

## OZONE GROUND-BASED MEASUREMENTS BY the "GASCOD" NEAR-UV AND VISIBLE DOAS SYSTEM

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## ABSTRACT

GASCOD, a near-ultraviolet and visible differential optical spectrometer, was developed at CNR's FISBAT Institute in Bologna, Italy, and first tested at Terra Nova Bay station in Antarctica (74.6°S, 164.6°E) during the summer expeditions 1988-1990 of PNRA (PNRA is the national research program in Antarctica, "Programma Nazionale di Ricerche in Antartide"). A comparison with coincident O<sub>3</sub> total column measurements taken in the same Antarctic area is presented, as is another comparison performed in Italy. Also introduced is an updated model for solar zenith measurements taken from a ground-based, upward-looking GASCOD spectrometer, which was employed for the 1991-92 winter campaign at Åre-Ostersund in Sweden (63.3°N, 13.1°E) during EASOE (European Arctic Stratospheric Ozone Experiment).

The GASCOD can examine the spectra from 300 to 700 nm, in 50 nm steps, by moving the spectrometer's grating. At present, it takes measurements of solar zenith radiation in the 310-342 nm range for O<sub>3</sub> and in the 405-463 nm range for NO<sub>2</sub>.

## 1. Introduction

A wide range of atmosphere trace gases, including O<sub>3</sub>, NO<sub>2</sub>, OClO, NO<sub>3</sub>, BrO, HNO<sub>2</sub>, CH<sub>2</sub>O, SO<sub>2</sub> and OH can be detected in the UV and visible spectral regions via differential optical absorption spectroscopy (DOAS). The basic difference between the differential and absolute absorption methods is that the former, unlike the latter, requires no knowledge of the unattenuated spectrum during measurement, which is very useful in remote atmospheric sensing. Other advantages of the DOAS approach include simultaneous determination of multiple absorbers with high sensitivity and specificity and high-precision calibration without need for a reference gas.

A DOAS spectrometer working in the UV and Vis spectral regions can use the linear diode-array sensors as a detector, thus becoming a multi-wavelength device. The data from measurements made with such a UV/Vis diode-array spectrometer, called GASCOD (gas-absorption spectrometer correlating optical differences) for zenith solar radiation, and the O<sub>3</sub> differential

absorption cross-sections measured in laboratory by a multi-path spectrometer are presented and discussed.

## 2. Stepwise description of GASCOD and its data analysis

The DOAS system was developed in two configurations: the GASCOD (fig.1), a ground-based remote sensor for measuring direct and diffuse solar radiation [1, 2], and the 1-meter multi-path configuration (fig.2) to measure absolute gas cross-sections [3]. Both versions have the same spectral dispersion values [1] and use the same DOAS method for data analysis [4]. The DOAS method in the remote-sensor configuration is used with the atmospheric transfer model to interpret zenith diffuse solar spectrum measurements.

The very narrow field of view of the input optics (a Cassegrain telescope featuring 1500 mm focal length and 300 mm diameter) provides the best approximation of the atmospheric transfer equation model for the interpretation of the solar light radiation scattered along the zenith. The GASCOD spectrometer features a Jobin-Yvon holographic spherical grating with a throughput that is about the same as the input telescope's. The detector is a Hamamatsu PCD linear diode array detector with 1x512 format: each pixel of the array is 0.050x2.5 mm and the array is 2.54 cm in length. The spectral dispersion is about 0.12 nm/diode and the overall optical resolution 0.5 nm.

The grating can be moved by a stepper motor, and an internal Hg lamp is used for wavelength calibration each time the motor moves the grating: the spectrum is held to be calibrated only when its two highest values match the position of the array detector's two central diodes. This makes it possible to ensure a spectral accuracy of 0.2 nm.

Our spectral interpretation of the DOAS method during zenith solar radiation measurements is based on the following steps:

1. The measurement of the solar zenith scattered spectrum (I<sub>s</sub>) as recorded by the spectrometer.
2. The measurement of the sun reference spectrum (I<sub>o</sub>) inferred from the Langley-plot method (solar spectrum at the top of the atmosphere or background diffused solar spectrum I<sub>b</sub>).

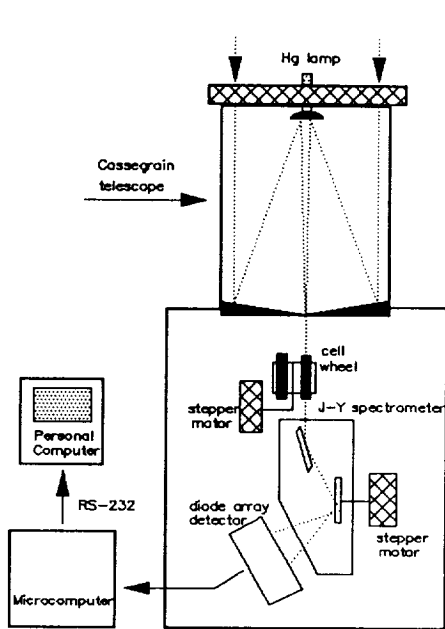


Fig.1 GASCOD set-up

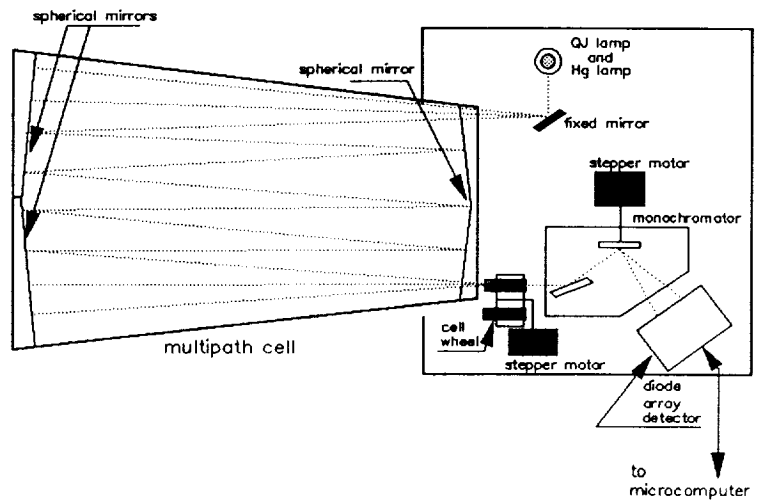


Fig.2 Multipath Cell Spectrometer configuration

3. Laboratory measurement of the absolute absorption cross-sections either with the same spectrometer used in field or one having identical characteristics to it.

The analytical procedure employed can be divided into the following steps:

- A. **Spectral alignment:** it is applied to all spectra recorded by the instrument.
- B. **Smoothing:** it determines via non-linear least square regression analysis (or applying other smoothing procedures) the values of the absorption differential cross-sections of the gases being analyzed by subtracting the resulting regression function from their absolute, laboratory-measured values; it is also applied to all the aligned (step 1) atmospheric spectra so as to determine the ratio to their regression function.
- C. **Regression analysis:** correlation of the narrow ratioed features of the solar zenith spectrum to the differential cross-section of the gas being analyzed by means of linear least square regression analysis applied to an atmospheric transfer equation given by parameterizing the atmosphere in 50 layers of 1 km each and taking into account only the single scattering:

$$\ln \left( \frac{\bar{I}_s}{I_s} \cdot \frac{I_o}{\bar{I}_o} \right) = \sum_{g=1}^n \Delta\sigma_g(\lambda) \tau_g,$$

which supplies after several simplifications the value of the gas slant column and where:  $I_o(\lambda)$  is the incident solar radiation flux density at the top of the atmosphere,

$I_s(\lambda)$  the irradiance scattered along the vertical path to the ground,

$\bar{I}_o(\lambda)$  and  $\bar{I}_s(\lambda)$  are the smoothed values of  $I_o(\lambda)$  and  $I_s(\lambda)$  respectively computed via point "b" procedure,

$\sigma_g(\lambda)$  with  $g=0,1,2,\dots,n$  is the absorption cross-section of the  $g$ -th gas. Among the  $\sigma_g(\lambda)$  there are several non-gas cross-sections in trace, such as  $\sigma_o$  (molecular cross-section for Rayleigh scattering),  $\sigma_M$  (Mie cross-section for the large particle scattering), and  $\sigma_R$  (Ring cross-section), and  $\tau_g$  with  $g = 0,1,2,\dots,n$  the slant column abundance of  $g$ -th absorber.

- D. **Shift & Stretch:** minimizing the value of the sum of squares (SOS) of the residual of the linear least-square regression can yield the best values of the absorbers' slant columns. To minimize the SOS, we used the procedure of "Shift & Stretch" which removes slight spectral displacement of  $I_s/\bar{I}_s$  in respect to  $I_o/\bar{I}_o$ .
- E. **Intensity-weighted optical path computation:** it is normally used to overcome the calculation difficulties of the atmospheric transfer model for interpreting the zenith solar radiation measurements.
- F. **Air-mass factor:** it is computed to determine the vertical column amounts of the absorbers under investigation.

In ground-based measurement of zenith scattered solar radiation the intensity flux can be calculated by integrating the value of the radiation flux along the vertical path. The calculations can be simplified by dividing the atmosphere into equal layers. Our atmospheric model is divided into 50 spherical layers, each  $\Delta z = 1$  km thick; the summation is used instead of the integral. The present study employs the 310-342 nm spectral range for the determination of the  $O_3$  slant column amounts and the 405-463 nm range for the  $NO_2$  slant column amounts.

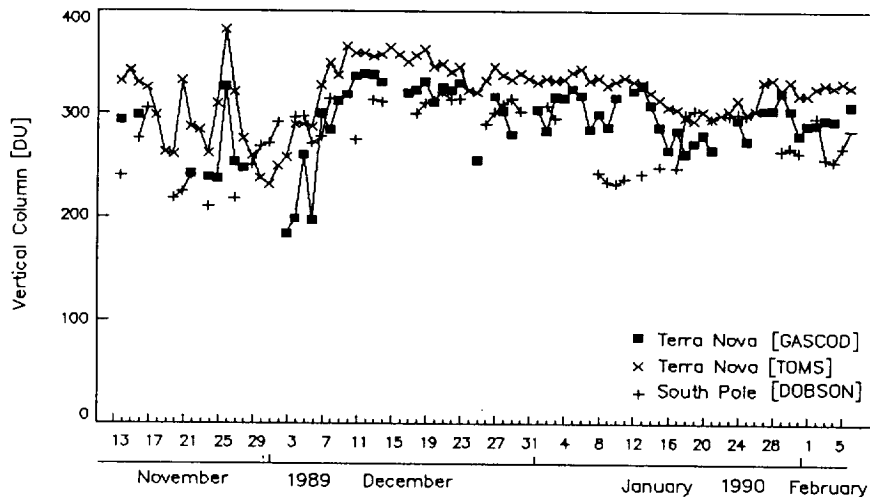


Fig.3 Ozone vertical column amounts as measured by GASCOD and TOMS in the same Antarctic area and by Dobson spectrometer at South Pole.

### 3. Data Comparison

The GASCOD was installed at the Icaro Camp (74.6°S, 164.4°E, 42 m a.s.l.), which is approximately 4 km from the Italian base at Terra Nova Bay on the Ross Sea, during the 1988-99 and 1989-90 summer expeditions. Figure 3 shows the values of the vertical column amounts of O<sub>3</sub> measured by GASCOD and those simultaneously measured by TOMS satellite over the same area and a Dobson spectrometer located at the South Pole station. The data exhibit substantial agreement between the GASCOD and TOMS (Version 6, [6]) values and, given the difference in sites, an essentially acceptable agreement, especially in the overall trend rather than in the individual values, between the GASCOD and Dobson readings. The detailed frequency analysis of the distribution of the differences between the GASCOD and TOMS data in figure 4 shows the former's values to be systematically underestimated: less than 40 DUs (average 25 DUs) in 76% of the cases and over 50 DUs in 16%. This lack of precision is likely attributable to the fact that the GASCOD was being used here for the first time in the field.

Subsequently, the GASCOD was upgraded as to its optics, detection device (Hamamatsu MOS linear diode array) and in its computational program, and the comparison was repeated during March 1991 in Italy between the O<sub>3</sub> vertical column data recorded by the GASCOD at Bologna and those taken by two Dobson spectrometers: one deployed at San Pietro Capofiume near Bologna, station 297 of the World Ozone Data Center, and the other 60 km from Bologna at Sestola, station 201 of WODC. The compared data sets are presented in figure 5; here, too, they show a good agreement.

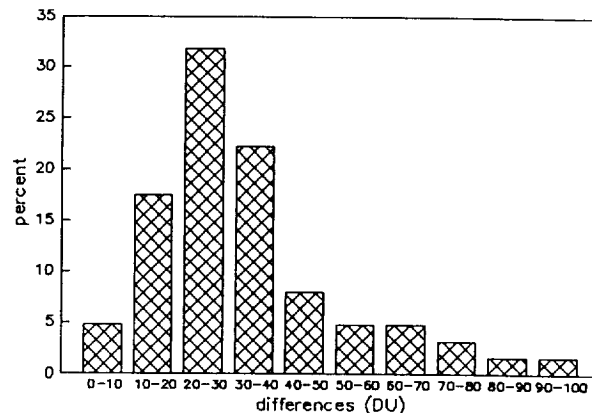


Fig.4 Frequency analysis of the distribution of differences between GASCOD and TOMS dataset in figure 3.

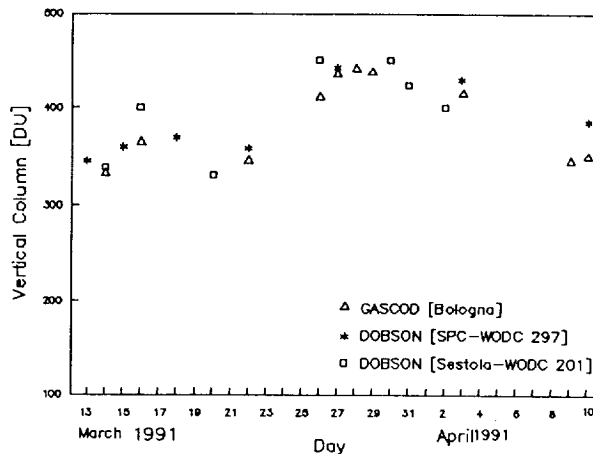


Fig.5 Ozone vertical amounts as measured by two Dobson spectrometers and by GASCOD at Bologna (Italy)

#### 4. Conclusions

DOAS UV/Vis systems are very valuable approaches to the study of the atmosphere's optical properties. The use of linear diode array detectors, which can simultaneously monitor extended spectral ranges without diminished resolution, also makes it possible to analyze the spectral features due to more absorbers, or to make the best fit on the signals due to several weak absorption lines of the same gas. DOAS also brings to the column content measurements of trace gases in the atmosphere enormous advantages in that it is non-invasive, i.e. it is an absolute method that does not require simultaneous knowledge of the unattenuated source spectrum.

The DOAS system reported herein features several innovative developments. Given the GASCOD's overall performance, it is possible to evaluate its strengths and weaknesses. The former include:

1. Operation in spectral ranges where the gases under investigation present the strongest absorption features.
2. Wavelength calibration in automatic mode by means of a mercury lamp placed along the axis of the telescope.
3. Telescope can be easily substituted by a different input optic (e.g. fiber optic) and the spectrometer can also be used for direct radiation measurements (sun or moon light by a solar tracker, artificial lamp light in horizontal path measurements).
4. Each of the spectrometer's operations can be executed in automatic mode (Hg-lamp calibration, auto ranging input light, positioning of gas cell wheel and pass-band filter wheel, sequence selection of spectral range, and so on).

The latter include:

1. Nitrogen gas and water flow are necessary for the cooling of the detector.
2. During sunset and sunrise periods time is lost for the movement of the grating when different spectral intervals are investigated.
3. At sunset and sunrise periods, longer integration times are needed due to the narrow field of view of the input telescope.

Although these initial results can be considered as extremely positive, we feel it is necessary to check the GASCOD in comparative measurements with other, equivalent instruments. At present, the GASCOD is being employed in several ground-based campaigns, such as EASOE. It was also used in the "NDSC UV/Vis Intercomparison of Stratospheric NO<sub>2</sub> Measuring Instruments" held at Lauder (NZ) from 11th to 24th May 1992, a totally blind experiment whose findings are scheduled for presentation in October 1992 at Boulder, Colorado (USA).

#### 5. Acknowledgments

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