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Simultaneous measurement of volatile sulfur compounds using ascorbic acid for oxidant removal and gas chromatography–flame photometric detection

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Abstract

A method for the simultaneous measurement of volatile sulfur compounds (COS, H₂S, CS₂, CH₃SH, DMS) is established with preconcentration and GC–flame photometric detection (FPD). Prior to preconcentration of ambient air, it was necessary to remove SO₂, water vapor and atmospheric oxidant. SO₂ and water vapor were removed using a glass fiber filter and a cooled PTFE water trap loop, respectively. In order to remove atmospheric oxidant, the efficiency of an ascorbic acid scrubber was examined. It was found that an ascorbic acid scrubber enabled measurement of volatile sulfur compounds without adsorption and reaction loss. The detection limits for COS, H₂S, CS₂, CH₃SH and DMS were 20, 34, 35, 263 and 44 pg of S, respectively. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Volatile sulfur compounds in the atmosphere include carbonyl sulfide (COS), hydrogen sulfide (H₂S), carbon disulfide (CS₂), methylmercaptan (CH₃SH), dimethyl sulfide (DMS) and sulfur dioxide (SO₂), and so on. DMS appears to be the significant portion of the natural sulfur flux [1]. COS, H₂S, CS₂ and CH₃SH are also produced from natural origins, but these emission rates are a minor contribution to the total sulfur budget. However, in polluted areas, COS, H₂S and CS₂ levels are considerable as a result of human activities [2].

Because of high chemical activities, except for COS, these compounds are finally converted to non-sea-salt sulfate (nss-SO₄²⁻) and methane sulphonate

(MSA, CH₃SO₃³⁻) aerosols resulting from the photochemical oxidation [3]. Sulfate and MSA contribute largely to the formation of aerosols in the troposphere. These aerosols are thought to be a major source of cloud condensation nuclei (CCN). The abundance and size distribution of CCN are influenced by the radiative properties of clouds. Therefore, these could affect the climate due to a change in the back scattering of solar radiation and the albedo of clouds in the troposphere [4,5].

On the other hand, COS is a relatively stable compound in the troposphere and diffused into the stratosphere. In the stratosphere, most COS is oxidized by the strong ultraviolet radiation, and it would be a main precursor of the background stratospheric sulfate aerosols. These aerosols might also be affect-

ed by the earth's radiation balances and the ozone budget by heterogeneous reaction [6,7]. Consequently, volatile sulfur compounds are important in the atmospheric environment. However, our understanding of the sulfur cycle on the global scale is quite unsatisfactory. Measurement of small amounts of volatile sulfur compounds is required for the understanding of the biogeochemical sulfur cycle and the evaluation of the influence on the earth's climate.

Only few methods for the simultaneous measurement of volatile sulfur compounds have been reported [8,9]. The difficulties of simultaneous measurement are (1) there is few adequate column packing materials to separate the compounds completely. In the atmosphere, the concentration of volatile sulfur compounds is quite variable over the wide range of ppt (v/v)–ppb (v/v). Therefore, an enrichment procedure is required which makes it more difficult to separate the peaks. (2) Atmospheric oxidants, such as ozone (O_3), nitrogen dioxide (NO_2), hydrogen peroxide (H_2O_2) and reactive radicals such as hydroxyl radical (OH) and peroxide radicals (HO_2 , RO_2), gave rise to variable loss of DMS during the preconcentration procedure [10–12]. For the removal of oxidants, a variety of materials such as sodium carbonate (Na_2CO_3), potassium hydroxide (KOH), potassium iodide (KI), have been tested. The results of a comparison of the various oxidant scavenging methods indicated that KI containing scrubbers, such as KI buffer solution, KI impregnated filter and KI crystals, are adequate to measure DMS. However, it is possible that oxidant removing materials interfere with quantifying of other volatile sulfur compounds except DMS. In addition, it was also pointed out that the recovery of CH_3SH was severely affected by cotrapped water vapor existing in ambient air [9,13].

In this paper, we describe a preconcentration and analytical procedure for the simultaneous measurement of volatile sulfur compounds from a single ambient air sample.

2. Experimental

The concentration of volatile sulfur compounds was determined by preconcentration and subsequent

analytical systems. Fig. 1 is a schematic diagram of the system developed in this study.

2.1. Analytical systems

The analyses of volatile sulfur compounds were performed on Shimadzu GC/8A gas chromatograph equipped with a flame photometric detection (FPD) system. Shimadzu Chromatopac CR-6A was used for recording the detector signal. The separation of peaks was achieved chromatographically using a glass column (3 m \times 2.6 mm I.D. \times 5.0 mm O.D.) packed with β,β' -ODPN (60/80 mesh, Uniport HP, GL Science) at a constant temperature of 50°C. The temperature of the injection and detection ports was maintained at 90°C.

Helium was used as a carrier gas at a flow-rate of 53 ml min⁻¹. Hydrogen and compressed air were used as combustion gases. The FPD response was optimized with hydrogen and air flow-rates of 50 and 36 ml min⁻¹, respectively. These carrier and combustion gases were purified by passing through activated charcoal (Granular, Wako) and molecular sieves 5A (1/8 pellet, GL Science) to remove water vapor and other gaseous impurities before use. This GC–FPD system was connected to the preconcentration system with three-way valve, as illustrated in Fig. 1.

2.2. Preparation of adsorption tube

An adsorption tube for preconcentration of ambient air was made from a U-shaped PTFE tube (12 cm \times 3 mm I.D. \times 4 mm O.D.) packed with 200–300 mg Tenax TA (60/80 mesh, GL Science). Silanized quartz wool (GL Science) was plugged at both ends of the Tenax TA in the absorption tube. Tenax TA was cleaned by passing helium with a temperature of 250°C for about 12 h before the preparation of the adsorption tubes.

2.3. Procedure for sampling and analysis of ambient air

In our preconcentration system, two absorption tubes were connected to two six-way PTFE valves and these valves were interfaced to GC–FPD by a three-way stainless steel valve. It was possible to

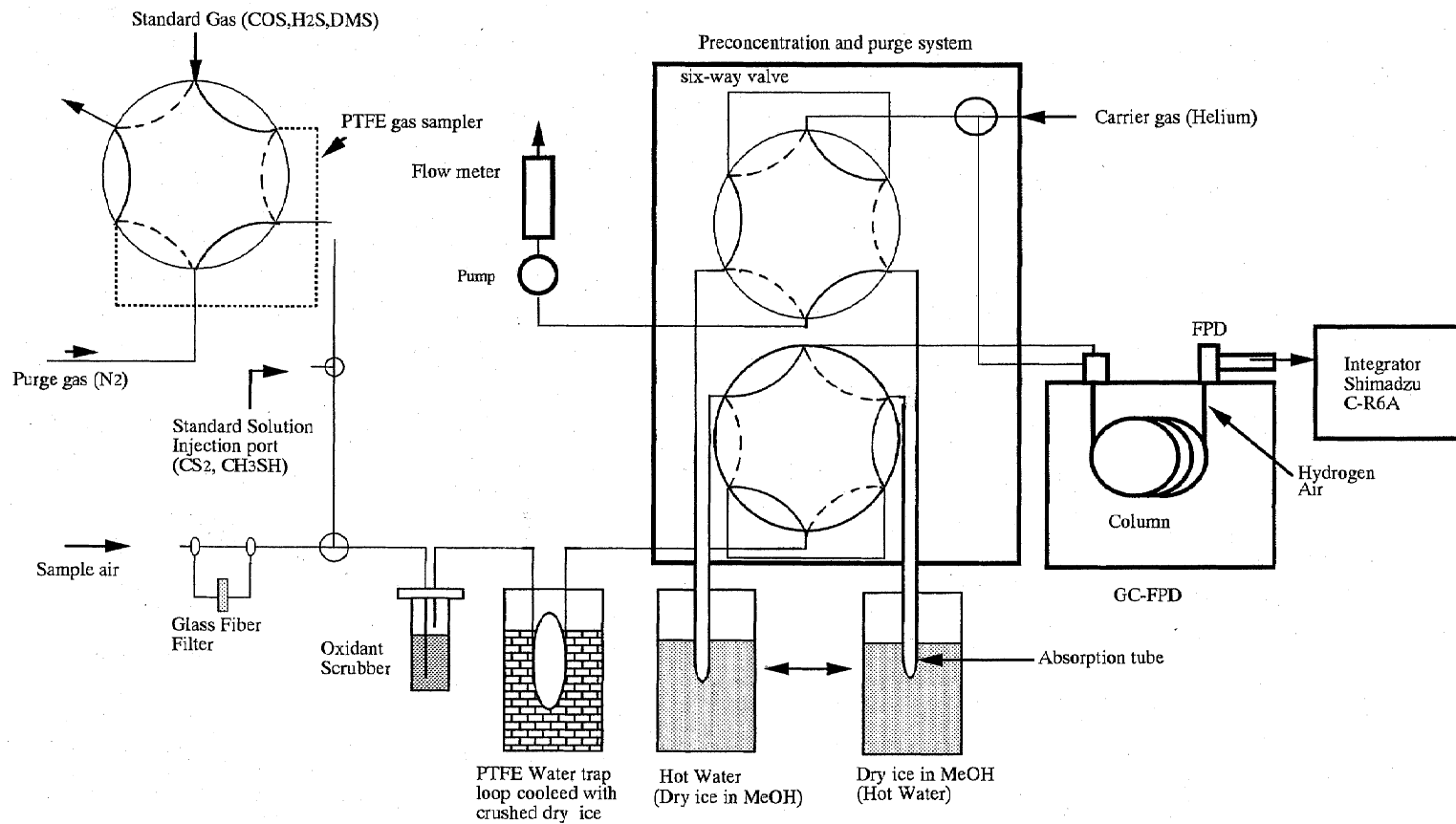


Fig. 1. Schematic diagram of the preconcentration, purge and analytical systems.

concentrate and analyze of ambient air simultaneously by switching six-way valves. These six-way valves and connected lines were placed into an aluminum box controlled temperature at 90°C to prevent volatile sulfur compounds from adsorbing onto the PTFE tube surface.

Ambient air was sampled by pumping through a PTFE tube (4 mm I.D.×5 mm O.D.) at a flow-rate of 200 ml min⁻¹. The air streams were passed through a PTFE water trap loop cooled with crushed dry ice to remove water vapor. For removing of SO₂ and oxidant, glass fiber filter and an oxidant scrubber were placed in front of the PTFE water trap loop. Subsequently, volatile sulfur compounds in ambient air were preconcentrated on the adsorption tube immersed into a dry ice–methanol solution (−70°C). When the preconcentration procedure was complete, the adsorption tube was removed from the dry ice–methanol solution and six-way valves were switched to the other portion. Then, the adsorption tube was immersed immediately into the hot water (90–95°C). The preconcentrated volatile sulfur compounds were desorbed from the adsorption tube with helium, and then injected directly onto the column. During this time, the other adsorption tube began the preconcentration of volatile sulfur compounds in ambient air.

In this system, all materials coming in contact with ambient air were made of PTFE materials which were cleaned with methanol and acetone solution (3% phosphate) to minimize adsorption loss and to avoid contamination of volatile sulfur compounds.

2.4. Standard materials and calibration

The calibration curves of volatile sulfur compounds were made by using standard gas for COS, H₂S and DMS (nitrogen dilution, Nihon Sanso) and standard solutions for CS₂ and CH₃SH (Wako, special grade). Concentrations of COS, H₂S and DMS standard gas were 9.0 ppm (v/v) 10.4 ppm (v/v) and 12.4 ppm (v/v), respectively. A PTFE gas sampler equipped with a six-way valve was used to inject the aliquots of standard gases with nitrogen streams.

For CS₂ and CH₃SH, stock solutions were prepared by diluting with distilled benzene. The aliquots of standard solution were injected into the heated

T-shaped glass tube placed in front of the PTFE water trap loop using a microsyringe and purged with nitrogen streams. In this procedure, only benzene was selectively trapped on the PTFE water trap loop cooled with dry ice.

These preconcentrated aliquots of standard gases and solutions were injected onto the column, and the procedure was same as for the ambient air analysis.

2.5. SO₂ and oxidant scrubber

For the analysis of volatile sulfur compounds, it is required to remove SO₂ and oxidant. In order to remove SO₂ from ambient air, glass fiber filter (GF/F, 25 mm diameter, Whatman) was used. For the removal of oxidant from ambient air, KI (granule, Wako, special grade) and ascorbic acid (granule, Wako, special grade) were investigated. These granules were packed into a polypropylene centrifuge vessel (Iwaki grass, 15 ml). Silanized quartz wool (GL Science) was put on the outlet of the vessel to prevent scavenging materials from entering into the analysis line.

3. Results and discussion

3.1. SO₂ scrubber

Fig. 2 shows chromatograms of volatile sulfur compounds in ambient air. COS, H₂S, CS₂, CH₃SH, SO₂ and DMS peaks were detected. Sufficient separation of COS, H₂S, CS₂ and CH₃SH peaks was achieved. However, it was impossible to separate SO₂ and DMS peaks completely, because a large SO₂ peak overlapped a small DMS peak (Fig. 2a). In addition, the recovery of SO₂ fluctuated so much that it could not be quantified.

We attempted to remove SO₂ for the purpose of quantifying DMS. According to the previous reports for the measurement of DMS, basic substances such as Na₂CO₃ and KOH have been used to remove SO₂ [14]. However, these basic substances might be given rise to loss of H₂S. In this study, we tested a glass fiber filter as a SO₂ scrubber. When ambient air was passed through the glass fiber filter, SO₂ was removed completely. Following this, it was possible to detect the DMS peak (Fig. 2b).

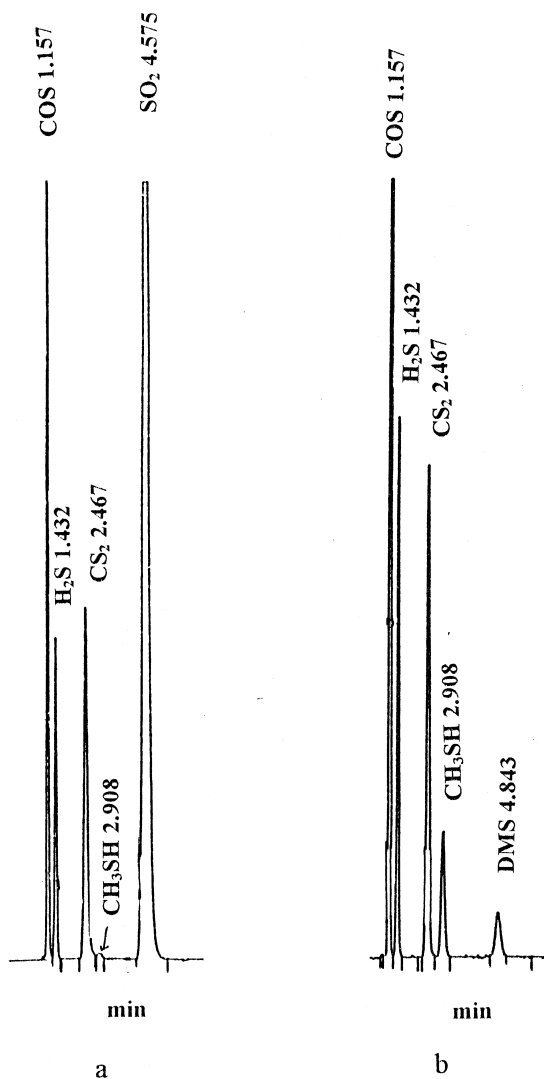


Fig. 2. Chromatograms of volatile sulfur compounds in ambient air. Figures indicate the retention time (min) of peaks (a) without passing through glass fiber filter, (b) with passing through glass fiber filter.

In order to investigate the efficiency of a glass fiber filter as a SO_2 scrubber, ambient air was collected into the polyvinyl fluoride bag (PVF bag, 50 l, Oumi odo air). Aliquots of DMS and CH_3SH standard solutions were added to the air in the bag. These were injected to the levels existing in ambient air. Fig. 3 shows the concentration of volatile sulfur compounds in the stocked air in the bag, with and without passing through a glass fiber filter. Passage

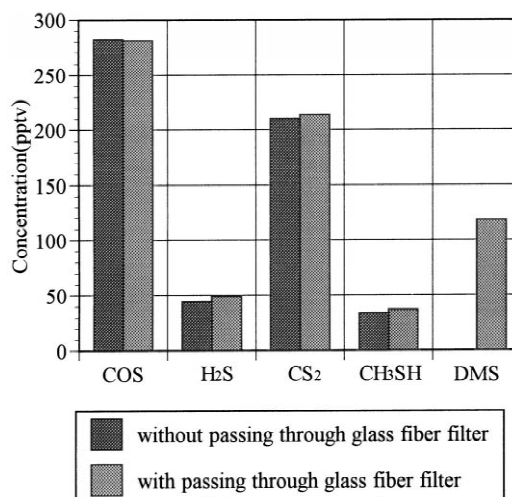


Fig. 3. Comparison of the concentration of volatile sulfur compounds in stocked air into the bag with and without passing through the glass fiber filter.

through the glass fiber filter did not significantly affect the concentrations of COS, H_2S , CS_2 and CH_3SH in the stocked air. The SO_2 peak interfered with the estimation of DMS concentration. In the case of the SO_2 -free air in the bag, the concentration of DMS was measured with no difference between the two cases. These results show that a glass fiber filter might be effective as a SO_2 scrubber to measure volatile sulfur compounds.

3.2. Ascorbic acid scrubber

In order to measure volatile sulfur compounds with GC-FPD, it was necessary to conduct a pre-concentration procedure because of the low levels of atmospheric concentration. The pre-concentration procedure was achieved either by cryogenic condensation [15] or chemisorption on the solid support material using porous polymers or metal surface such as gold materials [9,11]. It was pointed out that atmospheric oxidant caused a variable and extensive sampling loss of DMS during the pre-concentration procedure. The depletion tendency of DMS was remarkable in the presence of high concentration levels of ozone and anthropogenic materials [10–12].

In a study of the methodology reported for atmospheric DMS measurement, a variety of oxidant

removal materials were investigated, for example impregnated filter (NaOH, KOH, Na₂CO₃ and KI), chromatographic support (coated with Na₂CO₃, ferrous sulfate (FeSO₄), KI and potassium bromide (KBr)), and granules (FeSO₄, KI, KBr), etc. [4,10,15,18,19]. A comparison of these materials shows that a KI containing scrubber (KI buffer solution, KI impregnated glass fiber filter, KI crystal, etc.) has a significant capacity for oxidant removal, based on the large oxidant breakthrough volume of ambient air and the effectiveness in prevention of DMS sampling loss [16,17]. In this study, the usage

of KI for simultaneous measurement was attempted. However, KI gave rise to slightly diminished levels of H₂S, and so was inadequate for the simultaneous measurement of volatile sulfur compounds.

As with other oxidant scavenging materials, ascorbic acid (crystals), based on the nature of the neutral reducing agent, was investigated [20] for simultaneous measurement. First, the possibility of reaction and adsorption loss of volatile sulfur compounds with ascorbic acid was investigated by passing through aliquots of standard gases and solutions in nitrogen gas streams. Added aliquots of standard

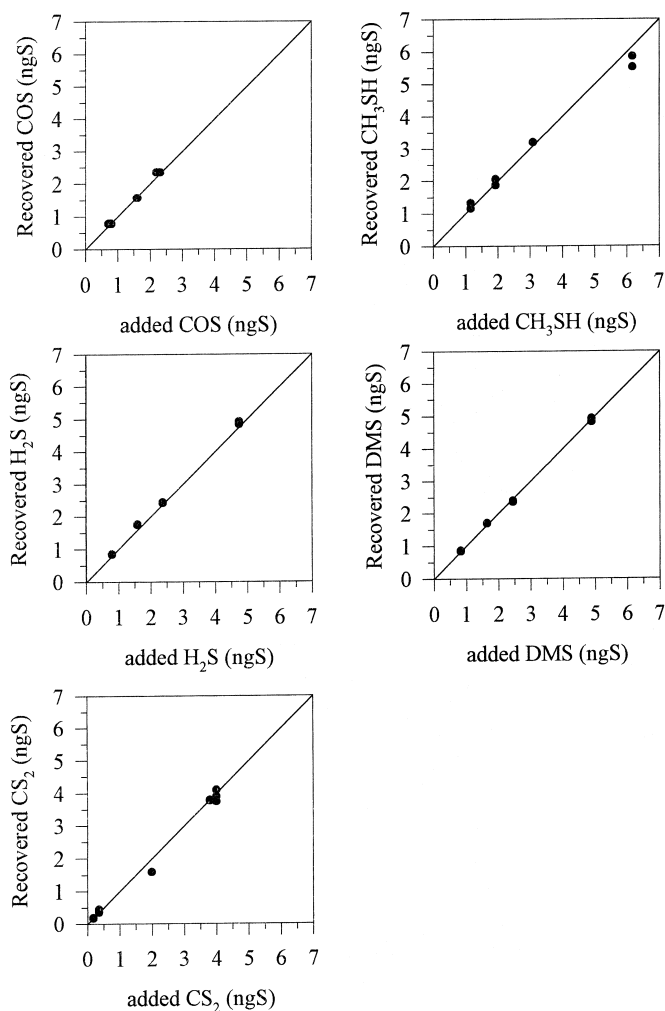


Fig. 4. Recovery of volatile sulfur compounds added in nitrogen gas streams which passed through an ascorbic acid scrubber. The straight lines indicate complete recovery.

gases and solutions were quantitatively recovered (Fig. 4). It was thought that ascorbic acid hardly affected the recovery of volatile sulfur compounds. The recoveries were COS $102\pm 3\%$; H_2S $105\pm 3\%$; CS_2 $100\pm 17\%$; CH_3SH $101\pm 8\%$ and DMS $101\pm 3\%$.

Second, ascorbic acid was investigated as an oxidant scrubber. In this experiment, a cold trap and purge line connected in six-way valves was rearranged so as to operate two independent sampling lines, allowing the collection of duplicate samples at the same time. In order to investigate the recovery of

volatile sulfur compounds during the sampling of ambient air, aliquots of standard gases and solutions were added only to one line at the beginning of the ambient air collection. The other line was used to estimate the already existing abundance of volatile sulfur compounds in ambient air. These trials were conducted to two preconcentration method with and without passing through ascorbic acid scrubber with every compounds. The results are shown in Fig. 5. The concentration of O_3 in ambient air was 40–50 ppb (v/v) during these experiments. When ambient air was passed through the ascorbic acid scrubber,

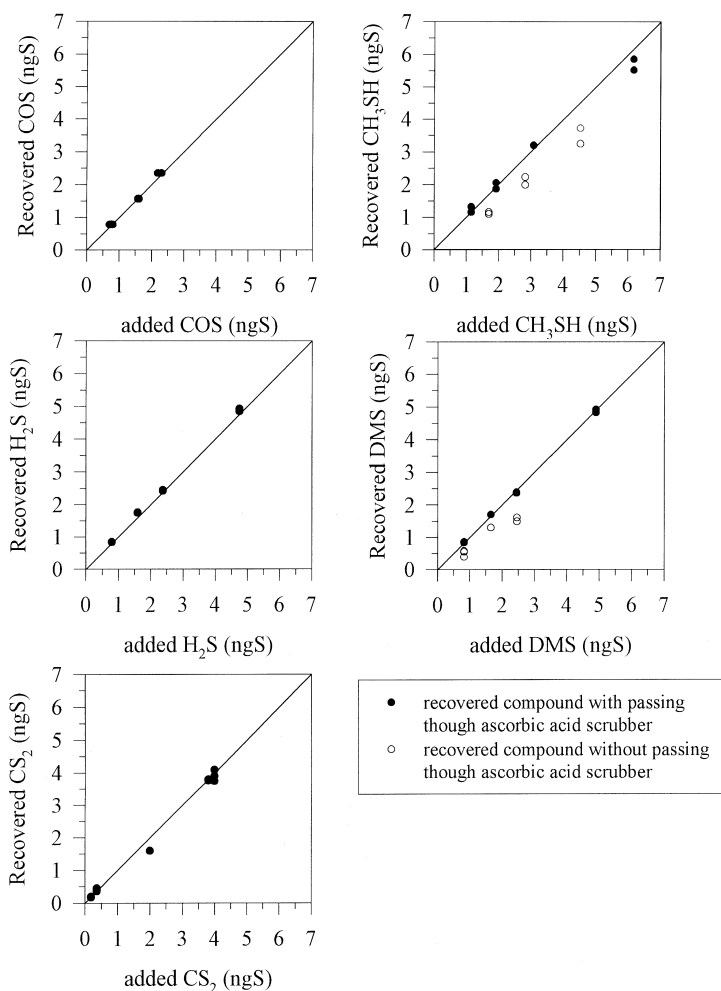


Fig. 5. Recovery of volatile sulfur compounds added to ambient air with and without passing through ascorbic acid scrubber. The straight lines indicate complete recovery. With respect to COS, H_2S , and CS_2 , the recovery is shown for the ascorbic acid scrubber passed sample, because there is no significant difference between passing through ascorbic acid scrubber and without it.

complete recovery of added standard compounds were achieved. On the other hand, when ambient air was passed through without ascorbic acid scrubber, the diminution of added DMS and CH_3SH were observed. In this experiment, the recovery of COS, H_2S and CS_2 were hardly affected. Therefore it is clear that ascorbic acid is adequate to measure volatile sulfur compounds simultaneously.

Furthermore, water vapor also strongly influenced the measurement of CH_3SH by GC [13]. If the preconcentration methods are useful for the analysis of volatile sulfur compounds, we need a method for the removal of water vapor, which blocks up the air flow in the absorption tube. For water vapor removal in this system, a PTFE loop cooled with dry ice and a Nafion dryer (GL science) was compared. The result showed that the PTFE loop method removed the water vapor better than the Nafion dryer method.

The recovery of added aliquots of standard gases and solutions into ambient air was COS $99\pm 3\%$; H_2S $105\pm 3\%$; CS_2 $107\pm 17\%$; CH_3SH $103\pm 8\%$; DMS $100\pm 3\%$; respectively. Detection limit was COS 20 pg, H_2S 34 pg, CS_2 35 pg, CH_3SH 263 pg and DMS 44 pg of S, respectively.

3.3. Effect of ozone on recovery of volatile sulfur compounds

In order to estimate of the efficiency of ascorbic acid as an oxidant scrubber, the concentration of O_3 in ambient air was also measured (model 1006HJ, Dasibi). In this trial, ambient air was preconcentrated in two adsorption tubes at the same time with and without passing through ascorbic acid scrubber (Figs. 5 and 6). When the concentration of O_3 was less than 8 ppb (v/v), no significant difference in the concentration of volatile sulfur compounds was observed between the samples taken with and without passing through the ascorbic acid scrubber. On the other hand, the diminution of DMS was observed in the presence of a high concentration of O_3 (more than 8 ppb). During experiment shown in Fig. 5, the concentration of O_3 was 40–50 ppb. Therefore, the loss of DMS corresponded to the presence of a high abundance of O_3 . However, gas phase reaction of DMS with O_3 is too slow to compete with OH and NO_3 reactions in the atmosphere [21–24]. It is unlikely that the diminished DMS is directly reacted

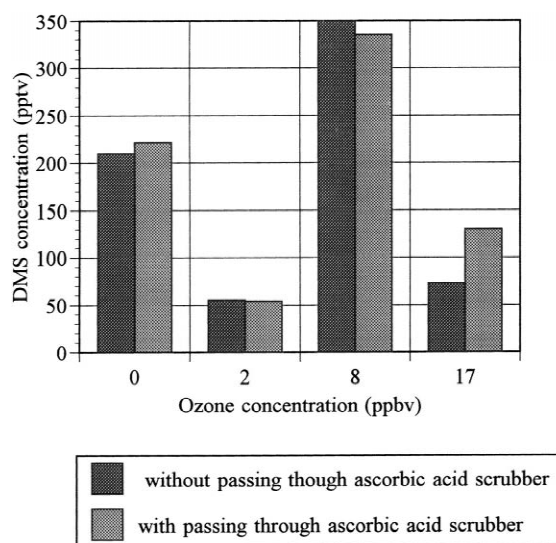


Fig. 6. Comparison of DMS concentration in ambient air, with and without passing through an ascorbic acid scrubber, against O_3 concentration.

with O_3 . However, it is reported that the lowering of DMS was observed in a synthetic air mixture in the presence of O_3 or NO_3 [25]. Concentrated O_3 on the adsorption tube might be degraded and produce radicals on the adsorbent surface, which might cause loss of DMS [10]. It was thought that CH_3SH had a similar tendency with regard to DMS.

The results of this experiment in an urban atmosphere in the presence of high concentration of oxidant indicated that ascorbic acid might be appropriate for analysis of volatile sulfur compounds under various atmospheric environments.

4. Conclusion

In order to understand the sulfur cycle and emission flux, it is required to measure volatile sulfur compounds simultaneously at short time intervals. In this study, simultaneous measurement of volatile sulfur compounds (COS, H_2S , CS_2 , CH_3SH and DMS) has been developed equipped with preconcentration and GC–FPD analysis systems. Ambient air was preconcentrated on the absorption tube packed with Tenax TA immersed into a dry ice–methanol solution. After sample collection, the absorption tube

was immersed in hot water and the pre-concentrated sample was directly injected onto the column with helium. These sulfur compounds were chromatographically separated with β, β' -ODPN and detected with a flame photometric detector. However, in the pre-concentration procedure, it was necessary to remove oxidant, SO_2 and water vapor from ambient air. In order to remove oxidant for measurement of DMS, KI was thought to be the most adequate material. However, KI caused a loss of H_2S . The efficiency of an ascorbic acid scrubber was investigated as another oxidant removal material and it proved to be effective for simultaneous measurement of volatile sulfur compounds. The removal procedure of SO_2 and water vapor from ambient air were conducted by passing through a glass fiber filter and PTFE water trap loop cooled with crushed dry ice, respectively.

In this system, it was possible to operate sampling and analysis continuously by using manually operated six-way valves. Furthermore, this system might be applied for not only atmosphere but also other environments, for example, sea water, soil, plants and so on.

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