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# Development of a new real-time method for measuring $S(IV)$ in cloud water using a counter-flow virtual impactor

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## ABSTRACT

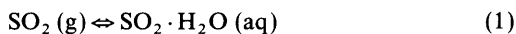
A new method of analysis for  $S(IV)$  is described incorporating a counter-flow virtual impactor for collection and evaporation of cloud droplets with an  $SO_2$  analyzer. This technique allows analysis of aqueous  $S(IV)$  concentration in real-time and overcomes some sampling or analysis problems of conventional sampling with bulk cloud water collectors and wet chemical analysis methods. The technique is demonstrated by the correlated responses of the  $S(IV)$  instrument and instruments measuring physical properties of clouds while passing in and out of clouds. Measured aqueous  $S(IV)$  concentrations ranged from the detection limit ( $0.1 \text{ nmol per m}^3$  of air) to  $1.8 \text{ nmol m}^{-3}$  in clouds in Ohio.  $S(IV)$  molar concentrations (moles/l of cloud water) were not calculable from these measurements, but can be calculated when a measurement of the liquid water content of the collected cloud water is made simultaneously.

## 1. Introduction

Because of the importance of the chemical and physical properties of acidic  $SO_4^-$  in the atmosphere, it is of interest to understand the processes governing its formation. Acidic  $SO_4^-$  is produced by the oxidation of natural or anthropogenic  $SO_2$ , which can occur in the gas phase (e.g., by the hydroxyl radical), or in the aqueous phase following dissolution into cloud droplets (Calvert et al., 1986). In the presence of sufficient concentrations of oxidants ( $H_2O_2$ ,  $O_3$ , or  $O_2$  with trace metals), the oxidation of  $SO_2$  dissolved in cloud water is expected to occur rapidly (Calvert et al., 1986).

The first step of the aqueous phase oxidation of

$S(IV)$  is the dissolution of  $SO_2$  into cloud droplets as described in the following equilibria:



where eq. (1) describes Henry's law and eqs. (2) and (3) describe subsequent acid base reactions. By combining the above equilibria, an "effective" Henry's law is produced (given below). This can be used to calculate

$$K_{EH} = \frac{[S(IV)]}{P_{SO_2}} = K_1 \left( 1 + \frac{K_2}{[H^+]} + \frac{K_3}{[H^+]^2} \right), \quad (4)$$

an expected  $S(IV)$  concentration (where  $[S(IV)]$  is defined here as the sum of  $[SO_2 \cdot H_2O]$ ,  $[HSO_3^-]$ , and  $[SO_3^{=}]$ ) from a known gas phase

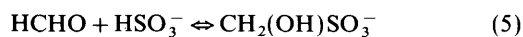
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SO<sub>2</sub> concentration and a measured cloud water pH. However, a number of factors including the reaction of *S(IV)* within droplets and the presence of droplets of different pH complicate the application of Henry's law and associated equilibria to the atmosphere. Thus, an accurate method for measuring *S(IV)* in cloud droplets is useful for understanding the dissolution process as well as the partitioning of *S(IV)* between gaseous and aqueous phases.

While there is a need for field measurements of *S(IV)* in cloud water to test the validity of using the effective Henry's law, few measurements of *S(IV)* have been made. A summary of previous *S(IV)* measurements is listed in Table 1. Often, however, sampling artifacts occur during the collection and analysis of aqueous *S(IV)*, which falsely may be attributed to deviation from the effective Henry's law equilibrium. One example is when *S(IV)* measured in collected cloud water contains *S(IV)* reaction products which are detected as *S(IV)*. It has been observed that hydroxymethanesulfonate (HMS), a reversibly formed product of *S(IV)* and HCHO (shown below), often is present in cloud or rain water



in concentrations similar to *S(IV)* (Munger et al., 1986; Keuken et al., 1987; Chapman, 1986). Thus, HMS detected as *S(IV)* will lead to an apparent positive deviation from Henry's law (where a positive deviation is defined as more *S(IV)* in the aqueous phase than expected). While it is possible

to include HMS and HCHO in a more detailed equilibrium calculation (Warneck, 1989), such a calculation is of limited use because of the expected kinetic limitations to this reaction (Munger et al., 1984).

Furthermore, past measurements all have involved the collection of cloud droplets on surfaces forming a liquid stream or volume. During the collection, a number of processes may occur which may lead to a different amount of *S(IV)* detected than is actually present in the droplets. Such processes may include the oxidation from simultaneous collection of *S(IV)* and oxidants, the variation of (bulk) cloud water pH during the time of collection, or through volatilization of SO<sub>2</sub> through the mixing of droplets of different pH (in which the collected [*S(IV)*] becomes greater than that predicted from Henry's law and the bulk pH, Perdue and Beck, 1988). Following the collection of cloud water, the collected *S(IV)* has been preserved in some previous measurements by the addition of HCHO (Richards et al., 1983; Munger et al., 1984; Munger et al., 1986) or tetrachloromercurate (TCM) (Radojevic et al., 1990). The addition of such chemicals strongly reduces any further oxidation before analysis. However, the addition of HCHO makes the discrimination between *S(IV)* and HMS impossible. Addition of TCM also may lead to the detection of some of the HMS as *S(IV)* depending on specific conditions (see Chapman (1986) for details).

The goal of this research is to produce a method for measuring *S(IV)* that is less susceptible to artifacts from collection and that discriminates

Table 1. *Previous measurements of S(IV) in cloudwater*

Investigator	Preservation used	Analysis method	species determined	Concentrations (μM)
Richards et al. (1983)	HCHO	colorimetric	<i>S(IV)</i> + HMS	5 to 365
Munger et al. (1984)	HCHO	colorimetric	<i>S(IV)</i> + HMS	1 to 2980
Munger et al. (1986)	HCHO; none	colorimetric; ion chromatographic	<i>S(IV)</i> + HMS; HMS	9 to > 230 ( <i>S(IV)</i> + HMS); 0 to 140 (HMS)
Keuken et al. (1987)	none	FIA, colorimetric with pre-reactions	<i>S(IV)</i> ; HMS	23 to 56 ( <i>S(IV)</i> ); 33 to 45 (HMS)
Radojevic et al. (1990)	TCM	colorimetric	<i>S(IV)</i> or <i>S(IV)</i> + some HMS	1 to 14.1
Joos and Baltensperger (1991)	none	ion chromatography	<i>S(IV)</i> + HMS	3 to 450

between  $S(IV)$  and HMS. The described method involves the separation of cloud droplets from their environment and the transfer of dissolved  $SO_2$  back to the gas phase where it is measured readily. The other significant improvement over past measurement methods by this work is real-time sampling which reduces the labor intensive work of analyzing each sample separately and leads to improved time resolution. One limitation to this method is that a direct measurement of the  $S(IV)$  molar concentration (per volume of liquid water) is not possible and requires a measurement of the collected liquid water content.

## 2. Experimental

### 2.1. Apparatus

To separate cloud droplets from their environment and to transfer aqueous  $S(IV)$  to the gas phase, a counter-flow virtual impactor (CVI) (Ogren et al., 1985) was combined with a gas phase  $SO_2$  instrument. CVI instruments have been described previously (Ogren et al., 1985; Noone, 1987; Twohy, 1988). The CVI works by inertial impaction of droplets into a clean, warm air stream in which the droplets subsequently evaporate. This evaporation transfers volatile components such as  $S(IV)$  to the gas phase along with water vapor. The use of a CVI for the measurement of volatile components in cloud droplets has been achieved for water (which can be a measure of the cloud liquid water content, Zuber and Witt (1987)) and for  $H_2O_2$  (Noone et al., 1991). The CVI also has an advantage over conventional cloud samplers by having a cut-size (or size at which 50% of the intercepted particles are collected) which can be adjusted. This allows the possibility of measuring the concentration of  $S(IV)$  as a function of drop size.

Measurements with the CVI described in this paper were performed from Battelle, Pacific Northwest Laboratories' Gulfstream G-1 aircraft during the Frontal Boundary Study (FBS). Flights of the G-1 during this study occurred during October and November of 1989 in northern Ohio. 5 flights included significant cloud samples when the CVI was operational. In addition to the CVI, other cloud instruments used during this study included a Johnson and Williams hot wire probe

used for liquid water content (LWC) measurements and dual Mohnen-type slotted rods for collection of bulk cloud water. These instruments were mounted on the roof of the aircraft through an emergency escape hatch.

The CVI was mounted out of a window in the fuselage of the G-1 with the probe tip about 5 m behind the aircraft's nose and 25 cm out from the window. The probe also was tilted downward at a  $3^\circ$  angle to compensate for the airplane's angle of attack at level flight. With a tip area of  $0.318 \text{ cm}^2$ , and at a typical airplane speed of  $100 \text{ m s}^{-1}$ , a flow of droplets into the inlet at a rate of  $190 \text{ l min}^{-1}$  is sustained. With a typical sample flow rate of  $5 \text{ l min}^{-1}$  cloud components are concentrated by a factor of 38. It should be noted that recent work has shown that the collection efficiency for aircraft-mounted aerosol probes often is quite low for some particle sizes (Huebert et al., 1990). However, for the  $S(IV)$  measurements, collisions of droplets with tubing walls should be less important because, except at the very tip, they should still evaporate and release  $SO_2$  within the sample line.

The CVI is schematically depicted in Fig. 1. Cabin air was scrubbed of  $SO_2$  and water vapor by soda lime and molecular sieve, respectively, before going to the probe tip. A heater was connected at the probe tip to facilitate evaporation of cloud

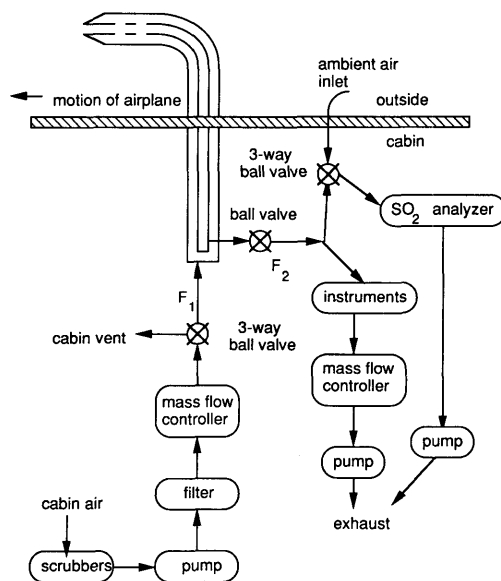


Fig. 1. Schematic diagram of CVI flow.

droplets. The sample air, containing gaseous and particulate residue from the evaporated droplets, then was directed to instruments. Teflon tubing was used for the sample lines, although some of the connections contained other plastics. One stainless steel valve was used following the failure of a Teflon valve in the field.

A condensation nuclei counter (CNC) (TSI model 3020) and a gas phase  $\text{SO}_2$  analyzer (Thermo Electron model 43S) were used in conjunction with the CVI for measurements of the cloud droplet number concentration (CDNC) and the  $S(\text{IV})$  concentration of the collected cloud droplets, respectively. Both concentrations refer to the concentration in the droplet size range larger than the CVI cut-size. The use of this model of pulsed-fluorescence  $\text{SO}_2$  analyzer on board aircraft has been described by Luria et al. (1990) and Kok et al. (1990). The listed detection limit and response time of this instrument are 0.1 ppbv and 2 minutes (for a 95% relaxation of the signal), respectively. Use of this instrument in conjunction with a CVI should result in a detection limit of cloud water  $S(\text{IV})$  of about  $0.1 \text{ nmol m}^{-3}$  (based on an aircraft speed of  $100 \text{ m s}^{-1}$  and an internal flow rate of  $5 \text{ l min}^{-1}$ ). A 3-way valve allowed the selection of either air from the CVI or ambient air for measurements with the  $\text{SO}_2$  analyzer.

A critical requirement for this method is that aqueous  $S(\text{IV})$  is transferred quantitatively to the gas phase as droplets evaporate within the sample line. This means that reactions (1), (2), and (3) must occur in the reverse direction to free  $\text{SO}_2$ . Reactions (2) and (3) have been shown to occur quickly relative to the mass transfer of  $\text{SO}_2$  (Schwartz and Freiberg, 1981) allowing equilibrium between the  $S(\text{IV})$  species to be assumed. The loss rate of both  $\text{SO}_2$  and water vapor from the droplet may be estimated to determine if the  $S(\text{IV})$  concentration is expected to increase or decrease during evaporation. The molar loss rate of a gas from a droplet through gas phase diffusion is given by (derived from Pruppacher and Klett, 1980):

$$\frac{dn_g}{dt} = -\frac{4\pi r D_g P_g F_v}{RT}, \quad (6)$$

where  $n_g$ ,  $D_g$ , and  $P_g$  are the moles within the droplet, the diffusion coefficient, and the vapor pressure at the droplet surface for a given gas,

respectively,  $R$  is the universal gas constant,  $r$  the droplet radius,  $T$  the drop temperature, and  $F_v$  the ventilation factor for air flow around the droplet. Eq. (6) assumes gas  $g$  is not present in the inlet line (the initial condition). By applying eq. (6) to both  $\text{SO}_2$  and  $\text{H}_2\text{O}$ , the ratio of the loss rates is calculated:

$$\frac{dn_s/dt}{dn_w/dt} = \frac{D_s P_s}{D_w P_w} = 0.64 \frac{P_s}{P_w}, \quad (7)$$

where  $s$  refers to  $\text{SO}_2$  and  $w$  to water ( $D_s = 1.4 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$ ,  $D_w = 2.2 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$ ). By substituting from eq. (4) and calculating relative loss rates (dividing by the molar ratio of  $S(\text{IV})$  to water in the droplet), eq. (7) is transformed to a

$$\frac{dn_s/(n_s dt)}{dn_w/(n_w dt)} = 0.64 \frac{\rho [H^+]^2}{P_w M_w K_1 ([H^+]^2 + K_2 [H^+] + K_3)} \quad (8)$$

more useful equation where  $\rho$  is the density ( $\text{g l}^{-1}$ ) and  $M_w$  is the molecular mass of water. Using the equilibrium constants of Maahs (1982) at  $25^\circ\text{C}$  ( $K_1 = 1.242 \text{ M atm}^{-1}$ ,  $K_2 = 0.0132 \text{ M}$ , and  $K_3 = 6.48 \times 10^{-8} \text{ M}$ ) and a typical cloud droplet pH of 5, a relative loss rate ratio of 0.47 was calculated indicating an increasing  $S(\text{IV})$  concentration initially. However, because much of the initial  $\text{H}^+$  will be conserved in the droplet, the pH will be forced to decrease as the droplet evaporates, and this eventually will lead to relatively greater loss of  $\text{SO}_2$  (which occurs when the pH value decreases below 4.8).

These calculations demonstrate that  $\text{SO}_2$  should be released from acidic droplets. Additionally, because the lifetime of droplets in the CVI is short (about 1 second for a  $10 \mu\text{m}$  radius droplet, Anderson, 1992), little time is present for  $S(\text{IV})$  to react with oxidants concentrated in the droplet during evaporation. In the unusual case of alkaline droplets some of the  $S(\text{IV})$  may remain as an  $\text{SO}_3^-$  salt.

While  $S(\text{IV})$  is expected to leave evaporating cloud droplets, HMS, having a structure similar to methanesulfonate, a compound of low volatility (Brimblecombe and Clegg, 1988), should remain in the aerosol particle formed from droplet evaporation. Besides loss through direct volatiliza-

tion, HMS may dissociate (the reverse direction of reaction (5)), yielding  $\text{SO}_2$ . The dissociation reaction, however, is very slow with the characteristic time (defined as the inverse of the rate constant) varying from 5 h at pH 6 to 230 days at pH 0 (at 25°C, Martin et al. (1989)). While significant dissociation of HMS during the short time period of droplet evaporation seems impossible, slow dissociation of HMS collected on filters up stream of the  $\text{SO}_2$  analyzer could conceivably contribute to the signal. For hydrated aerosol particles with a pH of 0 originating from clouds with a LWC of  $0.15 \text{ g m}^{-3}$  and a HMS concentration of  $100 \mu\text{M}$ , about an hour long collection period would be required before the  $\text{SO}_2$  released would reach the analyzer's detection limit (0.1 ppbv). HMS in aerosol particles with higher pH values coming from neutral cloud droplets dissociates more rapidly but also is more likely to form stable salts such as NaHMS where no dissociation will occur. Additional evidence of HMS stability comes from a study of laboratory produced aerosols from a NaHMS solution acidified with  $\text{HNO}_3$  (Dixon, 1991). In this study, loss of HMS from the aerosol phase was small (11% of that nebulized) and probably insignificant based on the uncertainty of the measurements and due to wall losses. From these considerations, it appears that insignificant levels of  $\text{SO}_2$  are released from HMS. However, additional laboratory experiments using more realistic solution compositions (e.g., HMS in the acid form with  $\text{H}_2\text{SO}_4$  and buffered with  $\text{NH}_4^+$ ) and measuring any released  $\text{SO}_2$  are required to definitively prove that HMS is not an interferent under certain conditions.

## 2.2. Tests

The demonstration of the combination of a CVI and an  $\text{SO}_2$  instrument to measure S(IV) in cloud water consists of three parts: tests showing  $\text{SO}_2$  released in the CVI is quantitatively detected, tests showing that  $\text{SO}_2$  is not detected in clear air flights, and actual measurements made in clouds.

A true calibration of this instrument would involve the introduction of droplets containing a known amount of S(IV) into the CVI inlet. Due to the difficulties of such a calibration because of the instability of such droplets,  $\text{SO}_2$  gas from a calibration source was released directly in the inlet of the CVI. This was compared to the  $\text{SO}_2$  signal when the calibration source was connected through the

ambient air line with the  $\text{SO}_2$  analyzer. Two such calibrations were carried out in a hanger. Using a calibration source of about 10 ppbv, losses of  $\text{SO}_2$  in the CVI of 7 and 9% were observed. A similar in-flight comparison of the two inlets acting as ambient air inlets in clear air showed no significant difference but was not very conclusive due to large variations of encountered  $\text{SO}_2$  during the test. Tubing losses by  $\text{SO}_2$  in tubing has been discussed previously by Kuster and Goldan (1987), and the use of non-ideal materials in the connections may have resulted in the observed loss of  $\text{SO}_2$  in the tubing. No attempt was made to correct for such losses.

Beside the "calibration" described above, the instrumental response under conditions outside of clouds also was tested to determine the "zero signal". In these tests, the CVI was operated in the same manner as operated during cloud sampling, except that measurements were made outside of clouds. Under these conditions, no unusual features were observed in the zero signal which were significantly different from features observed during an instrumental zero achieved by passing cabin air through a scrubber. It should be noted that the average zero signal obtained with the CVI often was different than the instrumental zero. This could be due to differences in pressure between the CVI manifold and the cabin or due to instrumental drift often associated with changes in elevation. The CVI zero signal was used in the calculation of the S(IV) concentrations whenever possible, ideally with measurements just before and just after entering clouds.

## 3. Results

### 3.1. Comparison of CVI/S(IV) data with other cloud data

The performance of the CVI method of measuring S(IV) was tested through the comparison of the results with other simultaneous cloud measurements. The CVI measurements result in an aqueous phase S(IV) concentration per volume of air. An actual S(IV) molarity (e.g., moles of S(IV) per liter of cloud water) could not be obtained because the fraction of the liquid water collected by the CVI was unknown. The LWC and the cloud droplet number concentration (CDNC),

also measured with the CVI, were used for the comparison.

During 2 of the 5 flights with a functioning CVI and clouds present, measurements were close to or below the detection limit of the SO<sub>2</sub> analyzer. During Flight 8, measurements were above the detection limit, but the LWC instrument was not operational, and the CDNC measurements indicated unbroken clouds. During Flights 13 and 16, measurements occurred as the aircraft passed between clear and cloudy air, thus demonstrating the response of the *S(IV)* measurements under changing conditions.

Figs. 2a, b show the LWC, CDNC, and *S(IV)* concentration for Flights 13 and 16, respectively. The LWC and *S(IV)* data were baseline corrected during periods of clear air between clouds or in the case of the *S(IV)* data for Flight 16, immediately after leaving the clouds. The CVI cut-size for Flights 13 and 16 were 6.2 and 5.8 μm (radius), respectively. Lag times, due to the time required for analytes to reach detectors, were corrected by moving the CDNC and *S(IV)* data ahead by 10 and 30 s, respectively. Figs. 2a, b show similar variation between the LWC and CDNC data with the exception of the disparity at times of higher LWC during flight 16. The general agreement provides evidence that both instruments were measuring similar cloud properties, and the region of poorer agreement may have resulted from poor performance of the CNC at higher number concentrations. (The CNC has different modes of operation below and above 1000 cm<sup>-3</sup>, and comparisons of the values in the two modes of operation indicated poor agreement at times during flight 16). On the other hand, the *S(IV)* data show much broader and slightly lagging peaks which is a result of the slow response time of the pulsed-fluorescence SO<sub>2</sub> instrument from a built-in RC filter to remove high frequency noise.

Normally, such a response time limits the use of such data to one or two minute averages. However, because the flight showed interesting variability on shorter time scales, a different approach was used. An RC filter "averages" data by applying an exponential weighting function to the data whereby older data is weighted less (by the factor  $e^{-t/RC}$  where  $t$  is the time before the data point and RC is the decay constant). The RC filter can be numerically applied to the LWC and CDNC data so that all data are treated com-

parably. It should be noted, that all the data will be distorted in the same manner as the *S(IV)* data is distorted relative to the true cloud parameters, but the treatment is valid for the sake of comparison. The following equation was used to apply a numerical RC filter to the CDNC and LWC data (derived from Wilson and Edwards (1976)):

$$\text{filtered } S(t) = \frac{ts}{RC} \sum_{i=t-11}^t S(i) e^{(ts/RC)(i-t-0.5)}, \quad (9)$$

where  $ts$  is the time step between data (10 s), RC is the decay time constant (measured to be 32 s),  $t$  is the data interval number or time from the first data point to be filtered divided by the time step, and  $S(i)$  is the LWC or CDNC at data interval number  $i$ . The use of 12 data steps (e.g., from  $t-11$  to  $t$ ) was chosen with the assumption that data from more than 2 min before the measurement would not contribute significantly to the filtered data.

Figs. 3a, b show the implementation of eq. (9) to the LWC and CDNC data during Flights 13 and 16, respectively. Following the application of the RC filter, the *S(IV)* data is demonstrated to agree better with the LWC data. During Flight 13, the 1st 3 cloud periods show somewhat broader *S(IV)* peaks than corresponding LWC or CDNC peaks. It is possible that a memory effect in which SO<sub>2</sub> temporarily sticks to the tubing walls could have caused such a disparity. Such disparities are more readily observed during brief cloudy periods and were not noticed in the last 10 min of the Flight 13 period or during Flight 16. Around 14:30 during Flight 13, the *S(IV)* and CDNC values are relatively low compared to the LWC values for a brief period. At this time, the aircraft started to descend, and the change in attitude may have caused an anomaly in either the CVI or the Johnson and Williams LWC instrument which were located at different positions on the fuselage. Both flight periods show relatively high *S(IV)* concentrations for the first 30 s, which are due to the decaying signal of SO<sub>2</sub> from the ambient sample before the valve to the SO<sub>2</sub> monitor was switched to the CVI line. Other disparities, such as lower *S(IV)* concentrations after 14:42 during flight 13 or from 13:32 to 13:33 during Flight 16 relative to the LWC and CDNC, are likely to be due to real differences between cloud physical properties observed by the LWC and CDNC and the chemi-

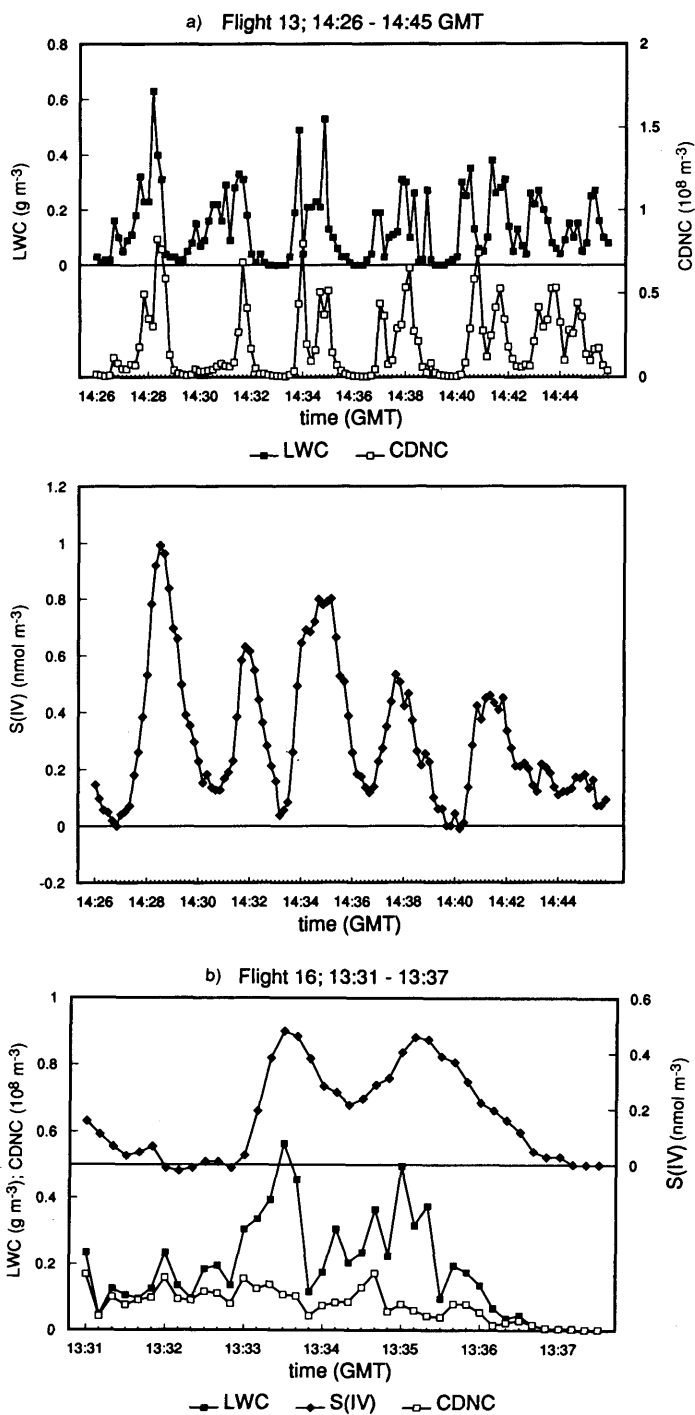


Fig. 2.  $S(IV)$  concentration (diamonds,  $\text{nmol m}^{-3}$ ) and unfiltered LWC (closed squares,  $\text{g m}^{-3}$ ) and CDNC (open squares,  $\times 10^8 \cdot \text{m}^{-3}$ ). (a) Flight 13, 14:26 to 14:45 GMT; (b) Flight 16, 13:31 to 13:37 GMT.



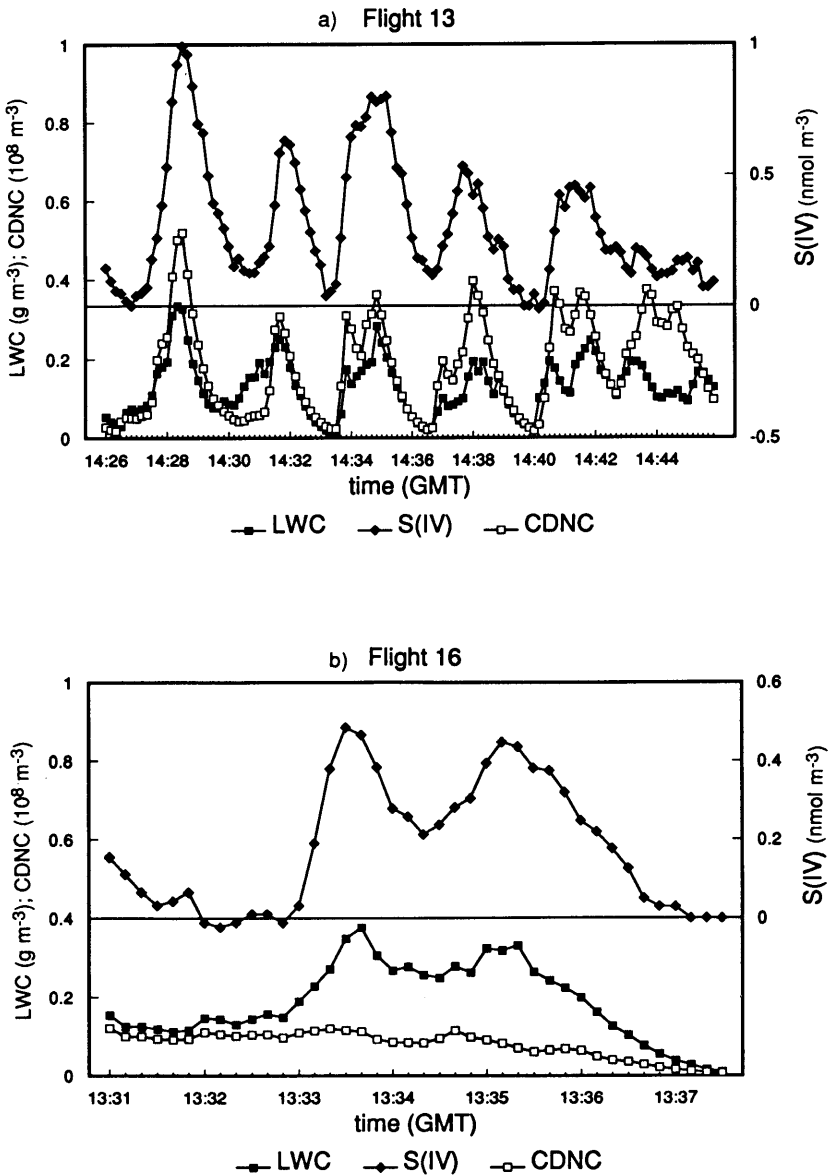


Fig. 3.  $S(\text{IV})$  concentration ( $\text{nmol m}^{-3}$ ) and filtered LWC ( $\text{g m}^{-3}$ ) and CDNC ( $\times 10^8 \cdot \text{m}^{-3}$ ). (a) Flight 13, 14:26 to 14:45 GMT; (b) Flight 16, 13:31 to 13:37 GMT.

cal concentration. Based on observations of short scale variability in gas phase  $\text{SO}_2$  measurements during the FBS flights, it is expected that  $S(\text{IV})$  concentrations would not entirely follow other cloud parameters.

Two minute averages, which should not be

affected by the RC filter, are listed for the flight periods discussed above as well as for a period during Flight 8. Flight 8 occurred under more homogeneous cloud conditions as indicated by the less variable CDNC. A smaller CVI cut-size of  $5.4 \mu\text{m}$  was used during this flight period. The

higher concentration of  $S(IV)$  was probably a result of more polluted conditions at the altitude where sampling occurred.

### 3.2. Estimation of $S(IV)$ molarity

Because the liquid water collected by the CVI neither was measured nor was estimated accurately (e.g., from optical cloud droplet size distributions), an accurate measure of  $S(IV)$  molarity could not be obtained. It was possible, however, to estimate a range of  $S(IV)$  molarity from the measurements. A minimum  $S(IV)$  molarity was calculated from the measured  $S(IV)$  concentration and the measured LWC. For a case where the collection efficiency of the CVI for cloud water was unity (e.g., where all cloud droplets were larger than about  $6\ \mu\text{m}$  in radius), this value would be

the true volume-weighted molar concentration. A maximum concentration was calculated by assuming all of the collected cloud droplets were equal in size to the cut-size (e.g., the minimum size for collection), and calculating a minimum collected LWC as the product of this drop volume and the CDNC.

The estimated  $S(IV)$  molarity range also is shown in Table 2 for periods during Flights 8, 13, and 16. Due to the lack of LWC measurements during Flight 8, only  $[S(IV)]_{\text{max}}$  could be calculated. During Flight 13,  $[S(IV)]_{\text{max}}$  was 5 to 12 times higher than  $[S(IV)]_{\text{min}}$ , but during Flight 16, due to previously mentioned problems with the CDNC values, a much greater ratio was observed. The  $[S(IV)]$  concentration ranges are comparable to measurements of Radojevic et al.

Table 2. 2-min average values

Time (GMT)	LWC ( $\text{g m}^{-3}$ )	CDNC ( $\times 10^7 \text{ m}^{-3}$ )	$S(IV)$ ( $\text{nmol m}^{-3}$ )	$[S(IV)]_{\text{min}}$ ( $\mu\text{M}$ )	$[S(IV)]_{\text{max}}$ ( $\mu\text{M}$ )	Altitude (m.a.s.l.)
Flight 8						
14:06	NM	5.01	1.02	NM	31	900
14:08	NM	5.76	0.93	NM	25	901
14:10	NM	5.46	0.86	NM	24	900
14:12	NM	6.28	0.86	NM	21	906
14:14	NM	6.11	1.17	NM	29	904
14:16	NM	5.67	1.75	NM	47	902
average	NM	5.72	1.10	NM	29	902
Flight 13						
14:27	0.140	2.06	0.27	2.0	13	3114
14:29	0.135	1.42	0.52	3.9	37	3118
14:31	0.177	1.47	0.35	2.0	24	3080
14:33	0.079	1.39	0.33	4.2	24	2987
14:35	0.141	1.57	0.55	3.9	35	2887
14:37	0.107	2.23	0.33	3.1	15	2723
14:39	0.086	0.93	<0.1*	<1.2*	<11*	2618
14:41	0.179	2.79	0.35	2.0	13	2586
14:43	0.142	2.66	0.17	1.2	6	2454
average	0.137	1.90	0.32	2.3	17	2841
Flight 16						
13:32	0.159	1.03	<0.1*	<0.6*	<12*	1982
13:34	0.300	0.93	0.35	1.2	45	1983
13:36	0.128	0.40	0.16	1.3	50	1817
average	0.193	0.75	0.19	1.0	31	1927

\* Below detection limit.

NM: not measured.

(1990), although our highest  $[S(IV)]_{\max}$  values are a few multiples higher than their highest values. The variability of  $[S(IV)]$  measurements may reflect variability in the spatial distribution of  $SO_2$ , or in the variability of other factors such as the cloud water pH.

## 4. Discussion and conclusions

### 4.1. Applications and limitations of CVI/ $S(IV)$ based tests

The tests of the combination of a sensitive  $SO_2$  analyzer and a CVI demonstrate a feasible method for measuring  $S(IV)$  in cloud water in-situ and on a minute time scale. The applicability of these measurements to various conditions requires an assessment of the detection limits and the conditions encountered during the measurements. Measurements of noise levels during flights indicated detection limits of about 0.1 ppbv (based on 2 times the standard deviation of the noise for time periods of 2 min). Based on the flight speed, and CVI sample flow setting, this corresponded to a minimum detection limit for  $S(IV)$  of about 0.1  $nmol\ m^{-3}$ . The CVI sample flow could be reduced to decrease further the detection limit. However, the flow setting of  $5\ l\ min^{-1}$  allows the CVI to work properly for LWC values below about  $0.8\ g\ m^{-3}$  without saturation of water vapor occurring in the CVI sample lines, and a lower flow setting only would be possible at low LWC. The response time, although relatively fast at 2-min time resolution, results in measurements averaged over 12 km for an aircraft flying at  $100\ m\ s^{-1}$ . This response time could be improved, at the expense of the sensitivity, by removing the RC filter. Following sample collection, data always can be averaged to improve the signal to noise without the type of distortion that a RC filter induces. Such averaging of data requires zero periods of the same time length outside of clouds. Assuming that the noise of the  $SO_2$  instrument is random, further reduction of the detection limit may be possible for longer averaging periods.

A more useful detection limit would be the minimum molar aqueous  $S(IV)$  concentration by this technique. This requires assumptions of the collection efficiency of the CVI and the LWC for which a value of  $0.5\ g\ m^{-3}$  is used. Based on a size distribution for typical for continental cumulus given

by Schwartz (1986) and 100% collection efficiency for droplets above the cut-size of  $6\ \mu m$ , a total collection efficiency and a collected LWC are calculated to be 70% and  $0.35\ g\ m^{-3}$ , respectively. This results in a minimum detectable  $S(IV)$  molar concentration of  $0.3\ \mu M$ . Under the conditions of most of our measurements, a more typical detection limit was calculated to be  $1\ \mu M$ .

Ohio is in the middle of a highly industrialized region of the United States and has large  $SO_2$  emissions (NRC, 1983). Nevertheless, most airplane flights occurred during or following frontal passage, so that high concentrations of  $SO_2$  (above 50 ppbv) were encountered infrequently during CVI measurements. During Flight 13, an average gas phase concentration of 1.1 ppbv was observed during an ascent at the same location just before the  $S(IV)$  measurements shown in Fig. 2a although  $SO_2$  mixing ratios greater than 1 ppbv during the CVI measurements may have occurred from the transport of higher concentrations of  $SO_2$  from the boundary layer. During Flight 16,  $SO_2$  ranged from 0.1 to 1.4 ppbv at 2100 m.a.s.l., measured before and 100 m above the altitude of the CVI, and  $SO_2$  ranged from 3.4 to 4.7 ppbv at 1000 m.a.s.l., at the same latitude and following the CVI measurements. During Flight 8,  $SO_2$  generally ranged between 2 and 15 ppbv, and during the two flights with little or no detectable  $S(IV)$ ,  $SO_2$  remained below 1 ppbv except when crossing plumes. Cloud water samples collected with the bulk cloud water samplers gave a pH range of 3.9 to 4.5 for all flights indicating consistently acidic conditions (R. Lee, personal communication). From the five flights, it appears that  $S(IV)$  is measurable by this method at the pH encountered when the  $SO_2$  concentration is at or higher than about 1 ppbv.

### 4.2. Comparison of CVI method to other methods

Because of inherent differences in the collection method discussed in the introduction, other measurement techniques may not be directly comparable to the CVI method described here. Nevertheless, a discussion of the performance of various methods of analysis provides insight into relative advantages of different methods. Detection limits for a number of wet analytical techniques are about  $0.1\ \mu M$  (equivalent to  $0.03\ nmol\ m^{-3}$  for a LWC of  $0.3\ g\ m^{-3}$ ; Keuken et al. (1987), Chapman (1986), Kok et al. (1984)). A lower

detection of  $0.003 \mu\text{M}$  was found for an IC technique (Davies and Ivey, 1987), but this technique used a 5.5 ml injection loop. With an injection loop more typically used in the analysis of cloud samples (e.g.,  $200 \mu\text{l}$ ), a detection limit similar to the others is achieved. Thus, the detection limit is slightly poorer for the CVI method. For most of the above methods, several mls of sample is required for the analysis (more is required for large injection loops). For aircraft slotted rods with large collection areas, this requires several minutes for clouds with a LWC of  $0.5 \text{ g m}^{-3}$ . Because the changing of sample vials generally is done manually, it would be very difficult to reduce the collection time below 2 min. In addition, when cloud water is required for other analyses, even longer collection times are required. The CVI method has additional advantages that analysis occurs within a short time period after reaching the inlet and no sample treatment is required (other than evaporation) following collection. Because of the ease in changing the CVI's cut-size, the concentration of  $S(IV)$  also can be measured in different drop size ranges.

#### 4.3. Conclusions

Simultaneous real-time measurements of cloud water  $S(IV)$ , LWC, and CDNC qualitatively demonstrated proper response of a new technique for measuring cloud water  $S(IV)$  through combining a CVI with a  $\text{SO}_2$  analyzer. Of the 5 flights in which this method was employed,  $S(IV)$  was measured in three flights and was close to or below

the detection limits for two flights. During the flights in which  $S(IV)$  was detectable, it ranged from the detection limit of  $0.1 \text{ nmol m}^{-3}$  to  $1.8 \text{ nmol m}^{-3}$  (for 2-min averages). This analysis method is limited by the requirement of simultaneous measurements of the LWC collected by the CVI to calculate molar concentrations (moles per liter of cloud water) and by remaining uncertainties regarding the behavior of  $S(IV)$  in alkaline droplets and HMS during droplet evaporation. However, the ability to measure  $S(IV)$  in real-time, the absence of required preserving solutions, and the elimination of other potential loss mechanisms during cloud water collection represent advantages of this method over previously used methods. From this method of analysis, a better determination of whether  $\text{SO}_2$  follows Henry's law and associated equilibria should be possible.

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