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Comparison of Cleanroom Samplers for Inorganic Airborne Molecular Contaminants

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Abstract: The performances of inorganic airborne molecular contaminants (AMCs) via silica gel tubes, impingers, and diffusion denuder sampler (DDS) were compared in a cleanroom. The results showed silica gel tubes were not applicable for cleanroom sampling due to high blanks. While with optimal sampling conditions both impingers and DDS have much better performances, of which DDS has the lowest detection limits of the method for HF, HCl, HNO₂, HNO₃, SO₂, and NH₃ gases to be 0.15, 0.11, 0.13, 0.03, 0.07, and 0.42 µg/m³, respectively. Results indicated no significant difference for the HF and SO₄²⁻ concentrations made by the DDS and impingers.

Keywords: Airborne molecular contamination (AMC), cleanroom, micro-contamination, semiconductor device, diffusion denuder sampler (DDS), impinger air sampler

INTRODUCTION

Ever since the semiconductor devices have been miniaturized to be less than 100 nm, the airborne molecular contaminants (AMCs) in cleanroom environment have been recognized as contamination sources causing yield reduction and performance deterioration of semiconductor devices (1–4). Large amounts of inorganic acids and bases are used in plants of integrated circuit

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manufacturing, cleaning, and etching processes. Acid gases of interest including HF, HCl, HNO₂, HNO₃, and SO_x are known to create corrosion problems throughout the fab. Molecular basic contaminants cause the resist line to be widening at the top and result in the so-called "T-topping" effect (5–7). Sophisticated filtration techniques and efficient purging of wafer boxes with inert gas are currently being developed to reduce the level of contamination in sensitive production areas (8, 9). Increasing concerns over inorganic airborne molecular contaminants led to a technical specification of SEMI (Semiconductor Equipment and Materials International) to recommend maximum allowable airborne molecular contaminant concentrations (10).

There have been online methods such as ion mobility spectrometry, continuously wetted denuders with ion chromatography, and chemiluminescence's instrument for inorganic AMCs measurements. These online systems have the advantage of continuous monitoring the critical point-of-use locations but they are so expensive that their application in detecting the gas species in a cleanroom is limited. On the other hand, sampling methods using silica gel tubes, impingers, denuder systems, and coated filters provide the advantages of inexpensive as well as high mobility, thus they are widely used in the monitoring of inorganic gases in cleanroom.

Lue et al. (11) and Lue and Huang (12) sampled the acidic and basic airborne contaminants in a cleanroom by SUPELCO ORBO-53 and SUPELCO ORBO-554 (Bellefonte, PA, USA) silica gel tubes, respectively. Their results showed that the measurement of acidic gas contaminants had high resolution and sensitivity at 216 ml/min sampling rate based on 24-h sampling. And for basic contaminants sampling, the sampling rate was recommended at 50 ml/min. However, concerns of no discussion on the blanks and spike analysis of Lue's study were raised by Vanatta (13). Possible negative sampling errors caused by the silica gel tube were also discussed by Cassinelli (14) that HF could react with the silica gel and glass fiber of the sampler and cause the reaction products trapped on the sorbent.

On the other hand, although the impinger sampler is widely employed for AMCs and industrial hygiene sampling purposes of inorganic gases (8, 15–17), its accuracy on the inorganic AMCs sampling with the characteristic of low concentrations has seldom been studied. The studies of Lue et al. (11) compared the performances of silica gel tubes and impinger samplers in a typical semiconductor cleanroom and concluded that impingers are not applicable due to bubbling volatility of the solution. However, this might be due to the fact that their impinger sampling flow rate was too high. And such high flow rate has been commonly used for the AMCs sampling (8, 11, 15). When the impingers were operated at a sufficiently high sampling flow rates, the liquid would be easily escaped from the impinger (17). Thus finding optimal gas flow rate and the liquid volume in the impingers sampler are essential.

Recently, condenser-type diffusion denuders were used for trace SO₂ contamination sampling in cleanroom air (18). The use of denuders followed by

ion chromatography has been addressed to be capable of detecting low ppb (parts per billion) levels of contaminants in a cleanroom and in a mini-environment (19). Although the geometry of diffusion denuder systems may be different from one to another, however, they all have the advantages of measuring particulate matter and gases separately. In contrast, with the impinger and the silica gel tube it is impossible even when they are operated behind a separate front filter. Besides, the diffusion denuder systems have been widely investigated for their precision and accuracy (20–24), however, the simultaneous sampling and comparison on the performances of silica gel tubes, impingers, and diffusion denuder samplers have never been investigated neither in the open atmosphere nor in the cleanroom for the measurement of inorganic gases.

This study intends to evaluate the gas collection efficiencies of the currently used silica gel tubes and impingers samplers in cleanroom environments, with a diffusion denuder sampler (DDS, MSP Corporation, USA) as a reference for the measurements of trace amounts of inorganic gases. The optimal sampling conditions for achieving lower sampling errors are suggested for each sampler. And then the field sampling data in an integrated circuit manufacturing plant are compared.

EXPERIMENTAL METHODS

Sampling and Analysis

The measurements of cleanroom inorganic gases were conducted at a cleanroom photo area of a semiconductor fab in Taiwan. The relative humidity in the sampling area was $45 \pm 3\%$ and temperature was $22 \pm 1^\circ\text{C}$. A number of wafer fabrication processes could be major sources of airborne contamination in this cleanroom besides possible contamination from the air supply. Types and arrangements of samplers, absorption or extraction solutions, as well as the sampling conditions of the silica gel tubes, impingers, and diffusion denuder samplers used in this study are listed in Table 1. Sampling time for all samplers was 24 hours.

Two commercially available silica gel tubes, SKC silica gel tube (SKC Cat. No 226-10-03, PA, USA) and SUPELCO silica gel tube (SUPELCO ORBO-53, PA, USA), which contain two sections of washed silica gel were evaluated. The SUPELCO and SKC silica gel tubes are recommended by USA NIOSH (National Institute for Occupational Safety and Health) method (25) and Taiwan IOSH (Institute of Occupational Safety and Health) method (16), respectively. Each front section of SKC tubes has glass fiber foam, PVC (polyvinyl chloride) filter, and 400 mg of silica gel, and the back-up section contains glass fiber foam and 200 mg of silica gel. Each front section of SUPELCO tubes has glass fiber filter, and 400 mg of silica gel, and the back-up section contains urethane foam and 200 mg of

Table 1. Sampling arrangements and sampling conditions of silica gel tubes, impingers and denuder samplers for evaluating their sampling efficiencies

Sampler	Manufacturer	Sampling compounds	Absorption or extraction solution	Sampling conditions
Silica gel tube (front and back up sections)	1.SKC (226-10-03)	HF, HCl, HNO ₂ , HNO ₃ , H ₂ SO ₄	Extraction solution: 2.7 mM Na ₂ CO ₃ /0.3 mM NaHCO ₃	1. Flow rate: 50 ~ 500 ml/min
	2.SUPELCO (ORBO-53)			2. Sampling time: 24-h
Impinger (two in series)	Corning Pyrex glass	HF, HCl, HNO ₂ , HNO ₃ , H ₂ SO ₄	Absorption solution: 2.7 mM Na ₂ CO ₃ /0.3 mM NaHCO ₃	1. Flow rate: 50 ~ 1000 ml/min
		NH ₃	Absorption solution: 0.01 N H ₂ SO ₄	2. Sampling time: 24-h
DDS (four plates in series)	Model 450 (MSP Corp. USA)	HF, HCl, HNO ₂ HNO ₃ , SO ₂ , NH ₃ , and inorganic species on particle filters	Absorption solution (26):	
			<ol style="list-style-type: none"> 1. For HF, HCl and HNO₂; at least 2 plates coated with 1% (w/v) Na₂CO₃, 1% (w/v) glycerol in 1:1 methanol/water solution 2. For HNO₃; at least 2 plates coated with 0.1% (w/v) NaCl in 1:9 methanol/water solution 3. For SO₂; at least 1 plate coated with 0.1% (w/v) NaCl in 1:9 methanol/water solution and 2 plates coated with 1% (w/v) Na₂CO₃, 1% (w/v) glycerol in 1:1 methanol/water solution 4. For NH₃; at least 2 plates coated with 1% (w/v) citric acid in methanol solution 	<ol style="list-style-type: none"> 1. Flow rate: 10 l/min 2. Sampling time: 24-h
			Extraction solution:	
			<ol style="list-style-type: none"> 1. For HF, HCl, HNO₂, HNO₃ and NH₃: plates extracted with deionized water 2. For SO₂: plates extracted with 0.1% hydrogen peroxide 	

silica gel. The flow rate was adjusted to be 50, 100, 200, 300, or 500 ml/min by a precision valve on the flow meter. After sampling, the front and the back-up sections (including the front filter) of silica gel tubes were placed in separate PE (polyethylene) containers and extracted with 2.7 mM Na_2CO_3 /0.3 mM NaHCO_3 for further analysis by the ion chromatography (IC) method.

For impinger sampler, two impingers in series with detailed structural drawing shown in Fig. 1(a) were filled with IC eluent absorbent (2.7 mM Na_2CO_3 /0.3 mM NaHCO_3) for acid gases sampling. While for basic gases sampling two impingers in series were filled with 0.01 N H_2SO_4 absorbent. The impinger sampler was made of Corning Pyrex, and the maximum capacity of impinger liquid volume was 60 ml. The bubble tube was a modified standard midget with a fritted nozzle tip designed for increasing contact between the air sample and the liquid. The air sample was bubbled through the collection solution either at 50, 100, 200, 300, 500, or 1000 ml/min for the evaluation of optimal sampling flow rates. It is noted that although the impinger samplers used herein were homemade due to availability at the time of study; however, commercial Teflon impingers of the same capacity of 60 ml is also available (e.g. from SKC, Inc).

The commercial diffusion denuder system (DDS, MSP Corporation, USA) consisted of three major parts: an impactor, denuder plates, and particulate filters. The cut-off aerodynamic diameter of the impactor was 2.5 μm . Denuder plates were porous metal discs coated with different solutions. For HF, HCl, HNO_2 , and SO_2 gases sampling, the plates were coated with 10 ml of 1% (w/v) Na_2CO_3 /1% (w/v) glycerol in 1:1 methanol/water solution. While if coated with 10 ml of 0.1% (w/v) NaCl in 1:9 methanol/water, the target compounds were for HNO_3 and SO_2 gases (24). For NH_3 basic gas sampling, the plates were coated with 10 ml of 1% (w/v) citric acid in methanol solution (26). After the gaseous species had been separated from the air stream by diffusive deposition on denuder plates, the liquid droplets such as H_2SO_4 or fine particles that penetrate the denuder plates were then deposited on the Teflon (Gelman Science, 2- μm pore size) and Nylon (Gelman Science, 1- μm pore size) filters.

A sketch of the regular coating sequence of each denuder plate was shown in Fig. 1(b). The 1st and 2nd plates were coated with NaCl solution, and the 3rd and 4th plates were coated with Na_2CO_3 and citric acid solutions, respectively. The coating sequence was in accord with that suggested by one of the authors' previous study (24) to minimize the HNO_3 sampling error. After coating, the diffusion denuder plates were dried by passing nitrogen gas through them. The flow rate of the DDS was kept at 10 ± 0.2 l/min. After 24-h sampling, the denuder plates coated with Na_2CO_3 solution were extracted with 10 ml of 0.1% hydrogen peroxide. And those coated with NaCl solution were extracted with 10 ml de-ionized water, and then 0.1% hydrogen peroxide was added into the extracted solution to oxidize SO_2 into SO_4^{2-} for ion-chromatography analysis. At the same time those coated with citric acid solution were extracted with 10 ml of de-ionized water. The

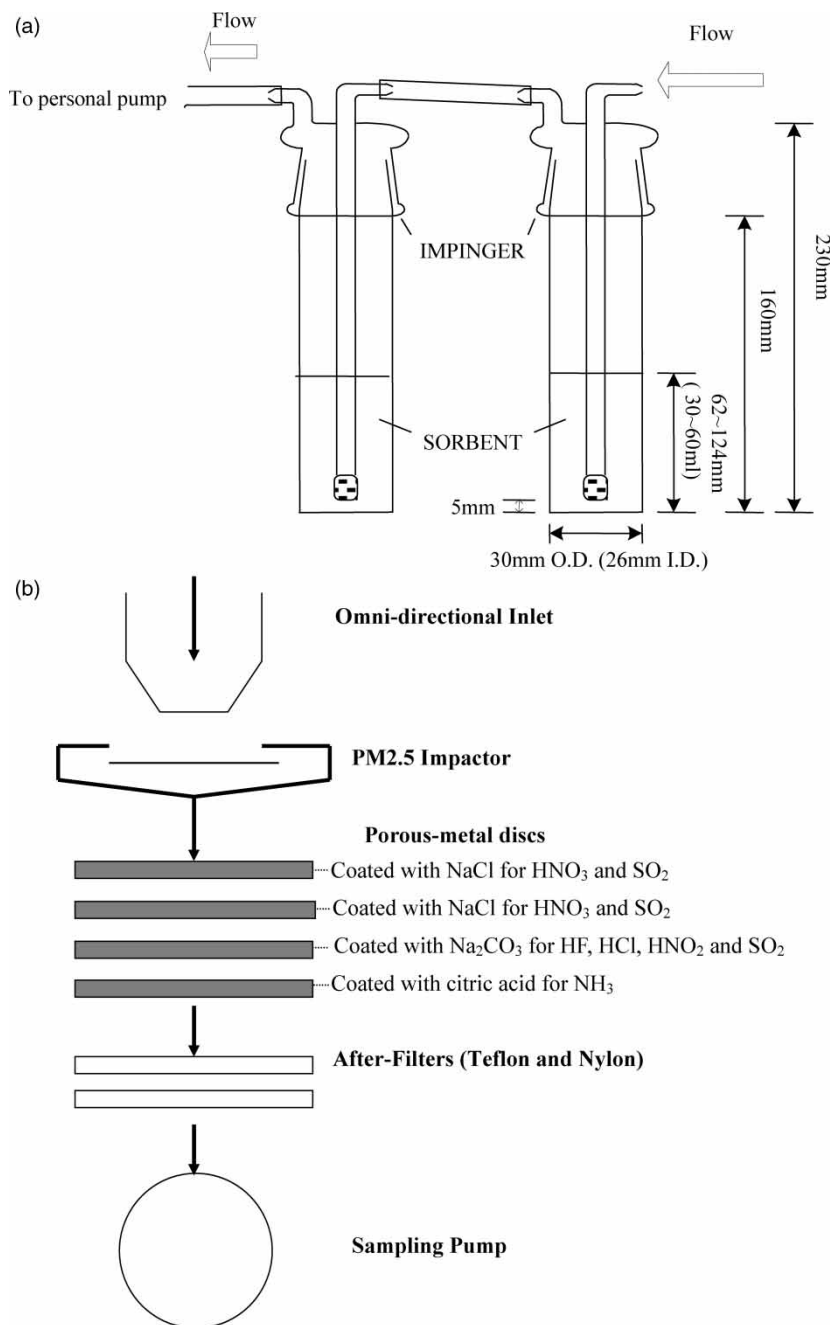


Figure 1. Schematic diagram of (a) an impinger with 60 ml liquid capacity and (b) diffusion denuder system (DDS) used in this study.

Teflon filter was extracted with 2 ml ethanol and 10 ml de-ionized water and the Nylon filter was extracted with 10 ml of de-ionized water. The extraction was preceded via placing the solution in ultrasonic bath for 30 min.

The extracts of silica gel tubes, impingers, and DDS for inorganic gas analysis were then injected into DIONEX DX-120 ion chromatography (DX-120, Dionex, USA) with AS12A column for anion samples and CS12A column for cation samples. The IC chromatograms for a typical air sample containing the anion and cation species are shown in Fig. 2.

QA/QC Program

A quality assurance and quality control (QA/QC) program was performed during sampling and analysis to ensure that measured contaminants were not from failure of the QA/QC program. Table 2 shows concentrations of

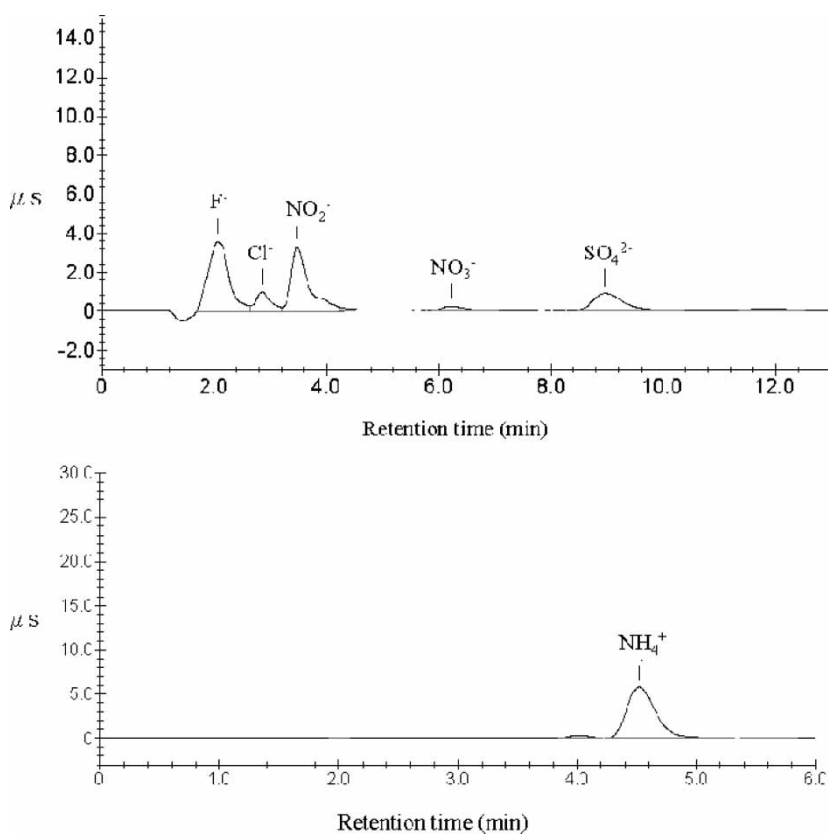


Figure 2. IC chromatograms of anion and cation samples.

Table 2. Blank analyses and detection limits of the method (MDL) of the three samplers

Section	Sample	Silica gel tubes							
		SKC		SUPELCO		Impinger		DDS	
		Mean (μg)	MDL ^b ($\mu\text{g}/\text{m}^3$)	Mean (μg)	MDL ($\mu\text{g}/\text{m}^3$)	Mean (μg)	MDL ($\mu\text{g}/\text{m}^3$)	Mean (μg)	MDL ($\mu\text{g}/\text{m}^3$)
Front (first)	F ⁻	1.37	4.75	5.48	19.02	ND ^a	0.39	ND	0.15
	Cl ⁻	1.08	3.75	0.51	1.77	ND	0.18	ND	0.11
	NO ₂ ⁻	0.12	0.41	0.12	0.41	ND	0.38	ND	0.13
	NO ₃ ⁻	0.19	0.65	0.26	0.90	ND	0.08	ND	0.03
	SO ₄ ²⁻	4.19	14.54	27.32	94.86	ND	0.22	ND	0.07
	NH ₄ ⁺	—	—	—	—	ND	1.24	ND	0.42
Back-up (second)	F ⁻	1.08	—	2.78	—	ND	—	ND	—
	Cl ⁻	0.54	—	0.43	—	ND	—	ND	—
	NO ₂ ⁻	0.3	—	0.15	—	ND	—	ND	—
	NO ₃ ⁻	0.19	—	0.39	—	ND	—	ND	—
	SO ₄ ²⁻	1.55	—	13.04	—	ND	—	ND	—
	NH ₄ ⁺	—	—	—	—	ND	—	ND	—

^aND: Non-detectable.^bMDL: Detection limit of the method, in equivalent to gas-phase concentration of 24-h sampling, $\mu\text{g}/\text{m}^3$.

The flow rate of silica gel tubes: 200 ml/min.

The flow rate of impinger: 50 ml/min, 300 ml/min for acidic gases and NH₃ gas, respectively.

The flow rate of DDS: 10 l/min.

blank for each sampler. It is observed that the blank concentration of SUPELCO silica gel tube is higher than that of SKC silica gel tube. And both SUPELCO and SKC silica gel tubes have higher blank concentrations than those of the impingers and DDS samplers, especially for the SO₄²⁻ and F⁻ species. The blank values of impingers and DDS samplers for the ion species were non-detectable and hence are negligible in sampling acidic or basic gases.

Results on the detection limits of the method (MDL) of the three samplers are also shown in Table 2. It was observed that the MDLs of all species for silica gel tubes (SKC and SUPELCO) are higher than those for the impingers and DDS samplers. This is due to higher blank concentrations for the SKC and SUPELCO silica gel tubes. The MDLs of all species for the DDS sampler appear to be the lowest among the three samplers. And the MDLs of all species for impingers and DDS samplers are lower than the maximum allowable AMCs concentrations suggested by ITRS (International

Technology Roadmap for Semiconductors) (27). In addition, additives at the concentration of 1 mg/l were added to the samples, and the recovery percentages of spike analysis were within $100 \pm 10\%$ for all three samplers.

Calculation of Sampler Efficiency

The collection efficiency of each sampler was obtained from the field in order to know possible interferences on the targeted AMCs for each sampler. The field collection efficiencies (η_1 , %) of the first section of silica gel tube, the first impinger and the first porous-metal plate of denuder sampler were calculated by

$$\eta_1(\%) = \left(1 - \frac{C_2}{C_1}\right) \times 100\% \quad (1)$$

where C_1 and C_2 are the measured inorganic gas concentrations of the first and second piece of sampler, respectively. For the silica gel sampler, C_1 was measured from silica gel and the front filter, and C_2 was measured from the 2nd section (the back up section) silica gel. Although these two sections contained different materials as well as different amounts of silica gel and may not be appropriate for the calculation of the actual collection efficiency, however, it does provide some information on whether the first section of silica gel can collect most of the inorganic acid gases and particles.

And for the two identical “pieces” of sampler in series such as the impingers or the denuder plates, they should have the same collection efficiency between the two identical pieces. However, it is often not possible to have more than two collection pieces in a sampler in practice, thus an assumption was made in equation (1) that the second piece collects all the remaining parts of the gas molecules. This is a reasonable assumption because η_1 is expected to be over 90% for a high efficient sampler so that the overall collection efficiency can be over 99%. As a result, only 1% maximum difference from the actual condition would be encountered using equation (1).

For an evaluation of diffusion denuder sampling efficiency, the field collection efficiencies for most species were determined by using Equation (1). But because SO_2 gas was collected by the plates coated with NaCl and Na_2CO_3 solutions (26), the field collection efficiency for SO_2 gas coated with NaCl, Na_2CO_3 , and Na_2CO_3 solutions in the 1st, 2nd, and 3rd plates, respectively, was calculated as:

$$\eta_{1+2(\text{SO}_2)}(\%) = \left(1 - \frac{C_3}{C_1 + C_2}\right) \times 100 \quad (2)$$

RESULTS AND DISCUSSION

Performances of the Three Samplers

A total of 8 samples for each sampler were obtained in the field and the results are shown in Figs. 3 to 5 with error bars indicated standard deviations of all sample results.

Silica Gel Tubes

Figure 3 shows the effect of the sampling flow rate on the field collection efficiencies of samples with correcting the blanks and without correcting the blanks of SKC silica gel tube. At 200 ml/min sampling flow rate, the measured average concentrations after correcting the blanks for HF, HCl, HNO₂, HNO₃, and H₂SO₄ gases of the first section were 1.81, 1.67, 2.60, 0.63, and 3.78 $\mu\text{g}/\text{m}^3$, and the second section were 0.41, 0.20, 0, 0.12, and 2.04 $\mu\text{g}/\text{m}^3$, respectively. It is observed that the collection efficiencies of all gas species without correcting the blanks are much lower than those with correcting the blanks except for the H₂SO₄ measurement data. This reveals that blank concentrations of the silica gel tube have significant interferences on its performance.

The collection efficiencies of the first section of SKC silica gel tube are higher at sampling flow rates range of 200~300ml/min for almost all species. When the sampling flow rate is under 200 ml/min, blank

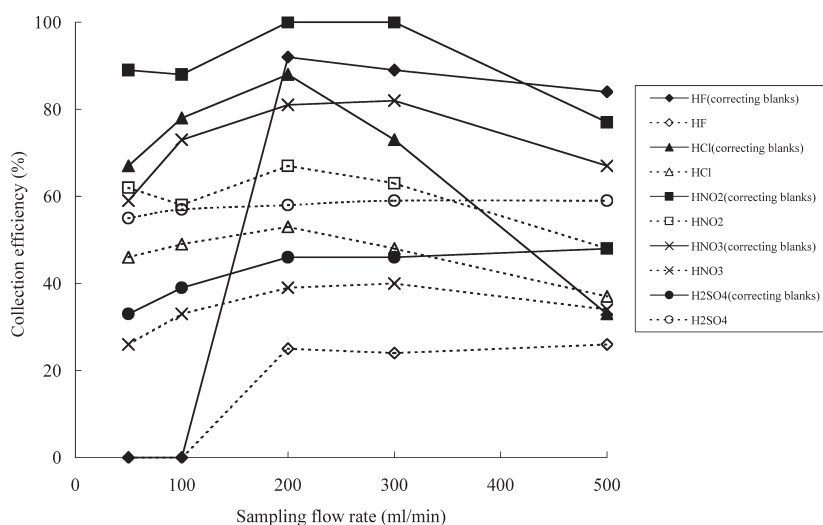


Figure 3. Gas collection efficiency of SKC silica gel tube as a function of sampling flow rate (at sampling time of 24 hours).

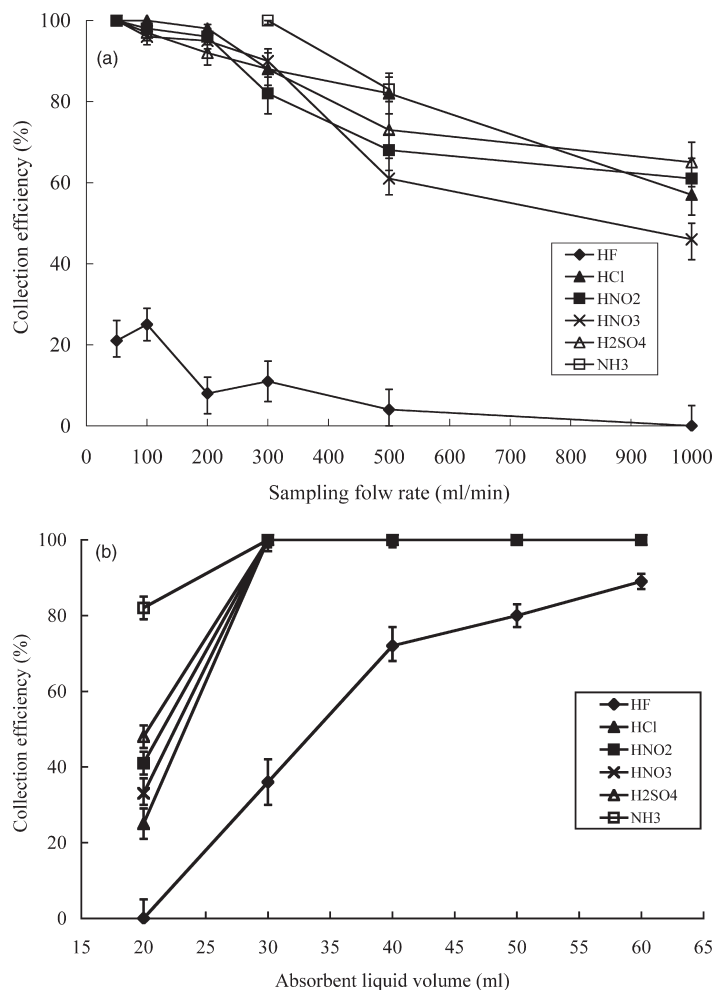


Figure 4. Gas collection efficiency of the first impinger as functions of (a) sampling flow rate (at 30 ml absorbent volume), and (b) absorbent liquid volume (at 50 ml/min and 300 ml/min sampling flow rates for acidic gases and NH₃ gas, respectively).

concentrations of the silica gel tube are the main reasons for the low collection efficiencies of the AMCs. On the other hand, when the sampling flow rate is over 300 ml/min, the collection efficiency of SKC silica gel tube is decreased due to either insufficient residence time for adsorption or the collected amount of gas was beyond the loading capacity of SKC silica gel tube. As a result, only HNO₂ and HF gases of correcting the blanks can reach over 90% collection efficiencies at 200 ~ 300 ml/min sampling flow rate after correcting the blank. But for HCl, HNO₃, and H₂SO₄ gases, the silica gel tubes have less than 90% collection efficiencies. The higher

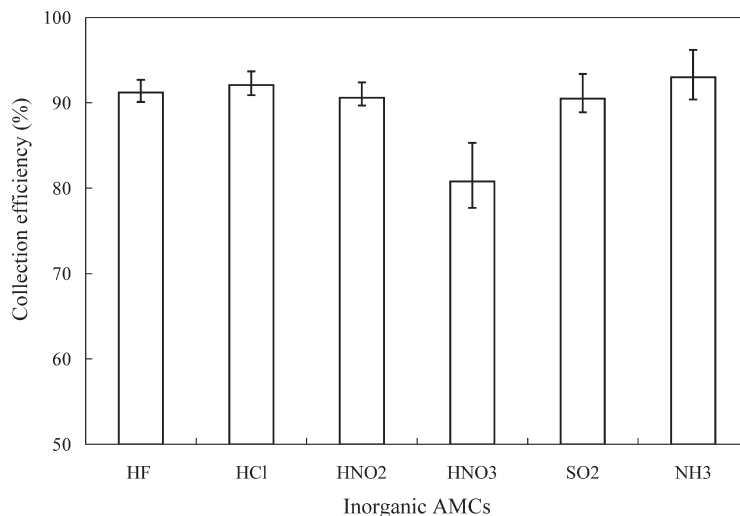


Figure 5. Gas collection efficiency of DDS for sampling inorganic airborne molecular contaminants using one denuder plate for each species.

collection efficiency at 200~300ml/min sampling flow rates are similar to the suggested flow rate of 216 ml/min by Lue et al. (11).

Impinger

The sampling errors could be influenced by the sampling flow rates, absorbent volume, as well as particles collected by the first impinger, but the effect of particles was difficult to be measured using the impinger alone. Thus Figs. 4(a) and (b) present the effects of sampling flow rates and absorbent volume on the collection efficiency.

Figure 4(a) shows the effect of sampling flow rate on the collection efficiency of the first impinger. It was observed that the collection efficiencies for HCl, HNO₂, HNO₃, and H₂SO₄ gases are very high (over 90%) at gas flow rate up to 100 ml/min with 30 ml absorbent liquid. A further increase in the gas flow rate leads to decrease in the gas sampling efficiencies. And at sampling flow rate of 300 ml/min, only NH₃ and HNO₃ gases can remain a high efficiency of over 90%. When bubbling at flow rate of over 300 ml/min, the solution in the first impinger tends to be escaped into the second impinger and results in a slightly decrease (5%~10%) of the solution. On the other hand, the breakthrough problem of HF gas exists even at low sampling flow rate of 50ml/min. Thus it is necessary to further evaluate the influence of other parameters such as liquid volume of absorbent so that the collection efficiency of HF gas can be increased.

Figure 4(b) shows the effect of absorbent volume on the sampling efficiencies of acidic gases and NH_3 gas at the sampling flow rate of 50 ml/min and 300 ml/min, respectively. It was observed that when increasing the absorbent liquid volume to 60 ml, the collection efficiency of HF gas can be enhanced to 90%. And the collection efficiencies of HCl, HNO_2 , HNO_3 , H_2SO_4 , and NH_3 gases at the first impinger can be almost 100%. The result that the gas collection efficiencies made by impingers are higher than those by silica gel tubes is inconsistent with that of Lue et al. (11), in which they reported that the impinger solution had a severe bubbling influence and fluoride interaction with the glass material of the impingers. This is possibly caused by that the absorbent volume was only 7 ml in the study of Lue et al. (11).

Under the optimal sampling conditions, the measured average concentrations for HF, HCl, HNO_2 , HNO_3 , and H_2SO_4 gases of the first impinger were 4.72, 2.07, 2.97, 0.47, and 1.88 $\mu\text{g}/\text{m}^3$, and those of the second impinger were 0.51, 0, 0, 0, and 0 $\mu\text{g}/\text{m}^3$, respectively, at 50 ml/min sampling flow rates and 60 ml absorbent volume. The measured average concentration for NH_3 gas of the first impinger was 9.64 $\mu\text{g}/\text{m}^3$, and that of the second impinger was 0 $\mu\text{g}/\text{m}^3$, respectively, at 300 ml/min sampling flow rates and 60 ml absorbent volume.

Diffusion Denuder System (DDS)

At least two plates coated with the same solution for targeted species were employed to evaluate the sampling efficiency of each species. The measured average concentrations for HF, HCl, HNO_2 , HNO_3 , and NH_3 gases sampled by the first DDS plates were 4.76, 1.87, 2.65, 0.38, and 8.89 $\mu\text{g}/\text{m}^3$, and by the second plates were 0.42, 0.15, 0.25, 0.07, and 0.62 $\mu\text{g}/\text{m}^3$, respectively. The measured average concentrations of the first and second plates for SO_2 gas were 1.17 $\mu\text{g}/\text{m}^3$ and the third plate was 0.11 $\mu\text{g}/\text{m}^3$.

Figure 5 shows the collection efficiencies of a DDS sampled by the first plates for HF, HCl, HNO_2 , HNO_3 and NH_3 gases, and that by the first and second plates for SO_2 gas. The sampling flow rate was set at 10 l/min as suggested by the DDS manufacture. It was seen that the average collection efficiencies for HF, HCl, HNO_2 , HNO_3 , SO_2 , and NH_3 gases are 91.2, 92.1, 90.6, 80.8, 90.5, and 93.0%, respectively. The lower collection efficiency of HNO_3 gas indicates that two plates are needed to increase the HNO_3 gas sampling efficiency. This is in accord with results of the atmospheric studies using denuder samplers. Dasch et al. (22) and Durham et al. (23) found that the HNO_3 gas was subjected to a high potential of sampling biases in field studies. The results of the authors' prior studies (24, 28) demonstrated that the atmospheric HNO_3 gas sampling errors were from both interfering N-containing gases and nitrate-containing particles and were higher than 40% if the ambient concentration was lower than 0.4 $\mu\text{g}/\text{m}^3$, hence two NaCl denuder tubes were suggested to minimize the error. In this study, tests via three NaCl coated plates showed that using two NaCl coated

plates could increase the collection efficiency to $91.1 \pm 2.3\%$ under typical cleanroom concentrations.

Coating the denuder plate with Na_2CO_3 may have higher efficiency for HNO_3 sampling (29), however, it is also suffered from high interference of the HNO_2 gas (24). But as also indicated by Fitz (29), NaCl -coated denuders were more effective in removing HNO_3 in ambient air than indicated by laboratory testing. Thus it is recommended that at least two NaCl coated plates must be used for sampling HNO_3 gas in a cleanroom to reduce sampling errors due to its relatively low concentration.

On the other hand, it may not necessarily require two Na_2CO_3 or citric acid coated plates to collect other gases if 90% of gas collection efficiency is acceptable. As a result, the assembly of the DDS train used in a cleanroom is recommended (as shown previously in Fig. 1(b)) that the first and second plates be coated with NaCl solution for the collection of HNO_3 and SO_2 gases, the third plate be coated with Na_2CO_3 solution for the collection of HF , HCl , HNO_2 , and SO_2 gases, while the fourth plate be coated with citric acid solution for the collection of NH_3 gas. In addition, particles are deposited on a Teflon filter. And the second stage of the Nylon filter collects the evaporated acid gases from the particles being collected on the first filter. Thus the DDS provides a further advantage of simultaneous sampling of inorganic gases and particles.

It is noted that the collection efficiency of HF gas by DDS was approximately the same as other gases, which was quite different from the low collection efficiency of the HF gas by the impinger sampler. This may be explained by the fact that the low collection efficiency of impinger sampler is probably caused by the high reactivity of HF with the glass materials to form the stable fluosilicic acid (H_2SiF_6) in the solution (11, 14), thus some HF could not be measured by the ion chromatography.

Suggestion of Sampling Conditions

Table 3 suggests the sampling conditions for the three samplers in measuring inorganic airborne molecular contaminants in a cleanroom. Both the impinger and the DDS sampling devices are recommended for clean room sampling of AMCs. The two impingers in series which contained 60 ml absorbent liquid volume in each impinger and at a sampling flow rate of 50 ml/min was suggested for the 24 hours sampling of inorganic acidic gases. And for NH_3 gas sampling, it was suggested that the gas flow rate can be up to 300 ml/min and the absorbent liquid volume be 30~60ml. Under the suggested sampling condition the impinger sampler has near complete sampling efficiency for HCl , HNO_2 , HNO_3 , H_2SO_4 , and NH_3 gases, but only 90% collection efficiency for HF gas if only one impinger is employed.

The assembly of 1st~4th plates of DDS is recommended to be coated in sequence with NaCl , NaCl , Na_2CO_3 , and citric acid solutions in series. Under the recommended sampling condition all inorganic basic and acidic gases can

Table 3. Suggest sampling conditions for measuring inorganic airborne contaminants in a cleanroom

Sampler	Targeted AMCs	Gas flow rate (ml/min)	Gas sampling volume (liter)	Sampling time (hrs)	Liquid volume of absorption or extraction (ml)	Comments
Silica gel tubes	Acidic AMCs (HF, HCl, HNO ₂ , HNO ₃ , H ₂ SO ₄)	Not applicable for cleanroom detection unless a better adsorbent of lower blank concentration is available				Higher blank concentrations
Impinger (two in series)	HF, HCl, HNO ₂ , HNO ₃ , H ₂ SO ₄	50	72	24	60	1. Higher collection efficiency for HCl, HNO ₂ , HNO ₃ , H ₂ SO ₄ , and NH ₃ gases (~100%), but can not separate gas from particles.
	NH ₃	300	432	24	30~60	2. Only 90% collection efficiency for HF gas at the first impinger
DDS (four plates in series)	Gases: HF, HCl, HNO ₂ , HNO ₃ , SO ₂ , and NH ₃ Particles: F ⁻ , Cl ⁻ , NO ₂ ⁻ , NO ₃ ⁻ , SO ₄ ²⁻ , and NH ₄ ⁺	10000 ^a	~14400	~24	10	1. Higher absorption efficiency for acidic and basic AMCs even at high flow rate of 10 l/min (>90%) 2. Simultaneous sampling of inorganic gas and particle contaminants 3. Lowest MDLs 4. Complex analytical procedures

^aNote: The sampling efficiency of a diffusion denuder can be further enhanced by reducing sampling flow rate (18).

have over 90% sampling efficiency. The DDS has a further advantage of sampling inorganic gas and particulate contaminants separately as compared to the impinger sampler. Besides, the DDS has lower MDLs than the impinger sampler. If the DDS can be operated at a lower gas flow rate, then the sampling efficiency of a DDS shall be further improved (18) but the MDLs will be higher.

Field Comparison of Inorganic Gas Concentrations by Impingers and DDS

Sampling conditions as suggested in Table 3 were used for the field measurements at the cleanroom photo area of a Taiwan semiconductor fab. The concentrations of all species measured from both impinger and the DDS samplers were obtained based on the sum of all collected plates. The sampling results made by impingers and DDS samplers were compared and shown in Fig. 6. The cleanroom concentrations of all inorganic AMCs were frequently above $1.0 \mu\text{g}/\text{m}^3$ except for the concentrations of HNO_3 , which has never been exceeded $1.0 \mu\text{g}/\text{m}^3$. The measured average concentration of NH_3 appeared to be the highest among all inorganic gases. And the most important inorganic acidic AMC in the cleanroom was HF.

One can see that many of the measured concentrations of HCl, HNO_2 , HNO_3 , and NH_3 gases from the DDS are lower than those from impinger sampler. This may be due to the fact that an impinger retains not only gases but also a considerable fraction of particulate matter and lead to higher measured gas concentrations as compared to the DDS which can separate the gas and particles well. It is well known that particles large than about $1 \mu\text{m}$ are captured by inertial mechanisms (30) and end up suspended in the liquid of impingers. The average concentrations in the $\text{PM}_{2.5}$ particles as measured by the DDS sampler for F^- , Cl^- , NO_3^- , SO_4^{2-} , and NH_4^+ were 0.16, 2.11, 0.41, 0.66, and $3.46 \mu\text{g}/\text{m}^3$, respectively. On the other hand, the results of one-way ANOVA indicated no significant difference ($P > 0.05$) for the concentrations of HF species made by the DDS and impinger sampler. This may be due to only a very small fraction of F^- is existed in the particulate matter.

And for the sulfur sampling, because the impinger sampler is targeted for H_2SO_4 sampling while the DDS sampler can differentiate SO_2 from the SO_4^{2-} collected on the filter, therefore the total concentration of SO_4^{2-} measured by IC is compared in Fig. 6(e). That is, the SO_4^{2-} concentrations taken by the DDS were made by the sum of SO_2 gas collected by denuder plate and the SO_4^{2-} particles collected by the filters. One can see from Fig. 6(e) that the SO_4^{2-} collected by the impinger sampler and the DDS sampler show very good agreement. This indicates that the measured H_2SO_4 concentration for impinger sampler is in fact the concentrations of all sulfur oxides species presented both in gas and solid phases.

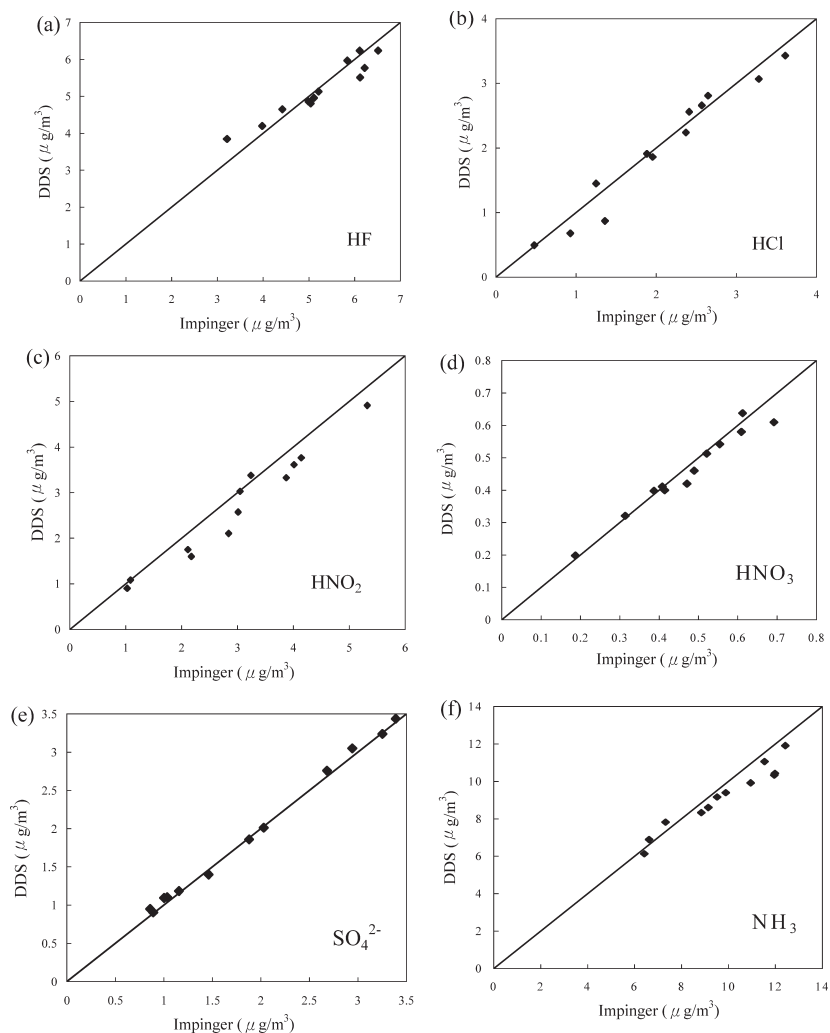


Figure 6. Comparison of field measurement data by impingers and DDS samplers under optimal sampling conditions listed in Table 3: (a) HF, (b) HCl, (c) HNO₂, (d) HNO₃, (e) SO₄²⁻ and (f) NH₃.

CONCLUSIONS

This study has evaluated the sampling efficiencies of silica gel tubes, impingers and DDS for the measurements of trace amounts of inorganic gases in a typical cleanroom environment. The results show that the SUPELCO and SKC silica gel tubes had higher sampling interferences due to their high values of blank concentrations. Thus silica gel tubes are not recommended unless new adsorbents of low blank AMC concentrations are

discovered. On the other hand, the impingers and DDS samplers have been proved to be more suitable for sampling acidic and basic AMCs in clean rooms. The 24 hours sampling conditions of the impinger is recommended at 50 ml/min sampling flow rate via absorbent liquid volume of 60 ml for HF, HCl, HNO₂, HNO₃, and H₂SO₄ gases sampling. For NH₃ gas sampling, the sampling flow rate can be further increased to 300 ml/min and the absorbent liquid volume be reduced to 30 ml. The MDLs of all species for impingers and DDS samplers are lower than the maximum allowable AMCs concentrations suggested by ITRS. Under optimal sampling conditions, the performance of an impinger sampler was much closer to that of DDS.

The ammonium species both presented in the gas and liquid phases have been found as dominant AMCs in the cleanroom environment. And although the sampling efficiency of NH₃ via DDS was higher than 90%; however, it was also indicated (31) that under high NH₃ loading the phosphoric acid is a better absorbing agent than citric acid. In addition, there are also possible errors on the ammonium (NH₄⁺) measured from the particulate phase since the back up Nylon filter might not completely collect the evaporated ammonia gas from the Teflon filter. Therefore, further studies should be conducted to evaluate the sampling and analytic accuracy of ammonium species.

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