

UV-VIS MEASUREMENTS OF STRATOSPHERIC TRACE  
SPECIES AT THE JUNGFRAUJOCH.

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1. INTRODUCTION : UV-VIS MEASUREMENTS AT MID-LATITUDE

Benefiting of latest improvements in diode array detectors technology, ground based ultraviolet and visible (UV-VIS) spectrometry has proved to be a simple and reliable technique for the measurement of total columns of stratospheric trace species. Not very sensitive to meteorological conditions, this technique has the capability of measuring O<sub>3</sub> and NO<sub>2</sub> and, in polar regions, OClO and BrO whatever the cloud cover. These advantages have led to an increase in the number of sites operating UV-VIS instruments, especially in Arctic and Antarctic regions. Having in mind this distribution, a coordination effort has been recently initiated for developing a UV-VIS network at the European and World scales. The development of such a network calls for reference stations located at mid-latitude.

The Scientific Station of the Jungfrauoch has been designated, together with the "Observatoire de Haute Provence" (OHP), as the mid-latitude reference site of the NDSC (Network for the Detection of Stratospheric Changes) in the Northern hemisphere. Located in the Swiss Alps at an altitude of 3580m, the Jungfrauoch is known for its good quality atmospheric conditions (dry and poorly polluted air). It has been performing high resolution infrared spectroscopy for many years (Delbouille et al., 1989).

Since June 1990, a UV-VIS spectrometer has been added to the equipment of the station. The instrument, named SAOZ ("Système d'Analyse par Observations Zénithales"), has been developed by the French group of J. P. Pommereau (Pommereau and Goutail, 1988). It is a fully automatic UV-VIS diode array spectrometer that covers the spectral range from 300 to 600 nm. It can be operated either by looking at direct sun-(or moon-)light or at the sunlight scattered at the zenith sky. Stratospheric amounts of O<sub>3</sub> and NO<sub>2</sub> are measured in the visible range in real time. Column amounts of tropospheric O<sub>4</sub> and H<sub>2</sub>O are obtained as by-products of the analysis.

The Jungfrauoch provides a permanent reference site for the SAOZ instruments installed at other locations (see Table 1). In this context its main role is to provide calibration spectra and good quality data needed for testing and improving SAOZ analysing procedures. This role will be extended in the future by exploiting the possible comparison of SAOZ data with results obtained by other techniques implemented -or to be implemented- at the Jungfrauoch (FTIR, medium and high resolution UV-VIS and microwave spectroscopies).

Table 1: Northern hemisphere permanent sites operating SAOZ spectrometers.

	Latitude	Longitude
- Haute Provence	44N	6E
- Kiruna	67N	22E
- Sondre Stromfjord	67N	51W
- Sodankyla	67N	27E
- Thule	77N	69W
- Ny-Alesund	79N	12E

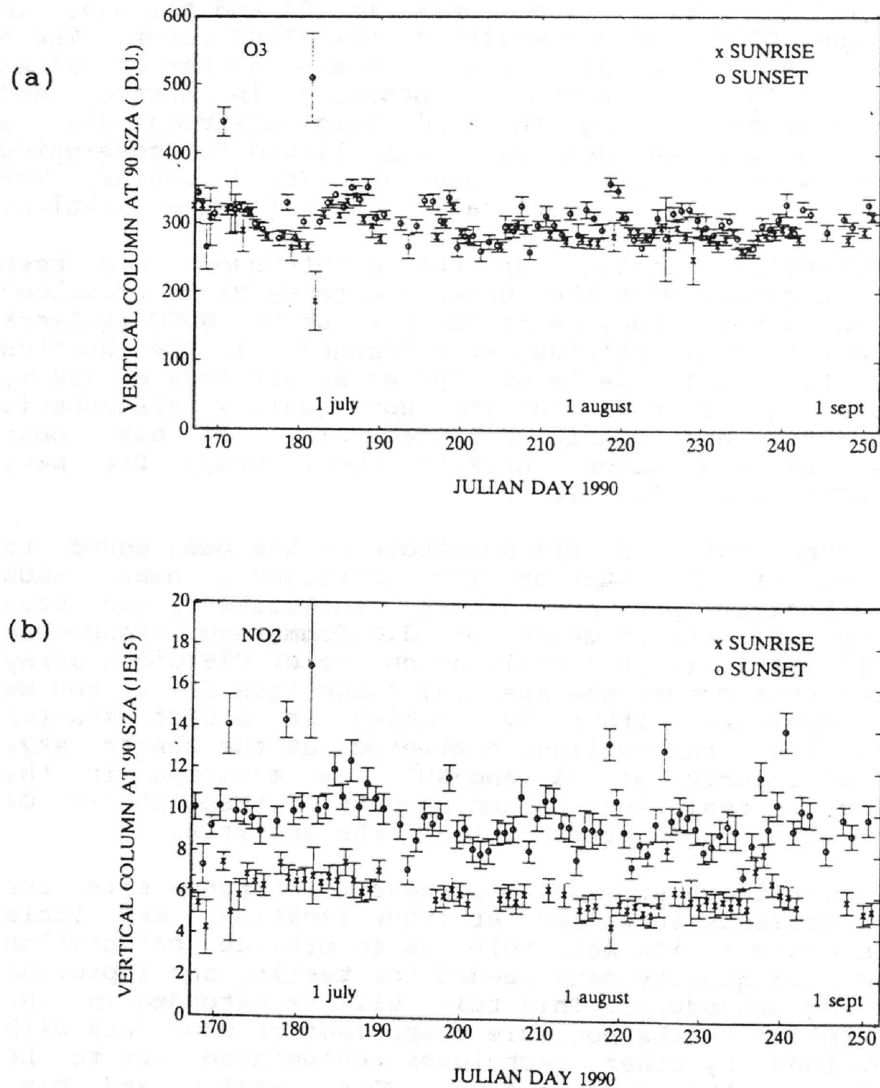


Figure 1 : Vertical columns of O<sub>3</sub>(a) and NO<sub>2</sub>(b) recorded at the Jungfraujoch between June and September 1990.

## 2. 1990 RESULTS

Three months measurements are presently available. Figure 1 presents vertical columns of O<sub>3</sub> and NO<sub>2</sub> determined at sunrise and sunset versus Julian days. Vertical amounts are evaluated on the basis of the data collected at 90° SZA (solar zenith angle) for which the highest measurement precision is obtained (see further discussion). The error bars associated with each point give a statistical estimate of the goodness of fit between molecular cross sections and atmospheric absorption spectra.

Besides the wellknown diurnal variation of NO<sub>2</sub> which appears clearly in figure 1(b), we also observe a variation of the NO<sub>2</sub> vertical column that seems to be correlated with O<sub>3</sub> column densities (figure 1(a)). More data together with ancillary informations -in particular pressures, temperatures and air mass trajectories- need to be gathered over a longer period of time in order to understand the origin of that correlation. Also the precision and the accuracy of the measurements need to be studied with great attention. This aspect is of particular importance for the validation of a reference station and will be addressed in the next section.

## 4. DISCUSSION : ERROR SOURCES

### a. Precision

The term precision usually refers to the random variations of values that an instrument would report when observing a constant value of the column density. With UV-VIS spectrometers using the Sun as light source, column densities are derived from an analysis of molecular absorption features superimposed on the Fraunhofer structure of the solar spectrum. The weakness of the optical depth in the visible requires to operate at high SZA values in order to obtain a few percent of absorption. Observations at very high SZA values obviously being limited by the light intensity incident on the detector, this leads to a balance between optical depth and light intensity which attains to an optimum at about 90° SZA. As illustrated in figure 1 the mean precision obtained with our instrument is 4 % for O<sub>3</sub> columns and 10 % for NO<sub>2</sub> columns.

### b. Accuracy

Accuracy refers to the amount by which the mean of a large number of individual observations of the same column density value could differ from the "true" value. Its evaluation involves the inventory of the different error sources that can affect the results in a systematic way. This has been done in Table 2 for the UV-VIS technique.

Error sources must be identified and quantified at the two stages of the analysis procedure:

(1) determination of the slant columns by fitting the atmospheric spectrum with the molecular cross-sections. The accuracy here is limited by spectral interferences between atmospheric species and by the uncertainties in molecular cross-sections measured in the laboratory. In case of NO<sub>2</sub> the error of the absolute value of the cross-section may be as high as 5 %, the temperature dependence being unknown.

Table 2 : Error budget of the UV-VIS technique (SAOZ spectrometer)

Error sources	Error values	
	O3	NO2
1. absorption cross-sections		
- absolute value	< 2 %	~ 5 %
- temperature dependence	-	?
2. spectral interferences between different atmospheric species	< 5 %	< 5 %
3. air mass calculation (*)		
- atmospheric profiles	< 4 %	< 4 %
- single scattering assumption	< 5 %	< 5 %
- photochemical effects	-	< 20 %

(\*) error values estimated at 90° solar zenith angle

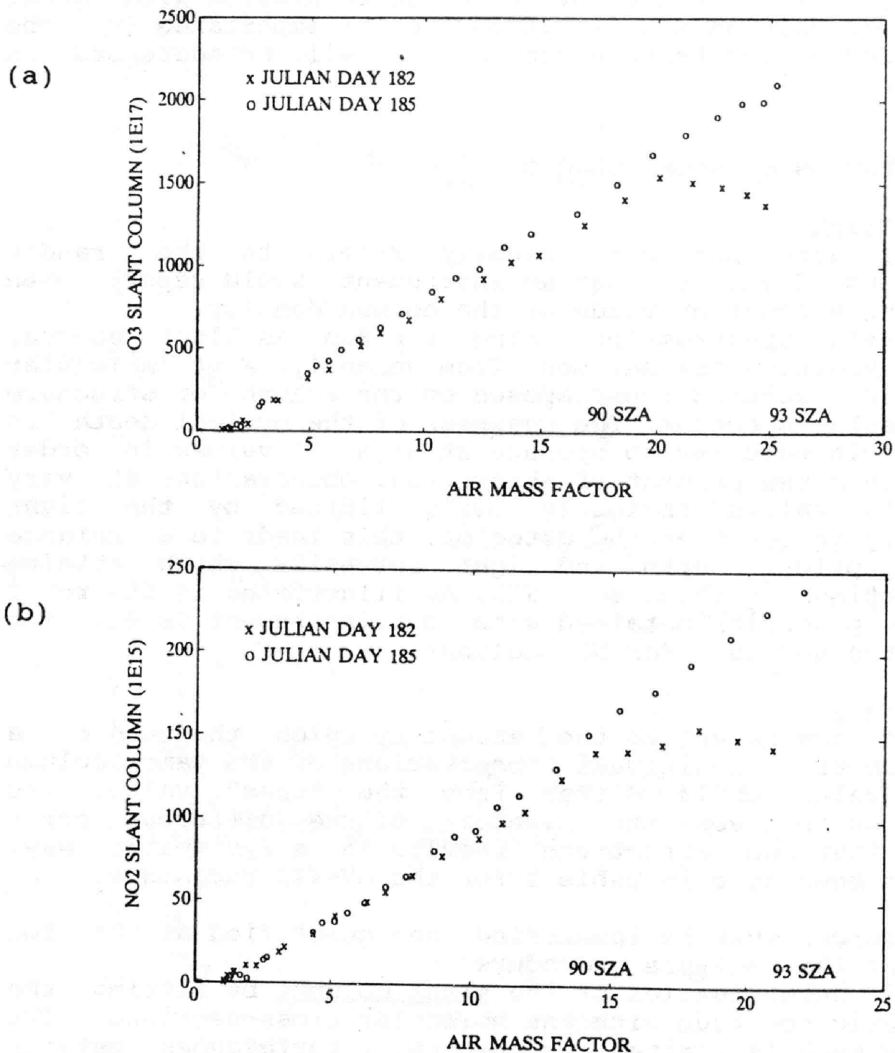


Figure 2 : "Bouguer-Langley" plots of the O3(a) and NO2(b) data recorded on Julian days 182 and 185 (at sunset)

(2) retrieval of the vertical columns by computation of the air mass factors. When experiments are performed by looking at the zenith sky (the most useful observation geometry) the evaluation of the air mass factors requires the choice of a radiative transfer model through the atmosphere. This calculation constitutes the most important contribution to the error budget of the UV-VIS technique. Its accuracy can be affected by a bad knowledge of the atmospheric profiles (pressure, temperature, absorbers and/or aerosols concentrations) and in some conditions by a failure of assumptions made such as single scattering (Noxon et al., 1979). In case of NO<sub>2</sub> important systematic errors originate in chemical effects (Solomon et al, 1987). For O<sub>3</sub> the accuracy can however be kept high by working at zenith angles lower than or equal to 90 degrees (Pommereau and Goutail, 1990).

An interesting way of testing the air mass calculation is to study the correlation between measured slant columns and calculated air mass factors by drawing "Bouguer-Langley" plots. An example of such plots is presented in figure 2 which compares the O<sub>3</sub> and NO<sub>2</sub> data recorded at sunset on Julian days 182 and 185. Figure 2 shows that, on day 185, calculated air mass factors are pretty well correlated with both O<sub>3</sub> and NO<sub>2</sub> slant columns up to 93° SZA, but that this correlation fails above 91° on day 182. These results indicate that, for some days, possible variations of atmospheric properties are not properly accounted for in the air mass calculation. Efforts will be made to better understand these effects both on a theoretical basis and by taking into account meteorological data. This is part of the ongoing activities at the Jungfraujoch.

#### 4. NEAR FUTURE ACTIVITIES

In the frame of EC ozone programmes:

- intercomparison between SAOZ and high resolution Fourier Transform Infrared (FTIR) spectroscopy results.
- studies of the UV-VIS technique at various spectral resolutions.

For the Arctic winter campaign of '91-'92:

- providing reference data at mid-latitude
- qualification of a transportable UV-VIS Silicon diode array spectrometer for the observation of the polar stratosphere.

#### 5. REFERENCES

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