Performance of the HPLC/Fluorescence SO_2 Detector During the GASIE Instrument Intercomparison Experiment.

M.S. Gallagher, D.B. King, P.-Y. Whung, and E.S. Saltzman

Rosenstiel School of Marine and Atmospheric Science
University of Miami
4600 Rickenbacker Cswy., Miami, FL 33149

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ABSTRACT

Sulfur dioxide (SO_2) in synthetic air and diluted ambient air was measured as part of the Gas Phase Sulfur Intercomparison Experiment (GASIE) using the HPLC/fluorescence technique. SO_2 was analyzed by equilibrating the gaseous sample with aqueous SO_2, sulfite and bisulfite, then converting the aqueous S(IV) to an isoindole derivative. The derivative was separated by reversed phase HPLC and was detected via fluorescence. The system was calibrated with mixtures of SO_2 in zero air prepared from an SO_2 permeation device through a two-stage dilution system. The instrument has a four minute sample integration time and a measurement period of nine minutes. During the GASIE intercomparison the lower limit of detection averaged 3.6 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 (H_2O, O_3, NO_x, DMS, CO, CO_2, and CH_4).

I. Introduction

The biogeochemical cycling of reduced sulfur gases in the marine troposphere has been a topic of contemporary interest due to the role of sulfate aerosols in the overall radiation budget of the earth (Charlson et al., 1987). The abundance and distribution of sulfur dioxide (SO_2) has been a central theme in 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. Due to relatively low precursor source strengths per unit area and efficient scavenging processes, the concentration of SO_2 in the remote marine troposphere is typically in the low tens of parts per trillion by volume (pptv) (Yvon et al., 1991; Bandy et al., 1992). Many of the measurements of sulfur dioxide in remote regions have been made by adapting analytical techniques which were originally designed for highly polluted environments (carbonate filter technique, TCM technique, GC with flame photometric detection), though several instruments have been developed recently which were specifically intended for use in environments with low concentrations of SO_2 (Driedger et al., 1987; Saltzman et al., 1993; Benner and Stedman, 1990).

The HPLC/fluorescence technique was developed primarily for use in the remote marine boundary layer. The original goals for the instrument were as follows: 1) sub-10 pptv detection limit, 2) 10 minute 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 performance of this instrument was evaluated during the Gas Phase Sulfur Intercomparison Experiment (GASIE) in Lewes, Deleware during September and October, 1994 (Stecher et al., this volume).

This paper describes the configuration of the HPLC/fluorescence instrument as it was operated during the GASIE intercomparison, including modifications which have been

made since it was originally described in Saltzman et al. (1993). This report assesses the performance of the instrument from the information available to the operators during the intercomparison. The formal results of the intercomparison, i.e. how this instrument compared with others, are given by Stecher et al. (this volume).

II. Instrument Description

A. Basic Principles

A schematic diagram of the instrument is given in Figure 1. The reagent concentrations and flow rates are as given in Saltzman et al. (1993). The instrument samples 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 is pumped through a continuous reaction system where it is sequentially mixed with: 1) a borate buffer (pH=9), 2) ethanolamine, and 3) o-phthalaldehyde. The reaction mixture flows through a reaction/delay coil, where S(IV) in solution is converted to a highly fluorescent isoindole derivative. The delay is timed to optimize the yield of the isoindole derivative while minimizing intra- and inter-molecular decomposition reactions. A strong acetate buffer (pH=5.7) is 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 HPLC. The reaction stream flows through a 600 ul injection loop which is periodically injected into an isocratic, reverse phase HPLC with continuous fluorescence detection. The mobile phase is a pH5.7 acetate/20% methanol buffer and a 1/4” x 5”C-18 reversed phase HPLC column (Spherisorb S5ODS2, PhaseSep, Queensferry, Clwyd, UK) was used. A dual monochromater spectrofluorometer (Hitachi model F-1080) fluorometer was used with excitation/ emission wavelengths of 330/380nm., which are the maxima for the derivative.

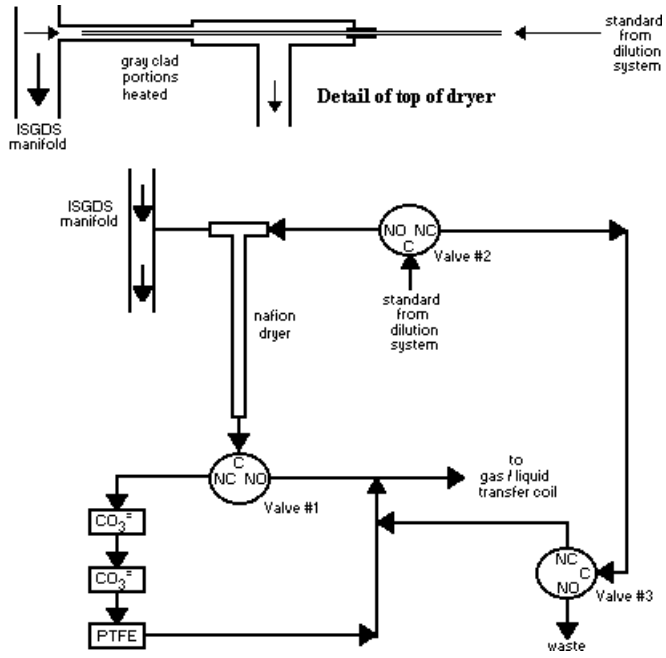

Figure 1. Schematic of the HPLC/fluorescence instrument.

B. Sample Inlet

The inlet for this istrument at GASIE was initially similar to that used by Saltzman et al. (1993), with the addition of a 1m PFA tube to connect to the manifold used to supply mixtures of SO_2 and various interferents in air from the Sulfur Gas Dilution System (SGDS) during GASIE. The inlet of the HPLC/fluorescence instrument was changed early in the the GASIE study (Phase 2a) when standard addition experiments demonstrated that there were significant losses of gaseous sulfur dioxide in humid air (see discussion in section III below). Although it was not known at the time, these losses were associated with sodium carbonate contamination of inlet valves which was inadvertantly 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, 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 PFAtube, 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 dryer was fitted with a 3-way PFA Teflon solenoid valve which was plumbed such that toggling the valve either sent sample directly to the air/liquid coil or first passed it through two carbonate treated filters and one PTFE Teflon

filter for blank determinations. A second 3-way PTFE Teflon solenoid valve was plumbed to direct standard gas mixtures to either a third valve or through the 1/8" o.d. PFA Teflon tubing to the upstream end of the inlet. The third 3-way PFA Teflon solenoid valve 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.

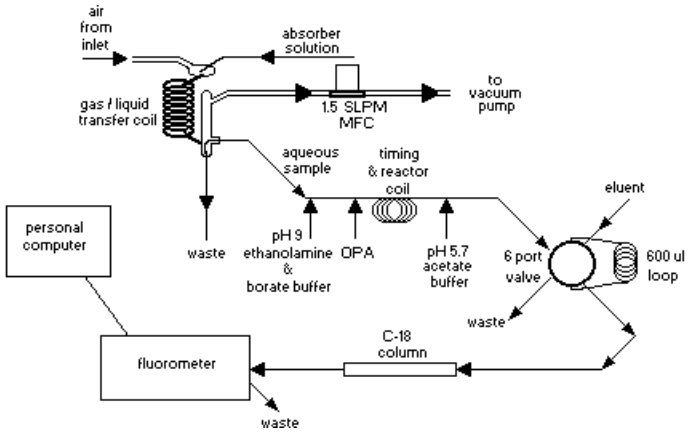

Figure 2. Schematic of the inlet used on the HPLC/fluorescence instrument at GASIE during intercomparison periods 2b-4.

C. Calibration

Gas standards were generated using a permeation source and gas dilution system, shown in Figure 3. The permeation tube was a certified, wafer-type permeation source (VICI Metronics, Santa Clara, CA), held at 30°C±0.3 in a PFA housing in a thermostatted aluminum block. The gas dilution is a two-stage system consisting of four 0-100 sccm mass flow controllers (Tylan General, San Diego, CA). 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. The operation of the gas dilution system is as follows. A mass flow controller (m_1 in Figure 3) provided a constant flow (approximately 85 sccm) of nitrogen over the permeation device. A second mass flow controller (m_2), located just downstream from the permeation device, is connected to a vacuum manifold. This controller is 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 sccm of nitrogen to dilute the remaining calibration gas stream. The gas stream was then passed through a PFA mixing volume (approximately 300 cc) to insure homogeneity. A final mass flow controller (m_4) is connected to the vacuum pump manifold, and is used to remove a fixed flow (approximately 70 sccm) from the calibration gas stream. The remainder of the calibration gas was directed to the inlet of the instrument.

Figure 3. Gas dilution system used to generate sulfur dioxide standards ranging from 12 to 610 pptv. The units labelled m_1 through m_4 are 0-100 sccm mass flow controllers.

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

(equation 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 (cc/min) as numbered in Figure 3. The constants at the end of the expression are conversion factors with units of pptv·cc/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. This data provides 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 (±0.2% of full scale) but considerably better than the overall absolute accuracy (±1% 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.

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. Using 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 SO_2 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. Under these conditions, we estimate the run-to-run uncertainty in the standards generated by the

calibration system to range from ±2.6% at 610 pptv to ±34% at 12 pptv. This uncertainty includes contributions from both the mass flow controllers and permeation oven temperature drift.

The output of the permeation device used in the GASIE study was certified by the manufacturer as 11.6 ng/min ±10% at 30 C when the device was manufactured 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 SO_2 output from the device with a standard generated by the dilution of a commercially prepared, certified SO_2 gas tank (10.18 ppmv ±1% SO_2 in N_2; Scott Specialty Gas, Plumsteadville, PA). The comparison was done using a Thermo-Electron Corporation pulsed fluorescence SO_2 monitor. The permeation rate determined in this way was 10.4 ng/min±12%, which was the value used in calculating all GASIE results. In order to assess the total uncertainty in our absolute calibration, this uncertainty should be added to those given above for the gas dilution system.

III. Instrument Operation and Performance During the GASIE Intercomparison

The GASIE experiment was carried out in four phases:

Phase 1	SO_2 in dry air with no interferents
Phase 2a	SO_2 in humidified air
Phase 2b	SO_2 in humidified air
Phase 3a	SO_2 in dry air with O_3 and NO ...
Phase 3b	SO_2 in dry air with CO, CO_2, CH_4, and DMS
Phase 4	Ambient air diluted with dry air.

Five different set points or “target” SO_2 concentrations ranging from 0 to 501 pptv were provided on a random basis by the SGDS during phases 1-3. Details regarding the concentrations of SO_2 and interferents and the performance of the SGDS are given in Stecher et al. (this volume). The GASIE sampling protocol called for five, ninety minute measurement periods each day. Measurement periods were followed by a thirty minute break during which the SGDS setpoint was changed to the value for the next measurement period and allowed to stabilize. At nine minutes per sample, this pace allowed the HPLC/fluorescence instrument to carry out thirteen 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). Any SO_2 losses occurring in the inlet should be detectable from the difference in (blank-corrected) response between standard addition runs and the sum of responses from standard runs and ambient runs. Daily calibration curves were generated from blank-corrected standard runs at four or five

SO_2 concentrations, typically ranging from 12 to 610 pptv. The variation in the calibration slopes from all days of the intercomparison was 6.5% (1σ), with no discernable trend. A system blank was always detectable, with a mean levels equivalent to 16 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 SO_2 environment, reagents were prepared in a positive pressure hood supplied with carbonate-filtered air. During the course of a single day, the blank varied randomly by an average of $\pm$12.3% (1σ). Day to day variation in blanks was larger.

Chromatograms from the first pair of ambient runs in a given measurement period were used to select the concentration of SO_2 standard to be used for that period. Concentrations were chosen such that instrument response to the subsequent standard addition runs was 160% to 200% of the response to the ambient runs.

Standard addition experiments with humid sample streams indicated that during phase 2a there were significant losses of SO_2 in the instrument inlet. The magnitude of these losses (up to 30%) was inconsistant from sampling period to sampling period, making it impossible to correct the data for the losses. Since losses of this magnitude were not detected during phase 1 sampling of dry gas streams, the formation of liquid water films and subsequent dissolution of SO_2 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 discovered the loss of SO_2 associated with a contaminated valve and adopted the inlet configuration shown in Figure 2. The port for the inlet was also relocated on the SGDS manifold to be upstream of two other instruments which had considerably higher flow rates. The contaminated valve contained white powder, thought to be sodium carbonate. This contamination was inadvertently introduced during a field project just prior to the GASIE experiment. 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 SO_2 quantitatively. Data from phase 2a was withdrawn from the intercomparison experiment. Data from phase 1 was not withdrawn because, although the contaminated valve was present in the system, it did not appear to significantly alter recoveries from dry air.

The performance of the instrument is best portrayed by the data obtained during phase 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 setpoint. For all periods in phases 2b, 3a, and 3b, this value averaged 4.4% at the lowest setpoint and decreased to an average of 1.3% at the highest setpoint. The variability calculated in this way reflects both the variability in the HPLC/fluorescence instrument and the SGDS system.

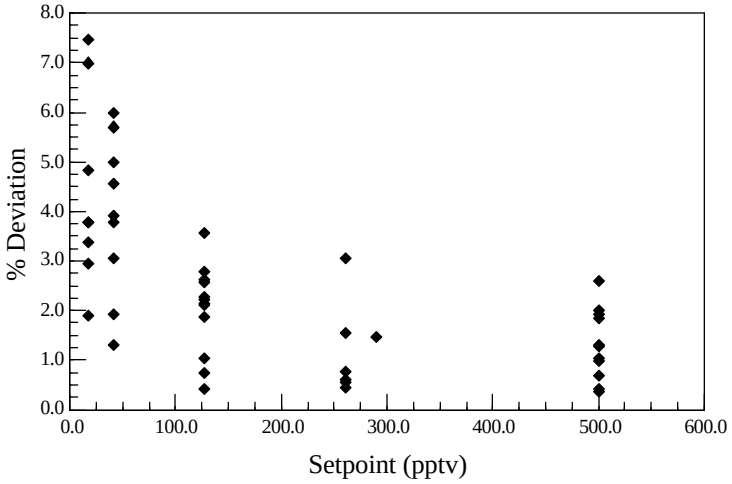

Figure 4 - Precision of the HPLC/Fluorescence instrument during the GASIE intercomparison. The data shown are 1σ/SGDS setpoint of the replicates for each measurement period, plotted against the SGDS setpoint.

The lower limit of quantitation for the HPLC/fluorescence instrument at GASIE was 12 pptv and the detection limit was 3.6 pptv (10σ and 3σ of the mean daily blank, respectively; Rubinson, 1987). The instrument reported SO_2 concentrations below the lower limit of quantitation for each measurement period that the SGDS setpoint was zero. However, non-zero concentrations were detected during each of these measurement periods. For the six periods with a SGDS setpoint of zero during Phases 2-4 we obtained a mean concentration of 3.1±1.8 (1σ) pptv. This suggests that the carbonate filter used to scrub air for our blanks was more effective at removing SO_2 than the clean air generator used in the SGDS.

The presence of interferents(H_2O, O_3, NO_x, DMS, CO, CO_2, and CH_4) during Phases 2 and 3 causes no detectable changes in instrument performance, with the exception of the water related inlet losses discussed previously. 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 SO_2 occur in the system at ozone levels up to 100ppbv. 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 overinterpreted. 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 SO_2 detection, but are difficult to model.

There was some evidence from the GASIE experiment that there may be compounds present in SGDS diluted ambient air which affect the HPLC/fluorescence technique. Averaging data from the portion of the experiment carried out with SO_2 standards during Phases 2b, 3a, and 3b for all methods except the denuder/SCD, the HPLC/fluorescence instrument response was close to the mean, with a response factor of 0.99. This is not to claim that the calibration of the system was "correct", but to establish a baseline for response to standard mixtures. In diluted ambient air (Phase 4) the response of the instrument dropped 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 was not entirely due to changes in other methods but was in part due to changes in the response of the HPLC/fluorescence technique. To illustrate this, the response of each instrument during a given period was ranked, with the instrument reporting the highest concentration assigned the rank of one and the instrument reporting the lowest concentration the rank of six. Examination of the relative ranks revealed systematic changes in instrument response. Of the six instruments considered, the average rank of four of the instruments showed little change between periods where standards were measured versus periods where diluted ambient air was measured. However the HPLC/ fluorescence method and the liquid chemiluminescence technique showed substantial changes in relative response (Figure 5). Note that during this phase of the intercomparison there was considerable temporal variability in concentration within analysis periods. For this reason it was not possible to do standard additions as we normally do in the marine boundary layer where the variability in concentration is much lower. Hence, we do not have data with which to assess whether loss of analyte occurred during these periods. It should be noted that the diluted ambient air tests during GASIE involved the passage of ambient air through a stainless steel bellows pump. It is likely that such treatment would significantly alter the oxidant speciation and concentrations in the outflow relative to that in the incoming ambient air. Pending further study, these results urge caution when using the technique in polluted or highly variable environments where the performance of the instrument cannot be internally verified.

Figure 5 - Average of the ranks for each instrument during periods in Phases 2b, 3a and 3b (standards in "scrubbed" air) and during Phase 4 (diluted ambient air).

IV. Summary and Conclusions

During the standards phases of the GASIE intercomparison, the HPLC/fluoresence instrument performed as expected. 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 exhibit any response to the interferents tested in this study. One of the most important attributes of the instrument is the capability to carry out standardization and standard additions tests at ambient sulfur dioxide concentrations in the low pptv range. The performance of the system during the ambient air phase of GASIE raises a question about the possible existence of interferents in some polluted air masses which might reduce the response of the instrument, but we caution that this conclusion is speculative.

V. References

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