Measurement of Atmospheric Sulfuric Acid Particles Using Diazomethane Methylation

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Abstract

A method of measurement of atmospheric sulfuric acid particles was developed by modifying a method proposed by Penzhorn and Filby (1976). This method used an assembly for the generation of diazomethane and methylation of sulfuric acid. The minimum detection of H_2SO_4 was 3 ng. The amount of sulfuric acid particles generated in a test chamber determined by this method agreed well with those by barium chloranilate and titration methods. On field sampling gaseous NH_3 which converted H_2SO_4 to $(\text{NH}_4)_2\text{SO}_4$ was eliminated by using an NH_3 denuder.

In Tokyo, in August of 1981 the concentrations of sulfuric acid particles were 0.3–4.7 $\mu\text{g m}^{-3}$. In Sapporo they were 0.2–1.3 $\mu\text{g m}^{-3}$ between May and July in 1981, and 0.1–1.4 $\mu\text{g m}^{-3}$ between November in 1981 and January in 1982 respectively. The cumulative fraction by weight of sulfuric acid particles less than 2.1 μm in diameter was 90%. The ratio of $\text{H}_2\text{SO}_4/\text{SO}_4^{2-}$ increased with decreasing particle diameter.

1. Introduction

Since atmospheric sulfuric acid particles are responsible for their effect on human health and acid rain, numerous methods have been developed for their determination such as barium chloride vapor-deposited thin film method, extraction into organic solvent, gas phase titration, infrared spectroscopy, acid-base indicator, sublimation, and titration. Of these methods, a vapor-deposited thin film method developed by Bigg *et al.* (1974) can determine individual sulfuric acid particles effectively. However, it requires much expertise and labor for its operation. Further,

other methods have not been tested at length in the field. According to the evaluation by Appel *et al.* (1980), even with the popular extraction with benzaldehyde and titrimetry the recovery of sulfuric acid was not quantitative.

In this report, the methylation of H_2SO_4 by means of diazomethane proposed by Penzhorn and Filby (1976) is modified to be applicable to the field measurement of sulfuric acid particles.

2. Diazomethane method

Penzhorn and Filby (1976) washed off H_2SO_4 with ether solution of diazomethane from an

Fig. 1 An assembly for the generation of diazomethane and methylation of sulfuric acid.

- A: Teflon bag B: Rotameter
C: Impinger D: Bubbler
E: Impinger F: Pump

aerosol collection filter, and dimethyl sulfuric acid thus produced was detected by FPD-GC. However, since diazomethane is noxious and explosive, the following simple procedure is adopted in the present study. Figure 1 shows an assembly for the generation of diazomethane and methylation of sulfuric acid. An impinger C contains 10 ml of ether, a bubbler D contains a mixture of 10 ml of diethylene glycol and 1 to 2 ml of water which dissolves 5 to 6 pellets of potassium hydroxide, and an impinger E contains 10 ml of ether and a filter on which H_2SO_4 particles are collected.

On introducing N_2 gas with a flow rate of 20 to 40 ml min^{-1} through the assembly while 5 ml of 1% (w/w) acetone solution of N-methyl-N-nitro-N-nitroso guanidine (MNNG) is placed into D, the diazomethane gas is immediately liberated and methylation is conducted in E. At equivalence point color of the ether solution in E turns yellow. When no yellow color does not develop even at 10 minutes after the addition of MNNG, further MNNG solution is added into D. Diethyl sulfuric acid is added to the methylated solution in E as an internal standard, and then the solution is concentrated to 100 μl on a water bath at 40°C. The concentrated solution is subjected to flame-photometric gas chromatographic analysis.

Table 1 shows the operating condition of the flame-photometric gas-chromatograph (FPD-GC), and Fig. 2 shows a calibration curve for dimethyl sulfuric acid.

For the calibration 0.5–2 μl of 2–10000 ppm ether solution of dimethyl sulfuric acid was injected into FPD-GC by means of a micro-

Table 1 Operating condition of gas chromatograph.

Column:	Glass column, 3 mm dia., 1.5 m length
Column packing	
Liquid phase:	Ucon oil 50 HB 2000, Wt 15%
Support:	Uniport B, Mesh 60/80
Condition of GC-FPD	
Injection temperature	180°C
Column temperature	80°C
Detector temperature	170°C
Flow rates	
Carrier gas (N_2)	80 ml/min .
H_2	160 ml/min .
Air	90 ml/min .
Retention time	
$(\text{CH}_3)_2\text{SO}_4$	12 min.
$(\text{C}_2\text{H}_5)_2\text{SO}_4$	23 min.

Fig. 2 Calibration curves for dimethyl sulfuric acid $((\text{CH}_3)_2\text{SO}_4)$ (Abscissa is amount of $(\text{CH}_3)_2\text{SO}_4$ in ngS).

syringe. The amount of sulfur contained in each injection was ranged from 1.3 to 6520 ng at 13 different levels. At each level three to five samples were taken.

The detection limit of H_2SO_4 was 3 ng. Then if the H_2SO_4 particles are sampled on a filter for 3 hours at flow rate of 20 l min^{-1} ,

Fig. 3 Methylation efficiency (E).

the extract of the sampled filter is concentrated to 100 μ l, and 5 μ l of the concentrated solution is injected into the gas chromatograph, the minimum measurable concentration of H_2SO_4 particles in the air is $0.02 \mu\text{g m}^{-3}$.

1 to 10 μ l of H_2SO_4 solution of 3.6 to 18 N in concentration is soaked to a quartz fiber filter and methylation is conducted. As shown in Fig. 3, with H_2SO_4 amount of less than 500 μg methylation efficiency is greater than 95%. If the sample contains moisture or methanol, the reactions

gives negative interference, so that it is necessary for the sample to be dessicated before the methylation.

The ambient air is sampled on two quartz fiber filters of 4.7 cm in diameter simultaneously and H_2SO_4 in the aerosol is determined by the methylation technique as shown in Table 2. The concentrations of H_2SO_4 aerosols in I and II series in Table 2 indicate that the difference of the simultaneous measurements is within 10%. In the field measure-

Table 2 Comparison of two parallel measurements of H_2SO_4 particles (Flow rate 20 l min^{-1} , Sampling time 3 hours)

Run No.	$\text{H}_2\text{SO}_4 (\mu\text{g m}^{-3})$	
	I	II
1	0.52	0.54
2	0.81	0.91
3	0.80	0.88

Fig. 4 Comparison of diazomethane method with barium chloranilate method ($\circ$) and titration method ($\bullet$) for sulfuric acid particles generated in a test chamber.

ment, just after sampling, each aerosol collected quartz fiber filter is packed in a plastic case of 5 cm in diameter and 0.5 cm in thickness, and dessicated before the methylation.

3. Comparison of diazomethane method with barium chloranilate and titration methods

Sulfuric acid aerosol generated by using an atomizer in an acrylate chamber 700 l in volume is simultaneously sampled on two or three quartz fiber filters and determined by diazomethane method for H_2SO_4 , barium chloranilate method for SO_4^{2-} , and titration method for H_2SO_4 (Gran, 1952). Figure 4 indicates the close agreement of the amounts obtained by the three methods.

4. Interferences

(1) Dimethyl sulfate ($(\text{CH}_3)_2\text{SO}_4$)

Lee *et al.* (1980) found that the amounts of $(\text{CH}_3)_2\text{SO}_4$ on fly ash and coal ash are 100 and $10\text{--}40 \mu\text{g g}^{-1}$ respectively. According to our measurement they are $7 \mu\text{g g}^{-1}$ for coal ash, $300 \mu\text{g g}^{-1}$ for coal soot and $8000 \mu\text{g g}^{-1}$ for oil ash. Therefore, usually the presence of $(\text{CH}_3)_2\text{SO}_4$ does not interfere H_2SO_4 measurement. The three day air sampling on the campus of Hokkaido University did not detect

$(\text{CH}_3)_2\text{SO}_4$.

(2) NH_3

Since atmospheric NH_3 would react with H_2SO_4 particles to produce $(\text{NH}_4)_2\text{SO}_4$, the NH_3 denuder developed by Hara *et al.* (1982) was attached to the air inlet of the particle collection filter.

(3) $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4

Aqueous solution with proper concentration of $(\text{NH}_4)_2\text{SO}_4$ or NH_4HSO_4 is dropped onto a quartz fiber filter with a microsyringe. The filter is dried in a dessicator and the sample is analyzed by the diazomethane method.

No interference of $(\text{NH}_4)_2\text{SO}_4$ was found in the H_2SO_4 measurement, but methylation of NH_4HSO_4 produced $(\text{CH}_3)_2\text{SO}_4$ with an efficiency 85-95%. Therefore, the H_2SO_4 and NH_4HSO_4 particles are defined as H_2SO_4 particles in the following sections.

5. Size distribution of H_2SO_4 particles

A combination of an Andersen sampler (Kanomax Inc. Model 5600) and a diffusion battery is used for the measurement of size distribution of H_2SO_4 particles. The diffusion battery is of plate type and its structure and operating condition are as follows. Length: 56 cm, width: 20 cm, spacing between plates: 1 mm, channel numbers: 20, and total air flow rate: 20 l min^{-1} . The theoretical efficiency of particle penetration had been obtained by De-Marcus and Thomas (1952), to agree well with the experimental one measured by using an electrical aerosol analyzer. The diameter of 50% particle penetration is found to be $0.02 \mu\text{m}$.

6. Results and Discussion

During August 4 to 13 in 1981 aerosol sampling was made on a roof of a six-story building of the National Institute of Public Health (IPH) located in the downtown of Tokyo. Figure 5 shows the concentration of atmospheric H_2SO_4 particles. High concentrations of $4.7 \mu\text{gm}^{-3}$, $3.9 \mu\text{gm}^{-3}$ and $3.0 \mu\text{gm}^{-3}$ were measured in the daytime of August 9, 10 and 12 respectively. During the sampling period temperature, relative humidity, and wind velocity were $24\text{--}28^\circ\text{C}$, $50\text{--}78\%$, and

Fig. 5 Concentration of atmospheric sulfuric acid particles in Tokyo in August, 1981.

Fig. 6 Concentration of atmospheric oxidant at the Minato-ku air pollution observation station in Tokyo in August, 1981.

$1.5\text{--}5.0 \text{ m sec}^{-1}$, respectively. Figure 6 shows the concentration of atmospheric oxidants measured at the Minato-ku air pollution observation station near IPH. On August 9 the oxidant concentration rose to 70-83 ppbv in the afternoon.

Therefore, high concentration of H_2SO_4 particles on August 9 seemed to be due to the photochemical conversion from SO_2 in the atmosphere. On the other hand, oxidant concentration on August 10 was not so high, and on August 12 it was the lowest in the period, so that it seems that high concentrations of H_2SO_4 particles on these days were not due to photochemical production. Besides photochemical production, H_2SO_4 particles are also emitted directly in the air from diesel exhaust and heavy oil combustion furnace. On August 10 and 12 the wind directions were SW and SE, respectively, and wind speed was 2 m sec^{-1} . As there are heavy industrial areas in the southwest and southeast of Tokyo known as Keihin and Keiyo industrial areas, respectively, high concentration of H_2SO_4 on these days seemed to be due to the advection of H_2SO_4 particles emitted primarily by industrial activity in those areas.

Aerosol sampling was also made in Sapporo on a roof of our laboratory building, which is

Table 3. Concentration of atmospheric sulfuric acid particles in Sapporo from May to July, 1981.

Date	Time	H ₂ SO ₄ ($\mu\text{g m}^{-3}$)
May 1	14:30-17:00	1.3
May 2	11:00-14:00	0.9
	14:00-17:00	0.9
May 4	14:00-17:00	1.0
Jun. 8	5:30-12:00	1.1
Jun. 22	12:00-20:15	0.5
Jun. 23	12:30-20:30	0.9
Jul. 3	8:15-20:15	0.3
Jul. 4	8:20-20:00	0.5
Jul. 7	9:00-21:30	0.7
Jul. 9	10:30-17:30	0.3
Jul. 10	12:45-20:30	0.2

26 m above the ground, in the university campus from May to July in 1981 and from November in 1981 to January in 1982. The concentration of H₂SO₄ particles in summer (May–July) shown in Table 3 ranged from 0.2 to 1.3 $\mu\text{g m}^{-3}$. Temperature and relative humidity during the sampling were 10.7–20.5°C and 54–90% respectively. High concentrations of H₂SO₄ particles as observed May 1, May 4 and June 8 were not correlated with high temperature and relative humidity.

The arithmetic mean concentration of H₂SO₄ particles was 0.7 $\mu\text{g m}^{-3}$.

The H₂SO₄ concentration in winter (Nov., 1981–Jan., 1982) in Sapporo is shown in Fig. 7, which also shows the concentrations of sulfate, nitrate, chloride, ammonium, and their ionic balance ($[\text{H}^+] + [\text{NH}_4^+] - 2[\text{SO}_4^{2-}] - [\text{NO}_3^-] - [\text{Cl}^-]$). The concentration of H₂SO₄ particles ranged from 0.1 to 1.4 $\mu\text{g m}^{-3}$, and its arithmetic mean was 0.5 $\mu\text{g m}^{-3}$, which was a little lower than that in summer. Sulfuric acid was comprised of sulfate by about 20% in mass. The temperature and relative humidity during the measurement were $-5 \sim 7^\circ\text{C}$ and 50–90% respectively, and high concentration of H₂SO₄ particles did not correlate with high temperature and humidity. The negative deviation from the ionic balance was observed in most cases, which suggested the presence of other cations such as Na⁺ and Ca²⁺. On the other hand, the positive deviation, which presupposed the presence NH₄HSO₄, was seldom observed.

Size distributions of H₂SO₄ and sulfate particles were measured in Sapporo from Dec. 21 to 29, 1981 and from Jan. 16 to 23, 1982. As the distribution pattern in the two cases were similar, only the former is shown in Figs. 8 and 9. H₂SO₄ particles (Fig. 8) had the highest

Fig. 7 Concentrations of atmospheric sulfuric acid particles (H₂SO₄), sulfate (SO₄²⁻), nitrate (NO₃⁻), chloride (Cl⁻), ammonium (NH₄⁺) and their ionic balance ($[\text{H}^+] + [\text{NH}_4^+] - 2[\text{SO}_4^{2-}] - [\text{NO}_3^-] - [\text{Cl}^-]$) in Sapporo from November, 1981 to January, 1982.

Fig. 8 Size distribution of atmospheric sulfuric acid particles in Sapporo. Sampling period was from December 21 to 29, 1981. M denotes the concentration of sulfuric acid particles ($\mu\text{g m}^{-3}$) and D is the diameter of the particles.

Fig. 9 As in Fig. 8 but for sulfate.

peak between 0.7 and 1.1 μm in diameter, whereas sulfate particles (Fig. 9) had the peak between 4.7 and 5.8 μm . Cumulative fractions by weight of H_2SO_4 and sulfate particles less than 2.1 μm in diameter were 90 and 60% respectively. This means that most H_2SO_4 particles were contained in the fine particle regime less than 2 μm in diameter. Generally it is thought that the fine particles are generated from combustion or formed by atmospheric reaction. Since in this period no photochemical reaction seemed to occur, it is presumed that H_2SO_4 particles were directly discharged from combustion sources. In the atmosphere, water-soluble inorganic particles less than 2 μm in diameter may be composed of $(\text{NH}_4)_2\text{SO}_4$, NH_4HSO_4 , NH_4NO_3 and NH_4Cl as well as H_2SO_4 because they are produced

Fig. 10 Variation of the ratio of $\text{H}_2\text{SO}_4/\text{SO}_4^{2-}$ with particle diameter.

○ : Sampling period was from Dec. 21 to 29, 1981.

● : Sampling period was from Jan. 16 to 23, 1982.

in the combustion furnace or in the atmosphere (Whitby, 1978). If this is true, then by collecting the particles less than 2 μm in diameter by means of a cascade impactor and by analyzing the amount of H_2SO_4 , SO_4^{2-} , NH_4^+ , NO_3^- and Cl^- , we can estimate the amount of NH_4HSO_4 from the difference of these ionic balance ($[\text{H}^+] + [\text{NH}_4^+] - 2[\text{SO}_4^{2-}] - [\text{NO}_3^-] - [\text{Cl}^-]$) in which $[\text{H}^+]$ is determined from the amount of H_2SO_4 measured by the diazo-methane method.

Figure 10 shows the variation of the ratio of $\text{H}_2\text{SO}_4/\text{SO}_4^{2-}$ with particle diameter in the two measurements. The ratio increased with decreasing particle diameter, although it had a dip at 0.5 μm .

In conclusion, by using the present method, atmospheric sulfuric acid particles can easily be measured. However, as the method cannot distinguish NH_4HSO_4 from H_2SO_4 , we may overestimate the amount of H_2SO_4 particles in the field.

References

- Appel, B.R., S.M. Wall, M. Haik, E.L. Kothny and Y. Tokiwa, 1980: Evaluation of techniques for sulfuric acid and particulate strong acidity measurements in ambient air. *Atmos. Environ.*, **14**, 559-563.
- Bigg, E.K., A. Ono and J. Williams, 1974: Chemical tests for individual submicron aerosol particles. *Atmos. Environ.*, **8**, 1-13.
- De-Marcus, W. and J.W. Thomas, 1952: Theory of a Diffusion Battery. USAEC Report ORNL-1413, Oak Ridge National Laboratory, Oct. 16.
- Gran, G., 1952: Determination of the equivalence point in potentiometric titrations. *Analyst*, **77**, 661-671.

- Hara, H., M. Kurita and T. Okita, 1982: Ammonia denuder for field sampling of sulfuric acid particles. *Atmos. Environ.*, **16**, 1565-1566.
- Lee, M. L., D. W. Later, D. K. Rollins, D. J. Eatough and L. D. Hanson, 1980: Dimethyl and monomethyl sulfate: Presence in coal fly ash and airborne particulate matter. *Science*, **207**, 186-188.
- Penzhorn, R. D. and W. G. Filby, 1976: Eine Methode zur spezifischen Bestimmung von schwefelhaltigen Säuren im atmosphärischen Aerosol. *Staub-Reinhalt. Luft.*, **36**, 205-207.
- Whitby, K. T., 1978: The physical characteristics of sulfur aerosols. *Atmos. Environ.*, **12**, 135-159.

ジアゾメタンによるメチル化法を用いた大気中の硫酸粒子の測定

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大気中の硫酸粒子の測定法について Penzhorn と Filby (1976) によって行われた方法を改良した新しい測定法を考案した。この新測定法では、ジアゾメタンを発生させて直接硫酸をメチル化する装置を用いている。硫酸の検出限界は 3 ng である。テストチャンバー内に発生させた硫酸粒子について、本方法とクロラニル酸バリウム法及び滴定法とで測定を行ったところ、良く一致した。野外測定において硫酸を硫酸アンモニウムに変換してしまうために問題となるアンモニアガスは、アンモニア除去管を用いることにより除去した。

1981年の8月の東京における大気中の硫酸粒子の濃度は $0.3 \sim 4.7 \mu\text{g m}^{-3}$ であった。札幌においては、硫酸粒子濃度は、1981年の5月～7月は $0.2 \sim 1.3 \mu\text{g m}^{-3}$, 1981年11月～1982年1月は $0.1 \sim 1.4 \mu\text{g m}^{-3}$ であった。直径 $2.1 \mu\text{m}$ 以下の硫酸粒子の重量累積頻度は90%であった。硫酸 (H_2SO_4) と硫酸塩 (SO_4^{2-}) の比は、粒径が減少するに従い増加した。