Development of a *DOAS* System for *ToTAL-DOAS* Applications with Temperature Control

**Javier A Ramos¹ and Erna Frins¹**  
¹ Instituto de Física, Facultad de Ingeniería, UdelaR, Uruguay  
E-mail: jramos@fing.edu.uy

**Abstract.** The ToTAL-DOAS (Topographic Target Light scattering – Differential optical Absorption Spectroscopy) is a novel atmospheric monitoring technique. The aim of our work has been enhancing a prototype, previously assembled within our research group, adding to it a temperature control and developing specific control software. The whole system offers the possibility of two dimension movement for spectra acquisition with a telescope of a field of view of approximately 0.03°, which let in signals in the near-UV and visible spectral range. The enhanced DOAS system is intended to be located on the roof of our faculty building to monitor SO2 and NO2 traces above the city of Montevideo. We are presenting the results of device’s characterization.

1. Introduction  
The Differential Optical Absorption Spectroscopy (DOAS) is a widely applied method for the detection of a large number of trace gases e.g. NO2, ClO, IO, O3, SO2, HCHO as well as some aromatic hydrocarbons [1]. A great advantage of the DOAS is its ability to determine the concentration of several trace gases simultaneously without disturbing their chemical behavior. DOAS measurements can be done using a spectrometer that measures either scattered sun light (called passive DOAS) or light from an artificial light source that has passed through a certain gas volume containing the trace gases of interest. In the later case, the DOAS system requires the adjustment of a long path optical system (in the km range), while passive DOAS demands are on the quality of spectra and evaluation procedure. Tomographic Target Light scattering – Differential Optical Absorption Spectroscopy (ToTAL-DOAS), also called Target-DOAS [2], is a novel experimental procedure to retrieve trace gas concentrations present in the low atmosphere. Scattered sunlight (partially or totally) reflected from natural or artificial targets of similar albedo located at different distances is analyzed to retrieve the concentration of different trace gases like NO2, SO2 and others. The aim of this work was to enhance a prototype, previously assembled within our research group as we will describe next.

2. Device description  
The device named ITDOAS (Intelligent Target Differential Optical Absorption Spectroscopy), offers the possibility of two dimension movement for spectra acquisition with a telescope of a field of view of approximately 0.03°, which let in signals in the near-UV and visible spectral range. An Ocean Optics spectrometer USB 2000+ with optical range 297-505nm was installed.
The lack of a temperature control on a device that has to work in field under extreme temperature variations implies noisy spectra acquisition and high detection limits. Therefore, a Peltier based cooling system was installed.

As shown in figure 1, in order to cooling down the spectrometer, it was covered by Polystyrene foam for thermal insulation. We placed a copper (Cu) block through the foam to conduct the heat to the outer surface of the ITDOAS case, pumped by the Peltier cell located over the copper block. The heat flow is then dissipated from the cell with a CPU fan cooler heat sink while air is forced by a fan through it.

![Figure 1. Spectrometer cooling setup.](image)

Once the cooling system has been set up, controlling the current through the peltier element is a must as well as a temperature feedback measurement. Both aspects were accomplished by using a SuperCool PR-59 controller. Through the installation of the temperature sensor on spectrometer’s side we get the temperature information input for our control system. According to that information output current is regulated. When achieved the desired temperature the controller reduces its output current, restoring it gradually back as the temperature drifts from the desired value. This behavior allows power optimization because the system drains a lot of power to achieve the final temperature. When this occurs, the power consumption drops off for maintaining it. This way, switching ON and OFF, is avoided (and so the peak starting currents) in continuous operation. Therefore after a transient the system keeps a constant temperature. After opening a window on the lid for letting the heat sink out, the device setup is as shown in figure 2.

![Figure 2.](image)

(a) ITDOAS with typical measurement setup.
(b) Detail of heat sink and front view with telescope detail.
For proper operation in fieldwork, reliable control software is required. In order to achieve the desired behavior, custom PC application was developed. The resultant Software interface is displayed in figure 3. Through it, Aiming Camera, Target List, Motion Control and Spectra among other controls were included looking forward for having all the relevant information at a glance.

![Control Software User Interface](image1.png)

**Figure 3.** Control software user interface.

### 2.1. Calibration

The correlation between wavelength and channel number was performed with the help of an Hg Lamp. The resulting calibration is shown in figure 4.

![Hg Lamp Spectrum](image2.png)

**Figure 4.** (a) Hg Lamp Spectrum acquired for calibration. (b) Polynomial fit of wavelength.

### 2.2. Dark Current & Offset

Two relevant corrections of measured spectra must be done in order to extract more precise information from the acquired spectra. These corrections are the Dark Current (DC) and Offset. Every pixel on CCD can be regarded as a capacitor with a proportional discharge to the number of incoming photons [3] [4]. Under dark conditions, (i.e. detector not exposed to light), thermal excitation causes a dark current proportional to integration time and the Boltzmann factor:
$I_{DC} \propto e^{E_g/kT}$,  \hfill (1)

where $I_{DC}$ is the dark current, $E_g$ is the silicon band-gap energy (in eV), $T$ is the absolute temperature of the CCD (in K) and $k$ is Boltzmann's constant (8.62 x 10^{-5} eV/K). The dark current signal exponentially decreases with decreasing detector temperature. Then, cooling the detector reduces the dark current signal. The remaining dark background is digitally corrected afterwards; a dark spectrum is measured by taking one scan with a long integration time (at least 1000 ms) under dark conditions. Every measured spectrum is corrected by subtracting a time-weighted dark current signal during the evaluation procedure:

$I_{corr}[n] = I[n] - \left( t_{int,\text{measure}} / t_{int,\text{dc}} \right) \cdot D_{offcorr}[n],  \hfill (2)$

where $I_{corr}[n]$ is the intensity in channel number $n$ after dark current correction, $t_{int,\text{measure}}$ is the integration time of the measurement spectrum and $t_{int,\text{dc}}$ is the integration time of the dark current spectrum. $I[n]$ denotes the intensity in channel $n$ before the dark current correction and $D_{offcorr}[n]$ the intensity of the offset corrected dark current signal in channel $n$.

The electronic of the spectrometer has a 12 bit analog to digital converter which turns the analog photon generated signal into a digital signal for the analysis procedure on a PC. If negative analog photo signals are produced by detector noise they cannot be interpreted by the A/D converter. Therefore, an artificial electronic offset signal is added to each measured scan to avoid this problem. Before the analysis process, the electronic offset weighted by the number of scans has to be subtracted from the measured spectra:

$I_{offcorr}[n] = I[n] - \left( \text{numscans}_{\text{measure}} / \text{numscans}_{\text{offset}} \right) \cdot O[n],  \hfill (3)$

where $I_{offcorr}[n]$ is the intensity in channel number $n$ after offset correction, $\text{numscans}_{\text{measure}}$ is the number of scans of the measurement spectrum and $\text{numscans}_{\text{offset}}$ is the number of scans of the offset spectrum. $I[n]$ denotes the intensity in channel $n$ before the offset correction and $O[n]$ the intensity of the offset signal in channel $n$.

To correct the electronic offset, a dark spectrum of a large number of scans (1000 or more) is taken at minimal integration time, which is 3ms for the CCDs used in the ITDOAS systems. The electronic offset signal of the ITDOAS is temperature dependant. In order to study about how much the collected data drift according to the temperature of the spectrometer we ran some basic tests. We measured Dark Current -DC- and Offset at different temperatures and the obtained data is shown in figure 5 and figure 6.

![Dark Current](image)

**Figure 5.** Dark Current measured at different temperatures.
Some test measurements were performed with UV-LEDs and the CCD at different temperatures. The aim is to see the way spectrums are affected at certain wavelength-ranges by the variation of temperature at the CCD. For this stage two different UV-LEDs were used. These tests involved a 335nm and 370nm LEDs (figure 7). From the acquired data could be seen that around the 335nm wavelength, the spectrums is quite temperature dependant, while for the 370nm this dependency does not seem to be too significant. This spectrums profile behaviour may be related to the cooling process. Decreasing temperature on the optical bench might cause optical misalignment as observed on former model of Ocean Optics’ spectrometer (USB 2000) by Bobrowski [3]. As we can see this effect is stronger the more we get into the UV range of the spectrometer’s CCD.

3. Conclusions
The instrument is being installed at the roof of our faculty building to monitor mainly SO2, NO2 and HCHO traces above the city of Montevideo. We have reach that through the reduction of DC very short acquisition times (few seconds) are possible.
Around the 335nm wavelength the spectra is quite temperature dependant, while for the 370nm this dependency does not seem to be too significant. This might be caused because of optical misalignment caused by the optical bench cooling process.

Two dimension movement and its aiming accuracy, makes this device a good choice for ToTaL-DOAS applications to monitor trace gases in large areas.

Acknowledgements
This work was supported by the CSIC of the Universidad de la República and PEDECIBA.

References
[1] Platt U and Stutz J 2008 Differential Optical Absorption Spectroscopy: Principles and applications (Heidelberg: Springer)
[2] Frins E, Bobrowski N, Platt U and Wagner T 2006 Tomographic MAX-DOAS observations of sun-illuminated targets: a new technique providing well-defined absorption paths in the boundary layer Appl. Optics 45 6227–40
[3] Bobrowski N 2005 Volcanic Gas Studies by Multi Axis Differential Optical Absorption Spectroscopy Doctoral Thesis University of Heidelberg Germany
[4] Janesick J R 2001 Scientific Charge-Coupled Devices (Washington: SPIE Press)