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# Stratospheric NO<sub>2</sub> Concentration Determined by DOAS Using Compact Spectrographs

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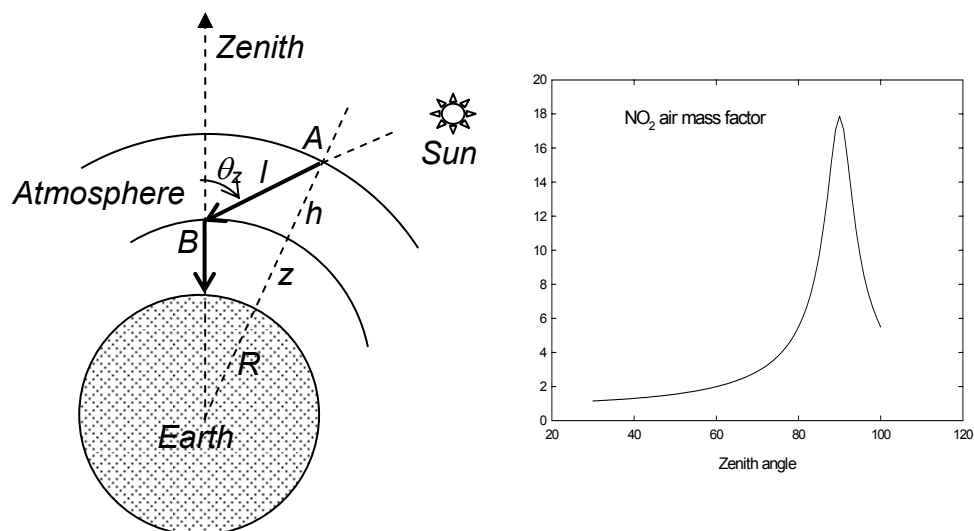
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**Abstract.** In this work we present the results for stratospheric NO<sub>2</sub>-total column concentration retrieved by DOAS (Differential Optical Absorption Spectroscopy) performed with compact spectrographs. The behavior for three different spectrographs (MonoSpec 27, Jarrell-Ash; HR4000, Ocean Optics and Mechelle 900, Multichannel Instruments) are analyzed making one intercomparison in the facilities of the LIDAR Division of CEILAP (CITEFA - CONICET), in Villa Martelli, Argentina (34.5° S, 58.5° W, 20 m amsl). The three instruments have a similar resolution (approximately 0.1 nm) but operate with different optical configurations and have optical sensors of different characteristics; two of them have cooling capability and the other one (HR4000) operates at room temperature. The NO<sub>2</sub> concentration was obtained from spectral results at twilight using solar noon spectra as reference. In all cases zenithal diffuse irradiance was used. The NO<sub>2</sub> absorption cross section given by S. Voigt and J. P. Burrows (University of Bremen - Institute of Environmental Physics) corresponding to 223 °K and 100 mbar is used. Results are compared with public data corresponding to ground-based device or to instruments mounted in satellites. These atmospheric soundings are of extreme importance to understand the roll that plays the stratospheric NO<sub>2</sub> in the associated phenomena of destruction and formation of ozone in the low stratosphere at middle latitudes.

## INTRODUCTION

Differential Optical Absorption Spectroscopy, DOAS, is a widely used technique for open-column atmospheric-gas pollution monitoring. Extinction of light coming from different sources of radiation such as conventional lamps, lasers or the sun, is produced by different interactions between radiation and matter (absorption or scattering). The concentration retrieval is based on the fitting of the measured extinction through the Lambert-Beer law. In our case, DOAS is based on the analysis of spectra acquired during twilight with the instrument pointing to the zenith as it can be seen in Figure 1. Under these conditions, the optic length of solar rays in the atmosphere - before reaching the point B, where they are scattered to the detector - is several times bigger than the corresponding to the Sun in the zenith. This simple way enhances the sensibility of the method and very small concentrations can be measured. Other main advantage of this method is that when the Sun is in the horizon, the biggest contribution in the zenithal radiation comes from the stratosphere and the gas in the troposphere can be ignored.

In these conditions, data retrieval is as follows. The spectra obtained during twilight are compared with the one taken with the sun near the zenith (reference), to eliminate the Fraunhofer's structure (one order of magnitude bigger than the absorptions that we wanted to measure). The slant columns (according to the trajectory of the twilight rays) are obtained solving the system of lineal equations generated when applying an adjustment of minima square to the logarithm of the ratio between the twilight spectra and the reference spectra.



**FIGURE 1.** Geometry of zenithal DOAS.  $\text{NO}_2$  air mass factor is calculated in a similar way as ozone (Microtops, Solar Light) with a different altitude for the layer.

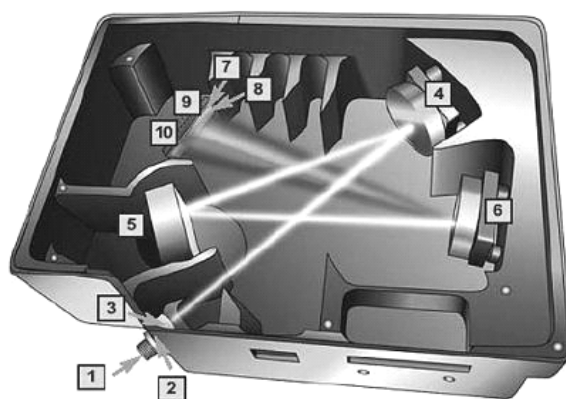
To obtain the stratospheric  $\text{NO}_2$ -total column concentration or vertical concentration, we divided the slant column by the  $\text{NO}_2$  - Air Mass Factor that depends on the solar zenithal angle and from other parameters like the altitude and the density profile of the gas in the atmosphere. In this work we calculate the Air Mass Factor as it was described for ozone [1], but more complicated models, like AMF calculated by radiative transfer models, will be tested in the future [2].

Usually, in any spectral range explored, the absorption's spectra of several molecules are superimposed, so that the algorithm should contemplate all the possible contributions to the extinction, like ozone, water, etc, in addition to Rayleigh's scattering, Mie's scattering, Raman's scattering and fluorescence that take place in the lowest layers in the atmosphere [3]. Taken all these factors into account, it is possible to simultaneously study different species that are in the atmosphere in very small concentrations [4].

## OPTICAL SPECTROMETERS

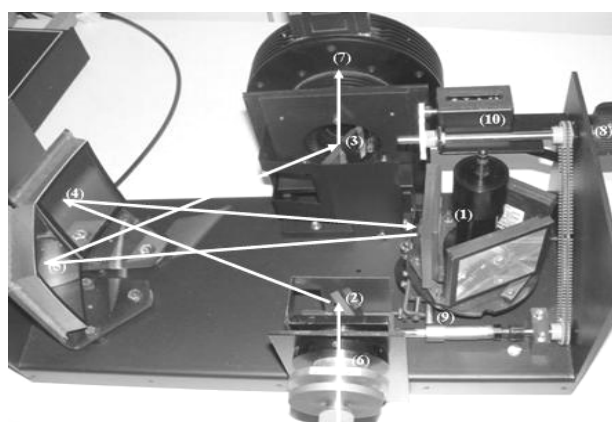
Systematic studies of the atmosphere behavior can be carried out by means of different instruments and remote sensing systems. According to the source that originates the radiation we could classify them in two categories: a) passive sensors and b) active sensing systems. In the first case, the radiation source is the Sun whose electromagnetic emission crosses the atmosphere and is captured by appropriate detectors at surface level, while in the second case, an artificial source (lamp or laser) emits light to the atmosphere to interact with the different molecules and particles. The active sensors possess reception and acquisition systems that usually consist of a telescope and ultrasensitive sensors (APD, photomultiplier, etc.) to gather backscattered light for the molecules and particles, to be analyzed by means of an appropriate algorithm. The sensing instrument can be located at ground-based level or mounted in airplanes, globes or satellites. For several years the LIDAR division, CEILAP (CITEFA-CONICET), Argentina, has been conducting investigations related to the study of the atmospheric contamination, the ozone's layer and the UV radiation ([www.division-lidar.com.ar](http://www.division-lidar.com.ar)).

In the present work we describe passive methods based on different compact spectrometers. The first one is a small and portable spectrometer (HR4000, Ocean Optics) derived of the space technology from now on referred to as "ERO". The device can measure solar spectral irradiance in the UV-VIS range (290-650 nm) through an optical fiber located outside the laboratory. In Fig. 2, the inner components of ERO can be appreciated as well as the hypothetical trajectory of a light beam. This instrument is a simple monochromator that has a fixed diffraction grating, collimating and focusing mirror, an entrance slit and a CCD (lineal array), among other elements. The spectral acquisition is carried out simultaneously in all wavelengths. The control of the acquisitions is made by software installed in a notebook, which communicates with the spectral analyzer via a USB port.



**FIGURE 2.** ERO's inner elements: 1) connector SMA 905, 2) entrance slit, 25  $\mu\text{m}$  (width), 1 mm (height), 3) filter, 4) collimating mirror, 5) diffraction grating, 600 grooves/mm, blaze 400nm, 6) focusing mirror, 7) cylindrical lens, 8) filter OFVL, 9) detecting UV2, 10) CCD Toshiba (lineal array of 3648 pixels, high sensibility).

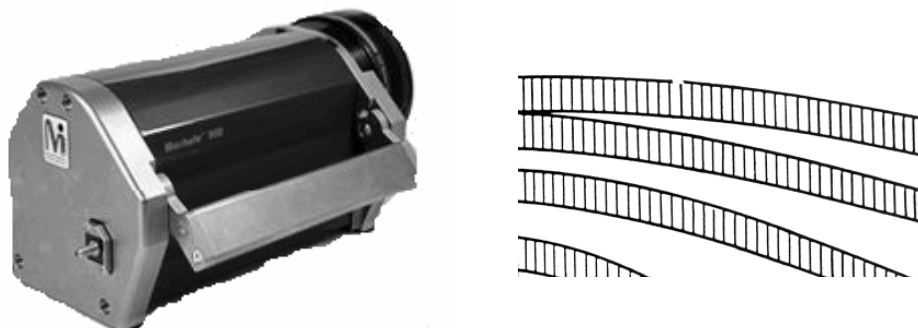
The second device used in this work was a Monochromator/Spectrograph Jarrell-Ash MonoSpec27 linked to a Peltier-cooled CCD camera that will be referred to as ERM, to differentiate it from the ERO (Fig. 3). The device, with a Czerny-Turner crossed configuration, was used for a fixed position of the grating with an optical window of 50 nm. The light coming from the roof is transported by a bundle of optic fibers in a similar way to the one described before.



**FIGURE 3.** Inner components of the spectrograph and trajectory of a hypothetical light beam. 1) Support for assembly of the diffraction gratings, 2) entrance mirror, 3) exit mirror, 4) collimating mirror, 5) focusing mirror, 6) connector/adaptor of the optic fibers bundle to the entrance of the instrument, 7) CCD camera, 8) crank associated to the spectral sweeping system (manual), 9) arm to make micrometric movements of the diffraction gratings, 10) wavelength counter.

The third instrument tested is a crossed dispersed spectrograph (Mechelle 900, Multichannel Instruments AB, Sweden). For high resolution spectroscopy, an echelle based spectrograph is preferred over common grating in low order. The main reason is its inherent higher throughput. Because the echelle grating has a large groove spacing, it is used at high order numbers but it is necessary to provide cross dispersion to avoid overlapping of diffraction orders. The cross disperser is simply a prism or another grating whose dispersion is at right angles with that of the echelle. The angular dispersion of the cross disperser is usually many times smaller, so the combination of the two elements gives a two-dimensional spectrum format. Figure 4 shows schematically this kind of format as would be seen at the exit plane of a spectrograph. The actual format outline is set by the relative dispersions of the two elements. Although this kind of spectrograph has been known for more than forty years, the advent of flat field spectrographs together with technology advances in CCD cameras and software overcame the difficulty in interpreting the spectrum.

The principles behind the wavelength calibration of the Mechelle are as follows. The exact position of any wavelength can be traced from the optics, using ray tracing. Thus from a given wavelength  $\lambda$ , the spectral order  $m$  and the focal plane co-ordinates  $x, y$  can be calculated. This coordinates would be the exact pixel coordinates  $x_p, y_p$  providing the CCD sensor could exactly be mounted to the theoretical position with proper orientation. However, as this never can be done in practice, a method of finding the coordinates on the sensor with respect to those calculated, is needed. Recording a spectral image of a calibration source (such as a low-pressure mercury lamp) containing well-defined known spectral lines provides the means for doing this calibration. The position of the lines in pixel coordinates is determined in both directions and constants in a mathematical expression relating these co-ordinates to the calculated co-ordinates are determined through a LSQ fit.



**FIGURE 4.** Mechelle 900. Location of the spectrum strips on the focal plane for a cross-dispersion echelle spectrograph.

### Determination of $\text{NO}_2$ by means of DOAS

Quantitatively, the absorption of radiation is described by the Lambert-Beer's law,

$$I(\lambda) = I_0(\lambda) \exp(-L \cdot c \cdot \sigma(\lambda)), \quad (1)$$

where  $I_0(\lambda)$  denotes the initial intensity emitted by some suitable light source,  $I(\lambda)$  is the radiation intensity after passing through a layer of thickness  $L$ , where the species to be measured is present at the concentration  $c$ . The quantity  $\sigma(\lambda)$  represents the absorption cross section at the wavelength  $\lambda$ . This cross section is a characteristic property of any species and can be measured in the laboratory or taken from the literature. Once these quantities are known, the average trace gas concentration  $c$  can be calculated from the measured ratio  $I(\lambda) / I_0(\lambda)$ ,

$$c = \log [I_0(\lambda) / I(\lambda)] / \sigma(\lambda) \cdot L = A / \sigma(\lambda) \cdot L, \quad (2)$$

where  $A = \log (I_0/I)$  denotes the absorbance of a layer of a given species. Typical absorbance values recorded in DOAS applications range between  $10^{-2}$  to  $10^{-4}$  [5]. Although the attenuation of a light beam by absorption due to a certain species is in principle described by equation 1, for practical purposes of measurements in the atmosphere this equation is oversimplified because it does not take into account other light extinction mechanisms such as scattering. Since in the real atmosphere there will usually be more than one absorbing species present, a more comprehensive description of atmospheric absorption is expressed by:

$$I(\lambda) = I_0(\lambda) \exp [-L (\sum (\sigma_i(\lambda) c_i))], \quad (3)$$

where  $\sigma_i(\lambda)$  and  $c_i$  denote the absorption cross section and the concentration of the  $i$ -th species.

DOAS makes use of the characteristic absorption features of trace gas molecules along a path of known length in open atmosphere. The problem of determining the true intensity  $I_0(\lambda)$ , as it would be received from the light source in the absence of any extinction is solved by working with the so called "differential absorption", which is defined as the part of the total absorption of any molecule "rapidly" varying with wavelength in a certain interval [6]. As a general fact, the absorption cross section of a given molecular species may be written as the sum of two terms:

$$\sigma_i(\lambda) = \sigma_{i0}(\lambda) + \sigma'_i(\lambda), \quad (4)$$

where  $\sigma_{i0}(\lambda)$  represents the monotonously “slowly” variation of the cross section with wavelength (due to scattering for example) and  $\sigma_i(\lambda)$  represents the “rapid” variation due to an absorption band. Obviously, the concept of “slowly” and “rapid” is meaningful taking into account the relation between the full wavelength range of the cross section and the width of the absorption band to be detected. Introducing equation (4) into equation (3), one obtains:

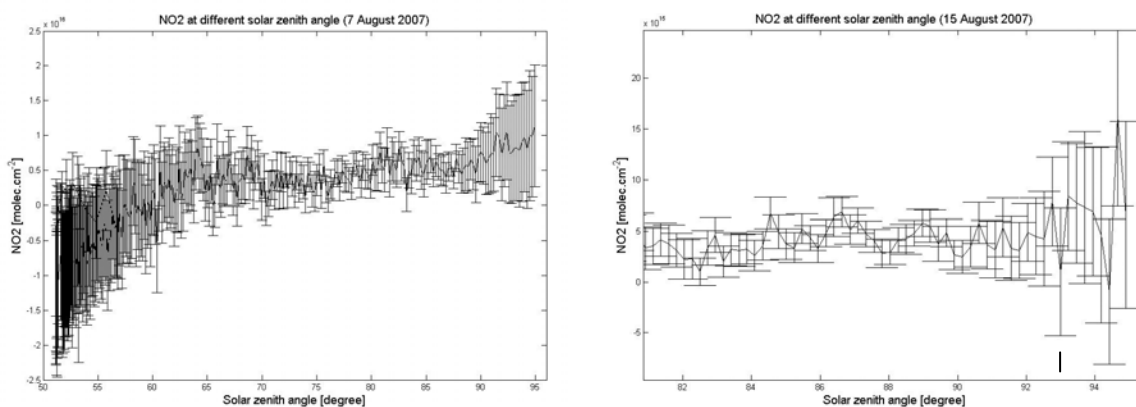
$$I(\lambda) = I_0(\lambda) \cdot \exp[-L (\sum \sigma_i(\lambda) c_i)] \cdot \exp[-L (\sum \sigma_{i0}(\lambda) c_i)] \cdot G(\lambda), \quad (5)$$

where the first exponential function describes the effect of the structured differential absorption due to the presence of absorption bands while the second exponential function gathers the effect of all the slowly variations due to extinction by scattering and other broadening processes. The G factor represents the smooth wavelength dependence of the transmission of the optical system used. With this condition, a differential absorbance can be defined similarly to equation (2) as:

$$A' = \log [I_0(\lambda) / I(\lambda)] = L \sum \sigma_i(\lambda) c_i. \quad (6)$$

Thus, the concentration of the atmospheric species under study can be calculated from equation (6) using the  $\sigma_i(\lambda)$  taken from the literature (or measured in the laboratory) and fitting  $I_0(\lambda)$  by a suitable polynomial. DOAS can only measure species with reasonably narrow absorption features but is insensitive to continuous absorptions of trace gases or to extinction processes which vary only monotonously with wavelength, like Mie scattering by aerosol, dust or haze particles. Likewise, slow variations in the spectral intensity of the light source or in the transmission of the optical system (telescope, spectrometer, etc) are also essentially eliminated [7, 8].

From the beginning of 2007, we have been carrying out measurements of diffuse zenithal irradiance to calculate the concentration of stratospheric NO<sub>2</sub>. Only ozone is considered as other absorbing species. Figure 5 shows some results of a “crude” estimate of NO<sub>2</sub> concentration corresponding to different times of the day. As it can be seen, signal to noise ratio is optimized near sunset, when the gas column length is maximized.



**FIGURE 5.** “Crude” results for measurements at different solar zenith angle.

Figure 6 shows the results of our DOAS calculations compared with public results of three SAOZ instruments located at similar latitudes. Data from HALOE (Halogen Occultation Experiment) on the UAR satellite were also included. Seasonal variation of NO<sub>2</sub> concentration can be seen but our results are systematically higher than literature values. This fact can be due in part to a mismatch in Air Mass Factors used for Ozone and for NO<sub>2</sub>. Other absorbing species must be included: water and aerosols are the principal species with absorbing features in the wavelength range used (420 – 450 nm). Ring effect must be considered also.

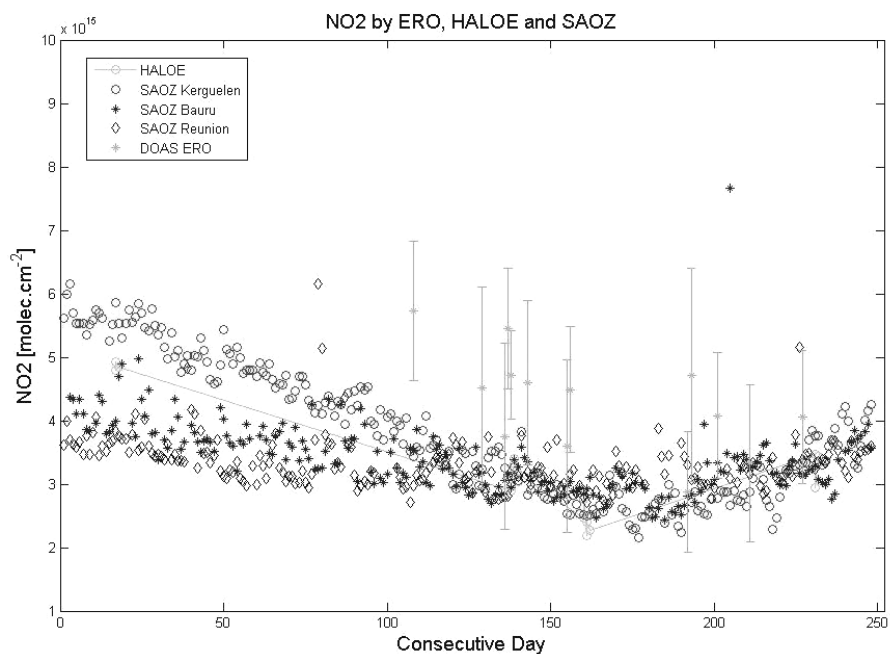


FIGURE 6. Comparison with SAOZ and HALOE results.

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