

## An intercomparison of ground-based UV-visible sensors of ozone and NO<sub>2</sub>

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**Abstract.** An intercomparison of zenith-sky UV-visible spectrometers was held at Camborne, UK, for 2 weeks in September 1994. Eleven instruments participated, from nine different European institutes which were involved with the Second European Stratospheric Arctic and Mid-latitude Experiment (SESAME) campaign. Four instruments were of the Systeme d'Analyse d'Observations Zénithales (SAOZ) type, while the rest were particular to the institutes involved. The results showed that the SAOZ instruments were consistent to within 3% (10 DU) for ozone and 5% for NO<sub>2</sub>. For ozone the results from these instruments agreed well with total ozone measurements by Dobson and Brewer spectrophotometers and integrated ozonesondes when the air mass factors for the SAOZ were calculated using the ozonesonde profiles. Differences of up to 10% in ozone and 30% in NO<sub>2</sub> were found between different instruments. In some cases these differences are attributable to the different absorption cross sections used in the analysis of the spectra, but other discrepancies remain to be investigated. A prominent source of error identified in the campaign was uncertainty in the derivation of the amount of absorber in the reference spectrum, which can contribute an error of up to 3% (10 DU) in ozone and  $1.5 \times 10^{14}$  molecules cm<sup>-2</sup> in NO<sub>2</sub>.

### 1. Introduction

An intercomparison of ground-based zenith-sky UV-visible spectrometers took place from September 12 to 23 1994 at the UK Met Office's station at Camborne, United Kingdom (50.2°N, 5.3°W). These instruments formed part of the ground-based network of the joint European Second European Stratospheric Arctic and Mid-latitude Experiment (SESAME) experiment, to study the evolution of the lower stratosphere in winter. The purpose of the intercomparison was therefore to ensure the self-consistency of the resulting measurements. Nine UV-visible groups participated, with 12 spectrometers. The Met Office provided Dobson and

Brewer spectrophotometer measurements of total ozone as well as ozonesonde profiles and standard meteorological observations.

The spectrometers exploited the technique of differential absorption to derive slant columns of ozone and NO<sub>2</sub> [e.g., Noxon 1975; Platt *et al.*, 1979, Mount *et al.*, 1987, Solomon *et al.*, 1987]. This is applied to the difference in optical depth between a zenith sky spectrum measured at high Sun (denoted the reference spectrum) and one measured at twilight, to derive a relative slant column of absorber  $S$ . The vertical column  $V$  is then derived from the expression:

$$V(\theta) = \frac{S(\theta) + R}{AMF(\theta)} \quad (1)$$

where  $R$  is the amount of absorber in the reference spectrum and AMF denotes the air mass factor at solar zenith angle  $\theta$ . This equation serves as a definition of AMF which for direct sun observations at  $\theta < 80^\circ$  is a simple geometrical factor. However, with zenith-sky observations the AMFs must be determined from a scattering model [e.g., Solomon *et al.* 1987], which must assume a particular profile of ozone and air density. The AMF is assumed independent of wavelength over the spectral range used to derive  $S$ . It is usual for each group to use standard air mass factors which are applied to each measurement; differences between these have been

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explored in an earlier intercomparison [Sarkissian *et al.*, 1995].

In a recent intercomparison of UV-visible sensors of NO<sub>2</sub>, Hofmann *et al.* [1995] showed similar differences in slant columns of NO<sub>2</sub> to those we show here. However, differences in AMFs and in the amount in the reference spectrum were not addressed. There have been many intercomparisons of Dobsons and of Brewer instruments which observe ozone in its UV bands, but this is the first reported intercomparison of zenith-sky spectrometers which measures ozone in its visible bands.

All the instruments used grating spectrometers coupled either to a charge coupled device (CCD) or a photodiode detector array to measure zenith-sky spectra. Four were of the Système Automatique d'Observations Zènithale (SAOZ) design [Pommereau and Goutail 1988]; three of these used a 512-pixel detector and the fourth (that of the Service d'Aeronomie) a new detector with 1024 pixels. These will be referred to as the SAOZ-512 and SAOZ-1024 types respectively. It is to be expected that the three nominally identical SAOZs give similar results, and one of the novel features of the intercomparison was to compare a number of instruments of this type and determine their relative precision. Discrepancies between the SAOZ and other instruments can arise from differences both in the instrument design and in the methods used to analyze the spectra. This paper does not seek to identify the reasons for each discrepancy and will concentrate on establishing how the measurements differ and whether these differences arise from the slant columns or the conversion from slant to vertical columns.

For ozone, some information was available on the absolute accuracy of the UV-visible measurements, in the form of coincident measurements by different techniques. ECC ozonesonde profiles were measured at 11 twilight periods during the course of the campaign, and Dobson spectrophotometer measurements (instrument 41) were taken every 2 hours during the day (1000 to 1800 UT). A Brewer spectrophotometer (instrument 75) measured ozone columns automatically throughout, although only direct Sun measurements will be presented here; the instrument had not been operating at Camborne for long enough to derive a zenith-sky calibration.

Spectra were measured by each spectrometer throughout the daylight hours. A reference spectrum was measured at 1215 UT each day (within 5 min of local noon) and used to derive relative slant-column amounts for ozone and NO<sub>2</sub> for that day's data. Each group also analyzed differential spectra using as a reference that at noon on September 15, chosen as a period of minimum cloud cover so that spectral interference by H<sub>2</sub>O and O<sub>4</sub> would be minimized.

In order that these measurements be used to derive vertical column totals, the air mass factors and the amount  $R$  of ozone or NO<sub>2</sub> in the reference spectrum must be known. For ozone,  $R$  must be determined either by minimizing the diurnal variation of the constituent or by constructing Langley plots of  $S$  against AMF for each twilight period (whence the slope gives  $V$  and the intercept

gives  $R$  from equation 1). Historically, this is the method used for the Dobson spectrophotometer, but some earlier zenith-sky visible spectrometers used the actual amount in the reference spectrum, determined from a simultaneous Dobson measurement and the solar zenith angle. Later, Roscoe *et al.* [1994] illustrated that the intercepts of Langley plots could contain artifacts which it was important to include; the effective amount in the reference spectrum was not necessarily equal to the actual amount. For NO<sub>2</sub> (which has a systematic diurnal variation) a value of  $R$  is normally chosen which produces a smooth, monotonic increase in column amount throughout the day. Johnson and McKenzie [1989] used an amount equal to the mean of the morning and evening twilight values on the day of the reference, multiplied by the AMF at noon. Lee *et al.*, [1994] used a 1-D photochemical model to predict the ratio of the NO<sub>2</sub> column at zenith angle  $\theta$  to that at 90°; by multiplying the AMFs by this ratio, straight Langley plots were obtained, from which the intercept could be used to estimate  $R$ . As it is the practice for most of the groups in the intercomparison to use a standard reference spectrum with well-defined values of  $R$  to analyze long runs of measurements at a particular site (this was the practice for SESAME), the choice was made that vertical columns provided for intercomparison would only be derived using the September 15 reference spectrum. Each group used its normal method to estimate  $R$  for this spectrum for O<sub>3</sub> and NO<sub>2</sub>; these estimates are compared below.

Differences in air mass factors arise from the different scattering models used by different groups, and the different standard profiles of ozone and temperature used therein. A feature of the Camborne intercomparison was the provision of 11 ozonesondes, launched at times of day to be selected by the campaign organizers. This enabled the correct profiles to be supplied to the scattering models for 11 twilight periods. It was found that AMFs calculated in this way were clearly of higher quality and allowed a more rigorous analysis of differences between zenith-sky ozone columns and those measured by sondes. This issue is discussed in detail in a companion paper [Sarkissian *et al.*, this issue], where it is shown that the average discrepancy between total ozone measured by one of the SAOZ spectrometers and ozonesondes was < 3 DU during the campaign. The issue addressed here is the agreement between different spectrometer measurements when coincident ozone profiles are not available. For this reason the analyses presented use the standard AMFs normally employed by the different groups.

## 2. Apparatus

A summary of the instruments used by each group is given in table 1. For ease of reference in the text and figures, a short code is defined in the table for each instrument. Note that the SE and IA2 instruments were only designed to measure NO<sub>2</sub>; their spectral range did not cover the ozone bands.

Table 1. Summary of Characteristics of Instruments Taking Part in the Intercomparison

Group	Code	Grating g/mm	Spectral Range, nm	Number of Pixels	Resolution nm/FWHM	Sampling Ratio pix/FWHM	Detector Type	Detector T, °C	Field of View, deg
Aberystwyth	AB	200	300-600	512	1.0	1.6	NMOS	ambient	30
NILU	NI	200	300-600	512	1.0	1.6	NMOS	ambient	30
DMI	DM	200	300-600	512	1.0	1.6	NMOS	ambient	30
Service d'Aeronomie	SA	360	300-635	1024	1.2	3.5	NMOS	ambient	30
IASB	IA1	1200	400-551	1024	0.6	4.0	diode	-40	15
IASB	IA2	1200	332-451	1024 x256	0.6	6.0	CCD	-56	15
Cambridge	CB1	600	130*	1152 x320	0.7	9.0	CCD	-80	1
Cambridge	CB2	600	130*	1152 x320	0.7	9.0	CCD	-80	1
IVL	SE	600	400-485	1024	1.3	15.8	PCD diode	-14	2.9
MPI	MPI	600	316-517	1024	1.1	5.0	diode	-68	1
Heidelberg	HD	600	362-677	1024	1.2	6.0	diode	-68	1

FWHM, full width half maximum; CCD, charge coupled device; NILU, DMI, IASB, IVL, MPI, refer to addresses of experimenters

\* The wavelengths observed by these instruments could be chosen by the experimenter, although the range observed was fixed at 130 nm.

Table 2: Spectral Ranges and Absorption Cross Sections Used for Analyses

	SAOZ-512	SAOZ-1024	IASB	Cambridge	IVL	MPI	Heidelberg
Spectral range for O <sub>3</sub> , nm	450-580	450-580	470-540	450-540	-	487-514	493-555
Spectral range for NO <sub>2</sub> , nm	405-498	405-498	415-455	420-455	439-471	432-455	435.7-461.6
$\sigma(\text{O}_3)$	Johnston, priv. comm., 293K	Brion <i>et al.</i> *, normalised on Anderson and Mauersberger [1992]	Johnston, priv. comm., 293K	Johnston, priv. comm., 293K	Burkholder and Talukdar [1994]	Measured in lab by investigators	Anderson and Mauersberger [1992]
$\sigma(\text{NO}_2)$	Johnston, priv. comm., 293K	Merienne <i>et al</i> [1995], normalised on Johnston, 293K	Measured in lab by investigators	Harwood and Jones [1994]	Johnston, priv. comm., 293K	Schneider <i>et al</i> [1987]	Amonso <i>et al</i> [1993]
$\sigma(\text{O}_4)$	Greenblatt <i>et al</i> [1990]	Greenblatt <i>et al</i> [1990]	Greenblatt <i>et al</i> [1990]	Greenblatt <i>et al</i> [1990]	Greenblatt <i>et al</i> [1990]	Greenblatt <i>et al</i> [1990]	Greenblatt <i>et al</i> [1990]
$\sigma(\text{H}_2\text{O})$	Measured in the atmosphere from ground	Measured in atmosphere from balloon	Measured by SAOZ from ground	Rothman <i>et al</i> [1992]	Rothman <i>et al</i> [1992]	Measured in the atmosphere from ground	Rothman <i>et al</i> [1992]

SAOZ, Systeme d'Analyse d'Observations Zénithales

J. Brion *et al.*, private communication [1994]

Each group analyzed the spectra using their own software. The analysis techniques for instruments of this type are not simple, and can lead to significant differences in the atmospheric measurements. The purpose of this intercomparison was to evaluate differences in the final measured column amounts and not to pursue issues of detail in the analysis methods. Nevertheless, certain features of the analyses have a direct bearing on the results and are briefly summarized here. One important point to note is that the three SAOZ-512 instruments used identical software for their analyses.

Slant columns are derived in all cases by comparing differential spectra with laboratory cross sections of the gases of interest (in this case the primary measured quantities O<sub>3</sub> and NO<sub>2</sub> and the spectrally interfering species O<sub>4</sub> and H<sub>2</sub>O), after correction for Rayleigh-Mie scattering and the Ring effect. The humid conditions encountered in Camborne made the correction for water vapor absorption more critical than is usually the case for SESAME observations (which were made at cold high latitudes in winter).

The wavelength intervals used to derive ozone and NO<sub>2</sub>, and references to the cross sections used ( $\sigma$ ) are given in Table 2. Although ozone cross sections from a number of sources were used by the various groups, the resulting variations in differential cross section were generally less than 2%, although the disagreement reached 5% at 530–555 nm. The O<sub>4</sub> cross sections were also very similar, but H<sub>2</sub>O cross sections differed significantly. The likely reason for this is that the lines are saturated so that a mean cross section is not strictly valid (it is a function of the amount of H<sub>2</sub>O in the spectrum). Substantial differences existed in the NO<sub>2</sub> differential cross sections, as discussed below.

Measurements from the Dobson spectrophotometer presented in this paper are daily mean values using the

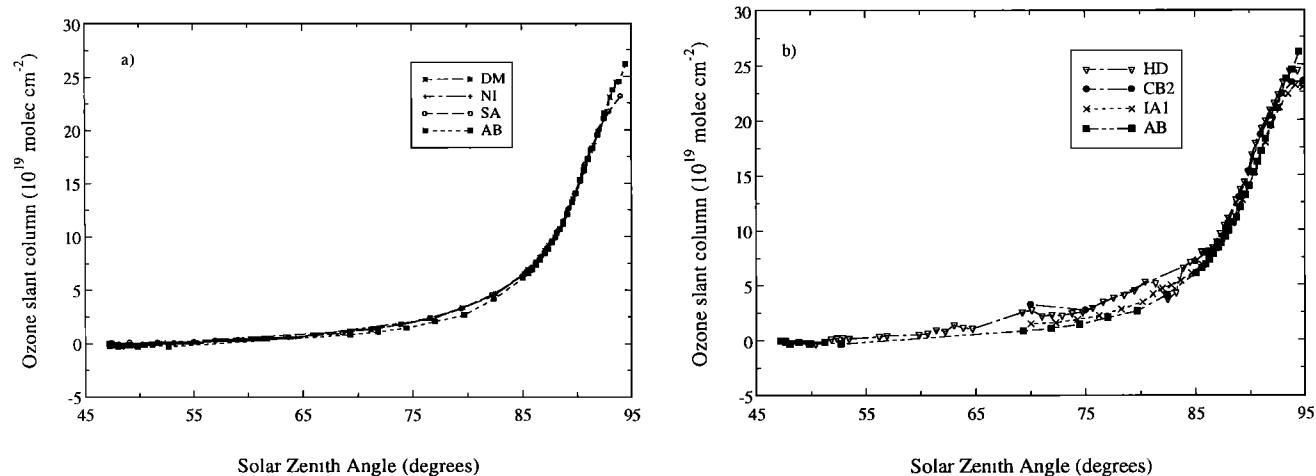
Bass-Paur absorption coefficients. A distinction is drawn between direct Sun and zenith sky AD-pair measurements and direct sun CD-pair measurements: the latter are known to be more sensitive to tropospheric pollution. AD-pair Dobson values are considered accurate to 3% (10 DU). Total ozone was also derived from the ozonesonde profiles by assuming a constant mixing ratio above burst height. This gives a good estimate when the balloon reaches 30 km or higher, as was the case with all but one of the sondes used here. The exception, on September 12, reached 26 km, and the value of 338 DU derived for total ozone may be too low by as much as 15 DU.

### 3. Results

#### 3.1 Comparison of Slant Columns

Direct comparison of slant-column amounts requires that instruments use the same wavelength region to measure each constituent, otherwise the AMF will be different, leading to a different slant column from the same vertical column. The MP1 instrument used a different wavelength range for ozone to the other groups and is not therefore included in this comparison. The Cambridge instruments experienced difficulties on September 15 and the only data available from these instruments are slant columns measured with respect to the daily noon reference spectrum.

Figures 1 (O<sub>3</sub>) and 2 (NO<sub>2</sub>) show typical sets of slant columns for one half-day period (morning of September 15), analyzed with respect to the daily noon reference spectrum. Note that the differences between instruments in the twilight period are small, often difficult to see on this scale. To display these differences better, an interpolated (not smoothed) curve  $S_{\text{Aber}}$  was drawn through the Aberystwyth SAOZ data for each half-day, and the differences between this curve and the data from the other



**Figure 1.** Examples of the agreement in ozone slant columns obtained by the different zenith-sky spectrometers at Camborne, in this case on the morning of September 15: (a) showing the excellent agreement between the different SAOZ instruments; (b) showing that agreement between some other instruments is not as good. Values from MP1 are not included because its use of a different wavelength region would give rise to significantly different air mass factors (AMFs), and so different slant columns, from the same vertical column.

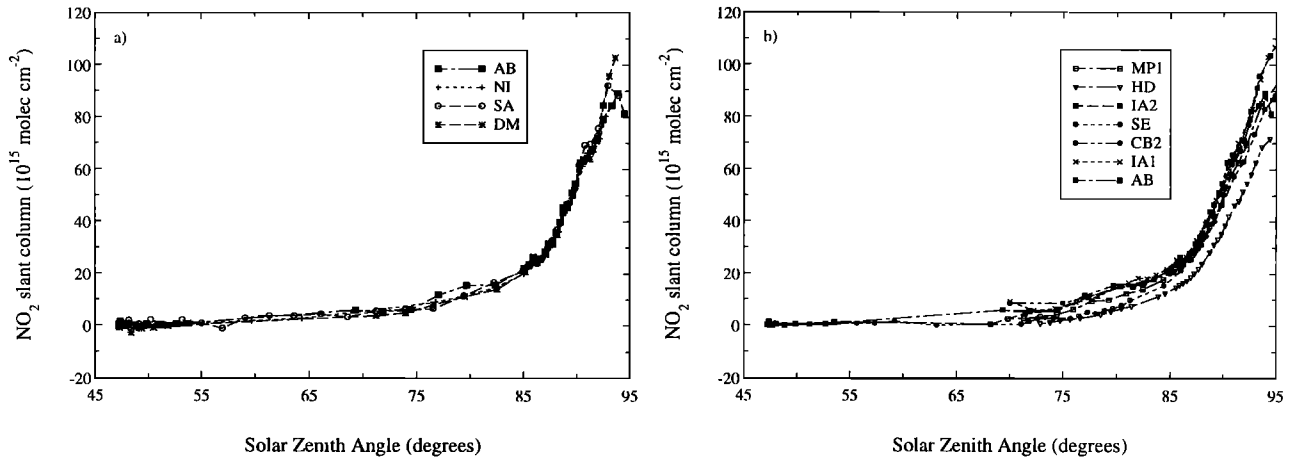


Figure 2. As figure 1 but for NO<sub>2</sub>.

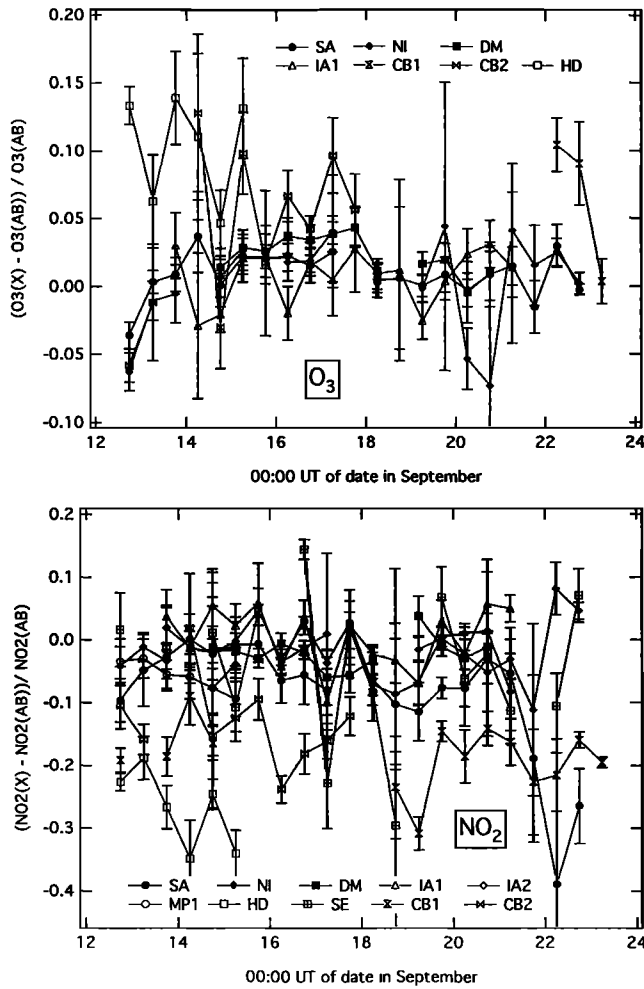
instruments ( $\Delta S$ ) was averaged for each twilight period ( $85^\circ \leq \theta \leq 91^\circ$ ). (This procedure was required because the instruments all measured at different times, so that simultaneous differences between instruments were not available). Typically, 10 measurements would be made by each instrument during this time. The resulting differences (expressed as  $\Delta S/S_{\text{aber}}$ ) are shown in Figures 3 (for analyses with respect to the daily reference spectrum) and 4 (for analyses with respect to the September 15 reference spectrum). Error bars on each point are derived from the standard deviation of  $\Delta S$  during each twilight period. The

mean and standard deviation of  $\Delta S/S_{\text{aber}}$  for each instrument are shown in Table 3.

There is considerable scatter in the values shown in Figures 3 and 4, with systematic and random variations. For ozone the four SAOZs track each other fairly well (certainly within the error bars), with agreement generally to within 4% but with occasional discrepancies as large as 10%. There is a systematic offset with respect to the AB instrument which is most marked with the September 15 reference spectrum. The IA instrument agrees well with the SAOZs, but the CB1, CB2, and HD values show a

Table 3. Mean and Standard Deviation of  $\Delta S/S_{\text{aber}}$  for Each Instrument

Instrument	Code	Mean Difference and Standard Deviation of Differences, % for O <sub>3</sub>				Mean Difference and Standard Deviation of Differences, % for NO <sub>2</sub>			
		Daily Reference		Sept 15 Reference		Daily Reference		Sept 15 Reference	
		Mean	s. d.	Mean	s. d.	Mean	s. d.	Mean	s. d.
Service d'Aeronomie SAOZ	SA	0.7	1.7	2.4	1.5	-5.4	3.6	-1.2	4.1
NILU SAOZ	NI	1.1	5.2	3.7	2.4	-2.8	2.3	-3.6	2.4
DMI SAOZ	DM	2.2	1.5	3.7	1.3	-2.1	2.5	-3.6	1.2
IASB 1	IA1	0.6	2.1	4.7	1.8	0.2	4.8	-1.3	5.3
IASB 2	IA2	-	-	-	-	-1.2	4.0	0.3	2.8
Cambridge 1	CB1	6.9	6.1	-	-	-18.3	6.2	-	-
Cambridge 2	CB2	4.4	6.0	-	-	-13.2	6.7	-	-
MPI ground-based	MP1	-	-	-	-	-5.8	2.5	-8.1	1.6
Heidelberg	HD	10.5	4.0	13.6	5.0	-26.9	6.4	-28.4	6.3
IVL	SE	-	-	-	-	-3.9	11.9	-4.6	11.5



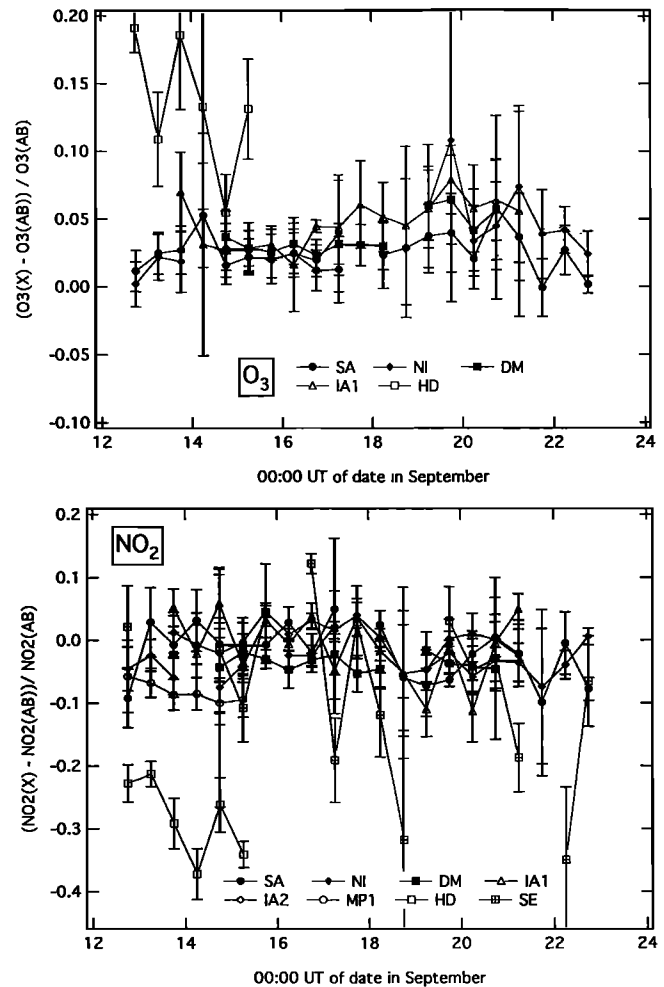
**Figure 3.** Fractional deviations of slant columns obtained by each instrument between 85° and 91° solar zenith angle (SZA) from those obtained by the AB instrument, using a daily noon reference spectrum (positive values imply slant columns greater than AB). The figure shows the averages and standard deviations of these relative differences for each half day.

consistent positive offset with respect to AB which exceeds the error bars. The scatter in Figure 4a is noticeably smaller (confirmed by the smaller standard deviations in Table 3), although there is a mean positive offset (i.e., most of the instruments measured more than AB). One reason for the smaller scatter is that the daily reference spectra were not measured at exactly the same time (the exposure time for each instrument to obtain a spectrum, for instance, was different). On cloudy or polluted days these small differences can cause significant changes in the relative slant columns.

A similar pattern was seen for NO<sub>2</sub>, but with much more scatter and larger error bars (Figures 3b and 4b). During the period September 20-23, persistent easterly winds brought a polluted air mass to Camborne, causing large tropospheric NO<sub>2</sub> values (see below) and rapid variations in the slant-column amount. The intercomparison is therefore most valid for the period September 12-20, and the statistics for NO<sub>2</sub> shown in

Table 3 apply to this earlier period only. The SAOZ-512 and IASB instruments are again consistent to about 4%, but there is a systematic discrepancy with the SAOZ-1024 (SA) when analyzed with the noon reference spectra which is not evident with the September 15 spectrum. Very large differences are seen with the other instruments, especially those of HD and CB.

Since the SAOZ instruments use the same analysis programs and cross sections the differences between these instruments are an indication of the accuracy attainable from instruments of this type. Some of the large differences between some of the other instruments can be traced unambiguously to differences in the cross-sections used: the Cambridge group, for instance, have measured the NO<sub>2</sub> cross section in the visible at a temperature of 50 °C and found a value 20% greater than at room temperature. This accounts for most of the difference between the CB instruments and the AB for NO<sub>2</sub>. The difference between the HD NO<sub>2</sub> values and the others can also be attributed to different cross sections. In contrast, this cannot explain the large difference for ozone between the HD group and the SAOZ-1024, which both nominally use the same cross sections (Table 2): those of SAOZ-



**Figure 4.** As figure 3 but using analyses with the reference spectrum measured at noon on September 15.

1024 are derived from the high-resolution values of *J. Brion et al* private communication [1994], normalized on *Anderson and Mauersberger* [1992], while the HD cross sections (taken from the latter) have been confirmed by independent laboratory measurements. A possible reason for the differences is excess absorption by tropospheric clouds, which may be sensitive to the instrumental field of view [*Erle et al.*, 1995]. These differences are currently being investigated.

### 3.2. Estimates of *R* in the September 15 Reference Spectrum

The value of *R* for ozone derived for the September 15 reference spectrum should be the same for all instruments. Figure 5 shows the spread of values derived by six of the instruments, either by averaging the intercepts of Langley plots or by minimizing the diurnal variation of ozone during the intercomparison period. An error of 10% in *R* introduces an error of about 1% in the vertical columns; thus the spread of values in Figure 5 corresponds to a difference of up to 3% between instruments arising from this source. Three of the values, for AB, MP1, and SA are the same at  $1.5 \times 10^{19}$  molecules cm<sup>-2</sup>. When divided by the air mass factor at the time of the reference spectrum, this value corresponds to 382 DU, in excellent agreement with the Dobson value (381 DU), the slope of the Langley plot for that day (379 DU), and the integrated sonde total ozone (376 DU). Unfortunately, this result is less convincing than at first sight: the standard deviation of the Langley-plot intercepts used to calculate *R* was about three times the standard error in each intercept given by the regression analysis. This means that an error bar of  $0.2 \times 10^{19}$  molecules cm<sup>-2</sup> must be associated with *R*, explaining to some extent the large differences in the estimates of *R* by different groups.

For NO<sub>2</sub>, *R* is normally chosen to produce a smooth, monotonic increase in column amount throughout the day; because of the photolysis of N<sub>2</sub>O<sub>5</sub>, the NO<sub>2</sub> columns increase during the day, rendering simple Langley plots inappropriate. The AB, DM, MP1, and SA groups all reported values of *R* between  $7.0$  and  $8.0 \times 10^{15}$  molecules cm<sup>-2</sup> (with uncertainty about  $1 \times 10^{15}$  molecules cm<sup>-2</sup>), corresponding to a vertical column between 4.6 and 5.2

molecules cm<sup>-2</sup> at noon. This is consistent with the actual column amount measured on the evening of 15 September (between  $4$  and  $6 \times 10^{15}$  molecules cm<sup>-2</sup>, figs. 9 and 10), given that the midday column should lie closer to the evening than the morning value. The other three groups report larger values which are not consistent with the evening measurements. The spread in Figure 5 of 30% corresponds to an uncertainty in vertical column amount of about 4%.

### 3.3 Comparison of Ozone Vertical Columns

For all but one instrument, slant columns were converted to vertical columns using equation (1). A single value for each twilight period was obtained by averaging individual vertical columns between  $\theta = 87^\circ$  and  $91^\circ$ , weighted according to the standard error of each measurement. A different procedure was adopted by the HD group, who derived the twilight ozone column from the slope of the corresponding Langley plot.

To understand more clearly the significance of differences between the instruments, a sensitivity test will first be presented using the AB data. Five slightly different methods were used to analyze the spectra and derive vertical columns: (1) Using the September 15 reference spectrum with the mean value of *R* ( $1.5 \times 10^{19}$  molecules cm<sup>-2</sup>). (This is the standard analysis conducted for such data by the Aberystwyth group.) (2) using the September 15 reference spectrum with *R* =  $1.7 \times 10^{19}$  molecules cm<sup>-2</sup> (1 $\sigma$  above the mean); (3) using a reference spectrum taken at another site (Aberdeen, Scotland, March 1994 during SESAME observations), with the *R* value determined at that site at that time ( $2.86 \times 10^{19}$  molecules cm<sup>-2</sup>); (4) as method 3 but with an *R* value determined for the Aberdeen spectrum from the Camborne data, using the intercepts of Langley plots as for method 1 ( $2.56 \times 10^{19}$  molecules cm<sup>-2</sup>); (5) using daily noon reference spectra and assuming constant ozone throughout each half-day. *V* was then derived from:

$$S(\theta) = V \times (\text{AMF}(\theta) - \text{AMF}(\text{noon})) \quad (2)$$

The results are presented in Figure 6 as differences between the standard analysis method and methods 2 to 5. The uncertainty in the value of *R* introduces an uncertainty of about 7 DU in the vertical columns, consistent with the argument in section 3.2. The use of an old reference spectrum for SAOZ analyses (i.e., that measured at Aberdeen) caused differences of < 2 DU in all but one case, provided the value of *R* was derived in the same way as for the standard analysis. Use of the *R* value derived at Aberdeen caused a mean offset of about 9 DU. This suggests that SAOZ analyses are not sensitive to the choice of reference spectrum provided changes in *R* are monitored; such changes were discussed in detail by *Roscoe et al.* [1994].

Differences arising from the use of equation (2) with daily noon reference spectra show much more scatter (standard deviation of 5 DU) but an average value of only

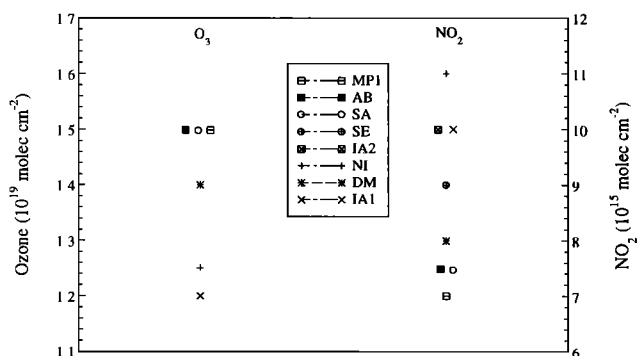
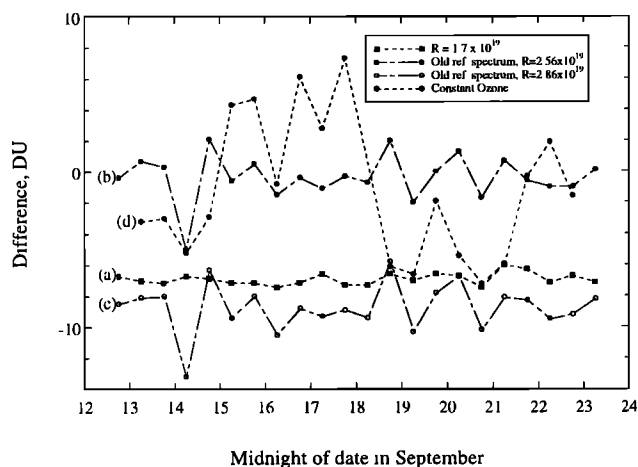


Figure 5. Estimates by each group of the amounts of O<sub>3</sub> and NO<sub>2</sub> in the reference spectrum of September 15.

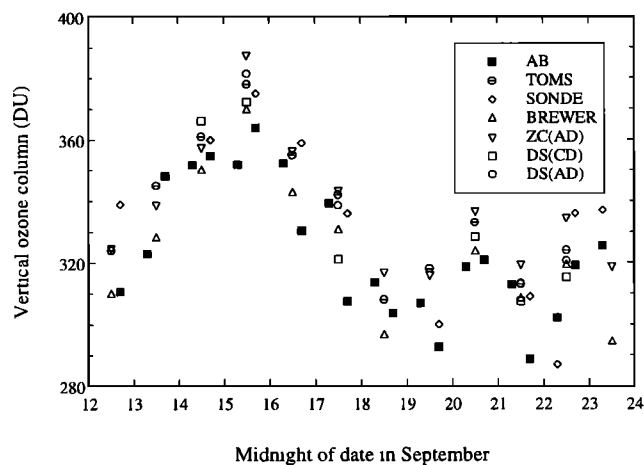




**Figure 6.** Analyses made with the AB data using different methods, shown as differences from the standard analysis (reference spectrum of September 15 with  $R = 1.5 \times 10^{19}$  molecules  $\text{cm}^{-2}$ ); (a) illustrating the sensitivity of the results to uncertainty in the value of  $R$ ; (b) using a reference spectrum measured at another site (Aberdeen, Scotland, March 1994), with the value of  $R$  determined from the Camborne data in the same way as for the standard analysis; (c) as (b) but with the value of  $R$  determined at Aberdeen; (d) using daily reference spectra and the assumption that total ozone remained constant during the day.

0.6 DU. A significant mean offset with this method would indicate an error in the estimate of  $R$ , so the excellent agreement is an encouraging indication that the analysis method used was robust and internally consistent. The scatter arises both from the assumption of constant ozone and from the use of different reference spectra, although the result using the Aberdeen reference spectrum indicates that changes in ozone are the dominant cause. The use of equation (2) suggests that the limiting precision of this kind of measurement is around 5 DU, with the accuracy of current measurements limited to 10 DU by the uncertainty in the derivation of  $R$ . (Accuracy is also, of course, limited by uncertainties in the absorption cross-sections used in the analysis.)

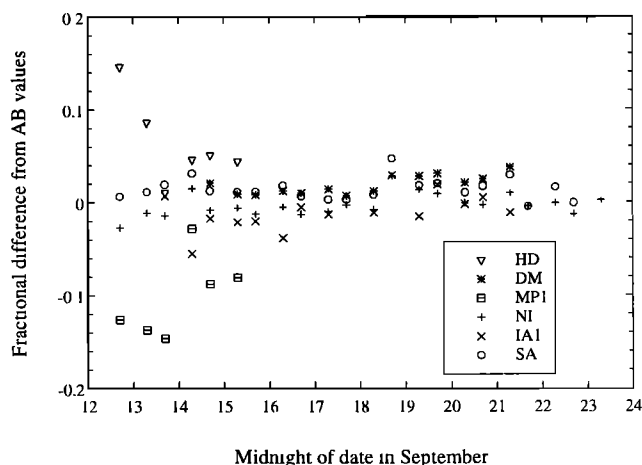
AB measurements analyzed with respect to the September 15 reference spectrum are compared with the Dobson, Brewer, TOMS and integrated ozonesonde measurements in Figure 7. The SAOZ is clearly 10 - 15 DU lower than the other techniques. In fact, this is entirely accounted for by the difference in AMFs factors discussed above: the standard SAOZ algorithms use AMFs calculated for 60°N in winter, where the ozone and temperature profiles differ from those measured at Camborne. There is considerable scatter between the points in Figure 7 (about 20 DU), but a close examination reveals that the direct sun Dobson values (marked DS(AD) and DS(CD) after the wavelength pairs used) agree with the SAOZ to within about 10 DU (note that the two Dobson values can differ by more than this). The conclusion from this is that the SAOZ measurements with daily airmass factors are consistent with the other



**Figure 7.** Vertical columns of ozone from AB, compared with values from the TOMS, Dobson, Brewer, and vertically integrated ozonesondes. Separate symbols are used for direct Sun (DS) and zenith cloud (ZC) Dobson observations, and for different wavelength pairs (AD, CD). Note that the ozonesonde on September 12 burst at 26 km, so that the corresponding ozone column is underestimated by up to 20 DU.

techniques to  $\pm 10$  DU but that with standard AMFs there was an offset of around -10 DU at Camborne in September [see also Sarkissian *et al.* this issue].

Vertical column averages from the other spectrometers are expressed as fractional differences from the AB measurements in Figure 8. The differences are summarized in Table 4. These figures should be compared with Figure 4, where the appropriate slant columns are compared. The four SAOZs and the IA1 instrument agree to about  $\pm 3\%$  (10 DU), with very small mean discrepancies, of the order of 1%. To some extent this arises because differences in slant-column amounts and in the value of  $R$  cancel out, but the agreement is nevertheless impressive: it is within the uncertainty for a



**Figure 8.** Comparison between zenith-sky spectrometer measurements of vertical ozone column, using the September 15 reference spectra. The values shown are fractional differences from the AB values shown in Figure 7.

**Table 4.** Differences Between UV-Visible Measurements of Ozone (percent deviation from AB) with Reference Spectrum of September 15

Instrument	Slant Column Differences		AMF Ratio to SAOZ	R for Sept 15 $\times 10^{19}$ molecules $\text{cm}^{-2}$	Vertical Column Differences	
	Mean	s.d.			Mean	s.d.
SA	2.3	1.5	1.0	1.5	1.4	1.2
NI	3.7	2.4	1.0	1.25	-0.3	1.2
DM	3.7	1.3	1.0	1.40	1.8	1.0
IA1	4.7	1.8	0.97	1.20	-0.9	2.0
MP1	-13.7	5.3	0.954 - 0.98	1.5	-10.1	4.4
HD	13.6	5.0	0.954 - 0.98	-	6.4	4.3

AMF, air mass factor

R for AB was  $1.5 \times 10^{19}$  molecules  $\text{cm}^{-2}$  for the September 15 reference spectrum. The MP1 and HD groups used different AMFs for different days, calculated from the ozonesonde profiles.

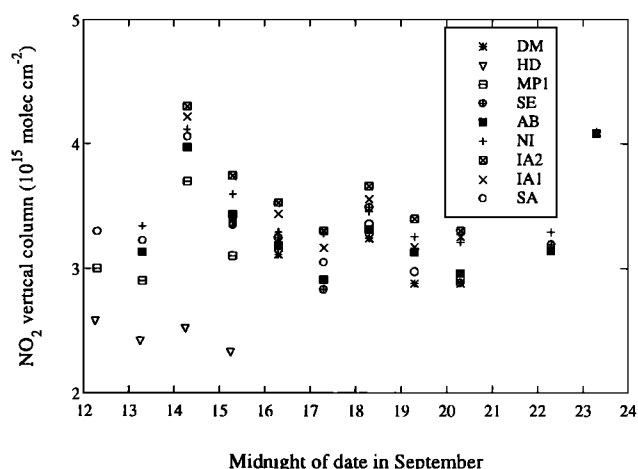
single instrument derived above. The values for MP1, on the other hand, were much smaller than those for AB, an average offset of -10% which appears to be largely attributable to the cross sections used in the analysis. A similar offset in the opposite direction is seen for the HD data. Because of concern about excess tropospheric absorption, vertical columns for this group were derived from the slopes of Langley plots; nevertheless, the large discrepancy in slant columns noted above persists in the vertical columns.

### 3.4 Comparison of NO<sub>2</sub> Vertical Columns

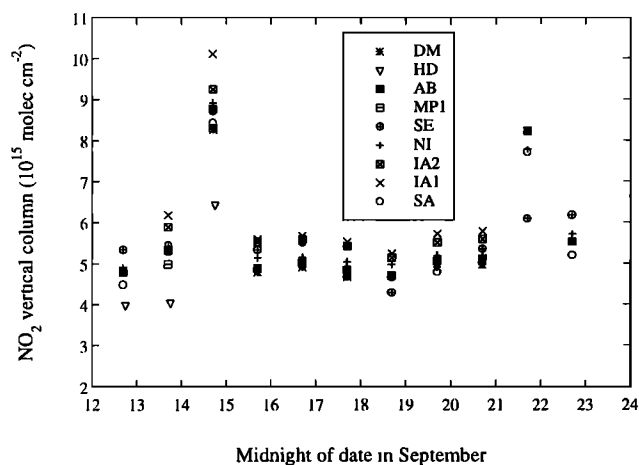
The AB data were again analyzed with respect to the Aberdeen reference spectrum to determine the sensitivity of the results from one instrument to the choice of reference spectrum. The results demonstrated a dramatic change in the value of R. The original value derived from the instrument at Aberdeen was  $5.5 \pm 1 \times 10^{15}$  molecules  $\text{cm}^{-2}$ , consistent with the AMF at the time the spectrum was measured (3.0) multiplied by the NO<sub>2</sub> total column derived that evening ( $2.6 \times 10^{15}$  molecules  $\text{cm}^{-2}$ ). However, when the Camborne data were used to derive R the value obtained was  $12 \pm 1 \times 10^{15}$  molecules  $\text{cm}^{-2}$ . Given the latter value, the average difference in NO<sub>2</sub> total columns derived from the Camborne data using the standard and Aberdeen reference spectrum was  $0.07 \times 10^{15}$  molecules  $\text{cm}^{-2}$  with a standard deviation of  $0.03 \times 10^{15}$ , a difference of about 2%, constituting excellent agreement within the stated error limit (the uncertainty of  $1 \times 10^{15}$  molecules  $\text{cm}^{-2}$  in R causes an uncertainty of  $0.07 \times 10^{15}$  molecules  $\text{cm}^{-2}$  in the vertical column). Use of  $R = 5.5 \times 10^{15}$  molecules  $\text{cm}^{-2}$  with the Aberdeen reference spectrum, however, introduced a very significant difference of about  $0.5 \times 10^{15}$  molecules  $\text{cm}^{-2}$  in the total NO<sub>2</sub> column. This amounts to 10% of the evening measurements and 16% of

the morning measurements at Camborne. The reasons for this discrepancy are currently being investigated.

The comparison of NO<sub>2</sub> total columns derived from the different instruments is shown in Figures 9 and 10 and summarised in Table 5. The SAOZ instruments agree to about 5% with one another. The difference of about 10% between the AB and the IA instruments arises partly from the difference in AMF (4%) and partly from the different estimates of R: there is very little scatter in the differences shown in Figures 9 and 10. A difference in R of  $2.5 \times 10^{15}$  molecules  $\text{cm}^{-2}$  leads to a difference in vertical column of  $0.17 \times 10^{15}$  molecules  $\text{cm}^{-2}$ , i.e., 5.6% of the morning values and 3.5% of the evening values. The mean offset in the slant columns for SE is also removed by the larger value of R used by the IVL group. In contrast, the differences with MP1 and HD arise conclusively from



**Figure 9.** Zenith-sky spectrometer measurements of NO<sub>2</sub> in the mornings, calculated using the September 15 reference spectra. Heavily polluted days have been excluded from this plot.



**Figure 10.** As figure 9 but for afternoon NO<sub>2</sub> measurements.

differences in the slant columns derived from the spectra and are attributable mainly to differences in the absorption cross sections.

#### 4. Conclusions

This paper has investigated the relative accuracy of ozone and NO<sub>2</sub> measurements by zenith-sky UV-visible spectrometers. Different analysis methods applied to ozone data from a single instrument led to differences of less than 10 DU, or 3%. A prominent source of error identified here was the value assumed for the amount of absorber in the reference spectrum, which can introduce an error of up to 10 DU in the vertical columns. Large

differences were seen in the value of  $R$  derived by different groups, consistent with this uncertainty. The effect was even more marked for NO<sub>2</sub>, where differences of 6% in vertical column amount were directly attributable to this cause. Indeed, two different determinations of  $R$  for the same reference spectrum (that measured by the Aberystwyth group at Aberdeen) were found to differ by a factor of 2. Further investigations of the large uncertainty in values of  $R$  are clearly required, but a recommendation that arises from this work is that for a "standard" reference spectrum; the amount of ozone is best estimated as the vertical column on the day the reference was taken, multiplied by the AMF at the time of measurement. This indeed is the practice followed in the past by the HD group [Fiedler *et al.*, 1993]. Currently, no such recommendation can safely be made for NO<sub>2</sub>. However, the results show that the use of a standard reference spectrum recorded on a day free of pollution is superior to the use of a daily reference spectrum.

Agreement in the vertical columns between instruments of the SAOZ type was generally within 10 DU (3%) for ozone and 5% for NO<sub>2</sub>. (In fact, this result is slightly flattering since differences in slant columns and the values of  $R$  tended to cancel). This is an indication of the repeatability of measurements made with these instruments. Differences between the SAOZ and other instruments can arise for a number of reasons, in particular the choice of absorption cross sections in the analysis of spectra. In fact, the IASB instrument was consistent with the SAOZ to 3% for O<sub>3</sub> and 10% for NO<sub>2</sub>, with the SE and MPI instruments also consistent to within 10% for NO<sub>2</sub>. For

**Table 5.** Differences Between UV-visible Measurements of NO<sub>2</sub> (percent deviation from AB) with Reference Spectrum of September 15

Instrument	Slant Column Difference		AMF ratio to SAOZ	$R$ for Sept 15 10 <sup>15</sup>	Vertical Column Differences			
					Morning		Evening	
	mean	s.d.			Mean	s.d.	Mean	s.d.
SA	-1.2	4.1	1.0	7.5	0.9	2.8	-3.4	2.4
NI	-3.6	2.4	1.0	11.0	5.4	3.2	2.0	3.0
DM	-3.6	1.2	1.0	8.0	-1.0	1.6	-3.3	1.5
IA1	-1.3	5.3	0.957	10.0	8.1	3.5	13.8	1.5
IA2	0.3	2.8	0.957	10.0	10.1	1.9	9.9	2.3
MP1	-8.1	1.6	0.953	7.0	-7.9	-	-4.1	-
HD	-28.4	6.3	0.953	-	-30.0	-	-23.0	-
SE	-4.6	11.5	1.019	9.0	-0.1	3.2	2.1	11.3

$R$  for AB was  $7.5 \times 10^{15} \text{ cm}^{-2}$  for the September 15 reference spectrum. Insufficient data to calculate standard deviation for MP1 and HD data

ozone, both the MPI and the HD instruments differed by > 6% from the others. For MPI this probably arises from differences in cross sections, but for HD the cause appears to involve a different sensitivity to low clouds. The large differences in NO<sub>2</sub> slant columns between the CB and the HD instruments and the others is directly attributable to the cross sections used. There is laboratory evidence that the cross-section of NO<sub>2</sub> is 20% larger at low temperatures such as pertain in the stratosphere than it is at room temperature [Harwood and Jones, 1994; Coquart et al., 1995], so that the SAOZ values, for instance, should be reduced by 20%. The results of this paper for NO<sub>2</sub> therefore relate to the relative accuracy of the different instruments and not to the absolute accuracy.

For ozone, the intercomparison exercise did provide valuable information on the absolute accuracy of measurements by zenith-sky UV-visible spectrometers. The average discrepancy between SAOZ spectrometer ozone measurements and other techniques (Figure 7) of around -10 DU was shown to be attributable almost entirely to differences in the air-mass factors [Sarkissian et al., this issue].

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