INTERCOMPARISON OF THE NO_2 VERTICAL COLUMN DENSITIES MEASURED OVER IZAÑA WITH TWO GROUND-BASED REMOTE SENSING TECHNIQUES: DOAS AND FTIR

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RESUMEN

En el marco del proyecto NORS se ha realizado una intercomparación de medidas de NO_2 con dos técnicas de detección remota desde superficie: DOAS y FTIR. Las columnas verticales de NO_2 medidas en Izaña por dos espectrómetros de alta calidad como son el RASAS basado en la técnica DOAS y el instrumento comercial BRUKER-120 basado en la técnica FTIR, han sido comparadas. Debido a la fuerte variación fotoquímica del NO_2, las medidas realizadas con el FTIR han sido corregidas con un Box-model fotoquímico para referenciarlas a la hora de medida del RASAS. Los resultados de ambos instrumentos se comparan bien, dando unas diferencias medias de 7±18%.

Palabras clave: NO_2, DOAS, FTIR, NORS, Izaña.

ABSTRACT

In the frame of the NORS Project, an intercomparison exercise of two ground-based remote sensing techniques is presented: DOAS and FTIR. Results form two high quality spectrometers located at the Izaña Atmospheric Observatory are shown and compared. DOAS based instruments are two RASAS, developed at INTA, working in the UV-VIS part of the spectrum. FTIR based instrument is a Bruker-120 that measures in the IR. To account for the NO_2 strong photochemical variation a Box-model has been used to refer the FTIR data to the DOAS measurement time. Results show a good agreement in the NO_2 concentrations. Mean differences are of 7±18%.

Keywords: *NO_2, DOAS, FTIR, NORS, Izaña.*

1. INTRODUCCIÓN

During the last decades the importance of nitrogen dioxide (NO_2) in the atmosphere has been discovered and studied (Crutzen, 1979). NO_2 plays a crucial role in stratospheric chemistry modulating the ozone budget through catalytic reactions. In the troposphere, NO_2 affects the ozone levels, causing respiratory problems in humans and is an acid rain precursor.

Long-term stratospheric NO_2 monitoring is required to understand the observed stratospheric ozone depletion and the foreseen recovery. Nowadays several instruments based on different techniques routinely measure stratospheric NO_2. Comparison and validation of the instruments is needed in order to improve the interpretation of the results and to explain the observed differences.

NORS (Demonstration Network Of ground-based Remote Sensing Observations in support of the Copernicus Atmospheric Service) project makes use of high quality and independent ground-based instruments to validate and improve satellite products delivered by Copernicus Atmospheric Service (CAS), previously known as GAS (GMES Atmospheric Service). Then, quality assured satellite products are assimilated in MACC-II (Monitoring Atmospheric Composition & Climate) models to provide data records on atmospheric composition for recent years. The instruments considered in NORS are part of the international Network for the Detection of Atmospheric Composition Change (NDACC).

Previous studies of Hendrick *et al*., 2012 and Adams *et al*., 2012 carried out comparisons of DOAS (Differential Optical Absorption Spectroscopy) versus FTIR (Fourier Transform InfraRed) instruments of the NDACC network. Results were also compared with satellite products showing seasonal variations in the NO_2 comparisons, suggesting systematic errors in measurements and/or in the photochemical models used. NO_2 comparison studies will help to understand inconsistencies found in works such as the Hendrick *et al*., 2012 or Gruzdez, 2009 that observed a negative trend in the concentration of stratospheric NO_2 in the North Hemisphere, in disagreement with the increase of emissions of nitrous oxide (N_2O), which is a precursor of NO_2. On the other hand, the trend in the South Hemisphere is positive as it would be expected (Gruzdez, 2009).

In this paper two ground-based remote sensing techniques for measuring NO_2 are shown and compared: DOAS and FTIR. The RASAS spectrometers make use of the DOAS technique working in the UV-VIS part of the spectrum. Bruker-120M is a FTIR instrument working in the IR part of the spectrum. Both instruments belong to the NDACC network and are installed at the Izaña Atmospheric Observatory (IZO) where they have been recording diffuse and direct solar spectra, respectively, from more than 13 years.

2. DOAS TECHNIQUE AND RASAS INSTRUMENTS

2.1. DOAS

DOAS technique (Platt and Stutz, 2008) is based on the detection of solar absorption spectra in the UV-VIS spectral range where NO_2 shows a structured cross-section.

In an optically thin atmosphere, the Beer–Lambert–Bouguer Law can be used to compute the solar radiation absorbed by the atmospheric gases:

$$I = I_0 \exp(-L\sigma(\lambda)\rho) \quad (1)$$

where I_0 and I are the incident and transmitted solar radiation intensities, ρ is the concentration of the gas (number density), σ(λ) denotes the effective cross-section at the wavelength λ and L is the thickness of the layer. DOAS technique requires that all the absorbers and their cross-sections are known in advance in the selected spectral range. After eliminating Rayleigh and Mie effects, the NO_2 Slant Column Density (SCD) is computed by least squares fitting. The last step is to compute the Vertical Column Densities (VCD) by dividing the SCD by the Air Mass Factor (AMF) which is mainly a function of the solar zenith angle (SZA) but also depends on the vertical distribution of the gas under consideration.

For stratospheric NO_2 measurements, DOAS instruments point to the zenith during the twilight in order to amplified stratospheric absorption compared to the tropospheric one (Solomon *et al*., 1987).

2.2. RASAS

INTA have been carrying out measurements of NO_2 at the Izaña observatory in the framework of NDACC since 1998. For this study data from two DOAS instruments have been used. From 1998 to 2010 the RASAS instrument has been operated. In 2010 a more versatile version of RASAS, a MAX-DOAS instrument (RASAS II) was installed at the station. Both instruments were simultaneously measuring for two months in order to overlap the data series.

RASAS instrument spectral range is of 340–600 nm for NO_2 and O_3 observations with an average FWHM resolution of 1.3 nm. The spectrograph and detector are housed in a thermostatised hermetic container keeping the spectrograph at a constant temperature maintaining the alignment of the spectra with time. A more detailed description of the instrument can be found at Gil *et al*., 2008.

RASAS-II MAX-DOAS spectrometer collects scattered radiation from the sky in the 415–530 nm spectral range. As in the case of RASAS, the instrument is thermally isolated to ensure the stability of the measurements on time. A detailed description of RASAS II can be found at Puentedura *et al*., 2012.

3. FTIR TECHNIQUE AND BRUKER 120 INSTRUMENT

3.1. FTIR

Ground-based FTIR instruments are used to determine zenith column amounts of NO_2 among other atmospheric gases. FTIR measures high resolution solar absorption spectra, in the IR part of the spectrum. FTIR instruments point towards the Sun and measures during the day at different SZA under clear sky conditions. A detailed explanation of the technique can be found in (http://www-imk.fzk.de/imk2/boden/bruker.htm).

3.2. Bruker 120M

FTIR instrument used is a BRUKER 120M that has a spectral resolutions of 0.0035 cm^{-1}. The Bruker region for absorption spectra measurements ranges from 2 µm to 14 µm using the Sun as natural radiation source. High spectral resolution is required to separate lines of different atmospheric species in the spectra. Bruker 120M is operated by the Institute for Meteorology and Climate Research (IMK) together with the Izaña Atmospheric Research Center, collecting measurements regularly under clear sky conditions since 1999.

4. METEOROLOGICAL STATION: IZAÑA, AEMET

The Izaña Atmospheric Observatory (IZO) belongs to the Meteorological State Agency of Spain (AEMET). It is located at the Island of Tenerife, 28º18'N, 16º29'W, on a mountain Plateau at 2373 m over the sea level, 300 km from the African cost and rather isolated from continental anthropogenic sources. IZO is normally above a temperature inversion layer, keeping the station free of local pollution influences and under clear sky conditions. Characteristics that make the observatory representative of Free Troposphere conditions.

5. METHODOLOGY

RASAS and Bruker morning data measured from 2000 to 2012 are compared. As it has already been explained, RASAS instruments measure diffuse solar radiation at twilight, with SZA varying from 89º to 91º. RASAS data used is the mean value of the twilight. Bruker measures during the day to direct Sun. Both measurement SZAs and conditions differ from each other. Due to the strong diurnal variation of NO_2

concentrations a box model is needed to make Bruker and RASAS data comparable. In our study a photochemical model (Chipperfield, 1999) has been used for this purpose.

To carry out the correction it has to be taken into account that the stratospheric NO_2 layer is located approximately at 25 km to 30 km height. Therefore the effective airmass scanned by RASAS is located about 360 km from the measurement station toward the Sun with an effective SZA of approximately 86.8º. FTIR data is corrected to the effective SZA for the comparison.

6. RESULTS

6.1. Cross-correlation

After the FTIR data correction, NO_2 columns can be directly compared. Figure 1 shows a cross-correlation between DOAS and FTIR data. In the image FTIR data without any correction and FTIR after correction are shown. Results of the correlation are shown in Table 1. Both the slope and the R-Square improve for the corrected FTIR data, even though correlation coefficient is not high (R^2=0.56).

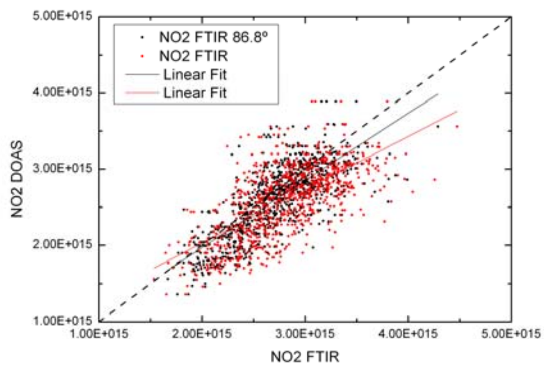

Figure 1. Scatter plot of the NO_2 VCD measured with the DOAS versus the FTIR instruments. Red dots represent the FTIR data without any correction. Black dots show the FTIR data corrected to the effective SZA.

6.2. Seasonal Evolution

Figure 2(a) shows the seasonal evolution of the NO_2 VCD for both datasets. **Figure 2** (b) presents the relative difference between both datasets, with a mean difference of -6.6±17.9%. Mean DOAS-FTIR value is shown in the plot with a solid red line while the dashed red lines represent one standard deviation. In general, the seasonal evolution observed for both instruments show a good agreement with lower differences during summer where most of the dots fall within the dashed lines. On the other hand, from October to April mainly negative differences are observed and most of the dots fall under the mean values. In addition the behaviour in spring and autumn months is different, showing higher differences in autumn. This seasonality effect can be related to the climatology used for retrieval or any other parameter dependent on the temperature of the stratosphere.

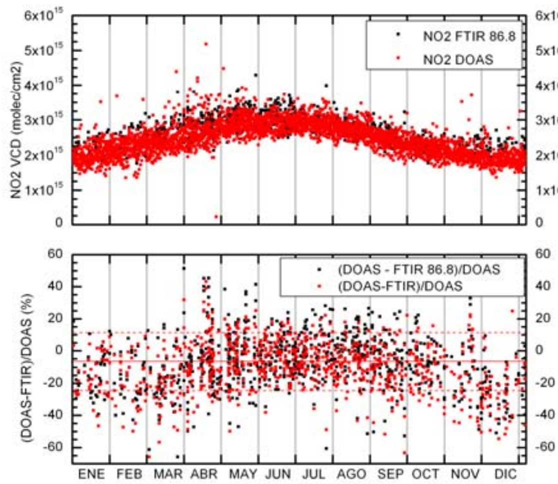

Figure 2. (a) Shows the seasonal variation of the NO_2 VCD measured with the DOAS (red dots) and the FTIR corrected (black dots) instruments. Relative differences are shown in (b)

Table 1. Results of the linear fit of DOAS versus FTIR NO_2 VCD

	Intercept	Slope	R-Square
NO2 FTIR	6.28E14	0.70	0.42
NO2 FTIR (86.8º)	2.05E14	0.88	0.56

6.3. Interannual evolution

The interannual evolution is in good agreement with other studies, see **Figure 3**. **Figure 3**(b) shows similar results as **Figure 2**(b). In addition, it is observed that the relative difference between datasets increase in 2009 and 2010 during summer.

7. DISCUSSION AND CONCLUSIONS

Results show that a photochemical correction has to be applied to the data to refer both instruments to a common hour of the day. The effective SZA for the DOAS air mass has been used to correct FTIR dataset. The comparison shows that results agree within -2E14±4E14 when no correction is applied to the FTIR data while comparison with the corrected FTIR data improves to -1E14±3E14. Table 1 and Table 2 show the improvement of the comparison after such correction, the R-Square of the linear fit increases (Table 1), and the mean difference decreases (Table 2) showing a better agreement between both dataset. For relative differences the mean also improves from -10% to -7% while the standard deviation increased from 16 to 18.

Figure 2 (a) and **Figure 3**(a) show, in general, the expected behaviour of the NO_2 VCD stratospheric seasonal evolution. While **Figure 2**(b) shows some differences that increase during cold months (from October to April). Seasonal differences in the NO_2 concentrations measured by the same both techniques have already been observed by Adams *et al.*, 2012 suggesting that there might be systematic errors in the photochemical model correction or in the measurements. Such differences can also be caused by errors of the spectroscopic data used for the data analysis. Gil *et al.*, 2008 also observed a spring–autumn asymmetry that is highly correlated to the temperature in the upper stratosphere which could also explained the observed differences in **Figure 2**(b).

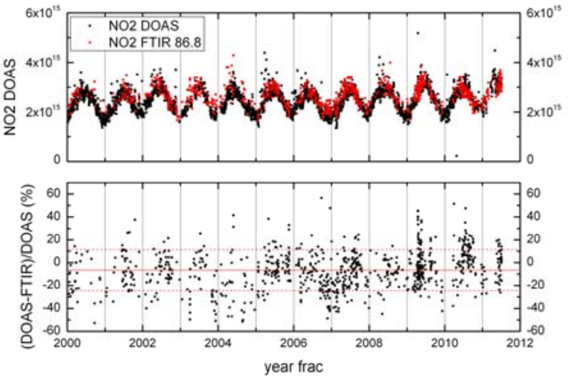

Figure 3. (a) Interannual evolution of NO_2 VCD. (b) Relative differences.

Table 2. Mean and standard deviation of the comparison is shown

N Total = 864	Mean	Standard Deviation
DOAS-FTIR	-2E14	4E14
DOAS-FTIR 86.8º	-1E14	3E14
DOAS-FTIR (%)	-10	16
DOAS-FTIR 86.8º (%)	-7	18

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