Remote sensing of stratospheric O$_3$ and NO$_2$ using a portable and compact DOAS spectrometer

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Abstract. The use of passive and active remote sensing systems has largely contributed to advance our understanding of important atmospheric phenomena. Here we present a compact and portable passive DOAS (Differential Optical Absorption Spectroscopy) system, developed for measuring the vertical column density (VCD) of multiple atmospheric trace gases. We highlight the main characteristics of the system components: a mini-spectrometer (HR4000, Ocean Optics), two optical fibers (400 µm of core, 6 m and 25 cm of longitude), an external shutter and the control/data processing software. Nitrogen dioxide (NO$_2$) and ozone (O$_3$) VCDs are derived from solar spectra acquired during twilights (87° - 91° zenithal angles) using the DOAS technique. The analysis is carried out by solving the Beer-Lambert-Bouger (BLB) law for the main atmospheric absorbers at selected wavelength ranges. The algorithm minimizes the fitting residuals to the BLB law, having as unknown the slant column density (SCD) of the species to determine. We present measurements carried out at the Marambio Antarctic Base (64° 14’ 25’’ S; 56° 37’ 21’’ W, 197 m asl) during January - February 2008. In addition, we compare our results with co-located measurements performed with EVA, a visible absorption spectrometer of Instituto Nacional de Técnica Aeroespacial (INTA, Spain), a Dobson spectrophotometer of Servicio Meteorológico Nacional (SMN, Argentine) and the Ozone Monitoring Instrument (OMI), on board AURA satellite.

1. Introduction

The development of remote sensing systems for monitoring of key chemical species, such as O$_3$, NO$_2$, bromine monoxide (BrO), chlorine monoxide (ClO) and other trace gases, is fundamental to understand the dynamic processes that occur in the stratosphere. The most important nitrogen species emitted to the atmosphere are nitrous oxide (N$_2$O), nitrogen oxides (NO$_x$ = nitric oxide (NO) + NO$_2$) and ammonium (NH$_3$). N$_2$O is an important greenhouse gas, which is naturally emitted by earth and sea bacteria, and also produced by human activities, mainly agriculture. In the middle and upper stratosphere N$_2$O is converted to NO by reaction with excited oxygen atoms O$^1$(D) produced mainly by UV photolysis of O$_3$ [1]. Stratospheric O$_3$ plays a critical role in the atmosphere by absorbing most of the biologically damaging solar UV radiation before it reaches the Earth’s surface. Within ~25-40 km of altitude, the NO$_x$ family is involved in a catalytic cycle that accounts for almost half the ozone...
removed by gas-phase reactions. Below 25 km, NO\textsubscript{2} moderates ozone loss caused by active chlorine and hydrogen by converting them into their inactive reservoir forms. Monitoring of stratospheric NO\textsubscript{2} is thus an important adjunct to international efforts to monitor the ozone layer health. During daylight a balance is established between NO and NO\textsubscript{2} concentrations through the reaction of the former with O\textsubscript{3} and the rapid photolysis and reaction with atomic oxygen of the latter (equation (1), (2) and (3)):

\begin{align}
NO + O_3 & \rightarrow NO_2 + O_2 \tag{1} \\
NO_2 + h\nu & \rightarrow NO + O \tag{2} \\
NO_2 + O & \rightarrow NO + O_2 \tag{3}
\end{align}

Equation (3) effectively determines the rate at which these reactions destroy odd oxygen (O + O\textsubscript{3}) since the first two constitute a null cycle. At night, photolysis of NO\textsubscript{2} (equation (2)) ceases and all the odd oxygen in the stratosphere is converted to ozone, so there is an almost-instantaneous change in the NO\textsubscript{2} concentration at twilight as the NO converts to NO\textsubscript{2} (in the evening) or is created by photolysis (in the morning). At night, NO\textsubscript{2} is converted first to nitrate radical (NO\textsubscript{3}) and via a three-body reaction to the dinitrogen pentoxide (N\textsubscript{2}O\textsubscript{5}) reservoir:

\begin{align}
NO_2 + O_3 & \rightarrow NO_3 + O_2 \tag{4} \\
NO_2 + NO_3 + M & \rightarrow N_2O_5 + M \tag{5}
\end{align}

This causes a build-up of N\textsubscript{2}O\textsubscript{5} during the night followed by a slow release during the following day through photolysis. The diurnal variation of NO\textsubscript{2} therefore comprises a maximum immediately after sunset, followed by a slow decrease throughout the night and a sharp drop to minimum at sunrise. As well as the diurnal variation there is a seasonal variation in stratospheric NO\textsubscript{2} at mid-latitudes due to the combined effects of photochemistry and atmospheric transport. During autumn and winter, NO\textsubscript{2} is converted to the long-term reservoir forms nitric acid (HNO\textsubscript{3}) and chlorine nitrate (ClNO\textsubscript{3}), either through gas-phase reactions (e.g. NO\textsubscript{2} + OH + M \rightarrow HNO\textsubscript{3} + M) or hydrolysis of N\textsubscript{2}O\textsubscript{5} on aerosol particles. A minimum in NO\textsubscript{2} occurs in winter, sometimes exacerbated, particularly in the polar vortex, by a quick conversion of N\textsubscript{2}O\textsubscript{5} to HNO\textsubscript{3} on Polar Stratospheric Clouds (PSCs). In spring and summer the reservoir species are photolysed or destroyed by hydroxyl radical (OH), re-generating NO\textsubscript{2} which therefore reaches a maximum around mid-summer [2]. In the Marambio Antarctic Base, the NO\textsubscript{2} VCD displays a strong (photochemically driven) seasonal variation ranging from 6x10\textsuperscript{15} molec/cm\textsuperscript{2} in summer to close to zero in winter and early spring. In September, when the rate of ozone depletion is maximum, NO\textsubscript{2} already start to increase by photodissociation of the HNO\textsubscript{3}.

Monitoring of stratospheric trace gases from the ground or space can be performed by absorption spectroscopy in the visible: an absorption band around 450 nm introduces measurable optical depth to an extraterrestrial light source if the atmospheric path is long. Such conditions apply to solar or stellar occultation measurements from satellites. A particularly notable application of the technique has been in measurements taken at high latitudes in late winter and spring, when the chemistry of the lower stratosphere is perturbed by PSCs. Stratospheric NO\textsubscript{2} and O\textsubscript{3} has been measured by a number of satellite instruments since 1979. One of them, the OMI, it is a nadir viewing, wide swath, UV-visible imaging spectrometer. It combines the advantages of the SCanning Imaging Absorption spectroMeter for Atmospheric CartographY (SCIAMACHY), Global Ozone Monitoring Experiment (GOME) and Total Ozone Mapping Spectrometer (TOMS) instruments, measuring the complete spectrum in the UV-visible wavelength range (270 - 500 nm) with a very high spatial resolution (13 × 24 km\textsuperscript{2}) and achieves daily global coverage of all products (2600 km wide swath). It uses two-dimensional detectors for simultaneous spatial and spectral registration (0.4 - 0.6 nm resolution).
The analysis of visible spectra based on the DOAS concept presents the advantage of allowing for simultaneous retrieval of VCDs of different species, over a wide range of meteorological conditions. It is based on the analysis of solar spectra obtained during the twilights referred to zenith spectra. The main difficulty in the analysis is the fact that the relative absorptions represent only a very small fraction (typically $< 10^{-3}$) of the observed signal, which implies a strong demand on measurement precision (signal-to-noise ratio).

2. Materials and methods

We present the development of a compact atmospheric remote sensing system, able to determine the VCD of multiple trace gases. We have developed a low-cost and portable passive DOAS system composed of a mini-spectrometer (HR4000, Ocean Optics), two optical fibers and a home-made automatic external shutter. We have developed a LabVIEW® based interface for spectrometer/shutter control and data acquisition, and a MATLAB® based algorithm for spectral data reduction. NO$_2$ and O$_3$ VCD are retrieved from zenithal solar spectra (in the visible range) acquired on “twilight” conditions (zenithal angle between 87° and 91°). Under these conditions, the solar ray path in the atmosphere (before reaching the detector) is about 20 times larger than when the sun is directly observed at their maximum elevation angle [3]. The largest contribution to twilight spectra comes from the stratosphere, thus the radiance spectra contains the information required for stratospheric trace gas retrieval. In the spectral range 400-550 nm there are some molecules that possess a very structured and intense absorption cross-section. The algorithm accounts for all contributions to the observed absorption, besides other phenomena, such as Rayleigh, Mie and Raman scattering. The twilight spectra are divided by the reference spectra to eliminate Fraunhofer’s structures (originated at the solar photosphere), which are one order of magnitude larger than the target absorptions. The analysis is carried out by solving the BLB law (equation (6)) for all the atmospheric absorbers over an adequately wavelength range [4]. Least squares fitting of equation (2) allow us to determine the NO$_2$ and O$_3$ SCD. The effects of Rayleigh and Mie scattering are subtracted out using a high-pass polynomial filter. The algorithm minimizes the fitting residuals to the BLB law, having as unknown the SCD of the species to determine and first order wavelength mapping coefficients (shift and stretching):

$$D = \ln \left[ \frac{I_o(\lambda)}{I(m\lambda + \Delta \lambda)} \right] = S_R + S_M + \sum_i (\sigma_i(\lambda) \otimes H) CD_i$$  \hspace{1cm} (6)$$

where $D$ is the optical density (due to absorption), $I_o(\lambda)$ is the reference spectra (measured at noon), $S_R$ and $S_M$ are the Rayleigh and Mie scattering respectively. $H$ is the instrumental function, $I(\lambda)$ the twilight spectra for a given zenithal angle, and $m$ and $\Delta \lambda$ the stretching and shift coefficients, respectively. $\sigma_i(\lambda) \otimes H$ is the convolved absorption cross section of the $i$-th species, $CD_i$ is the slant column density difference between reference and measured slant columns of the $i$-th species. After obtaining the optical density, the differential optical density is calculated as follows:

$$\Delta D \equiv \sum_i \Delta \sigma_{Hi}(\lambda_i) CD_i$$  \hspace{1cm} (7)$$

where

$$\Delta D = D - f LP(D)$$  \hspace{1cm} (8)$$

$f_{LP}$ is a polynomial and
The atmospheric gases absorb radiation at characteristic wavelength. The efficiency with which a given gas absorbs radiation is expressed by the absorption cross-section, which is a function of wavelength. At wavelengths where the absorption cross-section is small, we can expect solar radiation to reach the ground with little attenuation, while at wavelengths where the absorption cross-section is large, absorption is significant. Ozone has two absorption bands in UV (Hartley band with strong absorption between 200 and 300 nm and the Huggins band with a weak absorption between 320 and 360 nm), one absorption band in the visible (Chappuis band with weak diffuse absorption between 375 and 650 nm), and one near IR system (Wulf band with absorption beyond 700 nm). Our aim is to retrieve simultaneously the VCD of multiple gases (mainly \( \text{NO}_2 \), \( \text{O}_3 \), \( \text{O}_4 \), water vapour, etc.). Therefore, the visible spectral range where there are important absorptions of those gases, must be used. In this paper, the equations system is solved in the range 438.5 - 448 nm and 500 - 530 nm where \( \text{NO}_2 \) and \( \text{O}_3 \) display maximum differential absorption structure, respectively [5,6]. We are currently implementing the inclusion of water vapor, \( \text{O}_4 \) and the Ring effect contributions [1]. The analysis result is a \( \text{NO}_2 \) and \( \text{O}_3 \) SCD that we transform into VCD. The conversion factor among the slant and vertical values as a function of the zenithal angle (\( \theta_z \)) is denominated Air Mass Factor, AMF (equation 10). The \( \text{NO}_2 \) concentration profile shifts from sunrise to sunset and from winter to summer, due to its photochemistry [7]:

\[
\Delta \sigma_{HH}(\lambda) = (\sigma_i(\lambda) \otimes H) - f_{LP}(\sigma_i(\lambda) \otimes H)
\]

The spectra acquisition system consists of a portable spectrometer (HR4000), hereafter referred to as ERO, which measure solar spectral irradiance in the UV-visible range (290 - 650 nm), and two optical fibers (400 µm of core, 6 m and 25 cm of longitude) (figure 1).

![Figure 1](image1.jpg)

**Figure 1.** The components of DOAS system: a notebook, the software designed using Labview®, the spectrometer (HR4000), an automatic shutter and the optical fibers.
ERO is a simple spectrograph equipped with a fixed diffraction grating and a 3648-pixel lineal array CCD. It does not include mobile parts, thus the spectra acquisition is carried out simultaneously on all wavelengths [8]. The diffraction grating has 600 grooves/mm blazed at 400 nm, a characteristic that makes it appropriate for measurements in the spectral range mentioned. We developed an automatic shutter to determine the dark current of each measurement, and to remove this noise to the twilight spectra. We used Labview® to develop a software that controls start and end of spectral measurements, the retrieval of acquired spectra (via USB port) and the shutter (via LPT port). The software also reads a database that was created previously using Matlab®, and stamps begin/end local time to measurements (carried out at sunrise and sunset). The measurement location latitude, longitude and altitude, and the sun path in the sky are also recorded. The computer internal clock is daily updated to avoid possible time shifts and to maintain accuracy on zenithal and azimuth angles calculations. Furthermore, the software sets the CCD integration time to maximize sensing signal, varying the same one until the solar spectrum maximum intensity is within a predetermined intensity interval. This ensures a good signal/noise ratio. The dark (current) spectra are measured with the same integration time than the twilight spectra measured immediately before. This ensures that the subtracted dark noise is similar to the one actually measured over the illuminated period.

3. Results
We compare the data acquired by our DOAS system with co-located measurements performed with EVA, a visible absorption spectrometer operated by the INTA/Spain, and a Dobson spectrophotometer of the SMN/Argentine. Additionally, a comparative study is presented among the ground-based signals and those obtained by the instrument OMI. The instrumental function and the system resolution were determined using low pressure lamps spectra provided by the Instituto Tecnológico de Buenos Aires (ITBA). We retrieved the spectrometer instrument function from a helium lamp [9]. The full width at half maximum (FWHM) of the Voigt profile fitted to the He line was 1.03 nm at ~447 nm. We used the normalized fitted profile or “instrumental function” to convolve the literature absolute cross sections of NO\textsubscript{2} to the resolution of our spectral measurements. This operation is necessary because the twilight and reference spectra are acquired by an instrument of much lower resolution than the one used to measure σNO\textsubscript{2}. The lamp spectra were also used to recalibrate ERO’s wavelength mapping. This recalibration shows a shift of about -1.55 nm from the original (nominal) manufacturer calibration at the center wavelength of interest and time of the measurements.
Figure 2. NO$_2$ VCD variability at Marambio Antarctic Station during (a) the sunrise and (b) the sunset.

In the figure 2 we present the NO$_2$ VCD evolution during some days of January and February 2008, retrieved by the ERO-DOAS, EVA and OMI/AURA instruments. There is overall a good agreement between ERO-DOAS, Dobson and EVA measurements. The maximum relative difference found was 7% and 13% at sunrise and sunset, respectively. ERO-DOAS measurements were not adjusted for O$_4$, water vapor absorption and the Ring effect [10]. This source of error might account for some of the observed discrepancy. Likewise, we observe a better agreement among results at sunrise than at sunset. This is due to that the AURA meteorological satellite overpass over Marambio is closer to EVA’s and ERO-DOAS’ sunrise than sunset [7].
Figure 3. O$_3$ VCD variability at Marambio Antarctic Station, during (a) the sunrise and (b) the sunset.

In the figure 3, we can see the O$_3$ VCD variability at Marambio Station, during the sunrise and sunrise, retrieved by the ERO-DOAS, Dobson spectrometer and OMI/AURA instrument.

4. Conclusion

Unlike to other similar systems - as the EVA/NEVA instruments (INTA, Spain), SAOZ (CNRS, France), Dobson and Brewer spectrophotometer - our DOAS spectrometer (ERO-DOAS) has the capability of sensing automatically several chemical species and the advantage of being portable, which offers the possibility of easily moving the instrument to carry out measurements campaigns. A low cost and portable remote sensing instrument is a key tool to make stratospheric trace gases measurements along a large country like Argentina. Our instrument has achieved the design goals of low-cost and portable passive measurements of the vertical column concentration of multiple trace gases. The differences between OMI/AURA observations and the ground-based data might be due to: a) the NO$_x$ daily cycle, b) NO$_2$ natural variability, and c) tropospheric NO$_2$ variation. This last one is probably insignificant at Marambio, a non polluted remote location. We observe that NO$_2$ has a strong variability during the day. This variability is probably associated with the diurnal solar cycle, the NO$_x$ vertical distribution, the temperature in the high layers of the atmosphere and maybe the variability of other active species. In the case of the O$_3$, the daily variability of the gas is low, which is the reason why the comparison between satellite and ground-based data is very good.

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References

[1] Fish D J and Jones R L 1995 Rotational Raman scattering and Ring effect in zenith sky spectra Geophys. Res. Lett. 22 7 811-14
[2] Gil M, Yela M, Gunn L N, Richter A, Alonso I, Chipperfield M P, Cuevas E, Iglesias J, Navarro M, Puñetedura O and Rodríguez S 2007 NO$_2$ climatology in the northern subtropical region: diurnal, seasonal and interannual variability. *Atmos. Chem. Phys. Discuss.* 7 15067-103

[3] Gil M, Yela M, Gunn L, Richter A, Alonso I, Chipperfield M, Cuevas E, Iglesias J, Navarro M, Puñetedura O and Rodríguez S 2008 NO$_2$ climatology in the northern subtropical region: diurnal, seasonal and interannual variability. *Atmos. Chem. Phys.* 8 1635-48

[4] Jiménez R 2004 Development and application of UV-visible and mid-IR differential absorption spectroscopy techniques for pollutant trace gas monitoring Ph.D. Thesis, École Polytechnique Fédérale de Lausanne (EPFL), Thesis N° 2944

[5] van Roozendael M, Hermans C, Kabbadj Y, Lambert J C, Vandaele A C et al. 1995 Ground-based measurements of stratospheric OCIO, NO$_2$ and O$_3$ at Harestua, Norway (60° N, 10° E) during SESAME *Proc. 12th ESA Symp. on European Rocket and Balloon Programmes & Related Research, Lillehammer, Norway*, ESA SP-370 pp 305-310

[6] Mihalcea R M, Baer D S and Hanson R K 1996 Tunable diode-laser absorption measurements of NO$_2$ near 670 and 395 nm *Appl. Opt.* 35 4059-64

[7] Platt U and Stutz J 2008 Differential Optical Absorption Spectroscopy. Principles and Applications ISBN 978-3-540-21193-8 ed Springer chapter 2 pp 16-28

[8] Raponi M, González F, Wolfram E, Tocho J and Quel E 2008a Determinación de NO$_2$ estratosférico en columna vertical, utilizando un sistema portátil de sensado remoto pasivo Las Fronteras de la Física y Química Ambiental en IberoAmérica ISBN 978-987-1435-09-8 ed Universidad Nacional de San Martín, Buenos Aires pp 446-51

[9] Raponi M, Wolfram E, Quel E, Pedroni J, Rosales A and Tocho J O 2008b Stratospheric NO$_2$ concentration determined by DOAS using compact spectrographs ISBN 978-0-7354-0511-0 ed Niklaus Ursus Wetter and Jaime Frejlich *AIP Conf. Proc.* 992 pp 9-14

[10] Raponi M, Jiménez R, Tocho J O and Quel E J 2009 NO$_2$ vertical column retrieved by DOAS technique in Marambio, Antarctic. Current problems in atmospheric radiation (IRS 2008): Proceedings of the International Radiation Symposium (IRC/IAMAS) ISBN 978-0-7354-0635-3 ed Springer, Berlin, Germany. *AIP Conf. Proc.* 1100 pp 319-22

[11] Vaughan G, Quinn P, Green A, Bean J, Roscoe H, van Roozendael M and Goutail F 2006 SAOZ measurements of NO$_2$ at Abersystwyth *J. Environ. Monit.* 8 353-61