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Journal

Journal of Atmospheric Chemistry, 17(1)

ISSN

0167-7764

Authors

Saltzman, ES
Yvon, SA
Matrai, PA

Publication Date

1993-07-01

DOI

10.1007/bf00699115

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Low-Level Atmospheric Sulfur Dioxide Measurement Using HPLC/Fluorescence Detection

E. S. SALTZMAN, S. A. YVON, and P. A. MATRAI

Rosenstiel School of Marine and Atmospheric Science, University of Miami, 4600 Rickenbacker Causeway, Miami, FL 33149, U.S.A.

(Received: 24 April 1992)

Abstract. An automated technique for measuring SO_2 in ambient air has been developed. Air is passed through a gas/liquid exchange coil with an aqueous absorber solution containing $10 \mu\text{M}$ formaldehyde and $0.84 \text{ mM Na}_2\text{EDTA}$. The SO_2 rapidly equilibrates with bisulfite (HSO_3^-) and sulfite (SO_3^{2-}) in the aqueous solution. The aqueous S(IV) is subsequently reacted with *o*-phthalaldehyde in the presence of excess ethanolamine to form a fluorescent isoindole in a continuous flow stream. This derivative is then separated using reversed phase HPLC and detected via fluorescence with excitation and emission wavelengths at 330 and 380 nm, respectively. The lower limit of detection is 7 pptv ($\text{S/N} = 3$), with a measurement period of eight minutes per sample. The instrument response is linear over several orders of magnitude.

Key words. SULFUR dioxide, OPA, and HPLC.

1. Introduction

Sulfur dioxide plays a central role in the atmospheric sulfur cycle. It is a primary emission from pollutant and volcanic sources and a secondary oxidation product of both pollutant and biogenic emissions in the form of methyl sulfides, hydrogen sulfide, and thiols. In addition to its direct effects, sulfur dioxide plays a major role in atmospheric chemistry as a precursor of sulfate aerosol. Although there are numerous techniques for the determination of SO_2 at concentrations typical of highly polluted air (greater than 1 ppbv), the analysis of parts-per-trillion levels has proven difficult. Current techniques for this analysis include: (1) collection on filters impregnated with carbonate (Daum and Leahy, 1983; Berresheim, 1987; Ferek *et al.*, 1991) or hydroxide (Bates *et al.*, 1990) salts with ion chromatographic detection, (2) gas chromatography with cryogenic preconcentration and flame photometric detection (Thornton *et al.*, 1986), (3) isotope-dilution mass spectrometry with cryogenic preconcentration (Driedger *et al.*, 1987), (4) aqueous collection as mercuric complexes with chemiluminescent detection (Meixner and Jaeschke, 1981), and (5) aqueous collection in a mist chamber with ion chromatographic detection (Klemm and Talbot, 1991). The recent CITE-3 intercomparison of airborne measurements found poor agreement between various techniques (Gregory

et al., in press), illustrating the difficulty in making atmospheric sulfur dioxide measurements and demonstrating the need for new techniques.

We have developed a novel detection system for SO_2 in order to satisfy the following requirements: (1) sub-10 pptv detection limit, (2) near real-time concentration information, (3) an integration time of 10 minutes or less, (4) automated operation, and (5) operation without cryogenics which are often unavailable in remote regions. The most critical requirement is that the method should provide accurate response to SO_2 under the high relative and absolute humidity conditions typical of marine air. This instrument is relatively inexpensive to construct and maintain and, therefore, has potential widespread use as a monitoring device.

2. Principles of Operation

The detection system utilizes aqueous chemistry to absorb and preconcentrate sulfur dioxide from air, and to convert the resultant S(IV) to a highly fluorescent and easily detectable derivative. The absorption of SO_2 is accomplished in a gas/liquid exchange coil via the rapid acid/base equilibrium reactions forming bisulfite and sulfite ions. After collection, the S(IV) is converted to a fluorescent isoindole derivative by the following steps. First, a solution of ethanolamine in borate buffer is added, raising the pH of the reaction mixture to 9 and converting most of the S(IV) to sulfite. The second step is the addition of *o*-phthalaldehyde (OPA) followed by a two minute reaction period. Finally, a sodium acetate buffer is added to lower the pH of the reaction mixture to 5.7, in order to prevent dissolution of the silica-based HPLC column. The derivatization reaction is thought to proceed as shown in Figure 1 resulting in the formation of the *N*-alkyl-1-isoindole-sulfonate. Jacobs (1987) proposed this mechanism and obtained NMR results supporting the formation of the sulfonate. The isoindole derivative is intensely fluorescent and is easily separated chromatographically from other fluorescent by-products of the reaction by isocratic reversed phase HPLC.

The OPA reaction shown in Figure 1 is similar to that used widely for analysis of amino acids and other compounds containing primary amines in either pre-column

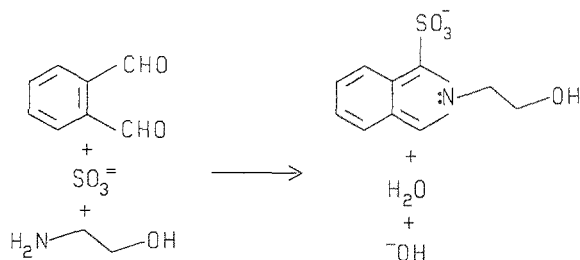


Fig. 1. Reaction converting aqueous sulfur dioxide to a fluorescent isoindole derivative.

or post-column derivatization modes. In those applications, the reagent includes OPA and a thiol such as methanethiol, ethanethiol, or mercaptoethanol, with the amines as the limiting reagent (Cronin *et al.*, 1979; Wong *et al.*, 1985; Rapsomanikis *et al.*, 1988, and references therein). An OPA-thiol-amine reaction has been used to analyze a variety of thiols in natural waters and biological samples, by providing excess OPA and ethanolamine and allowing the thiol to be limiting (Nakamura and Tamura, 1981; Mopper and Delmas, 1984). Mopper and Delmas (1984) noted that isoindole formation also occurs with sulfite in place of the thiol, and that the fluorescence spectra of the product isoindole was shifted from that of the organic thiols. The OPA-sulfite-amine reaction has subsequently been utilized for the detection of amino acids and alkylamines via HPLC with electrochemical detection (Jacobs, 1987) and for the detection of ammonia in flow injection mode (Genfa *et al.*, 1989).

As part of the optimization procedure for this study, we have measured the fluorescence spectra of the OPA-sulfite-ethanolamine isoindole derivative under the chromatographic conditions used for our instrument. This was done by derivatizing and injecting a large (μM) sample of sulfite into the HPLC and collecting the peak as it exited the fluorometer. The collected fraction was transferred to a Perkin-Elmer scanning fluorescence spectrophotometer with a xenon lamp source (model LS-3B). The resulting spectra, shown in Figure 2, have excitation and emission maxima of 330/380 nm. These spectra are not corrected for variations in lamp intensity with wavelength. The maxima we observed are somewhat different from the 346/390 nm maxima reported by Mopper and Delmas (1984) for the same derivative in 50% methanol.

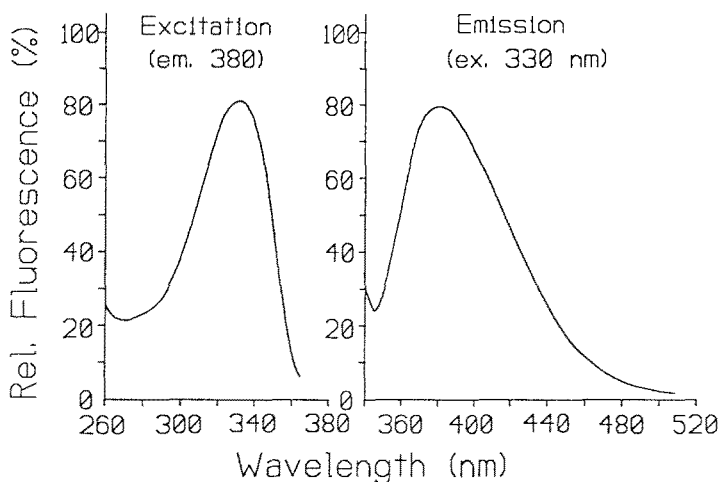


Fig. 2. Uncorrected fluorescence spectra of OPA-sulfite-ethanolamine derivative. Left-excitation scan with emission at 380 nm, right-emission scan with excitation at 330 nm.

3. Experimental: Materials and Instrument Design

3.1. Air Inlet Manifold

A schematic diagram of the instrument is shown in Figure 3. Air enters the system through a PTFE (Teflon PTFE, polytetrafluoroethylene) filter in a PFA (Teflon PFA, perfluoroalkoxy) holder. A PTFE solenoid valve is used to switch between the teflon filter for sampling and a carbonate-treated filter for calibrations. A 1/4"

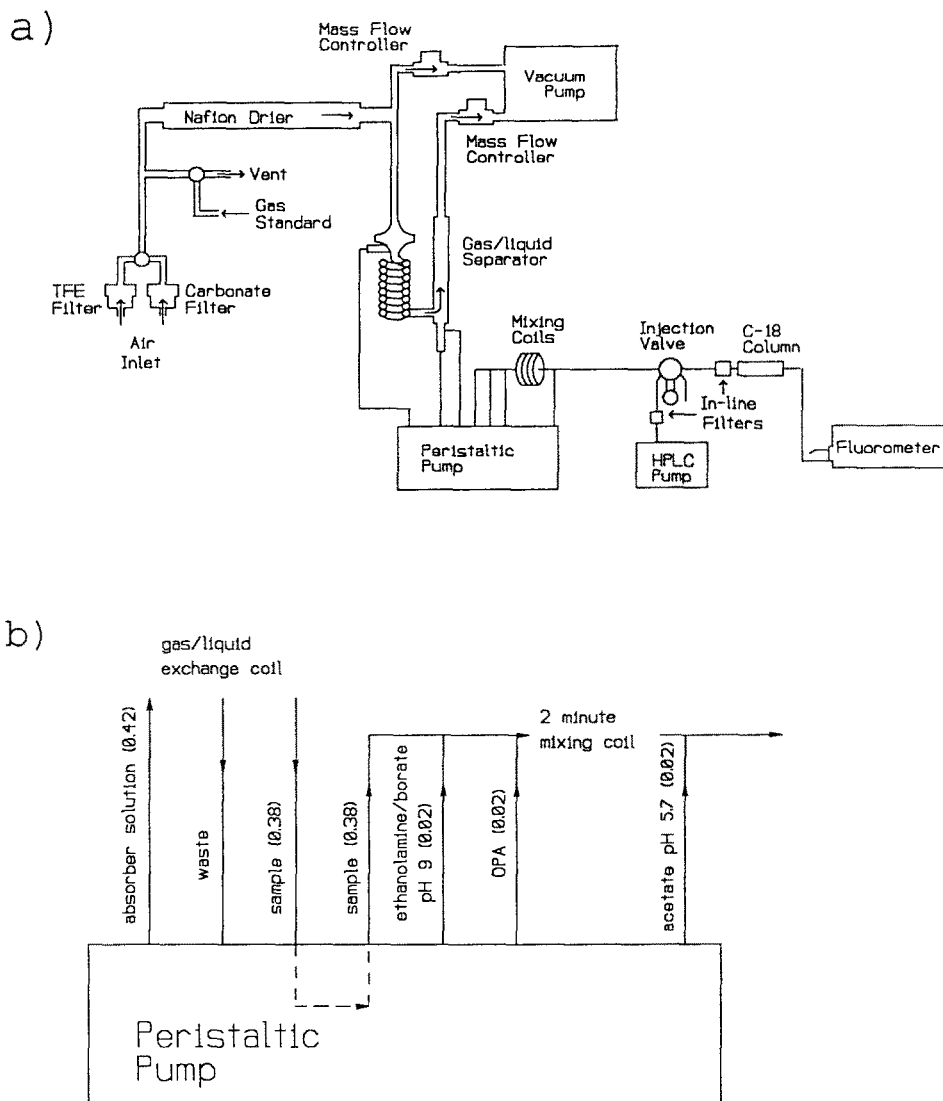


Fig. 3. (a) Schematic diagram of the sulfur dioxide detection system. (b) An expanded view of the precolumn reaction system. The flow rates are given in parentheses, and the units are mL/min.

PTFE union tee and a second solenoid valve are used to introduce gas standards into the flow stream. All tubing used in the inlet manifold is 1/4" o.d. PFA. The air flow rate into the system is 1-6 SLPM, with the higher flow rates needed for dilution during the addition of low concentration gas standards. During normal operation 1 SLPM is used. The sample air stream is drawn through a Nafion drier (Permapure Products, Toms River, NJ). This drier is positioned so that several inches of the inlet end remain outside the lab at ambient temperature to eliminate the potential for condensation. Dry air for the counterflow in the Nafion drier is provided by drawing laboratory air through a large silica gel reservoir at a flow rate 1.5 times the sample flow rate. A PFA tee is located just downstream of the Nafion drier connecting the Nafion drier to the gas/liquid exchange coil and the fast flow vacuum line. The analyte stream is drawn from the dry air stream at a flow rate of 1 SLPM. Both the main air intake flow and the analyte flow are mass flow controlled downstream of the analytical system so that the sampled air has not contacted any materials other than PTFE or PFA during passage through the intake manifold.

3.2. Gas/Liquid Exchange Coil

After passage through the drier, the analyte air stream is drawn through a 10-turn borosilicate glass gas/liquid exchange coil similar to that used by Kok *et al.* (1978). The tubing is 6 mm o.d. with a coil radius of roughly 1 cm. The interface between the drier and coil is a 15 mm glass o-ring joint with a 1/4" diameter glass tube attached as side-arm. The side-arm is converted to a liquid feed-through using a 1/4-1/16" PTFE connector drilled through to allow a 1/16" PFA tube to pump the aqueous absorber solution to the head of the coil. The outlet of the coil is attached to a vertical glass tube which serves as a gas/liquid separator. The air is pumped from the top of the separator, while the solution flows down into its base. At the base of the tube, two PTFE feed-throughs allow 1/16" tubes to enter for removal of the absorber solution. One of these tubes pumps solution to the analytical system. The other serves as an overflow which dumps excess absorber solution to waste.

3.3. Low Pressure Pumping System

An expanded view of the low pressure pumping system is shown in Figure 3b. A multichannel peristaltic pump with tygon pump tubing delivers the various reagents used to collect and derivatize the sample. The aqueous absorber solution is supplied to the gas/liquid exchange coil at 0.42 mL/min and removed from the coil for derivatization at 0.38 mL/min. The excess solution is pumped to waste. Three additional pumping channels are used to supply ethanolamine/borate, OPA, and sodium acetate at flow rates of 20 μ L/min. These are sequentially mixed with the sample stream in 1 mm i.d. PFA tubing using 1/16" PTFE tee unions as mixing tees. A 130 cm length of tubing is used as a mixing and delay coil prior to the addi-

tion of the sodium acetate channel to the reaction mixture. This mixture is continuously pumped through a 600 μL sample loop where it is automatically injected onto the column every 6–10 minutes.

The sample integration time of the instrument is a function of the absorber solution flow rate and the volumes of the reservoir at the base of the gas/liquid separator tube and of the peristaltic pump tubing containing the sample stream. The integration time was determined experimentally by flowing the reaction mixture from the HPLC loop directly through the fluorometer, bypassing the HPLC system. The system was allowed to sample sulfur dioxide-free air for several minutes after which a gas standard was instantaneously introduced. The increase in fluorescence began 5.5 minutes after the gas standard was introduced. The signal continued to increase for an additional five minutes, at which time it became constant. This five minute period is considered to be the integration time. The response time of the sampling system can be estimated at 8 minutes, the time it takes for the signal to reach 50% of its maximum. There is an additional delay of 6 minutes associated with the retention time of the derivative in the HPLC system. Thus the overall response time of the instrument is approximately 14 minutes.

3.4. *High Pressure Liquid Chromatography*

The high pressure side of the system is a modular HPLC consisting of the following components: a dual-piston stainless steel HPLC pump (model 100B; Eldex Laboratories Inc., San Carlos, CA), pressure gauge, an electrically actuated six or ten port injection valve, an in-line solvent filter (0.2 μm) and precolumn filter (0.2 μm), and a 15 cm C-18 Spherisorb column (Phase Separations, Norwalk, CT). All tubing in the system is Tefzel, 1/16" o.d., 0.02" i.d.. Mobile phases are selected using a PTFE solenoid valve. The mobile phase flow rate was 1.0 mL/min. The in-line solvent filter is located just after the pressure gauge. The precolumn filter is located before the chromatographic column to trap contaminants present in the sample which otherwise collect on the head of the column as a grayish-green coating. These contaminants appear to be by-products of the derivatization reaction, perhaps due to impurities in the reagents.

The detector used is a Hitachi model F-1000 fluorescence spectrophotometer. For this work, 150 watt Xe and Hg/Xe lamps (Hamamatsu, Bridgewater, NJ) were used. The Hg/Xe lamp provided increased sensitivity because of its overall higher emission intensity and an emission line at 333 nm. The excitation and emission bands of the fluorometer have a 7 nm bandpass and were centered on 330 and 380 nm, respectively.

3.5. *Reagent Solutions*

Distilled water used in this study was produced using a milli-Q system. All chemicals used were reagent grade unless otherwise noted. The sulfur dioxide absorber

solution (pH = 4.6) consisted of 10 μ M formaldehyde, with 0.84 mM of Na₂EDTA added to complex metals that may catalyze the oxidation of S(IV).

The reagent solutions for derivatization are prepared as follows: (1) 34 mM ethanolamine in a borate buffer (0.25 M borate, pH = 9), (2) 1.14 mM OPA (amino acid analysis grade; Sigma Chemical, St. Louis, MO) in an aqueous solution containing 10% MeOH, and (3) 2.5 M sodium acetate (HPLC grade; Fisher Scientific, Fair Lawn, NJ) buffered at pH = 5.7 using acetic acid. The mobile phase used for the chromatographic separation is 20% methanol (HPLC grade) in 0.01 M sodium acetate adjusted to pH = 5.7 using acetic acid (all buffers were filtered through 0.2 μ m nylon filters before use). A solution of 80% methanol in water was used to rinse the column and pump daily during system startup and shutdown.

In our laboratory, sulfur dioxide levels in air vary over several orders of magnitude and can reach ppbv levels depending on the meteorological conditions. In order to insure low and uniform blanks, reagents are prepared in a positive pressure Plexiglas box with air flow supplied through an 8 \times 10 inch cellulose filter impregnated with Na₂CO₃ (Ammons, 1980).

3.6. Instrument Control and Data Handling

The instrument timing and data acquisition is PC controlled by the E-Lab Chromatography Data System (OMS Tech, Miami, FL). The chromatographic data is collected from the fluorometer at 5 Hz, displayed and integrated in real time and stored on disk. For the field work discussed later in this paper a laptop PC (Toshiba model T1000SE) and bus expansion chassis (Connect Computer, Eden Prairie, MN) was used.

3.7. Calibration System

The gas calibration system is shown schematically in Figure 4. The design of the system was determined largely by the requirement that the low-level standard not pass through a mass flow controller; unacceptable losses were observed with stainless steel mass flow controllers in laboratory tests. A mass flow controlled dry nitrogen stream flows over a wafer-type permeation device (1.8 or 35 ng/min, VICI Metronics, Santa Clara, CA.), which is housed in a temperature controlled oven at 40 °C. These low loss rate tubes are calibrated against higher rate tubes (which can be accurately calibrated via weight loss) using the instrument itself. The permeation device is contained in a PFA vial and all tubing in the system is 1/8" or 1/4" o.d. PFA. After passing over the permeation device, a portion of the nitrogen flow is pumped away to waste through a second mass flow controller and vacuum pump. The remainder is connected to the air intake of the analytical system. The mass flow controllers used have a range of 0–100 SCCPM and are calibrated using an electronic bubble meter (A. P. Buck, Orlando, FL).

The calibration gas flow is normally used by addition to an ambient air flow

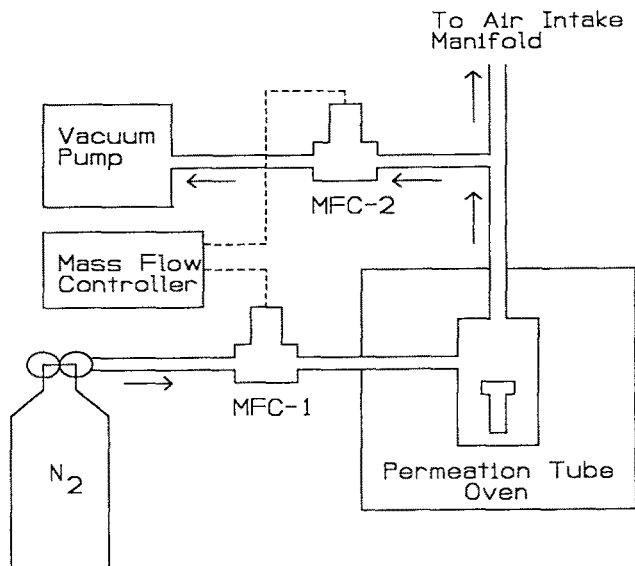


Fig. 4. Calibration system used to generate parts-per-trillion sulfur dioxide gas standards.

which has been passed through a Na_2CO_3 -treated filter to remove SO_2 . The standard gas is added just after this filter and before the Nafion drier. For standard additions experiments the PTFE filter is used, and the standard gas is added to ambient air. The standard is added to ambient air after the PTFE filter in order to prevent the standard line from becoming contaminated with aerosols when it is not being used. The results of standard addition tests in the laboratory and in the field indicate that SO_2 is not lost on the PTFE filter as long as the PTFE filter is changed periodically to prevent collection of large amounts of sea spray. After dilution by the 6 SLPM scrubbed or ambient air flow, final concentrations as low as 10 pptv can be reliably and repeatably generated using this system.

4. Results and Discussion

In this section, we briefly discuss some performance characteristics of the system and some design considerations which affect sensitivity and accuracy of the method. Data from an oceanographic cruise are presented in order to illustrate the performance of the system under field conditions.

An example of the detector output signal is shown in Figure 5. Each injection is followed by a negative (water) injection peak followed immediately by a positive system peak. The next peak is the sulfite derivative, with a retention time of approximately six minutes. The runs shown are part of a typical calibration sequence. The sulfite derivative peak area is integrated and converted to concentrations using a linear calibration curve. The resulting concentrations are reported in parts-per-trillion by volume.

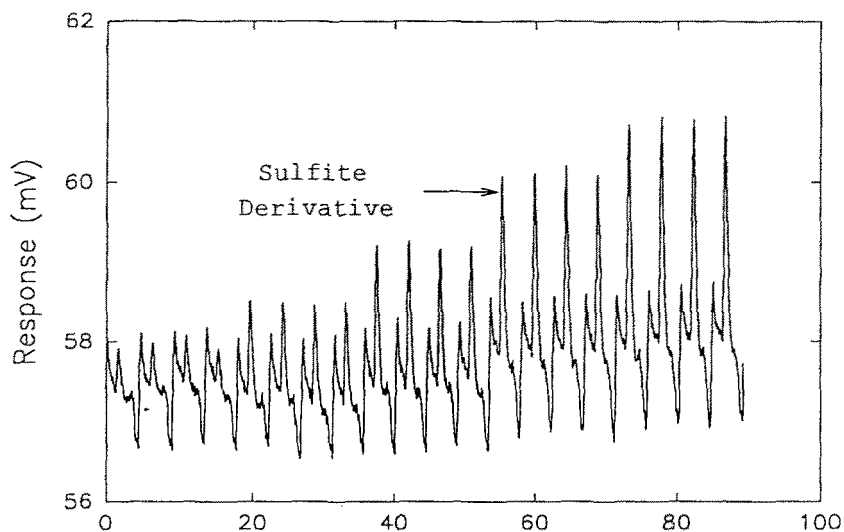


Fig. 5. Raw detector output from the system during calibration runs by addition of sulfur dioxide to scrubbed air over a concentration range of 10 to 100 pptv.

4.1. Optimization

We did not attempt to optimize all aspects of the system, but focused on those which most directly control the operational limit of detection. In this section we describe some of those efforts and mention some areas where future improvements may be made.

4.1.1. *Chromatographic peak shape.* The shape of the chromatographic peak is broad and slightly tailed during normal operation. This results from the use of a large (600 μ l) injection loop. Direct injection of loops larger than 600 μ l do not improve the signal to noise ratio because of deteriorating peak shape. However, larger sample volumes are possible using preconcentration. The choice of loop size also indirectly controls the frequency of sample injection onto the column since sufficient time must be allowed for the loop to be fully flushed with sample prior to each injection.

4.1.2. *Derivatization chemistry.* Although the formation of the isoindole occurs rapidly upon addition of the reagents, the net yield of the reaction can vary widely under different conditions. This is presumably a result of secondary reactions between the reagents and the derivative and intramolecular reactions causing breakdown of the isoindole product. Numerous authors have discussed these effects in the formation of OPA-thiol-amine isoindoles (Nakamura *et al.*, 1982; Stobaugh *et al.*, 1983; Allison *et al.*, 1984; Jacobs *et al.*, 1986) and the major loss is attributed to the reaction of excess OPA with the isoindole. The stability of iso-

indoles toward this attack is affected strongly by steric effects of both the S- and N-containing moieties, with larger substituents tending to stabilize the molecule. Jacobs (1986) demonstrated that OPA-methylamine-sulfite derivatives are significantly more stable than their 2-mercaptoethanol analogs toward OPA attack, but are subject to hydrolysis to the phthalimidine at low pH.

In order to optimize the system, we examined the effect of varying the delay time (1) between the addition of the reagents (ethanolamine and OPA) and injection into the HPLC system and (2) between the pH drop from pH 9 to 5.7 injection. Interestingly, quite different effects were obtained from the two experiments. When the mixture was allowed to stand after dropping the pH to 5.7 (Figure 6a), the signal decreased steadily with apparent first order kinetics. When the reaction mixture was allowed to stand at pH 9, the signal showed a rapid initial increase, attaining 90% of the ultimate signal during the first two minutes. After that time, the signal remained essentially constant, perhaps with a slight increase (Figure 6b). In terms of optimizing the flow derivatization system, the above results suggested that a reaction coil delay time of two minutes prior to the pH drop would provide a good yield of derivative, while the delay after the pH drop should be kept as short as possible to minimize losses.

Varying the reaction coil temperature showed that higher product yields were

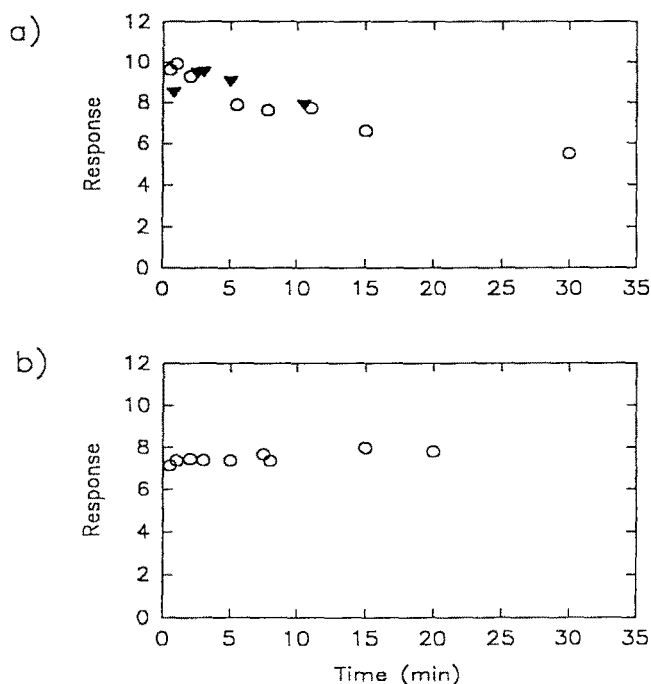


Fig. 6. Effect of reaction time on yield of the sulfite isoindole derivative using a $1 \mu\text{M}$ standard and: (a) delay at pH = 5.7 (triangles and circles refer to two experiments), (b) delay at pH = 9.0.

obtained at both 15 °C and 45 °C than at room temperature (23 °C). However, in both the elevated and reduced temperature cases, it took longer for the fluorescence response to stabilize, i.e. the reaction yield was more sensitive to the exact delay time in the coil. For this reason, operation at room temperature should provide greater precision and reproducibility from day to day. Since the system is not signal limited in terms of its overall detection limit, the added complexity of maintaining the coil at other than ambient temperature was not justified on the basis of sensitivity. However, the reproducibility of the response of the instrument would probably benefit from controlling the temperature of the reagents, tubing, and reaction coil.

4.2. Absorber Solution

The absorber solution has a pH of 4.6 and contains 0.84 mM Na₂EDTA and 10 μM formaldehyde. The Na₂EDTA is used to complex any metals that may act to catalyze the oxidation of S(IV). Assuming that equilibrium between the air stream and the absorber solution is attained, the efficiency of the absorber is determined by the mass flow rates of the air and solution and the pH of the solution. Mass balance calculations using equilibrium constants from Maahs (1982) at 298 K show that efficiencies of 57, 93, and 99% should be obtained for pH 4, 5, and 6, respectively, under the flow conditions used in this study. At the absorber pH of 4.6 the efficiency is 84%. We have kept the pH low in order to reduce the possible uptake and interference from carbonyl sulfide and hydrogen sulfide which may be absorbed along with the SO₂. Sulfide in solution would oxidize much more readily at higher pH (Millero *et al.*, 1987).

The use of formaldehyde in the absorbing solution was originally intended to assist in the trapping and stabilization of the S(IV) against oxidation through the formation of hydroxymethanesulfonic acid (HMSA). This adduct has been shown to stabilize sulfite against oxidation in cloud droplets and absorbing solutions (Dasgupta *et al.*, 1980; Munger *et al.*, 1984). However, in an effort to lower system blank levels, it was noted that the formaldehyde appears to remain effective at protecting S(IV) at levels below which HMSA formation should be important. In other words, according to published rate constants (Boyce and Hoffman, 1984; Olson and Hoffman, 1986), at the formaldehyde levels ultimately used in the system (10 μM) the rate of formation of HMSA at the absorber pH of 4.6 should be far too slow (by roughly a factor of 100) to have any impact on the speciation of S(IV) during the <10 minute residence time of the aqueous sample in the analytical system. If any HMSA was present in the absorbing solution due to the reaction of formaldehyde with sulfite and bisulfite, it would rapidly dissociate with the addition of the ethanolamine in borate buffer (pH = 9). Thus, it appears that HMSA is not an important species in the absorbing solution. The antioxidant effect of the formaldehyde may be related to its interaction with oxidizing species, for example as a free radical scavenger. Although the rate constant for the reaction between

formaldehyde and OH radicals in solution is not large ($k = 6.9 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, Farhataziz and Ross, 1975), it is present in the absorber solution at concentrations that are 2–3 orders of magnitude greater than the S(IV) concentrations being measured. At these levels formaldehyde reacts with OH at a rate 8–800 times that of bisulfite ($k = 9.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, Farhataziz and Ross, 1975) for SO_2 concentrations ranging from 1 ppbv to 10 pptv respectively. In this capacity, EDTA ($k = 2.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, Farhataziz and Ross, 1975) may be even more effective, reacting with OH 2×10^3 to 2×10^5 times faster than bisulfite over the same range of SO_2 concentrations. It is not known to what extent the formaldehyde is necessary. Initial work in Miami air suggested that it was effective as an antioxidant, but subsequent studies in marine air suggest that it may have no effect under clean conditions. We have maintained the use of formaldehyde at low levels, as it has no apparent disadvantages and does not contribute significantly to the blank signal.

4.3. Interferences

There are three principle types of potential interferences in this detection system. The most serious is wall losses of gas phase SO_2 in the delivery of the air to the absorption coil. These losses appear to be associated with water vapor and become particularly severe should visible condensation occur. Presumably the loss is caused by the dissolution of SO_2 into aqueous films. Experimentation showed that the losses occurred principally near the inlet to the absorption coil, rather than in the inlet manifold or inlet tubing prior to the manifold. This effect may be caused by condensation due to the pressure drop in that region. Addition of the Nafion drier to the system (Thornton *et al.*, 1986) immediately behind the standard addition mixing tee near the inlet alleviated the wall loss problem, as shown in a series of experiments with spiked carbonate-filtered ambient air and spiked humidified nitrogen gas streams. It was thought that the drier itself might cause some loss of SO_2 , as suggested by Thornton *et al.* (1986). This was investigated through experiments where low-level standards (50 pptv) were added to carbonate-filtered humid air streams at the inlet and also after the drier. No significant differences ($< 4\%$) in the measured concentrations were seen indicating that there were no significant losses of SO_2 in the drier. Experiments involving standard additions to ambient air have also been done and will be discussed in the following section.

The second interference type is oxidative loss of bisulfite in the absorption coil. Absorption of gas phase hydrogen peroxide is probably the most serious potential interferent because it reacts rapidly with bisulfite in aqueous solutions (Kunen *et al.*, 1983). Ambient levels of gas phase H_2O_2 range from 100 pptv to 1 ppbv in clean to moderately polluted environments. The rate of the reaction between H_2O_2 and bisulfite increases with decreasing pH (Kunen *et al.*, 1983). At the pH of the absorber solution (4.6) and assuming Henry's Law equilibrium with hydrogen peroxide at a gas phase concentration of 1 ppbv, the lifetime of bisulfite is 96 minutes. Under these conditions only 5% of the bisulfite would be oxidized in the

five minutes it takes to flush the gas/liquid exchange coil and raise the pH to a point where oxidation by H₂O₂ is too slow to be important. Therefore, we do not believe that oxidation by H₂O₂ in the coil is a significant interferent for this technique in marine air masses. However, in highly polluted areas where gas phase H₂O₂ may reach levels in excess of 1 ppbv, it could become a significant interference. Raising the pH of the absorber solution to approximately 6 should eliminate any potential for interference from H₂O₂ under ambient conditions.

The third type of potential artifact is positive interference from other sulfur-containing gases. The gases of particular concern are hydrogen sulfide and carbonyl sulfide, because both have straightforward conversion pathways to sulfite in aqueous solution. H₂S need only react with oxygen or hydrogen peroxide in the absorbing solution. Carbonyl sulfide must first hydrolyze to form sulfide, then oxidize. The direct reaction of sulfide via OPA-amine derivatization does produce a fluorescent isoindole product which is different from that of sulfite, however the yield is extremely low (Mopper and Delmas, 1984). As shown by those authors, the sulfide derivative would be chromatographically separated in our system; we have not observed peaks from sulfide in runs with either ambient air or standards. We have conducted laboratory tests in which high concentrations of H₂S and OCS (ppmv levels) are added to either nitrogen or ambient air and observed no artifact sulfite formation. Similar tests with other sulfur gases such as DMS, CS₂, and DMDS also yield no response. In principle, the system could be optimized to analyze for methylmercaptan or other mercaptans, which form a highly fluorescent derivative which is more hydrophobic than the sulfite derivative. The chromatographic conditions used in our work do not elute the methylmercaptan derivative during the run, but could easily be modified to do so.

4.4. Precision, Accuracy, and Detection Limits

The lower limit of detection of the instrument is approximately 7 pptv at a signal to noise ratio of three. This estimate was determined using 3 times the standard deviation in the peak areas of replicate blanks ($n = 11$) divided by the slope of the calibration curve (Rubinson, 1987). The precision ($2\sigma/\text{mean}$) of a given measurement ranges from 10% at 19 pptv ($n = 4$) to 4% at 186 pptv ($n = 11$), as determined from repeated measurements of a standard addition to ambient air passed through the carbonate-treated filter. The precision at very low concentrations is limited in part by the presence of a small reagent peak with a retention time slightly greater than that of the sulfite derivative. This peak is incompletely resolved from the sulfite peak in most cases. The peak area of a reagent blank is typically equivalent to 74 pptv. However, the variability of this blank within a given batch of reagents is approximately 4% (1σ), a signal equivalent to 3 pptv.

A calibration curve consisting of a number of replicate standards is shown in Figure 7. Some variability in the size of the blank has been observed when different batches of stock reagents are used. However, the slope of the calibration curve does

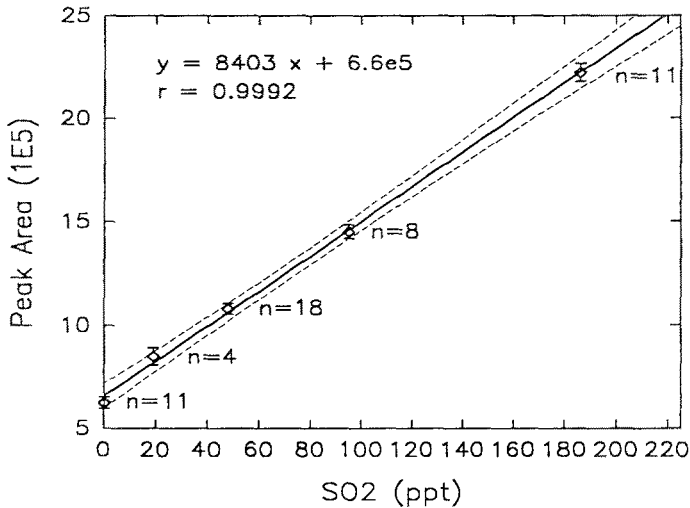


Fig. 7. A calibration curve for the SO_2 instrument. The dashed lines show the 95% confidence limits for the linear regression. The vertical error bars represent 1 standard deviation from the mean.

not change significantly from one batch to another. The variability in the blanks can be controlled when the stock solutions are prepared under SO_2 -free conditions. The blank level for a given batch of reagents remains stable for the duration of its use (3 days). Therefore, the blank does not vary from sample to sample and does not significantly affect the detection limit.

The accuracy of the method depends on the uncertainty in (1) the weight loss rate of the permeation tube and (2) the mass flow rates of the various dilution gases and air sampling streams. It also depends on the reproducibility of the slope of the calibration curve. The calibration curve intercept shifts with changes in the blank due to the use of different batches of reagents, but the slope does not change. The collection efficiency of the absorber solution does not affect the accuracy of the measurement as long as it remains constant. The overall uncertainty due to these factors is approximately $\pm 5\%$.

Experiments involving the addition of a standard to ambient air have also been carried out. Such experiments are useful in verifying the accuracy of the method with regard to system losses. However, because of the high variability in sulfur dioxide levels in coastal air, the precision with which the recovery can be determined at our laboratory is often poor. For one such experiment, ambient air was sampled on Virginia Key, Florida during a period of steady easterly winds which provided unusually low and steady sulfur dioxide concentrations. The results are shown in Figure 8. A 110 pptv gas phase standard was added to the air stream at the inlet on two separate occasions during the experiment. The first standard addition can be seen at approximately 1450 hr and the second at approximately 1630 hr. For the first standard addition, a $103\% \pm 9\%$ recovery of the standard was found. For the second standard addition, a $96\% \pm 13\%$ recovery of the standard

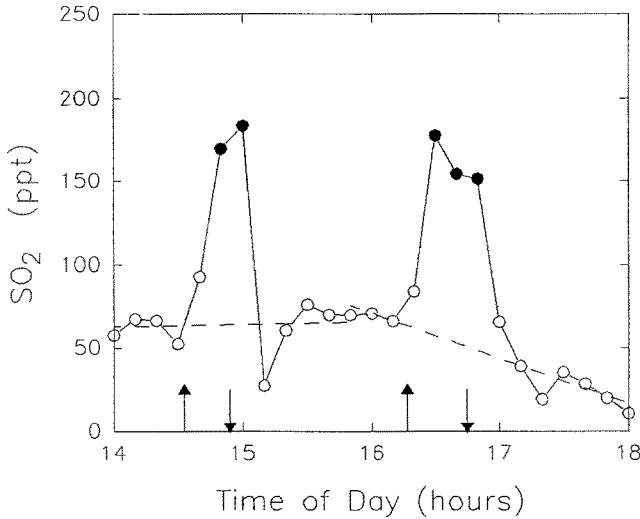


Fig. 8. The results of a standard addition experiment in Miami air during easterly winds. The dashed lines indicate average ambient air SO₂ concentrations. Filled circles indicate samples that include the standard addition. The up and down arrows mark the beginning and the end, respectively, of the addition of the standard.

was found. This variability is well within the natural variability of the ambient SO₂ levels during the course of the experiment.

4.5. Field Testing

This instrument was field tested during the Pacific Sulfur/Stratus Investigation (PSI-3) cruise aboard the R/V Discoverer in the Northeast Pacific Ocean. Some results are shown here to illustrate the performance of the system under field conditions. During this cruise the analytical system was housed in a van located forward of the ship superstructure, approximately 15 m above the sea surface. The air intake was located just outside the forward van wall with a 14 ft long 1/4" o.d. sampling line from the Nafion drier to the gas/liquid exchange coil. Calibration curves were run periodically during the cruise, and blanks were run more frequently to determine if the reagent solutions were becoming contaminated while in use. The blanks during the cruise varied by a factor of 2.5. Some precautions were taken to keep the blanks as low as possible; stock solutions were never prepared or open during periods of time when the ship's maneuvering caused stack gases to enter the lab van. However, on the ship we did not have the SO₂-free hood that we used to prepare solutions in the laboratory. It is likely that the higher blanks were due to some contamination during solution preparation.

The concentrations of sulfur dioxide measured during one day (22 April 1991) of the cruise are shown in Figure 9. It can be seen that while sampling clean marine

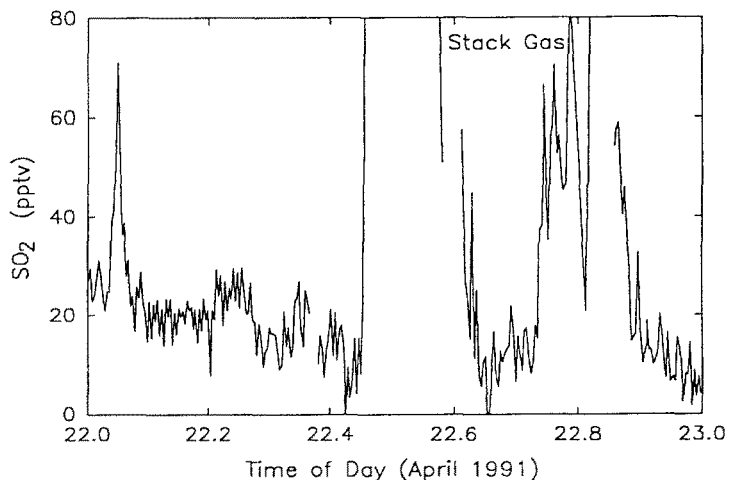


Fig. 9. The SO_2 levels measured on 22 April 1991 approximately 200 km off the Washington coast.

air the levels of SO_2 observed averaged 20 pptv. Several episodes of very high SO_2 occurred when maneuvering of the ship allowed plumes from the ship stacks to reach the system inlet. The concentration of SO_2 decreased rapidly when the ship was turned back into the wind, indicating that there is no significant memory effect in the instrument.

5. Conclusions

An automated instrument has been developed which is capable of accurate detection of atmospheric sulfur dioxide at low parts-per-trillion levels. The system allows standard additions at these low levels to be carried out in either ambient or scrubbed air, so the performance of the instrument can be monitored under field conditions. No interferences are known which significantly affect its reliability in moderately polluted to extremely clean air masses. For use in highly polluted air masses, further tests on the effect of peroxides should be carried out. The adaptation of this system to aircraft measurements is straightforward and such modifications are currently being made to the system.

This analytical system could easily be adapted for the detection of other thiols (e.g. methylmercaptan) or primary amines (e.g. ammonia) in air which undergo similar isoindole derivatization reactions to those of sulfite. The construction of a system for ammonia detection is currently underway.

Acknowledgements

We would like to acknowledge Ken Mopper, Dave Kieber, Robert Gawley, and A. Vairavamurthy for many helpful discussions and Albert Castellanos for assistance

in the laboratory. Discussions with Bill Dorko of NIST were helpful in the development of the calibration system. This work was supported by the National Science Foundation, grants ATM-8709802 and ATM-9120498. We also wish to thank Tim Bates and NOAA grant NA-90RAH00075 for the opportunity to participate in PSI-3.

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