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Measurement of Inorganic Acidic Gases and Particles from the Stack of Semiconductor and Optoelectronic Industries

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ABSTRACT

A method for sampling inorganic acids in the exhaust gas of semiconductor and optoelectronic industries was developed by using a porous metal denuder and an ion chromatograph analysis. The sampler consists of a Teflon filter to collect inorganic acidic aerosols followed by two coated porous metal discs for sampling inorganic acidic gases. The second disc was used to check if the gas broke through the first disc. The method detection limit of the sampler is appropriate for sampling the exhausted gas at semiconductor or photoelectric industries. Test results indicated that the calibration curves had good coefficients of correlation,

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and the concentrations of the laboratory and field blanks were found to be lower than the method detection limit. For the semiconductor and optoelectronic industries, the total concentration of acidic gases and particles for hydrofluoric acid, hydrochloric acid, nitric acid, phosphoric acid, and sulfuric acid was found to be 85–999, 40–820, 21–223, ND (not detectable)–404, and 49–535 $\mu g/Nm^3$ (at 0°C, 1 atm), respectively, by using the new method. The porous metal denuder is compact in size, sensitive in detection, and suitable for sampling several inorganic acids simultaneously in the exhausted gas for the semiconductor or photoelectric industries.

Key Words: Inorganic acids; Semiconductor and optoelectronic industries; Porous metal denuder; Detection limit.

INTRODUCTION

Large quantities of inorganic acids, including hydrofluoric acid, hydrochloric acid, nitric acid, phosphoric acid, and sulfuric acid, are commonly used in semiconductor and optoelectronic industries for cleaning and etching processes in the Hsinchu Science-Based Industrial Park (HSIP) in Taiwan. The industries usually use packed towers (or scrubbers) to control emission of these inorganic pollutants. The control efficiencies of the packed towers used in these industries are still unknown because that they are normally designed for abating air pollutants of high emission concentrations,[1] while the acidic concentrations from these industries are low, typically less than several parts per million by volume (ppmv). Thus, the measurement of the inorganic acids in the exhaust duct is very important to protect the environment and human health. The heath effect, evidence, concentration ranges, and epidemiological studies of acidic aerosols in the ambient air have been reviewed by Spengler et al.[2]

The standard methods of Taiwan Environmental Protection Administration (Taiwan EPA) use an impinger to absorb inorganic acidic pollutants in the exhaust duct of a stationary source. A colorimetric analysis is used to determine the concentrations of the hydrofluoric acid and the hydrochloric acid, and a titration method is used to determine the concentrations of the sulfuric acid. The standard methods can be used only in the cases when the concentrations of the inorganic acids are high enough. Table 1 lists the detection limit of the standard methods and the range of the emission concentrations of the inorganic acids. This table shows that the method detection limits are not low enough for most emitted inorganic acidic pollutants from the semiconductor and optoelectronic industries, the concentrations of which are usually less than 500 $\mu g/Nm^3$ (at 0°C, 1 atm). Presently, it is still not known whether a strict

Table 1. The detection limit of the standard methods and the range of emission concentrations.

Pollutant	Standard methods	Detection limit (standard methods) ($\mu g/Nm^3$)[a]	Emission conc. range	
			Semiconductor industry ($\mu g/Nm^3$)	Optoelectronics industry ($\mu g/Nm^3$)
Hydrofluoric acid	NIEA[b] A409.70A	179	54–11,607	179–7,143
Hydrochloric acid	NIEA A412.70A	2,925	49–13,000	65–3,250
Nitric acid	N/A[c]	N/A	28–1,125	28–563
Phosphoric acid	N/A	N/A	<429	<857
Sulfuric acid	NIEA A441.11B	109	30–2,500	20–1,000

[a]At 0°C, 1 atm.
[b]National Institute of Environmental Analysis (Taiwan EPA).
[c]Not available.

emission standard promulgated by Taiwan EPA in April 1999[3] can be met because of a lack of a sensitive method to determine the low concentration of the exhaust stream for the semiconductor manufacturing industry. In addition, for different mixed gases and particles in high-tech industries, many different standard methods must be used in sequence for sampling these inorganic acids, resulting in a very high sampling cost for the industries in the HSIP.

Diffusion denuder is a sampler for removing gases from an aerosol stream to measure their concentrations separately. Several commercial diffusion denuders have been designed and tested, including the annular denuder,[4] the compact coiled denuder,[5] and the glass honeycomb denuder,[6,7] to collect atmospheric gases and particles. Poon et al.[8] developed a high-efficiency compact diffusion denuder that uses porous metal discs. Because of its smaller size, it is possible to design a compact atmospheric and/or indoor denuder sampling system. By using the same porous metal discs, Tsai et al.[9] designed and tested a porous metal denuder in the laboratory. The porous metal discs were tested for adsorption efficiency and capacity of various inorganic gases.[9,10] Their results showed that the collection efficiencies of the porous metal denuder coated with 5% sodium carbonate/glycerin for inorganic acids were as high as 96%. The coating solution concentrations were higher than that of the denuder used for atmospheric sampling,[7,8] since the latter was found to be insufficient for the high gas concentration in the

workplace. Based on the test data, the maximum allowable inlet concentration without breakthrough can be as high from 22,321 to 56,250 $\mu g/Nm^3$ for inorganic acidic pollutants.

In this study, a new porous metal denuder was designed for measuring the inorganic acidic gases and particles in the exhausted gas of semiconductor and optoelectronic industries. The advantages of this new sampler are smaller size, corrosion-resistant, and the capability to sample several inorganic acidic gases and particles simultaneously. The porous metal denuder was used to sample inorganic acids in the stack at various optoelectronic and semiconductor manufacturing industries located at the HSIP in Taiwan.

METHODS

The schematic diagram of the porous metal denuder is shown in Fig. 1. The entire sampler was made of Teflon. The diameter of the porous metal denuder is 35 mm, and the total length is 97.5 mm. The sampler consists of a Teflon filter (Gelman Science, 2-μm pore size, Gelman Science, Ann Arbor, Michigan, USA) to collect inorganic acidic aerosols followed by two coated porous metal discs (diameter: 2.54 cm, pore size: 100 μm, thickness: 0.317 cm, P/N 1000, Mott Inc., Farmington, CT) to collect inorganic acidic gases. The porous metal discs were coated with 5% sodium carbonate/glycerin. In this sampler, particles of all sizes were collected by the Teflon filter, while inorganic acidic gases were collected by the two porous metal discs. Particulate and gaseous samples were analyzed separately by ion chromatograph. To avoid sampling loss of particles in the sampling tube, the entire sampler was inserted into the stack with the sampling inlet facing into the exhaust stream. The isokinetic sampling condition was achieved by installing an additional inlet nozzle in front of the inlet and by adjusting the sampling flow rate so that inlet air velocity was the same as the free-stream air-flow velocity. The sampling flow rate of the sampler was usually less than 2 L/min. After sampling, the samplers were sealed with parafilm and brought back to the laboratory. In the laboratory, Teflon filters were extracted with 6 mL, while porous metal discs were extracted with 15 mL of deionized water, by an ultrasonic bath for 20 min. The samples were kept in a refrigerator and subsequently analyzed by an ion chromatograph (Model 120, Dionex Corp.) within 24 hr.

High purity water (zenopure Quatra90) of 18 mΩ cm was used for all eluent, sample, and standard preparations. The standard solutions of sodium fluoride, sodium chloride, sodium nitrate, potassium phosphate, and potassium sulfate (E. Merck, Darmstadt, Germany) were used for the preparation of the calibration curves. Another standard solution containing these anions was obtained from High Purity (High Purity, Charleston, Southern Carolina,

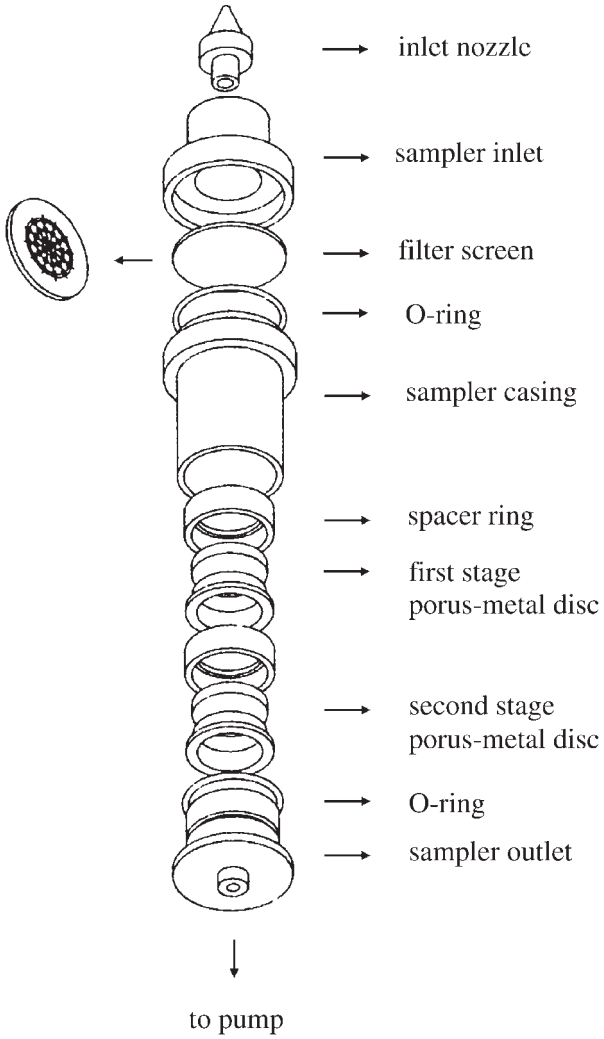

Figure 1. Schematic representation of the porous metal denuder used in this study.

USA) to verify the calibration curves and as the controlled samples. A Dionex (Sunnyvale, CA) Model 120 ion chromatograph was used for all analyses. Eluent for ion chromatograph (IC) analysis was a buffer solution of 0.3 mM of $NaHCO_3$ and 2.7 mM of Na_2CO_3 (Merck, analytical grade, E. Merck, Darmstadt, Germany). The eluent was pumped at a flow rate of 1.5 mL/min. A 500 μL sample aliquot was injected into the instrument. The analytical

column IonPac AS12A (200 mm × 4 mm, Dionex), with a guard column (IonPac AG12A, 50 mm × 4 mm), was used in the measurement. Post-column eluent suppression was accomplished with an anion suppressor (ASRS-Ultra 4 mm). Instrument control, calibration, integration, data collection, and printing control were performed with a personal computer and PeakNet (Dionex Corp.) software.

Inorganic acids have been measured at various industrial plants located at the HSIP. The HSIP has an area of 625 ha, stretching over both Hsinchu county and Hsinchu City, and it is the major high-tech industrial park in Taiwan. Two major industries: semiconductors [48 plants, mainly for DRAM (dynamic random access memory) and IC fab (integrated circuit fabrication)] and optoelectronics [16 plants, mainly for LED (light-emitting diode) and LCD (liquid crystal display)] use acidic chemicals extensively (i.e., hydrofluoric acid, hydrochloric acid, nitric acid, phosphoric acid, and sulfuric acid) during cleaning and etching processes. In this study, a total of eight flue gas samples (optoelectronics: stacks 1–3; semiconductors: stacks 1–5) were taken from June 2002 to May 2003, by using the porous metal denuder. The average temperature and the average relative humidity of the flue gas in the optoelectronic industries was from 19°C to 24°C, and 85% to 98%; and it was from 20°C to 22°C, and 93% to 100% for the semiconductor manufacturing industries.

RESULTS AND DISCUSSION

QA/QC (quality assurance and quality control) procedure in this study includes the establishment of the calibration curve, the method detection limit, blank analysis, repeated analysis, and spike sample analysis. The calibration curves showed excellent linear relationship with the correlation coefficient of the regression line greater than 0.998 for all ions. The verification of the calibration curve was determined by using standard solutions. The verification results showed that the relative deviations were within $\pm 6\%$. The accuracy and precision of the method was performed by using spiking standard solutions and repeat analyses in different days. The results showed that the precision (relative standard deviations) was within 5% and the accuracy (recovery efficiency) was from 85% to 115% for different ions. The method detection limit was determined as 2.681 times the pooled standard deviation of the expected method detection limit, which was determined as three times the standard deviation of the repeated analysis of seven samples at the lowest possible standard concentration. The recovery efficiencies were estimated by using spike samples with the sampling concentrations based on the sampling volume. The results of method detection limit, blank analysis, and recovery efficiency of the porous metal disc and Teflon filter are shown in Table 2. When the sampling volume

was 75 L, the method detection limits were 0.86, 1.31, 0.75, 1.46, and 2.49 μg/Nm^3 for hydrofluoric acid, hydrochloric acid, nitric acid, phosphoric acid, and sulfuric acid, respectively. The method detection limit is appropriate for sampling the exhausted gas from the stack in the semiconductor or photoelectric industries. The concentrations of the laboratory and field blank were found to be lower than the method detection limit. The recovery efficiency of hydrofluoric acid, hydrochloric acid, nitric acid, phosphoric acid, and sulfuric acid for the porous metal disc was 100.8% ± 3.9%, 95.3% ± 7.4%, 95.1% ± 6.1%, 97.8% ± 5.7%, and 93.6% ± 6.8%, and that for the Teflon filter was 99.5% ± 3.2%, 98.7% ± 2.9%, 94.0% ± 3.2%, 97.5% ± 3.3%, and 99.6% ± 3.3%, respectively. Repeated analysis results showed that the relative percentage differences of all inorganic acids were within ±17.7%.

The emission concentrations of the inorganic acids from the different stacks were determined by using the porous metal denuder for semiconductor manufacturing and optoelectronic industries. The concentrations of the inorganic acidic gases for the first and the second porous metal disc within the sampler were determined after the field sampling. The results showed that the concentrations of the inorganic acidic gases for the second disc were lower than the method detection limit, indicating the breakthrough did not occur and the capacity of the sampler was sufficient to collect the inorganic acidic gas from the stacks. Figure 2 shows the concentrations of acidic gases [Fig. 2(a)] and acidic particles [Fig. 2(b)] from the stack of optoelectronic industries. For

Table 2. Method detection limit, blank analysis, and recovery efficiency of porous metal disc and Telflon filter.

Species	MDL[a] (μg/Nm^3, at 0°C, 1 atm)	N[b]	Blank analysis		% Recovery efficiency (SD[c])	
			PMD[d]	TF[e]	PMD	TF
Fluoride	0.86	8	ND[f]	ND	100.8 (3.9)	99.5 (3.2)
Chloride	1.31	8	ND	ND	95.3 (7.4)	98.7 (2.9)
Nitrate	0.75	8	ND	ND	95.1 (6.1)	94.0 (3.2)
Phosphate	1.46	8	ND	ND	97.8 (5.7)	97.5 (3.3)
Sulfate	2.49	8	ND	ND	93.6 (6.8)	99.6 (3.3)

[a]MDL: method detection limit (at 0°C, 1 atm).
[b]N: number of samples.
[c]SD: standard deviation.
[d]PMD: porous metal disc.
[e]TF: Teflon filter.
[f]ND: detected value <MDL.

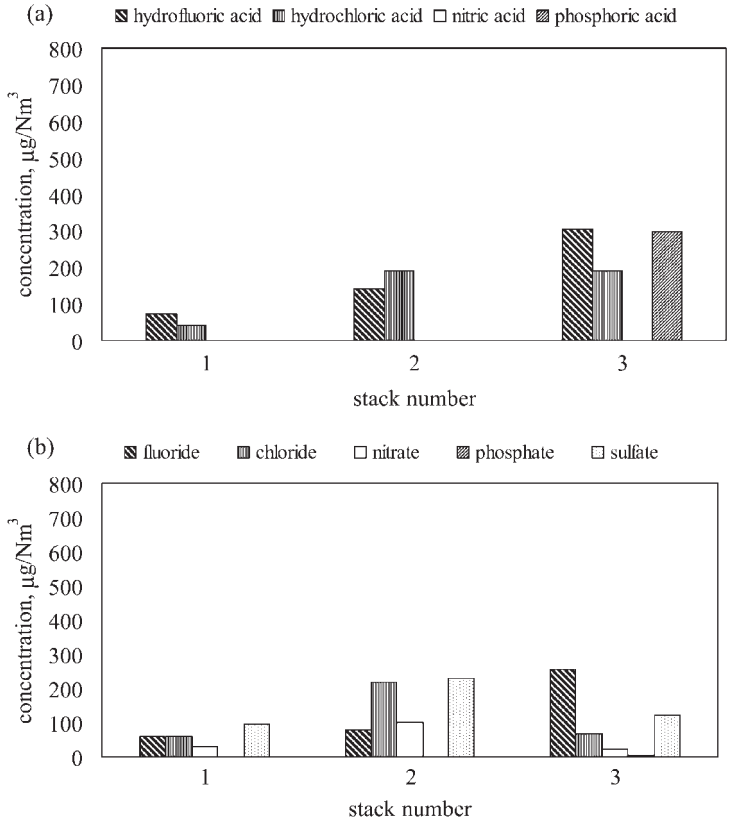

Figure 2. The concentrations of inorganic acids from the stack of optoelectronic industries (a) acidic gases and (b) acidic particles.

stack 1, the concentration of inorganic acidic gas, i.e., hydrofluoric acid and hydrochloric acid, was found to be 72 and 40 $\mu g/Nm^3$, respectively, and that for acidic particle, i.e., fluoride, chloride, nitrate, and sulfate was 61, 61, 29, and 98 $\mu g/Nm^3$, respectively. The gaseous and particulate concentrations of the phosphoric acid both in stacks 1 and 2 were found to be lower than the method detection limit. Compared with stack 1, the gaseous and particulate concentrations of the acidic species found in stack 2 were higher, and hydrochloric species was found to be the predominant acidic pollutant. For stack 3, the gaseous hydrofluoric acid and phosphoric acid were the predominant pollutants with the concentration of 306 and 297 $\mu g/Nm^3$, respectively. The particulate concentration of fluoride, chloride, nitrate, phosphate, and sulfate was 254, 65, 21, 3, and 122 $\mu g/Nm^3$, respectively. In stacks 1–3, the predominant pollutants

were hydrofluoric species and hydrochloric species. The sampling results showed that the fraction of the particulate concentration was 36–46% and 25–60% for the hydrofluoric species and the hydrochloric species, respectively. These particles might be formed in the exhaust gas due to the interaction of ammonia gas coexisting with acidic gases. However, the packed towers typically are used only to handle acid/base gases, and the removal efficiency for fine particles is low.

For semiconductor manufacturing industries, the concentrations of acidic gases and acidic particles are shown in Fig. 3(a) and (b). The figure shows that hydrofluoric species and hydrochloric species are the predominant acidic pollutants in stack 1. For stack 2, the gaseous concentration of hydrofluoric

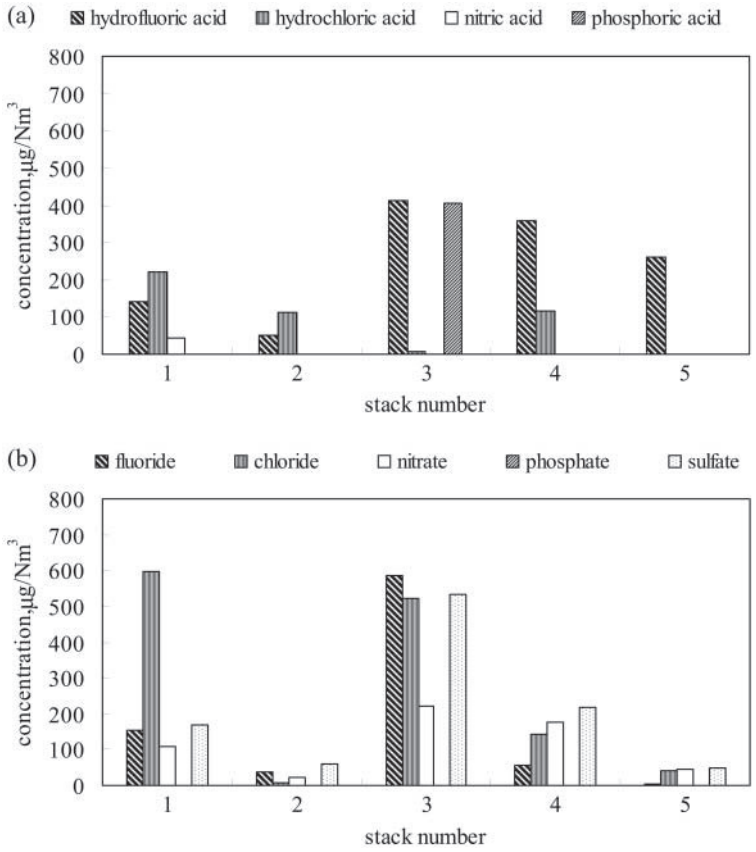

Figure 3. The concentrations of inorganic acids from the stack of semiconductor industries (a) acidic gases and (b) acidic particles.

acid and hydrochloric acid was found to be 49 and 112 $\mu g/Nm^3$, and the particulate concentration of fluoride, chloride, nitrate, and sulfate was found to be as low as 36, 9, 21, and 59 $\mu g/Nm^3$, respectively. In stacks 3–5, the gaseous concentrations of hydrofluoric acid were higher; they were 413, 358, and 260 $\mu g/Nm^3$. For stack 3, the particulate concentration of fluoride, chloride, nitrate, and sulfate was found to be as high as 587, 522, 223, and 535 $\mu g/Nm^3$, respectively. The sampling results showed that the several inorganic acids were emitted into the atmosphere from the stack after a packed tower. Although there were many parameters and operation conditions that could influence the performance of the packed tower, it seemed reasonable to suppose that the removal efficiency was not sufficient for the low inlet concentrations of the acidic gases.[11] In addition, the possible reentrainment of the scrubbing droplets of the packed tower into the stack also will cause the high emission concentrations of the aerosols.

In general, test results showed that the predominant pollutants were hydrofluoric species and hydrochloric species in the stacks of the semiconductor manufacturing and optoelectronic industries. Sample analysis at different industries indicated that the concentrations of inorganic pollutants were not the same between the stacks of the semiconductor manufacturing and optoelectronic industries. The proposed measured method can be used for sampling the inorganic species in a wide range of concentrations. The total concentrations of gaseous and particulate inorganic species were found to be 85–999, 40–820, 21–223, ND–404, and 49–535 $\mu g/Nm^3$ for hydrofluoric acid, hydrochloric acid, nitric acid, phosphoric acid, and sulfuric acid, respectively. With its compact size and capability to sample several inorganic acids simultaneously, the sampling cost and efforts will be reduced.

CONCLUSIONS

This study had proposed a sensitive porous metal denuder and an ion chromatograph to measure the concentrations of various inorganic acids in the exhaust gas at semiconductor and optoelectronic industries. The method detection limits were found to be 0.86, 1.31, 0.75, 1.46, and 2.49 $\mu g/Nm^3$ for hydrofluoric acid, hydrochloric acid, nitric acid, phosphoric acid, and sulfuric acid, respectively, based on the sampling air volume of 75 L. The recovery efficiency of hydrofluoric acid, hydrochloric acid, nitric acid, phosphoric acid, and sulfuric acid for the porous metal disc was 100.8% $\pm$ 3.9%, 95.3% $\pm$ 7.4%, 95.1% $\pm$ 6.1%, 97.8% $\pm$ 5.7%, and 93.6% $\pm$ 6.8%, and those for Teflon filter was 99.5% $\pm$ 3.2%, 98.7% $\pm$ 2.9%, 94.0% $\pm$ 3.2%, 97.5% $\pm$ 3.3%, and 99.6% $\pm$ 3.3%, respectively.

The porous metal denuder was used to sample inorganic acids in the stack at various optoelectronic and semiconductor manufacturing industries located at the HSIP in Taiwan. The results showed that the porous metal denuder is able to sample a wide range of concentrations for the inorganic acid. The new sampler has the advantages of lower method detection limit, convenience of operation due to its small size, and the ability to sample various inorganic acidic gases and particles simultaneously.

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