

Determination of Water Soluble Trace Gases in Ambient Air by Condenser-type Diffusion Denuder Coupled Ion Chromatography

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An automated method is developed for simultaneous determination of water soluble gases at parts per trillion level in the environmental air. The method involves temperature-humidity control of sample air using a thermostated humidifier, collection of analyte gases by condenser-type effluent diffusion denuder and subsequent effluent analysis by ion chromatography. The detection limits (3σ) of the method for CH_3COOH , HNO_2 and SO_2 gases are 0.022, 0.019 and 0.009 ppbv, respectively. The precisions range from 0.3 to 3.0% RSD. The method has been successfully applied to urban air analysis and some results for nitrous acid and SO_x in Seoul air are presented.

Introduction

Demands for the determination of trace gases in ambient air are high in various fields; acid rain, aerosol chemistry, microchip fabrication clean room air quality control are among the examples. In many cases, simultaneous monitoring of several species at low ppb to sub-ppb level is preferred. For this purpose gas collection in solution and subsequent solution analysis using multi-element analytical technique such as ion chromatography have been most frequently used procedures.¹⁻⁶

Diffusion scrubber (DS)^{1,2,7-11} and wet effluent diffusion denuder (WEDD)^{3-5,12} have been adopted for the collection of water soluble gases. DS is easier to fabricate and use than WEDD, but it suffers from low collection efficiency even at moderate gas flow rate. Because of this, periodic calibrations using gas standards are mandatory for accurate monitoring, but this is a non-trivial job. On the other hand, WEDD collects gases quantitatively, and thus it does not require gas standard for calibration. However, WEDD also has few drawbacks. First of all, fabrication and operation require delicate skills. It also needs high effluent flow rate to keep denuder surface wet and to minimize effluent flow variation caused by the change of sample air humidity.^{3,4} High effluent flow leads to low concentration factor for analyte gas and this is less desirable in trace gas monitoring.

Lately, a new wet effluent denuder called condenser-type diffusion denuder (CDD) was developed and successfully applied to trace gas monitoring in semiconductor clean room air monitoring.¹³ Basic design and operating principles are similar to conventional WEDDs. In CDD, wet effluent is *in-situ* generated at denuder surface by cooling denuder surface. Thus, CDD is simpler in design, and easier to fabricate and use than conventional WEDD. It can run with small volume of effluent; CDD can operate at an effluent flow of as low as $10 \mu\text{L}/\text{min}$. However use of CDD is limited to humidity and temperature controlled air and this is a serious drawback.

In the present work, we have extended the CDD to ambient air by introducing a temperature-humidity control unit upstream of CDD. The unit consists of a Nafion membrane

tubing humidifier and thermostated copper tubing. Construction details and analytical performances are described. Seoul air monitoring results for HNO_2 and SO_x are presented as well.

Experimental Section

Reagents and solution standard. Deionized water ($18.3 \text{ M}\Omega \text{ cm}$ resistivity at 25°C) was obtained from Milli-Q water purification system. All reagents used in this study are of analytical grade. Dilute working standard solution were prepared by serial dilution of 1,000 ppm stock standards (Dionex Co. Sunnyvale, CA, USA) and stored in polyethylene containers.

Analysis system configuration. The arrangement in Figure 1 was used for all experiments.

This system consists of three main components; temperature humidity control unit (THCU), condenser-type diffusion denuder gas sampler and ion chromatography unit. The role of THCU is to adjust temperature and humidity of sample gas to prefixed values. Instruction details for THCU fabrication are described below. When standard or sample gas

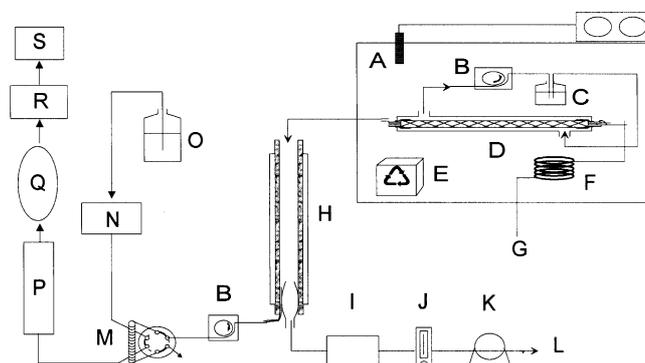


Figure 1. Schematic diagram of CDD/IC system. A: thermocouple, B: peristaltic pump, C: D. I. water, D: Nafion humidity controller, E: heater & fan, F: copper tubing, G: air inlet, H: CDD, I: pulse damper, J: flow meter, K: air pump, L: air outlet, M: injection valve, N: HPLC pump, O: eluent, P: IC column, Q: suppressor, R: detector, S: data analysis system

enters THCU, its temperature and humidity are adjusted to 40 °C and 85%. The gas is introduced to CDD upward by pumping with an air pump. The condensed effluent flowing down the glass column of CDD is collected at sample receptacle and aliquots are aspirated to the injection valve of ion chromatography system (Alltech 325 HPLC Pump, 350 conductivity detector, Dionex ASRS-1) using a peristaltic pump (Model MP3, Gilson). The sample flow rate was controlled using a flow controller at the inlet of the air pump.

The chromatographic conditions were as follows; 25 mM NaOH as an eluent, flow rate of 1.0 mL/min and a Dionex AS4A-SC column. The change of the eluent strength by the input of CO₂ during measurement was prevented by helium sparging. Under these conditions, the peak of the most retained species, SO₄²⁻ was eluted *ca.* 15 minutes. However, in real air monitoring, 30 min sampling interval was used so that memory effect of CDD was minimized.

Thermostat system. For the effective isolation from the room air, a low heat capacity acryl (10 mm thickness) was used and shaped into a box (53 cm×53 cm×53 cm). The thermostat system includes three subunits; (1) the heating assembly for heat generation, (2) heater with a fan for fast thermal equilibration, (3) thermocouple for accurate detection of exit stream. To enhance the heat capacity of the thermostat, several aluminium blocks (5 cm×10 cm×0.5 cm) were placed inside the box. For the fast thermal equilibrium, the air sample was introduced to the CDD through the copper tubing (1 cm o.d., 10 m long) in the thermostat at 40 °C. Typical sample gas flow rate was 3 L/min.

Nafion membrane-based humidifier. In order to control sample air humidity, a Nafion membrane based humidifier was used. Nafion humidifier is commercially available (VICI, USA), but in this study our own version was used. The humidifier schematics are shown in Figure 2.

A piece of Nafion membrane tubing (2.8 mm o.d.×61 cm long) is housed in glass tube (12 mm i.d.×61 mm long). Both ends of Nafion are connected to polyethylene tubing (4.0 mm i.d.) with an aid of Teflon tape. Nafion shows highly hydrophilic characteristics and permits rapid transport of water vapor because Nafion is a fluorocarbon polymer with pendant groups bearing sulfonic acid functionality. This is the reason why Nafion membrane tubing has been used commercially as a gas dryer for the reduction of water vapor in ambient air. The membrane withstands up to 160 °C in temperature and 560 kPa in pressure. The equilibrium of

hydration can be completed within 0.2 second in Nafion membrane due to the hydrophilic characteristic. The sulfonic acid functional group restricts the transport of acidic analytes in the air. Therefore, it can act as an effective humidifier without loss of atmospheric acidic gases such as organic acids, SO₂ and HNO₂. The gas sample flows continuously through the Nafion tube (G), while D. I. water simultaneously pass through the outside of the tube (G) with counter direction. In order to prevent condensation of water vapor caused by temperature change of the humidified air sample, the humidifier was placed in a thermostat.

Adjusting relative humidity. The relative humidity of the gas was adjusted by adding a variable amount of steam to dry N₂ in a glass mixing chamber. Super-heated steam was made by pumping a given amount of deionized water through a stainless tubing coiled with nickel-chromium wire and maintained about 150 °C. The effluent from the mixing chamber passed through the CDD and condensed on the surface of the CDD, which was cooled by water at 2.0±0.1 °C using a circulator (coolman pal C-302, Sibata). The air sampling rate was 3 SLPM, in most cases.

Condenser-type diffusion denuder (CDD). For the collection of trace gases a tubular-type CDD was used. Its basic design and operating principles are the same as conventional tubular wet effluent diffusion denuder (WEDD).^{3,4} CDD consists of a glass tubing with the scrubber liquid flowing down the interior wall of the tube and being collected at the bottom. The tubing (6.0 mm i.d.×1.2 mm wall×500 mm long) is jacketed with an acrylic outer tube (20 mm i.d.×450 mm long) through which coolant flows so that water vapor from sample air condenses on the tubing interior surface and serves as scrubber liquid. CDD is easier to fabricate and to operate than conventional WEDD. Detailed design and fabrication instructions will be described elsewhere.¹³

Standard gas generation. CH₃COOH and SO₂ standard gases were generated from a permeation device (VICI Metronics, Santa Clara, CA). The emission rates of SO₂ and CH₃COOH were 290 ng/min and 36,000 ng/min, respectively. HNO₂ gas was generated according to the method of Lee *et al.*¹⁴ Briefly, HNO₂ generation was based on the permeation of nitrous acid into dry air flowing through a PTFE tubing immersed in a mixed solution of NaNO₂ and H₂SO₄. The gas generation rates were determined by impinger absorption and subsequent ion chromatographic determination. Working standard gases of low concentration were made by further dilution with dry nitrogen gas.

Results and Discussion

Optimization and performances of temperature humidity control unit. Before introducing to CDD, the sample air should have constant temperature and humidity. Otherwise, the amount of water vapor condensing at denuder surface will vary and effluent flow variation will be resulted. When this happens, air gas concentration shall not be portionally reflected in effluent solution making it impossible to determine gas concentration from solution analysis.

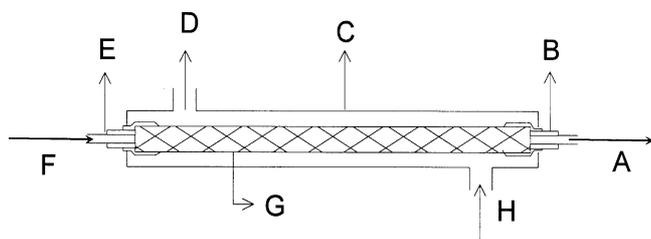


Figure 2. Schematic diagram of Nafion humidity controller. A: air outlet, B: tygon tubing, C: glass tubing, D: D. I. water outlet, E: PE tubing, F: air inlet, G: Nafion tubing, H: D. I. water inlet

The performance of the thermostat was evaluated by checking the stability of outflow air temperature upon the variation of incoming air temperature over a range from $-20\text{ }^{\circ}\text{C}$ to $40\text{ }^{\circ}\text{C}$, which most likely covers year round variation of air temperature in Korea and almost any regions. The thermostat was set at $40\text{ }^{\circ}\text{C}$ and air flow rate was set at 3 liters/min in the experiment. Over the tested range, outflow temperature varied within measurement uncertainty of $\pm 0.5\text{ }^{\circ}\text{C}$. At the air flow of 3 L/min which is maintained throughout this work, the temperature of air flowing out from the thermostat was constant at $40\pm 0.5\text{ }^{\circ}\text{C}$. Regardless of incoming air temperature over a range from $-20\text{ }^{\circ}\text{C}$ to $40\text{ }^{\circ}\text{C}$, $1\text{ }^{\circ}\text{C}$ difference corresponds to about 1 torr of water vapor pressure for 85% relative humidity (RH) of $40\text{ }^{\circ}\text{C}$ air and calculation shows that effluent outflow variation caused by this difference is less than 5%.

Humidity is another factor to determine effluent flow rate. So that extreme weather condition is covered, controlled humidity must be higher than potential maximum humidity. In case that air humidity exceeds a set value, a problem of water vapor condensation within the system may arise. In the course of experiment we find 85% RH to be most appropriate. When RH is further increased, condensation often occurs between CDD and the unit. Additionally it requires longer Nafion tubing, which will not only create air pressure drop/buildup problem, but increase the possibility of analyte gas loss. At the present experimental conditions, 60 cm Nafion tubing (2.8 mm o.d., 60 cm effective length) found to be adequate. Pressure drop/buildup was unnoticeable with this length. Performance of this humidifier was evaluated at two different air temperatures, $25\text{ }^{\circ}\text{C}$ and $40\text{ }^{\circ}\text{C}$ with RH 0 to 85% by measuring the amount of condensed effluent. The condensate amount was determined in batch mode; the effluent liquid following down the denuder was overaspirated to a tared collection PE bottle for a preset time interval and then the bottle was weighed again. The results are shown in Figure 3. The condensed amount increases slightly as air temperature and RH do. The increase is about 5% for a change from 0% to 85% RH and about 1% from $25\text{ }^{\circ}\text{C}$ to $40\text{ }^{\circ}\text{C}$. Correction could be made by monitoring the changes, but for most environmental analysis this magnitude of error might be acceptable.

Denuder performance. The collection efficiencies of the CDD for CH_3COOH , HNO_2 , SO_2 and NH_3 were determined

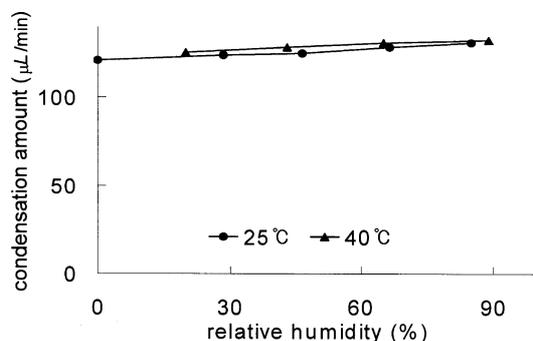


Figure 3. Dependences of condensation amount on the relative humidity of input air at $25\text{ }^{\circ}\text{C}$ and $40\text{ }^{\circ}\text{C}$.

Table 1. Precisions of This Method for CH_3COOH , HNO_2 , SO_2 at Various Concentrations

	standard gas concentration					
	low concentrations			high concentrations		
	CH_3COOH	HNO_2	SO_2	CH_3COOH	HNO_2	SO_2
n	14	17	14	16	16	21
mean (ppbv)	0.35	0.23	0.14	7.0	22	49
SD (ppbv)	0.0074	0.0061	0.0031	0.11	0.28	0.14
RSD (%)	2.1	2.6	2.2	1.6	1.3	0.29

n : number of determination.

using two different methods; serial denuder data and liquid-phase calibration. The two results agreed within experimental errors. The collection efficiencies measured by the former method were 98.4%, 97.0%, 97.0% and 0% for CH_3COOH , HNO_2 , SO_2 and NH_3 , respectively. Almost complete loss of ammonia should be occurred in the Nafion membrane humidifier. There are sulfonic acid functional groups in the Nafion which should serve as an excellent sink of any alkaline gases. Therefore, ammonia or any alkaline gases can not be determined with this system.

Analytical figures of merits. The measurement precisions and limits of detection (LOD) were evaluated by replicate analyses of standard gases of two different concentration. As shown in Table 1, the relative standard deviation varies from less than 0.3% to 3.0%.

LODs are estimated to be 0.022 ppbv, 0.019 ppbv, 0.009 ppbv for CH_3COOH , HNO_2 and SO_2 , respectively. Here LOD is defined by three times of the standard deviations for low concentration measurement.

Due to the lack of certified standard air for trace impurity gases, accuracy of the method cannot be evaluated directly. However, analysis of air spiked with standard gas gave near quantitative recoveries. In addition, simultaneous monitoring of SO_2 in Seoul air by the present method and by DS-IC method were in good agreement (Figure 4).

The calibration curve was made by the analysis of standard gases which had been prepared by serial dilutions using high purity nitrogen. The calibration curves were linear over the range of 0-50 ppbv; The regression coefficients, R^2 were 0.9981, 0.9985 and 0.9979 for CH_3COOH , HNO_2 , and SO_2 , respectively. In as much as the above calibration range, most ambient air concentration might be encompassed, so no fur-

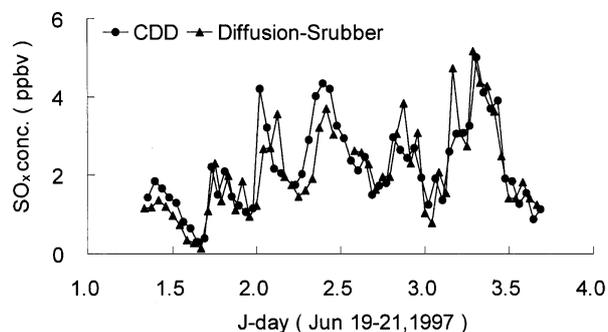


Figure 4. Temporal variation of SO_x gas in Seoul air monitored by CDD-IC and DS-IC method.

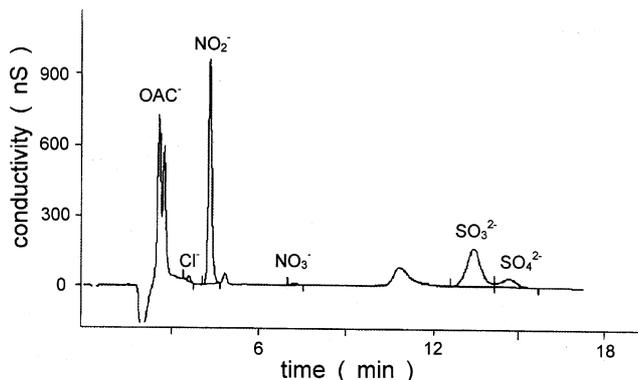


Figure 5. Typical ion chromatogram for Seoul air.

ther work was made to cover higher concentrations. However, actual linear range should extend to much higher concentration because the concentrations of ionic species in effluent solution, which are produced when gases are dissolved, are not only well below the gas equilibrium concentrations, but also well within linear dynamic range of ion chromatographic measurements.

Application to Seoul air. This method has been successfully applied for continuous and simultaneous measurement of atmospheric acidic gases at Seoul. Figure 5 is a typical chromatogram from Seoul air.

There are four major peaks which were identified to represent for acetate, nitrite, sulphite and sulphate from left. There are few minor peaks but they are neither identified nor determined in the present study. In this chromatographic condition formate eluates with acetate and thus they are not determined. Separation of sulphate from sulphite is excellent, implying that their interconversion reaction does not occur during separation. However we combined both peaks and the data are presented as SO_x ($\text{SO}_2 + \text{SO}_3$). Interestingly, chromatograms from CDD shows much more pronounced sulphite peak than those from conventional diffusion denuder or scrubber and this suggests that sulphite oxidation is slower in CDD. This can be explained by the difference of denuder effluent temperatures; CDD has effluent temperature of about 2 °C, which is at least 20 °C lower than the conventional one. Perhaps differentiation of sulphite and sulphate is possible with CDD collection method and no further study was made in the present work. In Figure 6 are HNO_2 monitoring results for two days, showing characteristic diurnal

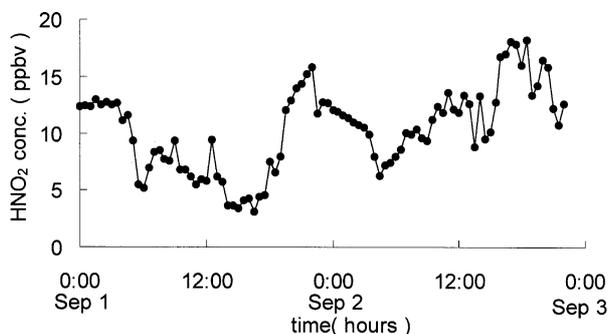


Figure 6. HNO_2 gas concentration in Seoul air measured by the present method (Sep 1-3, 1997).

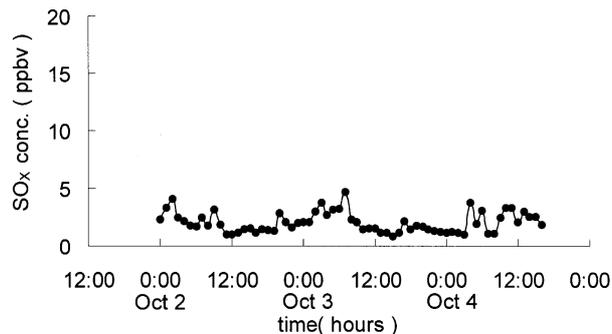


Figure 7. SO_x gas concentration in Seoul air measured by the present method (Oct 2-4, 1997).

variation of high at night and low during daytime which is caused by photochemical decomposition. In comparison to previous monitoring data,¹⁴ present data are 2-3 times elevated and this is most likely caused by increased NO_x emission from automobile.

SO_x monitoring results are depicted in Figure 7. Both daily and long term variations for SO_x are opposite from those of HNO_2 . SO_x concentration peaks at night and bottoms during the days. And this variation pattern is related to local emission from household heating which occurs mostly at night during fall season. SO_x concentration varies over a range of 1 to 5 ppbv and this is considerably smaller than late 1980's. Obviously recent decrease in SO_x is attributed to the progressive enforcement of air pollution control over the last fifteen years.

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