A Balloon Sounding Technique for Measuring SO₂ Plumes

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ABSTRACT

This paper reports on the development of a new technique for inexpensive measurements of SO₂ profiles using a modified dual-ozonesonde instrument payload. The presence of SO₂ interferes with the standard electrochemical cell (ECC) ozonesonde measurement, resulting in –1 molecule of O₃ reported for each molecule of SO₂ present (provided $[O_3] > [SO_2]$). In laboratory tests, an SO₂ filter made with CrO₃ placed on the inlet side of the sonde removes nearly 100% of the SO₂ present for concentrations up to 60 ppbv and remained effective after exposure to 2.8×10^{16} molecules of SO₂ [equivalent to a column ~150 DU (1 DU = 2.69×10^{20} molecules m⁻²)]. Flying two ECC instruments on the same payload with one filtered and the other unfiltered yields SO₂ profiles, inferred by subtraction. Laboratory tests and field experience suggest an SO₂ detection limit of ~3 pbb with profiles valid from the surface to the ozonopause [i.e., ~(8–10 km)]. Two example profiles demonstrate the success of this technique for both volcanic and industrial plumes.

1. Introduction

SO₂ is a trace atmospheric constituent with a lifetime of 1–2 days in the lower troposphere (Krueger et al. 2000; Benkovitz et al. 2004) and is emitted both naturally by volcanoes and anthropogenically by certain power plant and industrial facilities. The earth's radiative budget is impacted when SO₂ is converted to sulfate aerosols via reactions with H₂O₂ in clouds or OH (Seinfeld and Pandis 1998; Chin et al. 2000), although the extent of the influence of SO₂ on climate and atmospheric chemistry remains uncertain. The Intergovernmental Panel on Climate Change (Soloman et al. 2007) reports sulfate aerosol direct radiative forcing of -0.4 ± 0.2 W m⁻². Future implementation of pollution reduction policies, however, could lead to positive net forcings relative to today (Kloster et al. 2008).

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Retrieval techniques for the measurement of SO₂ from satellite instruments were suggested by Krueger (1983) and refined by Krueger et al. (1995) and Krotkov et al. (1997). Because of its available wavelengths and spatial resolution (\sim 50 km at nadir and \sim 100 km average), the Total Ozone Mapping Spectrometer (TOMS) SO₂ retrievals were limited to large amounts in volcanic eruptions (Krueger et al. 1995, 2000; Carn et al. 2003) and exceptional pollution events (Carn et al. 2004). Greatly improved sensitivity was demonstrated through the detection of volcanic and anthropogenic SO₂ in full-spectrum ultraviolet (UV) data provided by the Global Ozone Monitoring Experiment (GOME) (Eisinger and Burrows 1998; Burrows et al. 1999; Thomas et al. 2005; Khokhar et al. 2005) and the Scanning Imaging Absorption Spectrometer for Atmospheric Cartography (SCIAMACHY) (Bovensmann et al. 1999; Bramstedt et al. 2004; Richter et al. 2006; Lee et al. 2008). However, GOME needs 3 days and SCIAMACHY 6 days to acquire a contiguous global map and hence could miss short-lived pollution events. Recently, Kearney et al. (2008) have developed an SO_2 retrieval for Moderate Resolution Imaging Spectroradiometer (MODIS) data.

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The Ozone Monitoring Instrument (OMI) (Levelt et al. 2006a,b) launched on the National Aeronautics and Space Administration (NASA) Aura satellite (Schoeberl et al. 2006) in July 2004 offers better spatial resolution (13 km imes24 km at nadir) and contiguous global daily coverage, permitting high-resolution, daily space-based UV measurements of SO₂ (Krotkov et al. 2006, 2007; Yang et al. 2007, 2009a,b; Lee et al. 2009). Validation of these satellite observations has been limited to aircraft in situ measurements over the eastern United States (Taubman et al. 2006) and eastern China (Dickerson et al. 2007; Krotkov et al. 2008), ground-based remote sensing [e.g., the Brewer UV spectrometer network described in Fioletov et al. (1998) and Krueger et al. (1995)], and, most recently, with miniature differential optical absorption spectroscopy (mini-DOAS) instruments (Galle et al. 2010). However, these ground-based techniques provide little information on the vertical profile of SO₂, an important factor in satellite column SO₂ retrieval algorithms. To date, no inexpensive, regular in situ sampling program has been available to further these validation studies. The satellite community would find very valuable a sounding technique for in situ measurement of SO_2 of similar cost to the standard ozonesonde.

To review, the standard ozonesonde, originally presented in Komhyr (1969), uses an iodine–iodide redox electrochemical cell (ECC) made of two platinum electrodes immersed in potassium iodide (KI) solutions in separate cathode (0.5%–2% solution) and anode (saturated solution) polytetrafluoroethylene (Teflon) chambers (see Fig. 1). The chambers are linked by an ion bridge that allows for the exchange of charge but prevents mixing of the cathode and anode solutions. After charging the cells with the solutions, a transient potential difference results that is dissipated through the redistribution of charge across the ion bridge, such that the following equilibria are established:

$$3I^{-}AI_{3}^{-} + 2e^{-}(anode),$$
 (1.1)

$$2I^{-}AI_{2} + 2e^{-}$$
(cathode). (1.2)

When O_3 bubbles through the cathode solution, a chemical reaction imbalances the cathode solution in favor of I_2 :

$$2\mathrm{KI} + \mathrm{O}_3 + \mathrm{H}_2\mathrm{O} \rightarrow 2\mathrm{KOH} + \mathrm{I}_2 + \mathrm{O}_2. \tag{1.3}$$

To rebalance the cell, electrons must flow from the anode across the ion bridge to the cathode so that

$$3I^- \to I_3^- + 2e^-$$
(anode), (1.4)

$$I_2 + 2e^- \rightarrow 2I^-$$
 (cathode). (1.5)



FIG. 1. A schematic of the ECC sonde cathode and anode chambers, connected by an ion bridge and an external ammeter to measure the current between the cells, which is proportional to the O_3 concentration in the ambient air around the sonde.

If SO_2 is present, however, the cathode chamber chemistry is altered:

$$SO_2 + 2H_2O \rightarrow SO_4^{2-} + 4H^+ + 2e^-.$$
 (1.6)

In the presence of both O_3 and SO_2 , therefore, reaction (1.6), rather than the anode solution reaction (1.4), supplies the electrons needed to rebalance the ECC after reaction (1.3). The result is that in the presence of both species with $[SO_2] < [O_3]$, the standard ozone-sonde actually reports $[O_3] - [SO_2]$.

One approach to measure SO₂ directly, therefore, is to filter the incoming air to remove O₃ and electrically bias the cathode cell. When SO₂ enters, reaction (1.6) results in a flow of electrons from the cathode cell across the ion bridge to the anode. Figure 2 shows data previously unpublished from a flight in Pittsburg, Pennsylvania, on 24 February 1983 that used this approach. The figure shows a low-altitude peak of ~35 ppbv of SO₂ just above the mixed layer, with a broader SO₂ peak of ~65– 72 ppbv trapped between two temperature inversions at ~0.7 and 1.7 km. Such high levels of SO₂ are not observed in modern data, as U.S. emissions decreased by ~37% from the 1970 to 1996 (EPA 2000).

A second approach is to fly two instruments side-byside, one with a filter to remove SO_2 and the other without, as shown in Fig. 3. Since the filtered sonde will measure $[O_3$ and the unfiltered sonde will measure $[O_3]$ – $[SO_2]$, the concentration of $[SO_2]$ can be derived by subtraction. The technique relies upon finding a filter that effectively removes SO_2 without impacting the O_3 concentrations.

In this paper we describe the development of such a technique using a modified dual-ozonesonde payload.



FIG. 2. The first sounding of SO_2 with temperature and relative humidity profiles made by W. Komhyr in Pittsburg, PA, on 24 Feb 1983.

Laboratory tests demonstrate the effectiveness of the technique for measuring tropospheric SO₂ profiles for \sim 3 ppbv < [SO₂] < [O₃]. Two examples from field deployments demonstrate the effectiveness and utility of the technique: 1) volcanic emissions observed over Sapporo, Japan; and 2) industrial emissions observed over Houston, Texas. Since the filtered sonde and unfiltered sonde share the same balloon, parachute, payout-reel, and GPS and radiosonde units, the cost of a balloon flight with the dual payload is only about 40% higher than the cost of a standard ozonesonde.

2. Laboratory tests

We conducted a number of controlled laboratory tests during the development of our SO₂ sounding technique. The appendix describes tests performed on the various components used in the construction of the SO₂ filter, as well as the results of possible alternate SO₂ filter solutions. For all tests and flights, we use 0.5% buffered KI solutions in the cathode cell and saturated KI solutions in the anode cell (solutions prepared by B. Johnson, NOAA/Climate Monitoring and Diagnostics Laboratory, 2008–2009, personal communication), as recommended by the Jülich Ozone Sonde Intercomparison Experiment (JOSIE) (Smit et al. 2007).

The EnSci SO₂ filter consists of a Teflon cell (~5 cc) containing treated filter paper cut into ~3 mm × ~12 mm strips. The original filters used glass filter paper (2008 data; see the appendix), while the new filters use Teflon paper (2009 data, below). A 15-ml aqueous solution with 2.5 g of CrO₃ and 0.7 ml concentrated H₂SO₄ is used to



FIG. 3. The dual O_3 -S O_2 sonde payload. From left to right are the Väisälä RS80–15N radiosonde, the unfiltered ECC ozonesonde, and the S O_2 filtered ECC ozonesonde using the EnSci CrO₃ filter.

treat ~400 cm² of filter paper. The paper is then dried in an oven at 80°–90°C for 1 h. Each strip is folded in half and inserted into the Teflon cell. Before use, it is recommended that the filter be exposed to high ozone in dry air for several hours. If the filter paper becomes damp, drying in an 80°C oven followed by high-ozone conditioning is recommended. The original suggestion for use of such a CrO₃ filter to remove SO₂ from sample air can be found in Saltzman and Wartburg (1965), while use of such a filter in surface SO₂ measurements is described in Warmbt and Herrmann (1977).

Laboratory tests on this filter demonstrated its effectiveness. The University of Houston (UH) test consisted of a Thermo Electron Corporation (TECO) 49C-PS ozone calibrator, a TECO 146C multigas calibrator (used to control the SO₂ concentrations), a manifold for mixing and distributing the gasses, a TECO Model 49C ozone analyzer using the U.S. Environmental Protection Agency standard measurement technique (EQOA-0880–047), a modified TECO 43S SO2 analyzer (Luke 1997), an unfiltered ozonesonde, and a filtered ozonesonde. The experimental setup is shown in Fig. 4.

Tests were performed with O_3 concentrations of approximately 120, 80, and 40 ppbv (in that order) and SO_2 concentrations ranging from ~(2.5–65) ppbv. The data are shown in Tables 1–3. Each paired combination of O_3 and SO_2 was maintained for 3–5 min. An overall background level was established through data taken at $[O_3] = 0$ and $[SO_2] = 0$, and at each O_3 level, additional backgrounds are established with $[SO_2] = 0$. None of the data in Tables 1–3, however, have been adjusted for the background levels.

Within the 120- and 80-ppbv levels, the performance of the filter as a function of the integrated exposure to



FIG. 4. A schematic of the instruments used in the laboratory test of the EnSci CrO_3 version of the SO₂ filter conducted at the University of Houston in July 2009.

SO₂ changes very little. A linear regression analysis of the difference between the dual-sonde-derived and TECO-measured SO₂ concentrations as a function of integrated SO₂ exposure shows slopes of 0.005 \pm 0.011 ppbv per Dobson unit (DU; 1 DU = 2.69 \times 10²⁰ molecules m⁻²) and -0.0078 \pm 0.0081 ppbv DU⁻¹, respectively. Between the two tests, an offset of ~1 ppbv of SO₂ is observed, as seen in the data in Tables 1 and 2.

Integrating the SO₂ concentrations passed through the filter as a function of time through the first two of the three O₃ levels in our test, we find a cumulative exposure of $\sim 2.8 \times 10^{16}$ molecules of SO₂. We can compute an equivalent column of SO₂ in flight from the equation

$$\text{Column SO}_2(\text{DU}) = \frac{N\dot{z}}{\dot{V}},$$

where *N* is the total number of molecules passed through the filter in the test, \dot{u} is the rise rate of the balloon in flight (5 m s⁻¹), and \dot{V} is the pump volume flow rate

TABLE 1. Individual readings for the \sim 120 ppbv ozone test. The mean ozone difference (sonde – TECO) = 0.3 ± 4.8 ppbv, while the mean SO₂ difference (sonde – TECO) = -0.87 ± 2.3 ppbv.

TECO O ₃ (ppbv)	Sonde O ₃ (ppbv)	TECO SO ₂ (ppbv)	Sonde SO ₂ (ppbv)
121.64 ± 0.97	118.32 ± 0.50	-0.034 ± 0.082	0.49 ± 0.68
120.6 ± 1.2	120.27 ± 0.90	65.35 ± 0.64	66.12 ± 0.64
120.76 ± 0.69	121.13 ± 0.40	46.90 ± 0.49	48.10 ± 0.51
121.27 ± 0.71	121.48 ± 0.64	27.81 ± 0.51	28.54 ± 0.65
121.78 ± 0.68	122.57 ± 0.52	18.04 ± 0.33	18.92 ± 0.61
119.97 ± 0.84	122.3 ± 1.9	9.03 ± 0.28	10.13 ± 0.64
121.5 ± 1.9	122.9 ± 1.7	3.90 ± 0.27	5.03 ± 0.55
122.9 ± 1.3	123.9 ± 1.3	0.03 ± 0.16	0.77 ± 0.72

TABLE 2. Individual readings for the ~ 80 ppbv ozone test. The mean ozone difference (sonde – TECO) = 1.2 ± 8.0 ppbv, while the mean SO₂ difference (sonde – TECO) = -1.2 ± 1.9 ppbv.

TECO O ₃ (ppbv)	Sonde O ₃ (ppbv)	TECO SO ₂ (ppbv)	Sonde SO ₂ (ppbv)
81.0 ± 2.1	82.7 ± 1.9	-0.009 ± 0.090	-0.98 ± 0.70
82.0 ± 2.8	84.1 ± 2.7	65.85 ± 0.49	65.12 ± 0.68
80.4 ± 2.0	81.5 ± 1.6	47.20 ± 0.46	46.38 ± 0.55
80.8 ± 1.4	81.56 ± 0.92	27.85 ± 0.36	26.43 ± 0.34
79.9 ± 2.6	81.3 ± 2.0	18.85 ± 0.38	17.36 ± 0.51
80.7 ± 1.3	81.7 ± 1.0	9.05 ± 0.29	7.60 ± 0.56
81.7 ± 2.1	82.5 ± 1.5	3.95 ± 0.24	2.45 ± 0.51
80.1 ± 2.6	80.9 ± 2.2	0.02 ± 0.12	-1.24 ± 0.55

 (3.45 cc s^{-1}) . Thus the laboratory test was equivalent to an SO₂ column of \sim 150 DU. Even after such exposure, the filter performance was still quite good. For the 40-ppbv-level test, we used a new SO₂ filter of the same type as for the 120- and 80-ppbv tests. The same linear regression analysis as above reveals a slope of 0.0458 \pm 0.0083 ppbv DU⁻¹ exposure, with most of the change occurring over the last four levels of data [i.e., when SO₂ was lowered from \sim (20–2.5) ppbv]. While our dualsonde SO₂ measurement changed more with respect to the TECO SO₂ measurement for this test than the previous two tests, the changes are still <2 ppbv of SO₂ at a cumulative exposure of the equivalent of nearly 40 DU. Thus, the filters stand up well to high SO₂ concentrations for extended periods of time, consistent with the findings of Saltzman and Wartburg (1965).

Figure 5 shows the filtered ozonesonde reading as a function of the TECO O₃ reading. The regression of the overall data shows a line of best fit with a slope to within 1% of 1.00 and an intercept of less than one-half of one standard deviation from 0.00. Good agreement is seen at all levels: at the 120-ppbv O₃ level, the mean O₃ difference (sonde – TECO) = 0.3 ± 4.8 ppbv, while the mean SO₂ difference (sonde – TECO) = -0.87 ± 2.3 ppbv; at the 80-ppbv O₃ level, the mean O₃ difference

TABLE 3. Individual readings for the \sim 40 ppbv ozone test. The mean ozone difference (sonde – TECO) = -1.0 ± 5.3 ppbv, while the mean SO₂ difference (sonde – TECO) = -0.74 ± 1.5 ppbv.

$\begin{array}{c ccccccccccccccccccccccccccccccccccc$				
40.9 ± 1.8 40.6 ± 1.7 -0.020 ± 0.080 $-1.20 \pm 40.4 \pm 1.0$ 40.4 ± 1.0 39.44 ± 0.83 34.71 ± 0.35 $32.84 \pm 41.2 \pm 1.3$ 41.2 ± 1.3 40.1 ± 1.1 32.95 ± 0.41 $31.68 \pm 39.5 \pm 1.9$ 38.7 ± 1.8 27.92 ± 0.34 $26.63 \pm 42.4 \pm 1.4$	TECO O ₃ (ppbv)	Sonde O ₃ (ppbv)	TECO SO ₂ (ppbv)	Sonde SO ₂ (ppbv)
42.4 ± 1.4 41.0 ± 1.3 18.13 ± 0.49 $17.57 \pm 42.2 \pm 1.5$ 42.2 ± 1.5 40.8 ± 1.2 9.07 ± 0.30 $8.95 \pm 38.6 \pm 1.3$ 38.6 ± 1.3 37.6 ± 1.0 2.48 ± 0.16 2.56 ± 0.16	$\begin{array}{c} 40.9 \pm 1.8 \\ 40.4 \pm 1.0 \\ 41.2 \pm 1.3 \\ 39.5 \pm 1.9 \\ 42.4 \pm 1.4 \\ 42.2 \pm 1.5 \\ 38.6 \pm 1.3 \end{array}$	40.6 ± 1.7 39.44 ± 0.83 40.1 ± 1.1 38.7 ± 1.8 41.0 ± 1.3 40.8 ± 1.2 37.6 ± 1.0 42.0 ± 0.6	$\begin{array}{c} -0.020 \pm 0.080 \\ 34.71 \pm 0.35 \\ 32.95 \pm 0.41 \\ 27.92 \pm 0.34 \\ 18.13 \pm 0.49 \\ 9.07 \pm 0.30 \\ 2.48 \pm 0.16 \\ 2.48 \pm 0.16 \end{array}$	-1.20 ± 0.18 32.84 ± 0.28 31.68 ± 0.54 26.63 ± 0.26 17.57 ± 0.24 8.95 ± 0.20 2.56 ± 0.21



FIG. 5. The EnSci CrO₃ version of the SO₂ filter was tested at the University of Houston at three different O₃ concentrations. Within each O₃ concentration, SO₂ was varied from 0 to 65 ppbv. Shown here is the O₃ reported by the filtered sonde vs that measured by the standard TECO O₃ analyzer. The response is linear, with reasonably high accuracy and precision. See text for details.

(sonde – TECO) = 1.2 ± 8.0 ppbv, while the mean SO₂ difference (sonde – TECO) = -1.2 ± 1.9 ppbv; and at the 40-ppbv O₃ level, the mean O₃ difference (sonde – TECO) = -1.0 ± 5.3 ppbv, while the mean SO₂ difference (sonde – TECO) = -0.74 ± 1.5 ppbv. We note that the uncertainties in the (sonde – TECO) O₃ are rather large, owing to the fact that the O₃ calibrator instrument experienced difficulty in maintaining O₃ at constant concentrations. While we have not made adjustments for the offsets at [SO₂] = 0 for this test, we correct these offsets for flight data. The offsets can be corrected by adjustments in the background cell current of each ECC independently or through a subtraction from the postflight SO₂ concentrations.

Figure 6 shows the derived SO₂ concentration (filtered – unfiltered) as a function of the TECO SO₂ reading. Again, the regression of the entire dataset shows a line-of-best-fit slope to within 0.1% of 1.00 and an intercept of -0.36 ± 0.14 ppbv. The ~40 ppbv ozone level test was used to examine closely the limits of the SO₂ measurement (data in Table 3). It appears that this technique can distinguish 2.5 ppbv from 0 ppbv of SO₂ at the surface. In flight, the detection limit may be somewhat higher [~(3–5) ppbv] due to differing response time constants of the two ECC instruments.

One final laboratory test at Hokkaido University examined the SO_2 destruction properties of our 4-yr-old filters and used the experimental setup depicted in Fig. 7. The laboratory equipment consisted of a temperaturecontrolled oven for SO_2 production and a chemical ionization mass spectrometer (CIMS) for measurement



FIG. 6. As in Fig. 5, but here we examine the SO_2 measurements. The dual-sonde response is quite linear, accurately reproducing the measurements made by the standard TECO SO_2 analyzer. See text for details.

of the SO₂ concentration. The details of the CIMS instrument are described in Hirokawa et al. (2009). SO₂ gas was released at a rate of 120 ng min⁻¹ from a permeation tube in the oven controlled at 40°C and was diluted by N₂ at a flow rate of 200 cm³ min⁻¹ to prepare a test gas mixture containing approximately 200 ppbv of SO₂. The test gas mixture was sampled in the glass inlet of the CIMS instrument both with and without passing through an SO₂ filter. In the inlet, the SO₂–N₂ was further diluted by N₂ at a flow rate of 1000 cm³ min⁻¹ and then introduced into a chemical ionization region, in which SO₂ was ionized via the following ion–molecule reactions (Huey et al. 1995; Lovejoy and Wilson 1998):

$$SF_6^- + SO_2 \rightarrow SO_2F^- + SF_5, \tag{2.1}$$

$$\rightarrow \mathrm{SO}_2\mathrm{F}_2^- + \mathrm{SF}_4, \qquad (2.2)$$

$$\rightarrow SF_5^- + SO_2F. \tag{2.3}$$

The ions as well as the unreacted SF_6^- were mass-analyzed by a quadrupole mass filter and detected by a secondary electron multiplier. The SO₂ concentration was measured by monitoring ion signals of SO₂F₂⁻ detected at a mass-tocharge ratio (*m*/*z*) of 102.

Figure 8 shows the results of this test. The performance of two other tested filters, described in the appendix, is also shown in this figure. Despite their age, the CrO₃ filters resulted in an $(87 \pm 14)\%$ reduction of SO₂ at ~200 ppbv. We do not expect to encounter such high SO₂ levels during our flights, and tests described above (made with Teflon filter paper in 2009) suggest that these new filters are nearly 100% effective at removing SO₂.



FIG. 7. A schematic of the instruments used in the laboratory test of the several different SO₂ filters conducted at Hokkaido University in August 2008.

3. Field observations

a. Ozonesonde background

The example data presented here used the ECC type EnSci 2Z ozonesonde instruments (Komhyr 1986; Komhyr et al. 1995) with 0.5% buffered KI cathode solution. Meteorological measurements (pressure, temperature, and relative humidity) for all dual-sonde flights are provided by Väisälä RS80–15N radiosondes, as described in Thompson et al. (2003, 2007). Onboard global positioning systems (GPS) provided latitude, longitude, altitude, wind speed, and wind direction data. With a typical rise rate of ~5 m s⁻¹ and a measurement time constant of ~25 s, the effective vertical resolution of O₃ features is ~125 m (see also Smit et al. 2007).

Dual-ozonesonde payloads (Fig. 3) consisted of two such ECC cells, one with the EnSci SO₂ filter on the inlet side and one without, so that, by subtraction, an SO_2 profile was derived. (Note that the circuits of the two sondes have been modified by EnSci so that the data from the two instruments are combined and transmitted to the surface in the same datastream.) Differences in the measurement time constants between the two ECC units can result in the appearance of false SO₂ signals as the sonde moves through air with strong vertical gradients in O_3 . Thus, evaluation of SO2 profiles requires some care. Nevertheless, we have had good success in producing tropospheric O_3 and SO_2 profiles on 20+ dual-sonde payload balloon flights. (All of our data are available on our project Web sites: http://physics.valpo.edu/ozone, www.rice.edu/ ozone, and www.imaqs.uh.edu/ozone.)

Before each flight, the dual O_3 -SO₂ payloads are bench tested to make sure the SO₂ filter is properly conditioned and does not destroy O₃. Inlets from the filtered and unfiltered sonde are connected to the EnSci ozonizer unit, which is set to 0, low (10–40 ppbv), medium (40–80 ppbv), and high (80–300 ppbv) concentrations of O₃. Figure 9 shows that for the 14 flights from Sapporo in August 2008 and 2009, the O₃ readings reported by the two instruments agree extremely well, indicating that the filter is properly conditioned. The mean offset (secondary–primary) was -0.4 ± 2.3 ppbv, with a mean absolute offset (secondary–primary) of 1.5 \pm 1.8 ppbv.



FIG. 8. Results of a laboratory test of different SO₂ filters conducted at Hokkaido University in August 2008. The 4-yr-old EnSci CrO_3 version of the filter removed ~85% of the incident SO₂, while the KMnO₄ filter removed nearly 100%. However, after high ozone conditioning, the KMnO₄ filter no longer removed SO₂. See text for details.



FIG. 9. Preflight comparison of O₃ readings from the filtered and unfiltered ozonesondes conducted on the laboratory bench at 0, low (0–40 ppbv), medium (40–80 ppbv), and high (>80 ppbv) O₃ concentrations, with good agreement shown. Data shown are from 4 dual O₃–SO₂ sonde flights from Hokkaido University in August 2008 (dots) and 10 flights in August 2009 (stars).

Such results suggest that the technique may be able to identify SO_2 features of as little as 3 ppbv. This test should be performed before all dual O_3 - SO_2 flights.

b. Volcanic plume case—Sapporo, 22 August 2008

At 0424 UTC 22 August 2008, we released a dual sonde from the campus of Hokkaido University in Sapporo (43.07°N, 141.35°E; elevation 26 m). Figure 10 shows the SO₂ profile for this flight, with a prominent feature of ~17 ppbv between 0.45 and 0.95 km. Since this flight employed a 4-yr-old SO₂ filter, a correction factor was employed (this filter was determined to be ~65% effective). Newer filters do not require such corrections since they are nearly 100% effective (see above).

Figure 10 also shows that relative humidity (RH) increases steadily from the surface (\sim 38%) to \sim 1.85 km (87%), with values \sim 50% in the layer of elevated SO₂. Potential temperature (theta) is nearly constant at 295 K from the surface to 1.9 km, where the temperature data indicate a strong inversion (not shown). Ozone is nearly constant at \sim 40 ppbv from the surface to \sim 2.4 km. Elevated SO₂ is also seen up to \sim 3 km, but at much lower concentrations. If we integrate the SO₂ column from the surface to 3 km, we find 0.9 DU.

Figure 11 shows the OMI SO₂ map near Hokkaido for 0345–0349 UTC 22 August 2008, with a retrieval assuming a 3-km center for the peak height of the SO₂ cloud. The OMI data show a swath of elevated SO₂ (>2.5 DU) stretching from eastern Siberia across the Tatar Strait to the northeast coast of Hokkaido, then southward into the Pacific, with values ~(0.3–1.0) DU



FIG. 10. Profiles of SO₂ (black dots), O₃ (gray dots), RH (black line), and theta (gray line) from the 22 Aug 2008 dual-sonde released from Hokkaido University in Sapporo, Japan. The SO₂ peak near 0.7 km is most likely a plume from a volcanic eruption that has been transported to Hokkaido. See text for further details.

along the flight path of the dual sonde (due southeast of Sapporo).

There are two possible volcanic sources for the SO₂ plume. Mt. Kasatochi erupted violently three times during 2200 UTC 7 August to 0435 UTC 8 August 2008, sending emissions to >13.5 km. Eruptions continued through ~1800 UTC 9 August. Emissions from the eruption, quickly detected by MODIS and OMI, traveled around the world (see papers in the Okmok-Kasatochi special issue of J. Geophys. Res.). The Bezymianny volcano (55.98°N, 160.58°E) erupted at 1030 UTC 19 August 2008, producing an ash plume up to 9 km that drifted west ~1200 km (data available from the Alaskan Volcano Observatory online at http://www.avo.alaska.edu). The plume of the former can be followed in the OMI SO₂ data from the time of the eruption until its arrival in the vicinity of Hokkaido 2 weeks later. The arrival of the Kasatochi plume, however, coincides well with the arrival of the plume of the latter as well. Thus, identifying which of the two plumes our sonde actually detected may be difficult.

Back trajectories at 500 and 1500 m for this case (not shown, but found online at physics.valpo.edu/ozone/ fulbrightdata.html) were calculated using the NASA Goddard Space Flight Center (GSFC) Trajectory Model (Schoeberl and Sparling 1995) run in kinematic mode (hereafter referred to as the KTM) with National Centers for Environmental Prediction (NCEP) reanalysis ($1^{\circ} \times 1^{\circ} \times 6$ h) meteorological fields. The trajectories show the air masses over the previous 3 days arriving from the north-northeast, descending in altitude from ~1.5 to 0.5 km and from ~4 to 1.5 km, respectively, as they passed over the Sea of Okhotsk into Hokkaido. KTM forward trajectories run from the time of the Kasatochi eruption through 22 August 2008 indicate



FIG. 11. OMI SO₂ retrieval assuming a 3- km height for the arriving SO₂ plume shows a 2.5+ DU cloud moving across Hokkaido on 22 Aug 2008. The position of Sapporo is marked by the star in the figure. The balloon flight was due south-southeast from Sapporo, parallel to the high-SO₂ feature seen in the OMI data. See text for further details.

strong descent as the air mass arrived near Hokkaido (these trajectories can be found online at http://physics. valpo.edu/ozone/data/Fulbright/trajectory/kasatochi_ simulation/kasatochi_simulation.mov). Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model (Draxler and Rolph 2010) trajectories for the Bezymianny eruption are shown in Fig. 12. The air parcel initialized at ~5 km altitude arrives nearer to Sapporo than the Kasatochi plume seen in the OMI SO₂ data (Fig. 11).

Despite the theta profile that indicates that the peak was observed within the boundary layer, we believe this SO₂ peak is not of local origin. In particular, we have looked at the dependence of the dual-sonde-measured [SO₂] in the lower 1.0 km for all of our balloon flights in August 2008 and August 2009 from Sapporo, excluding the 22 August 2008 case. We find that northwesterly, northerly, or northeasterly winds (as was the case for the 22 August 2008 profile) produced mean [SO₂] = 1.11 ± 0.66 ppbv. Easterly, southeasterly, and southerly winds, on the other hand, produced mean [SO₂] = 1.8 ± 1.2 ppbv. Although not statistically significant given the limited number of profiles and the typically low local SO₂ concentrations, such differences can be explained by local

geography, with the sea to the north providing cleaner air and the industrial centers to the southeast providing more polluted air. It seems likely, therefore, that the source of the SO_2 peak is different than the usual urban centers southeast of Sapporo and may well be linked to one of the two volcanic eruptions (described above).

c. Houston plume case

The Study of Houston Atmospheric Radical Precursors (SHARP) campaign occurred from 15 April to 31 May 2009. As part of that campaign, 19 ozonesondes were released from the campus of the University of Houston (29.72°N, 95.34°W; el.19 m). On two occasions, dual O_3 -S O_2 sonde balloon payloads were flown to detect plumes emitted from industrial facilities in the Houston ship channel region (east of campus). It was found as part of this study that when light easterly winds were present, monitors on the UH Moody Tower frequently recorded higher levels of S O_2 .

Figure 13 shows the O₃, SO₂, RH, and theta profiles for the dual sonde released at 1323 UTC (shortly after dawn) on Saturday, 30 May 2009. Ozone increased from ~15 ppbv at the surface to 80 ppbv at 1.3 km. SO₂ increased from ~11 ppbv near the surface to ~55 ppbv near 400 m. Winds near 400 m as reported by the sonde were light (<4 m s⁻¹) and generally from the east-southeast direction. Moody Tower 1-min-average SO₂ readings on this morning peaked at 38 ppbv at 1154 UTC, while the hourly average at the nearby Continuous Ambient Monitoring Station 81 (29.73°N, 95.32°W) peaked at 1300–1400 UTC at 12.4 ppbv [data available online from the Texas Commission for Environmental Quality (TCEQ) at http:// www.tceq.state.tx.us].

Back trajectories were calculated at 250, 500, and 750 m with the UH Regional Data Assimilation System (UH-RDAS), with winds from the NCEP North America Mesoscale Model (NAM). The domain is interpolated to 12- and 4-km resolution, then adjusted by observations using the objective analysis module in the fifth-generation Pennsylvania State University-National Center for Atmospheric Research Mesoscale Model (MM5) (Grell et al. 1994). These trajectories suggest air arriving at UH from the east-northeast. HYSPLIT back trajectories, calculated at 300, 400, and 500 m, suggest sources to the east or southeast of UH. (A map of the 300- and 400-m HYSPLIT trajectories and the 750-m UH-RDAS trajectory can be accessed online at http://www.imaqs.uh. edu/ozone/ourdata.html via a link in the 2009 data table in the row labeled "20090530, 13:23.") The trajectories suggest that influences from sites along the Houston Ship Channel are possible. Examining the upset inventory maintained by the TCEQ (available online at http://www. tceq.state.tx.us), we find that Houston Refining (12000



FIG. 12. HYSPLIT forward trajectories [graphical output described in Rolph (2010)] from Mt. Bezymianny on the Kamchatka Peninsula started at 1100 UTC 19 Aug 2008 at the time of an observed eruption. The trajectories descend rapidly and arrive near Sapporo at the time of the dual-sonde release (data shown in Fig. 10). See text for details.

Lawndale St., very near to the 300-m HYSPLIT back trajectory) reported the emission of \sim 1900 kg of SO₂ between 0200 and 0710 UTC 30 May 2009. Thus, the most likely explanation for this plume is a primary source at this industrial plant along the ship channel.

4. Summary

This work has presented a new technique for inexpensively measuring tropospheric SO_2 plumes using a modified dual-ozonesonde approach. This technique is useful for validation of satellite SO_2 observations as well as transport studies of SO_2 plumes, both from natural (volcanic) and anthropogenic sources.

Laboratory tests found the EnSci SO₂ filter made with CrO₃ most effective at removing SO₂ from the inlet airstream, with $\sim 100\%$ removal by the new Teflon paper filters. These tests further showed that the filters did

not interfere with measurements of O_3 and demonstrated that the filters remained effective at removing SO_2 even after exposure to $\sim 2.8 \times 10^{16}$ molecules.

By flying balloons with two ozonesondes on the same payload, one with an SO₂ filter and one without, O₃ and SO₂ profiles can be measured simultaneously. Laboratory tests and field experience suggest that the detection limit is around 3 ppbv for altitudes below the ozonopause (i.e., < < 8-10 km). Readings near and above the ozonopause probably are not robust, as the derived SO₂ concentration becomes the difference between two relatively large numbers. Since reported ozonesonde measurement accuracy is 5%–10%, when O₃ concentrations reach 200 ppbv, these accuracy limitations can result in 10–20-ppbv SO₂ readings at altitudes where no SO₂ is present. Thus, we recommend our dual-sonde approach only for lower- to midtropospheric SO₂ profiles. Care must be taken in deriving the SO₂ profiles for



FIG. 13. As in Fig. 10, but for the dual-sonde from the University of Houston on 30 May 2009. A peak of >60 ppbv of SO₂ was observed near 0.4 km. See text for further details.

sondes with different time constants, particularly when the vertical O_3 gradient is large.

Before flight the SO₂ filters should be conditioned with 2–4 h of high-O₃ air. Furthermore, it is important that the filter paper be dry before high-O₃ conditioning. One hour of baking in an 80°C oven is sufficient to insure that the filter paper is dry.

Two examples demonstrated the effectiveness of the technique in measuring SO_2 plumes. The 22 August 2008 flight from Sapporo, Japan, detected an SO_2 plume near 700 m that most likely was emitted by a volcanic eruption. The 30 May 2009 flight from Houston, Texas, detected an SO_2 plume near 400 m that most likely was emitted by industrial processes.

For ECC sonde operators near SO₂ sources, it is recommended that SO₂ filters be deployed on the inlet to remove SO₂ and accurately retrieve O₃. If possible, dual sondes as described here should be flown in such locations to provide the most reliable O₃ profiles and simultaneous SO₂ profiles. Before launching the dual-sonde payloads, we recommend reviewing local air traffic regulations and contacting local air safety officials.

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APPENDIX

ECC Filter Tests

Many of the following tests employed the EnSci ozonizer unit to produce ozone and measure the current flowing between the cathode and anode cells, hereafter referred to as the intercell current (IC). The ozonizer consists of a UV lamp with an adjustable shield that produces ozone in a tube of air flowing next to the lamp. High ozone concentrations up to 4 ppmv can be achieved by turning off the ozonizer air pump, pulling the UV shield completely out, and drawing air past the UV lamp at the ozonesonde pump flow rate ($\sim 200 \text{ cc min}^{-1}$). Lower concentrations ($0 - \sim 500 \text{ ppbv}$) are achieved by running the ozonizer air pump and adjusting the shield until the desired IC is achieved. Descriptions of the ozonizer unit and its operation can be found in Komhyr (1999).

a. Empty cell and filter paper tests

We assessed the impact of the various materials from which our SO₂ filter is constructed. An ECC ozonesonde was run on ozone-free air for 5 min with a background cell current of 0.03 μ A, then run with ozonated air with a resulting IC = ~5 μ A for 5 min, with a final reading of 4.98 μ A. An empty Teflon cell of the same type that is used to hold the cathode and anode solutions was inserted between the inlet side of the pump and a constant known O₃ source. For an unconditioned cell, the IC dropped >50%, while for a high-O₃-conditioned (i.e., 5 h of high O₃ exposure) cell, the IC dropped 5%–12%. The fact that the empty, conditioned Teflon cell itself results in O₃ loss is interesting, as the ECC approach to measuring O₃ profiles has been used worldwide and demonstrated to be accurate and reliable for more than 35 yr.

When measuring ozone with the ECC ozonesonde, the incoming air bubbles through the cathode solution. Reactions in the solution in the presence of the platinum electrode, therefore, must take place on a time scale smaller than the diffusion of air in the solution to the Teflon cell walls. With a pump flow rate of $\sim 200 \text{ cc min}^{-1}$ and a Teflon cell volume of $\sim 5 \text{ cc}$, this puts an absolute upper limit of $\sim 1.5 \text{ s}$ on the reaction time constant.

We next placed an unshredded, unconditioned, 1.3-cmdiameter Teflon filter paper disk (the same size as the Teflon filter cell inner diameter) over the outlet port on the inside of the filter cell and inserted this filter between the inlet side of the pump and a constant known O_3 source. The IC dropped by 40%. This test was repeated using an unshredded, unconditioned, 2.0-cm glass fiber paper, which when placed between the constant ozone source and the pump led to an IC drop of 60%. It appears, therefore, that use of the Teflon filter paper is preferable to the glass fiber filter paper for construction of the SO_2 filter.

Finally, we shredded one untreated, unconditioned, 3.7-cm Teflon filter paper disk into approximately eight pieces, folded the pieces in half, and placed them inside the Teflon filter cell. When this filter cell was inserted between the inlet side of the pump and a constant known O_3 source, the IC dropped by >80%. The additional surface area provided by the shredded paper left a lot of surfaces for ozone deposition and destruction to take place.

b. H_2O version

We examined the impact of water on the measurement of SO_2 and O_3 . We conditioned a Teflon cell with high O_3 for 30 min, then ran for 10 min on O_3 -free air. Upon insertion of this Teflon cell between the outlet side of the pump and the cathode cell, the IC dropped 30%-40%. Water was added slowly to the Teflon cell until it was about half full; the IC was observed not to change, whether the incoming air was bubbled through the H₂O or cycled though the cell above the water level (i.e., sent through 100% relative humidity air).

We reran the test using a Teflon cell that had been high-O₃ conditioned with dry air for 4 h. As before, when inserted between the pump and the O₃ source, the empty, conditioned Teflon cell resulted in an IC drop of 13%. Water again was slowly added to the Teflon cell. This time, however, the IC dropped by 70% after about 1 min, then slowly rose to a ~24% deficit after 5 min, with the recovery likely due to the increasing dissolved O₃ content in the H₂O slowing its further absorption as saturation was approached.

Measurements by the CIMS (described above) of air after passing through the H_2O filter indicated nearcomplete destruction of SO₂. When the SO₂ air was passed through the H_2O filter cell without bubbling through the H_2O , little to no SO₂ was removed.

c. Other filters

We tested filters made from filter paper soaked in NaHCO₃ and KMnO₄ solutions, then dried. In the former case, the IC current dropped 50%, suggesting an interference with the measurement of O₃. In the latter case, IC current drops were >12%. Initially, the KMnO₄ filter removed nearly 100% of incident SO₂ (as indicated by tests using the apparatus in Fig. 7, described above), but 1 week after its construction, the filter no longer removed SO₂. Thus, we were unable to create successfully a filter using NaHCO₃ or KMNnO₄.

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