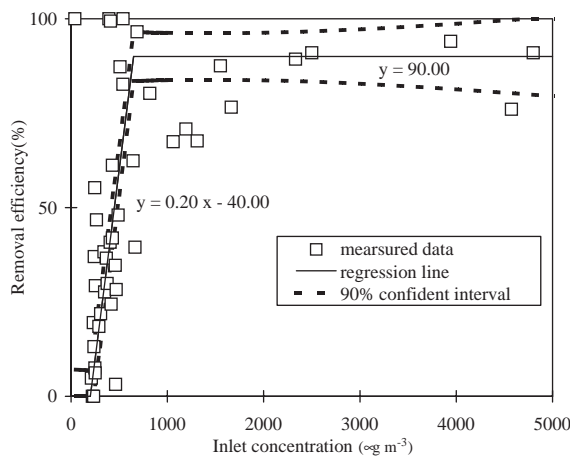


Fig. 1. Removal efficiency versus inlet concentration for gaseous HF.

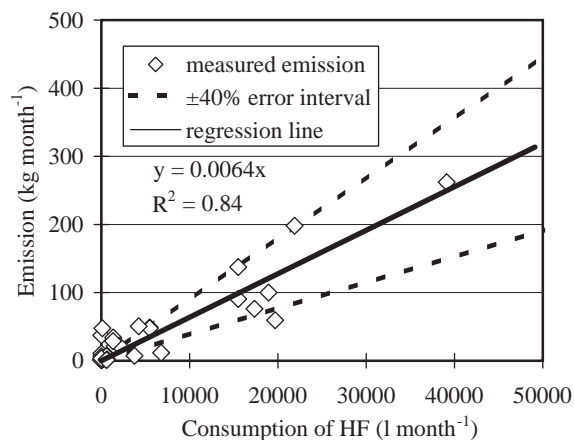


Fig. 2. Monthly emission rate (in kg) versus consumption of liquid chemical (in l) for gaseous HF.

Table 2  
Emission factor, range, and  $R^2$  value of linear regression of various species (unit: kg/l)

Pollutant	Emission factor ave <sup>a</sup> ( $\pm$ std)	Range (kg/l)	$R^2$ value	No. of samples
Gaseous HF	0.0064 ( $\pm$ 0.0010)	(0.0038, 0.0090)	0.84	31
Gaseous HCl	0.0191 ( $\pm$ 0.0045)	(0.0096, 0.0287)	0.70	35
Gaseous HNO <sub>3</sub>	0.0168 ( $\pm$ 0.0031)	(0.0101, 0.0235)	0.77	21
Particulate F <sup>-</sup>	0.0023 ( $\pm$ 0.0005)	(0.0012, 0.0035)	0.74	31
Particulate Cl <sup>-</sup>	0.0104 ( $\pm$ 0.0024)	(0.0052, 0.0156)	0.73	35
Particulate NO <sub>3</sub> <sup>-</sup>	0.0033 ( $\pm$ 0.0005)	(0.0017, 0.0050)	0.65	21
Particulate SO <sub>4</sub> <sup>2-</sup>	0.0017 ( $\pm$ 0.0003)	(0.0009, 0.0026)	0.79	31

<sup>a</sup>ave: average value from linear regression.

in semiconductor industry, explain why the predominant species in the stacks (after the control device) are HF and HCl. The emission factors obtained in this study are shown to be much lower than that of VOC, 0.0428 kg/l by Chein and Chen (2003), mainly because of relatively lower volatility of inorganic acids and ammonia.

#### 4. Conclusions

This study used a sensitive porous metal sampler and ion chromatograph to determine the emission rates, emission profiles, control efficiencies, and emission factors of various acidic and basic gases and particles for packed towers used in semiconductor and optoelectronic industries. Results show that predominant species from the scrubber is in gas phase. In the acidic scrubber, predominant acidic gases in the stack outlet are HF and HCl. NH<sub>3</sub> may co-exist in the duct neutralizing acidic gases to form small particles, which are not easily removed.

The emission factors before the control device determined in this study, provide a quick method to estimate the emission rate of various inorganic gases and particles. Results show that emission factor for HCl is the highest, followed by HNO<sub>3</sub> and HF. The emission factors for particulate pollutants (such as SO<sub>4</sub><sup>2-</sup>) are lower than those of gaseous pollutants.

It is found that HNO<sub>3</sub> removal efficiency is nearly 100%, and some species such as HF and HCl have low control efficiency when the inlet concentration is low. Control efficiency of other species, such as NH<sub>3</sub> and SO<sub>4</sub><sup>2-</sup>, is more variable. Equations were developed for various species for calculating the emission rate after the control device. This study has found that an emission standard based on the requirement that the control efficiency must be >95% is impractical for low concentration, in high-flow exhaust stream such as

in high-tech industry. For inlet concentration below 1 ppmv, the control efficiency is usually very low.

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