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Performance of the HPLC/fluorescence SO₂ detector during the GASIE instrument intercomparison experiment

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Abstract. Sulfur dioxide (SO₂) in synthetic air and diluted ambient air was measured as part of the Gas-Phase Sulfur Intercomparison Experiment (GASIE) using the high performance liquid chromatography (HPLC)/fluorescence technique. SO₂ was analyzed by equilibrating the gaseous sample with aqueous SO₂, sulfite, and bisulfite, then converting the aqueous S(IV) to an isoindole derivative. The derivative was separated by reversed phase HPLC and detected via fluorescence. The system was calibrated with mixtures of SO₂ in zero air prepared from an SO₂ permeation device through a two-stage dilution system. The instrument has a 4-min. sample integration time and a measurement period of 9-min. During the GASIE intercomparison the lower limit of detection averaged 3.6 parts per trillion by volume (pptv). The precision of replicate measurements over the entire intercomparison period was better than 5% at the 20 pptv level. Instrument performance was unaffected by the interferent gases included in the GASIE protocol (H₂O, O₃, NO_x, DMS, CO, CO₂, and CH₄). During diluted ambient air tests, the HPLC/fluorescence technique exhibited an approximately 10% reduction in response relative to some other techniques. The cause of this apparent calibration change is not understood.

Introduction

The biogeochemical cycling of reduced sulfur gases in the marine troposphere is the focus of current research due to the role of sulfate aerosols in the radiation budget of the Earth [Cambridge University Press, 1995; Charlson *et al.*, 1987]. The abundance and distribution of sulfur dioxide (SO₂) is an important component of such investigations since it is an intermediate in the oxidation of reduced sulfur gases and is the predominant anthropogenic sulfur gas released to the atmosphere. The analysis of tropospheric sulfur dioxide is difficult because it is a reactive gas which is often present at levels as low as a few tens of parts per trillion by volume (pptv). The Chemical Instrumentation Test and Evaluation Program (CITE 3) examined the performance of airborne SO₂ instrumentation and raised concerns about the current capability to measure tropospheric SO₂ levels [Gregory *et al.*, 1993]. The Gas-Phase Sulfur Intercomparison Experiment (GASIE), a ground-based experiment, was designed to further investigate the ability of current instrumentation to measure low levels of SO₂ under controlled conditions and to investigate possible interferences.

The HPLC/fluorescence technique was developed primarily for use in the remote marine boundary layer. The design goals for the instrument were as follows: (1) sub-10 pptv detection limit, (2) 10-min. time resolution, (3) detection of S(IV) only (i.e., no interference from sulfate), and (4) capability to verify instrumental response at ambient sulfur dioxide levels. The instrument design was discussed in detail by Saltzman *et al.* [1993], and it has been used in several scientific cruises [e.g., Yvon and Saltzman, 1996]. The

HPLC/Fluorescence technique was not tested in the CITE 3 program. The performance of this instrument was evaluated during GASIE in Lewes, Delaware, during September and October 1994 [Stecher *et al.*, this issue]. This paper describes the configuration and performance of the HPLC/fluorescence instrument as it was operated during the GASIE intercomparison, including modifications which have been made since it was originally described by Saltzman *et al.* [1993]. The formal results of the intercomparison are given by Stecher *et al.* [this issue].

Instrument Description

Basic Principles

A schematic diagram of the instrument is given in Figure 1, and the reagent composition and flow rates are listed in Table 1. The instrument sampled ambient air by absorbing gaseous sulfur dioxide into an aqueous scrubbing solution in the flowing aqueous film of a gas/liquid exchange coil. The resulting aqueous solution containing sulfur dioxide, bisulfite, and sulfite was pumped through a continuous reaction system where it was sequentially mixed with ethanolamine in a pH = 9 borate buffer and o-phthalaldehyde. The reaction mixture flowed through a reaction/delay coil, where S(IV) in solution was converted to a highly fluorescent isoindole derivative. The delay was timed to optimize the yield of the isoindole derivative while minimizing intramolecular and intermolecular decomposition reactions. A strong acetate buffer (pH=5.7) was then added in order to slow further reaction, raise the ionic strength, and lower the pH of the solution to render the sample compatible with analysis by high performance liquid chromatography (HPLC). The reaction stream flowed through a 600- μ L loop which was periodically injected onto an isocratic, reversed phase HPLC column (C-18; Spherisorb S50DS2, PhaseSep) with

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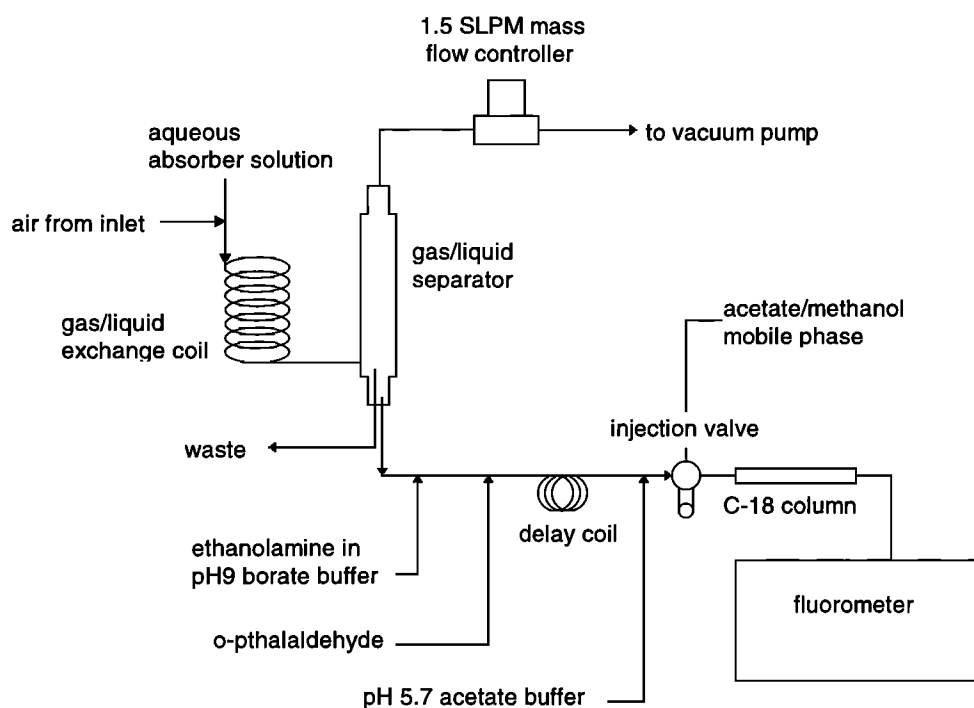


Figure 1. Schematic of the high performance liquid chromatography (HPLC)/fluorescence instrument.

continuous fluorescence detection. A dual monochromator spectrofluorometer (Hitachi model F-1080) was used with excitation/emission wavelengths of 330/380 nm, which are the maxima for the derivative.

Sample Inlet

The inlet for this instrument at GASIE was initially similar to that used by *Saltzman et al.* [1993], with the addition of a 1m long section of 0.635 cm OD perfluoroalkoxy (PFA) Teflon tubing to connect to the manifold used to supply mixtures of SO₂ and various interferences in air from the sulfur gas dilution system (SGDS) during GASIE. The inlet of the HPLC/fluorescence instrument was changed early in the GASIE study (phase 2a) when standard addition experiments demonstrated that there were significant losses of gaseous sulfur dioxide in humid air. Although it was not known at the time, these losses were associated with sodium carbonate contamination of inlet valves which was inadvertently introduced prior to shipment of the instrument to the GASIE experiment. In order to rectify the problem, the inlet was

changed in the field to the configuration shown in Figure 2. This configuration was used for the remainder of the GASIE intercomparison (phases 2b, 3a, 3b, and 4). The most important attribute of the inlet configuration is that it permits introduction of gaseous standards at the entry point for air samples into the instrument. Air is drawn into the system through a 10-cm PFA Teflon tube and a Nafion membrane drier. This tube and the first few centimeters of the Nafion drier were heated (45°C) to prevent condensation.

The downstream end of the Nafion drier was fitted with a three-way PFA Teflon solenoid valve (V_1 in Figure 2) which was plumbed such that toggling the valve sent the airstream either (1) directly to the air/liquid coil or (2) through two carbonate impregnated filters and one PTFE Teflon filter prior to the air/liquid coil. The carbonate impregnated filters quantitatively remove SO₂, providing an airstream for blank determinations and gas calibration. A second three-way PTFE Teflon solenoid valve (V_2) was plumbed to direct standard gas mixtures to either a third valve or through the 0.3175 cm OD PFA Teflon tubing to the upstream end of the

Table 1. Solution Composition and Flow Rates Used in the HPLC/Fluorescence Instrument [*Saltzman et al.*, 1993]

Solutions	Composition	Flow Rate, mL/min
Absorber solution	10 μ M formaldehyde, 0.840 mM Na ₂ EDTA	0.42
Reagent (1)	34 mM aminoethanol in 0.25M borate buffer, pH = 9	0.02
Reagent (2)	1.14 mM orthophthalaldehyde in 10% methanol	0.02
Reagent (3)	2.5M acetate buffer, pH=5.7	0.02
Mobile phase	0.01M acetate buffer, pH=5.7 in 20% methanol	1.0

All solutions are aqueous.

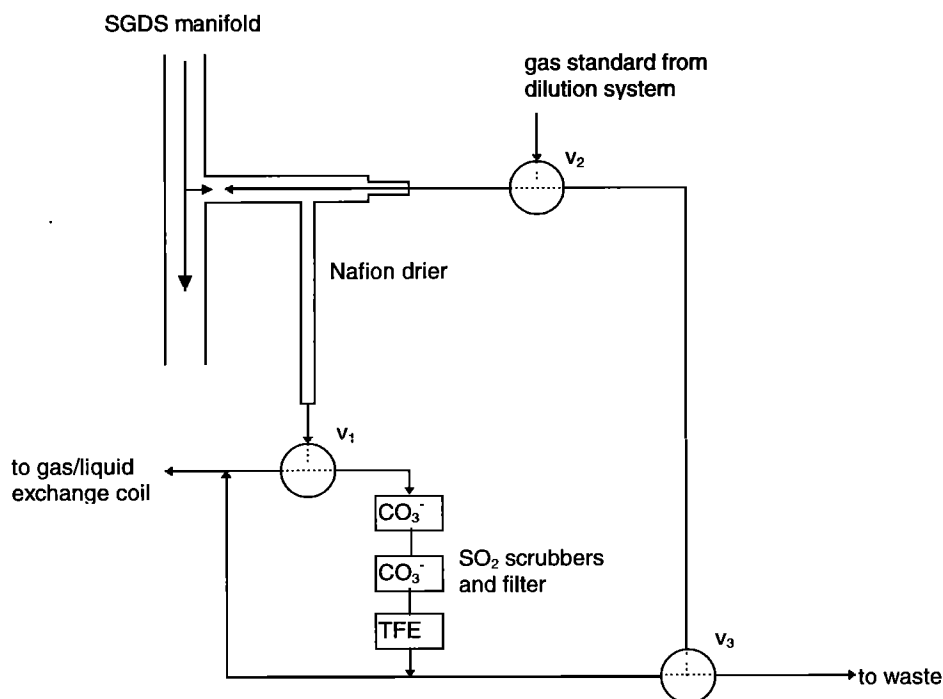


Figure 2. Schematic of the inlet used on the HPLC/fluorescence instrument at GASIE during intercomparison periods 2b-4.

inlet. The third three-way PFA Teflon solenoid valve (V_3) directed the standard gas mixtures either to waste or to the air/liquid coil. This arrangement allowed comparison of instrument response to standards introduced directly to the air/liquid coil, with response to standards added near the SGDS manifold.

Calibration

Gas standards were generated using a permeation source and gas dilution system, shown in Figure 3. The permeation tube was a wafer-type permeation source (VICI Metronics, Santa Clara, California), held at $30 \pm 0.3^\circ\text{C}$ in a PFA Teflon housing in a thermostatted aluminum block. Gas dilution was accomplished in a two-stage system consisting of four 0-100 standard cubic centimeters per minute mass flow controllers (Tylan General, San Diego, California). The gas dilution system has two particularly useful characteristics for reactive gases such as sulfur dioxide: (1) the analyte does not pass through any mass flow controllers and contacts only PFA and (2) both the concentration and the flow rate of the standard vary, allowing the system to generate a wide dynamic range of mass flow rates of the analyte without having the tubing experience a large range in analyte concentration, which may cause memory effects.

A mass flow controller (m_1 in Figure 3) provided a constant flow (approximately 85 standard cubic centimeters per minute) of nitrogen over the permeation device. A second mass flow controller (m_2), located just downstream from the permeation device, was connected to a vacuum manifold. This controller was used to dump a variable amount of the gas flowing over the permeation device (48% to 97%) to waste. A third mass flow controller (m_3) delivered an additional 85 standard cubic centimeters per minute of nitrogen to dilute the remaining calibration gas stream. The gas stream was then

passed through a PFA mixing volume (approximately 300 cm^3) to insure homogeneity. A final mass flow controller (m_4) was connected to the vacuum pump manifold and was used to remove a fixed flow (approximately 70 standard cubic centimeters per minute) from the calibration gas stream. The remainder of the calibration gas was directed to the inlet of the instrument.

The concentration of sulfur dioxide generated by the calibration system is governed by the following relationship:

$$SO_2(\text{pptv}) = \left[\frac{P}{F} \right] \left[\frac{m_1 - m_2}{m_1} \right] \left[\frac{m_1 - m_2 + m_3 - m_4}{m_1 - m_2 + m_3} \right] \left[\frac{22.4 \cdot 10^6}{64} \right] \quad (1)$$

where P is the permeation rate of the tube (ng/min), F is the air sampling flow rate (cc/min), and m_1 , m_2 , m_3 , and m_4 are the flow rates of the various mass flow controllers (cm^3/min) as numbered in Figure 3. The constants at the end of the expression are conversion factors with units of $\text{pptv cm}^3/\text{ng}$.

In this dilution system the relative (rather than absolute) response of the mass flow controllers is critical to the accuracy of the standards generated. The dilution system was periodically calibrated by connecting the four mass flow controllers in series and intercomparing their readouts over the range of flows used to generate standards. These data provide a function whereby the flow reading of each of the mass flow controllers can be normalized to that from one arbitrarily chosen unit. Three such calibrations were performed, at the start, middle and end of GASIE, with a variation of 0.6% between the most divergent pair. This is slightly worse than one would have predicted from the manufacturer's specification for repeatability ($\pm 0.2\%$ of full scale). A six-digit multimeter was used to read the mass flow controller output voltages in order to fully utilize the precision of the mass flow controllers.

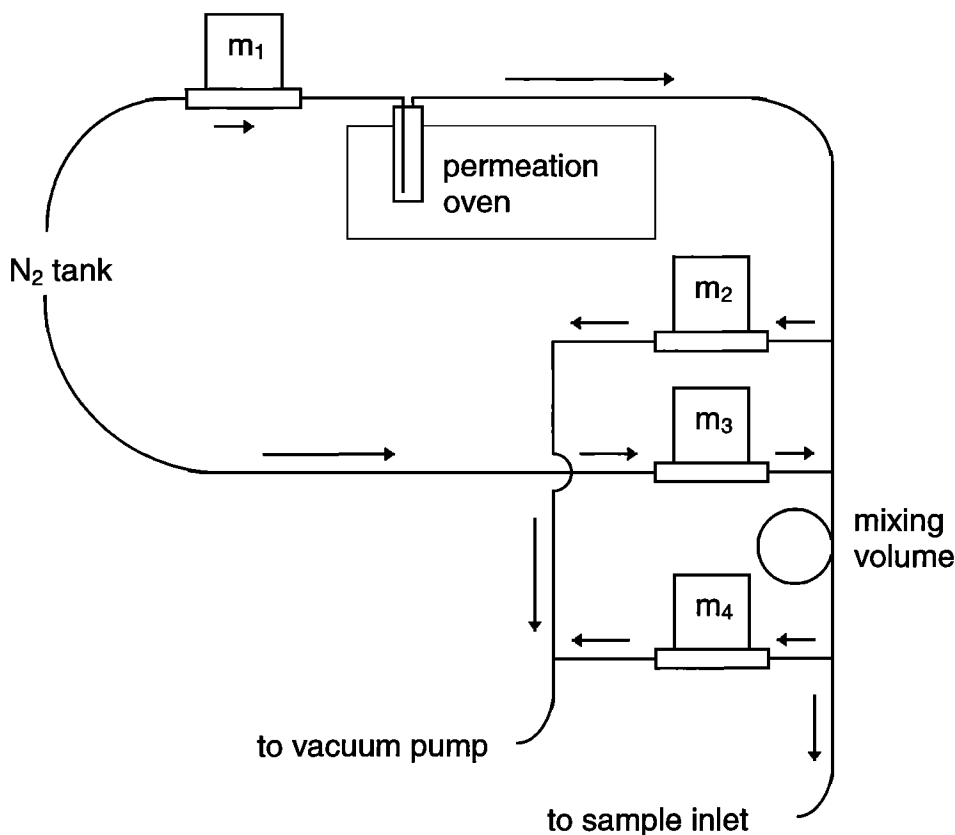


Figure 3. Gas dilution system used to generate sulfur dioxide standards ranging from 12 to 610 pptv. The units labeled m_1 through m_4 are 0-100 standard cubic centimeters per minute mass flow controllers.

During the GASIE intercomparison, this two-stage dilution system was used to deliver from 0.4% to 23% of the total output of the permeation device. A permeation device with a loss rate of 10.4 ng/min in a total sample flow of approximately 1.5 standard liters per minute allowed generation of calibration mixtures with SO₂ volume mixing ratios from 12 to 610 pptv. Lower-level standards could easily and reproducibly be prepared by using a permeation device with a lower loss rate and/or delivering a smaller percentage of the permeation device output to the instrument inlet.

The output of the permeation device used in the GASIE study was certified by the manufacturer as 11.6 ng/min \pm 10% at 30° C in July 1994. A record of the permeation device mass was maintained prior to, during, and after the GASIE study; however, this involved measurement on balances at the GASIE site and at the University of Miami. The use of different balances and the low permeation rate of the device cast doubt upon the accuracy of the gravimetric determination of the absolute permeation rate for this tube. Therefore the permeation rate was determined after GASIE by comparing the SO₂ output from the device with a standard generated by the dilution of a commercially prepared, certified SO₂ gas cylinder (10.18 ppmv \pm 1% SO₂ in N₂; Scott Specialty Gas, Plumsteadville, Pennsylvania). The comparison was done using a Thermo-Electron Corporation pulsed fluorescence SO₂ monitor. The permeation rate determined in this way was 10.4 ng/min \pm 12%, which was the value used in calculating all GASIE results. The uncertainty in the permeation rate was estimated from the stated uncertainty in the SO₂ concentration

of the commercial standard (\pm 1%) and uncertainty introduced by the flow controller used to dilute it.

The uncertainty in the concentration of the SO₂ standards was estimated by evaluating the total differential of equation (1) [Rubinson, 1987]. The total differential approximates the propagation of the individual uncertainties when the uncertainties in each of the variables are substituted as an incremental proxy for the differential of each variable. An evaluation of the total differential was done at the mass flow controller flow rates corresponding to the highest and lowest calibration standard set points, 610 and 12 pptv respectively. The uncertainty in the flow rates was estimated as \pm 1% of the mass flow controllers' full scale flow, which is the manufacturer's published accuracy for these controllers. The uncertainty in the permeation rate due to temperature variation was \pm 3% as calculated from an equation supplied by the manufacturer of the permeation device;

$$\log P_1 = \log P_0 + (\alpha (T_1 - T_0)) \quad (2)$$

where P_1 is the permeation rate at temperature T_1 , P_0 is the nominal permeation rate at the nominal temperature T_0 , and α is a constant specific to the permeation device. We observed \pm 0.3°C variation in the temperature of the permeation oven and substituted this value for the temperature difference in the equation. As mentioned above, there is a \pm 12% uncertainty associated with the absolute calibration of the permeation device. When the total differential of equation (1) is evaluated with these uncertainties, the uncertainty in the absolute calibration is \pm 12% at 610 pptv and \pm 43% at 12 pptv.

Instrument Operation and Performance During the GASIE Intercomparison

The GASIE experiment was carried out in four phases: phase 1, period 1-25, SO₂ in dry air with no interferents; phase 2a, period 26-50, SO₂ in humidified air; phase 2b, period 91-105, SO₂ in humidified air; phase 3a, period 51-70, SO₂ in dry air with O₃ and NO_x; phase 3b, period 71-90, SO₂ in dry air with CO, CO₂, CH₄, and DMS; and phase 4, period 106-115, ambient air diluted with dry air.

SO₂ Standards: Phases 1-3b

During the standards portion of the experiments (phases 1-3b), five different set points or "target" SO₂ concentrations ranging from 0 to 501 pptv were provided on a random basis by the SGDS. Details regarding the concentrations of SO₂ and interferents and the performance of the SGDS are given by *McTaggart et al.* (this issue). The GASIE sampling protocol called for five 90-min. measurement periods each day. Measurement periods were followed by a 30-min. break during which the SGDS set point was changed to the value for the next measurement period and allowed to stabilize. At 9 min. per sample, this rate allowed the HPLC/fluorescence instrument to carry out 13 runs for each combined measurement period and break. A typical sampling schedule consisted of (1) four measurements of SGDS test gas, (2) three measurements of SGDS gas with our standard added near the manifold (standard additions), (3) three measurements of carbonate-filtered SGDS gas (blanks), and (4) three measurements of carbonate-filtered SGDS gas to which our standard is added near the air/liquid coil (standards). Standard addition was used to detect losses of SO₂ in the inlet.

Daily calibration curves were generated from blank-corrected standard runs at four or five SO₂ concentrations, typically ranging from 12 to 610 pptv. The variation in the calibration slopes from all days of the intercomparison was 6.5% (1 σ), with no discernible trend. A system blank was always detectable, with a mean level during phases 2b, 3a, 3b, and 4 equivalent to 10 pptv. This blank is due primarily to sulfite present in the chemicals used to prepare the reagent solutions. Sulfite can also be absorbed from air during preparation of the reagents. Because GASIE was carried out in a high SO₂ environment, reagents were prepared in a positive pressure hood supplied with carbonate-filtered air. The average daily variation in the blank was $\pm 12.3\%$ (1 σ).

Chromatograms from the first pair of runs in a given measurement period were used to select the concentration of SO₂ standard to be used for that period. Concentrations were chosen such that instrument response to the standards was about the same as the response to the SGDS gas.

Standard addition experiments with humid air indicated that during phase 2a there were significant losses of SO₂ in the instrument inlet. These losses ranged up to 30% with considerable variability between intercomparison periods. Since losses of this magnitude were not detected during phase 1 sampling of dry air, the formation of liquid water films and subsequent dissolution of SO₂ in the liquid water was suspected as a possible mechanism for the observed losses. Visible condensation was noticed in the inlet during sampling period 32. Although the protocol called for relative humidity of 80%, this was exceeded because of uncontrolled temperature and pressure gradients across the manifold.

During this period we also discovered the loss of SO₂ associated with a valve contaminated with sodium carbonate. At this time we adopted the inlet configuration shown in Figure 2 and relocated the inlet port on the SGDS manifold to be upstream of two other instruments which had considerably higher flow rates. The inlet configuration depicted in Figure 2 was used from period 51 through the completion of GASIE. Standard additions experiments performed after phase 2a indicated that the inlet passed SO₂ quantitatively. Data from phase 2a were withdrawn from the intercomparison experiment. Data from phase 1 were not withdrawn because, although the contaminated valve was present in the system, it did not appear to significantly alter standard addition recoveries from dry air.

The performance of the instrument is best portrayed by the data obtained during phases 2b, 3a, and 3b since by that time problems with the SGDS had been corrected and the instrument was operating with the redesigned inlet. The precision of the replicate measurements within each sampling period is illustrated in Figure 4. The average of the absolute deviation of each replicate about the mean for a given sampling period is expressed as a percentage of the SGDS set point. For all periods in phases 2b, 3a, and 3b this value averaged 4.4% at the lowest set point and decreased to an average of 1.3% at the highest set point. The variability calculated in this way reflects both the variability in the HPLC/fluorescence instrument and the SGDS system.

The lower limit of quantitation for the HPLC/fluorescence instrument at GASIE was 12 pptv, and the detection limit was 3.6 pptv (10 σ and 3 σ of the mean daily blank, respectively [*Rubinson, 1987*]). The instrument reported SO₂ concentrations below the lower limit of quantitation for each measurement period that the SGDS set point was zero. However, nonzero concentrations were detected during each of these measurement periods. For the six periods with a SGDS set point of zero during phases 2-4 we obtained a mean concentration of 3.1 ± 1.8 (1 σ) pptv. This suggests that either the carbonate filter used to scrub air for our blanks was more effective at removing SO₂ than the clean air generator used in the SGDS or that the SGDS manifold itself was a weak source of SO₂ during zero set point runs.

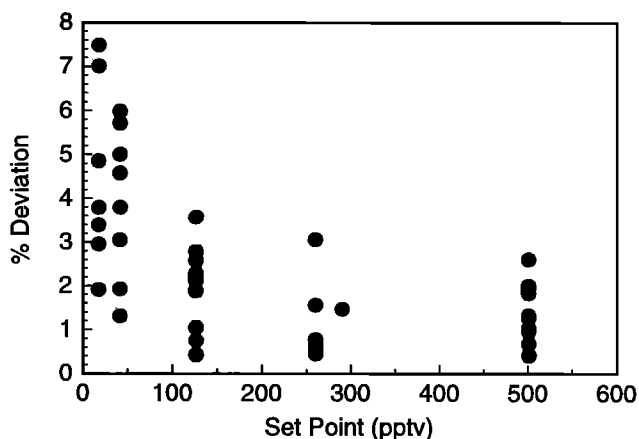


Figure 4. Precision of the HPLC/fluorescence instrument during the GASIE intercomparison. The data shown represent the variance of replicate analyses within each measurement period during phases 2b, 3a, and 3b, calculated as (1 σ /sulfur gas dilution system (SGDS) set point).

Table 2. Relative Response of SO₂ Instruments During Standards (Phases 2-3b) and Diluted Ambient Air (Phase 4) Phases of the GASIE Study

Technique	Aqueous CL	Modified Teco	ID-GC/MS	Mist-IC	HPLC/fluor	Filter-IC
Standards	4.2	2.8	1.6	4.2	3.9	3.9
Diluted ambient	2.2	3.2	2.5	3.8	5.5	3.8

The response is shown as a rank from 1 to 6 (highest to lowest response).

The presence of interferents (H₂O, O₃, NO_x, DMS, CO, CO₂, and CH₄) during phases 2b and 3 caused no detectable changes in instrument performance. Of the interferents tested, only ozone might be expected to be a potential problem for this technique. Ozone could interfere directly via dissolution in the aqueous scrubber solution and oxidation of bisulfite or indirectly via aqueous decomposition into reactive intermediates which produce hydrogen peroxide, which can oxidize sulfite. The GASIE results demonstrate that no significant losses of SO₂ occur in the system at ozone levels up to 100 ppbv. This result confirms our own experiments in which we have demonstrated the ability to quantitatively recover standard additions of SO₂ in marine air, where ozone is usually present in the range of 10-30 ppbv.

The fact that the HPLC/fluorescence instrument did not respond to the interferences tested should not be over-interpreted. The GASIE protocol did not test what we consider the most serious potential interference, which is hydrogen peroxide, particularly in humid air. As mentioned above, because the sampling principle for this instrument is aqueous absorption, the potential exists for oxidation of bisulfite during sample collection. Rate calculations suggest that such losses should be negligible during sampling of relatively clean air but may be significant in highly polluted air. The possibility also exists for oxidation of sulfite on hydrated surfaces on inlet lines. Such losses could apply to most analytical methods for SO₂ detection but are difficult to model.

Diluted Ambient Air: Phase 4

The final phase of the GASIE experiment consisted of the analysis of diluted ambient air. The ambient air was delivered into the dilution system via metal bellows pumps and diluted five- to tenfold with air from the SGDS clean air generator. Because of the potential for rapid fluctuations in the SO₂ concentration, we did not attempt to carry out standard additions experiments during this phase of the project. Instrument blanks and calibration slopes were similar to those obtained during the standards phase of the project. Qualitatively, the instrument appeared to track variations in the SO₂ concentration in the diluted ambient air [Stecher *et al.*, this issue]. However, there is some evidence that the response of the HPLC/fluorescence instrument decreased relative to other instruments in the study during the diluted ambient phase. The complete data set from this phase of the project is given by Stecher *et al.* (this issue).

During Phases 2b, 3a, and 3b the mean response of the HPLC/fluorescence technique was 0.99, relative to the mean of all methods (except the denuder/SCD [Stecher *et al.*, this issue]). During phase 4 the response of the HPLC/fluorescence instrument decreased relative to that of the other instruments, giving a response factor of 0.73 relative to the mean of the six methods considered. This change in the

response factor could be due to changes in the response of the HPLC/fluorescence technique, the response of the other techniques, or to changes in both. To better illustrate this the response of each instrument during a given period was ranked, with the instrument reporting the highest concentration assigned the rank of 1 and the instrument reporting the lowest concentration the rank of 6. The rankings were then averaged to give a single value for the standards and diluted ambient air phases, respectively. During the standards portion of the study, these ranks presumably reflect differences in the calibration of the instruments. The rank of the HPLC/fluorescence method increased during the diluted ambient air phase compared with the standards phase, indicating lower response relative to other techniques (Table 2). The rank of the isotope dilution-gas chromatograph/mass spectrometer (ID-GC/MS [Driedger *et al.*, 1987]) also increased during the diluted ambient air phase relative to the standards phase. The rank of the aqueous chemiluminescence technique [Meixner and Jaeschke, 1981] decreased during the diluted ambient air phase, which indicates a higher response relative to other techniques. The other three instruments showed little change.

To gain insight into this change in relative response, we attempted to carry out detailed comparisons between the HPLC/fluorescence and that of other instruments. Such comparisons are complicated by the differences in measurement frequency of the various instruments and the apparent variability of the atmospheric concentrations. As noted by Stecher *et al.* [this issue], it is impossible to rigorously intercompare measurements which are not completely overlapping in time. In order to carry out the comparison, we subjectively selected samples where the overlap was maximized and where the atmospheric trends were tracked by several techniques. We concluded that there was sufficient overlap among the HPLC/fluorescence technique, the Mist-IC technique [Klemm and Talbot, 1991], and the ID-GC/MS to form a reasonable basis for comparison of relative instrument response. Figure 5 shows the data from these three instruments for phase 4 sampling of diluted ambient air. SO₂ concentrations were high during period 111 [Stecher *et al.*, this issue]. These data were not included in the comparison since they could dominate a regression between the two-methods response.

The diluted ambient air data used for intercomparison were first normalized by the average response of each instrument during the standards phase of the GASIE study. The normalization factors were: HPLC/fluorescence, 1.010, Mist-IC, 1.052, and ID-GC/MS, 0.787 [see Stecher *et al.*, this issue, Table 7]. The resulting data are shown in Figure 6. The data sets were highly correlated, confirming that all instruments were responding to atmospheric variations. Because the data were normalized for instrument response to standards, one would expect a linear regression to yield a slope of 1 between instruments. The slope of the linear

regression was 0.96 ± 0.04 between the Mist-IC and the HPLC/fluorescence data and 0.87 ± 0.06 between the ID-GC/MS and the HPLC/fluorescence. This confirms a decrease in response of the HPLC/fluorescence relative to the other techniques by approximately 4-13% and suggests that the calibration of one or more instruments changed. There is sufficient uncertainty in the relationships that it is not possible to determine which instrument (or instruments) are responsible.

The high degree of correlation between instruments argues against a major chemical interference in ambient air as the cause of reduced response of the HPLC/fluorescence instrument. Unless the interferent was highly correlated with SO₂, one might expect to see a loss of correlation between instruments. In fact, the variance between instruments observed during the diluted ambient phase (based on the data in Figure 6) is approximately the same as that observed between the same instruments during the standards portion of the project.

Summary and Conclusions

During the standards phases of the GASIE intercomparison, the HPLC/fluorescence instrument performed as expected based on the design specifications. The instrument demonstrated the capability for measuring sub-10 pptv levels of sulfur dioxide in humid air, with the time resolution, precision, and accuracy needed for current scientific objectives involved in the study of the atmospheric sulfur cycle. The instrument did not respond to the interferents tested in this study. Most importantly, the instrument demonstrated the capability for standardization and standard additions tests at ambient sulfur dioxide

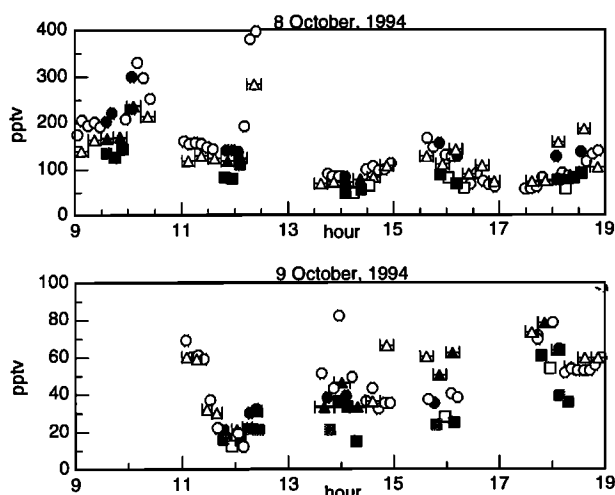


Figure 5. Diluted ambient air data from the ID-GC/MS (circles), the Mist-IC (triangles) and HPLC/fluorescence (squares) instruments. Open symbols denote data that were not used for comparison of relative instrument response. Solid symbols represent data that were used in the comparison. Gray squares denote HPLC/fluorescence data that were compared against both ID-GC/MS and Mist-IC data. Horizontal bars indicate each instrument's integration period. High [SO₂] data from period 111 (0900 to 1030 on October 9) were excluded from the comparison.

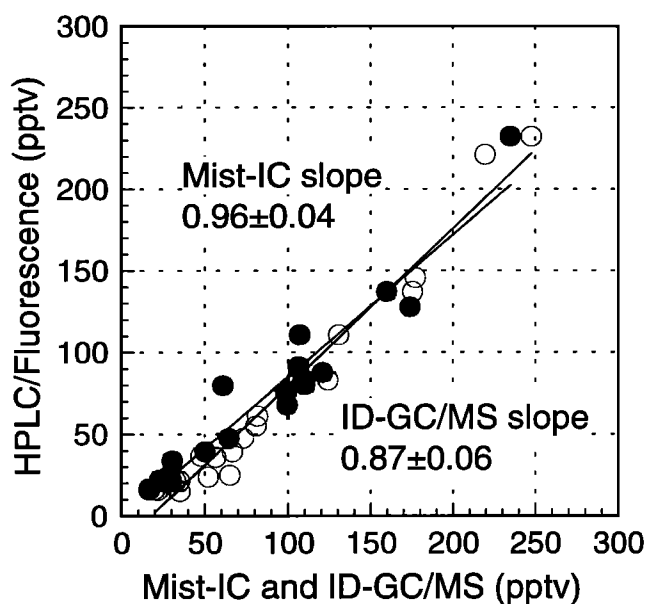


Figure 6. Diluted ambient air measurements using Mist Chamber-Ion Chromatography (open circles) and isotope dilution GC/MS (solid circles) instruments plotted against the HPLC/fluorescence technique. All data have been normalized to remove calibration differences.

concentrations in the low parts per trillion by volume range. During diluted ambient air tests, the HPLC/fluorescence instrument exhibited a $\approx 10\%$ decrease in response relative to some other techniques. The cause of this apparent calibration change is not known.

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References

- Cambridge University Press, *Climate Change 1995: The Science of Climate Change, Contribution of Working Group I to the Second Assessment Report of the Intergovernmental Panel on Climate Change*, edited by J.J. Houghton, L.G. Meiro Filho, B.A. Callander, N. Harris, A. Kattenberg and K. Maskell, New York, April 1996.
- Charlson, R. J., J. E. Lovelock, M. O. Andreae, and S. G. Warren, Oceanic phytoplankton, atmospheric sulfur, cloud albedo and climate, *Nature*, 326, 655-661, 1987.
- Driedger, A. R., III, D. C. Thornton, M. Lalevic, and A. R. Bandy, Determination of parts-per-trillion levels of atmospheric sulfur dioxide by isotope dilution gas chromatography/mass spectrometry, *Anal. Chem.*, 59, 1196-1200, 1987.
- Gregory, G.L., D.D. Davis, N. Bely, A.R. Bandy, R.J. Ferek, and D.C. Thornton, An intercomparison of aircraft instrumentation for tropospheric measurements of sulfur dioxide, *J. Geophys. Res.*, 98, 23,325-23,352, 1993.
- Klemm, O., and R. W. Talbot, A sensitive method for measuring atmospheric concentrations of sulfur dioxide, *J. Atmos. Chem.*, 13, 325-342, 1991.
- McTaggart, D. L., S. O. Farwell, T. J. Haakenson, W. L. Barnesberger, and W. D. Dorko, Generation and evaluation of test gas mixtures for the Gas-Phase Sulfur Intercomparison Experiment, *J. Geophys. Res.*, this issue.

- Meixner, F. X., and W. Jaeschke, The determination of low atmospheric SO₂ concentrations with a chemiluminescence technique, *Int. J. Environ. Anal. Chem.*, *10*, 51-67, 1981.
- Rubinson, K. A., *Chemical Analysis*, pp. 172-173, Little, Brown, Boston, Massachusetts, 1987.
- Saltzman, E. S., S. A. Yvon, and P. A. Matrai, Low-level atmospheric sulfur dioxide measurement using HPLC/fluorescence detection, *J. Atmos. Chem.*, *17*, 73-90, 1993.
- Stecher, H.A., III, et al., Results of the Gas Phase Sulfur Intercomparison Experiment (GASIE): Overview of experimental setup, results, and general conclusions, *J. Geophys. Res.*, this issue.
- Yvon, S.A., and E.S. Saltzman, Sulfur dioxide budget in the tropical South Pacific marine boundary layer (12°S, 135°W), *J. Geophys. Res.*, *101*, 6911-6918, 1996.
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