

## Practical Environmental Measurement Techniques:

# DOAS measurements of Atmospheric Species

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## Measurements

All your measurements are performed using the software running on the computer attached to the instrument. The software is a WINDOWS program designed to set-up and control the experiment and facilitate automated long-term measurements. You will need only a small part of the available commands and should **avoid changing any settings not explicitly mentioned here**. The supervisor will help you with the operation of the instrument, but with this document you should know about the basic points:

- The DOAS instrument is operated from a computer in the lab room
- The measurement program is usually running when you start with your practical. (If

not, you start it by double-clicking on the AMAX\_OMA icon  on the desk-  
top.)

- Most commands can be interrupted by the <ESC> key or by clicking on the STOP button, but it may take some time until the previous command is finished
- Taking the measurements consists of several steps:
  - stopping a running measurement (if necessary)
  - changing the settings if necessary
  - selecting the operation mode (SINGLE in your case)
  - STARTing the measurement
  - saving the results to a folder on the desktop, using a unique name for each measurement (see below)
- For each measurement, you need a corresponding dark measurement taken with the same settings except that the telescope is closed by putting a box or a cloth over the telescope. You should measure the dark signal before and after you have finished your time series with the NO<sub>2</sub> cell.
- If you want to determine the best exposure time, just type <i> when in the main menu
- For all measurements, you will be prompted to give a file name. Save your files in a folder on the desktop. Later you can copy it on your USB stick. Select meaningful names for the files and use the ASCII format option. The extension has always to be DAT.
- After you are finished, please phone the tutor. He will reset the instrument back to automatic measurements.

For the NO<sub>2</sub> cell measurements, the best exposure time might differ for the measurements with and without cell, and you will need different dark measurements for these data sets (see below).

### Example: taking one set of measurements:

- Step1: set MeasurementMode to <SINGLE>
- Step2: insert the NO<sub>2</sub> cell, **measurement with cell**
- Step3: click on <START>
- Step4: switch off the flag “Automatic Exposuretime”  
Based on your last measurements (or use of <i>), enter a good exposure time  
set Mirror Position to <90> (view to the zenith)  
set N average to <20>
- Step5: start measurement <Start Measurement>
- Step6: wait until measurement is finished
- Step7: set filename  
set <Use ASCII File Format>  
set <Save Binned>  
do NOT set <Save Image>  
save file <SAVE>
- Step8: take a note of which exposure time the program has selected for the measurement (e.g. 0.2s), this is important for the dark measurements
- Step9: remove the NO<sub>2</sub> cell, for **measurement without cell**, and repeat steps 3 to 8

In order to get a meaningful time series of the NO<sub>2</sub> concentration in the cell you have to repeat measurements with and without cell for at least 120 minutes. This depends on weather conditions: for low sun or rainy weather more time is needed (up to 3 hours). The time within the measurements with and without cell should be less than one minute. The time between one pair of measurements with/without cell should be less than 5 minutes.

After performing all the required measurements with and without cell you can perform the dark measurements necessary for the exposure times of your data set.

- Step10: **dark measurements:**  
Prevent light from entering the telescope by putting a box or a cloth over it  
repeat from step 3 to step 7 for every exposure time you have used for measurements with and without cell. In step 4 untag the flag “Automatic Exposure time” and select manually

### Off-axis measurements

After having finished the measurements with the NO<sub>2</sub> cell, take some real atmospheric measurements without cell. For that, take a series of measurements, one in zenith direction (90°) and one at each elevation between 1° and 15°. You can set the elevation angle in the dialogue for the SINGLE measurements.

Make sure that you use good exposure times and that you perform dark measurements for all of these exposure times as well.

start and stop

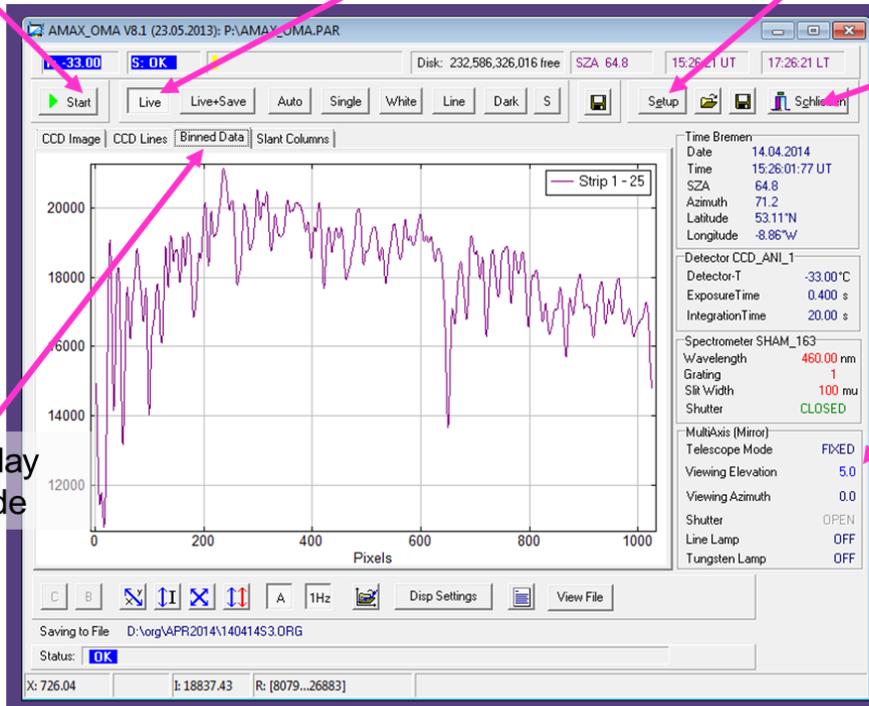
measurement mode

settings

close

Display mode

mirror setting



## Data Analysis

In the data analysis, you will use the spectra you have recorded to determine the NO<sub>2</sub> content in the cell and during the horizon measurements. Also, you will use simulated atmospheric spectra supplied to you to determine the atmospheric trace gas column (e.g. ozone or bromine monoxide or formaldehyde) for one sample day.

### NO<sub>2</sub> content in the cell

In the lab, you should have taken the following spectra:

- several pairs of measurements with and without cell
- a series of measurements towards the horizon and to the zenith
- dark current measurements for all exposure times used for the cell measurements

All the corresponding files are in ASCII format and can be read into MATLAB (or any other software you like) for further analysis.

The data analysis consists of the following steps, which will be explained in more detail below. Here, we concentrate on the cell measurements first:

1. read all files into MATLAB, try to program a loop to analyse all measurements in one step
  - a. measurements with cell
  - b. dark measurement for exposure time with cell
  - c. measurements without cell
  - d. dark measurement for exposure time without cell
  - e. differential cross-section for NO<sub>2</sub> [NO2\\_DIFFXSECTION.DAT](#)
2. subtract matching dark current from measured spectra
3. apply wavelength calibration to measured spectra using the simple polynomial formula provided
4. compute the optical density (OD) of measurement by taking  $\ln(I_0/I)$
5. compute differential optical density by fitting a polynomial to the OD and then subtracting this fit from the OD
6. determine slant column by fitting the provided differential cross-section to the determined differential OD
7. convert to mixing ratio for NO<sub>2</sub>

In practice, you will have to perform the following steps (if some command is not clear then use the MatLab help or write “[help command](#)” to get information about *command*.):

1. read data

```
[pixel, var] = textread(FILENAME, '%f%f', 'headerlines', 16);
```

where *var* is the variable you want to read from the file  
read raw spectra, I  
read data, I<sub>0</sub>  
read dark current (dark)  
read differential cross sections (NO<sub>2</sub> cross sections)
2. subtract dark current from I<sub>0</sub> and I

3. apply wavelength calibration using the formula

$$\lambda(i) = \sum_{j=0}^2 a_j \left( \frac{i-1}{N-1} \right)^j \quad i = 1 \dots N$$

where

$\lambda$  is the wavelength

N is the number of CCD pixels: for NO<sub>2</sub>: N = 1024

a0 .. a2 are the calibration coefficients which have the values

for NO<sub>2</sub> (ask the supervisor for current data):

a0 = 429.494

a1 = 93.112

a2 = -6.050

4. choose the values of I and I0 in the fitting window:

NO<sub>2</sub>: 432.5 – 465 nm

5. calculate ln(I0/I) (I and I0 have already to be dark current corrected!)

use function `log`

Note: make sure you get the sign of ln(I0 / I) right or else you might get 0 as fit result

6. fit a polynomial of order 3 to ln(I0/I)

use function `polyfit`

7. subtract the fitted polynomial from ln(I0/I) to get the differential ln(I0/I)

use function `polyval`

8. interpolate the differential cross section to the measurement wavelengths

use function `interp1`

Remember that in this practical only a simplified analysis is done. After the interpolation all the necessary corrections according to the full DOAS method are ready and therefore the result of the next function will be THE coefficient that you are looking for.

9. DOAS fit, fit the differential cross-section to the differential ln(I0/I)

use function `lscov`

Note: use column vectors for the cross-sections and the differential OD. The function also returns the standard error of the fitted parameter.

10. Calculate the concentration of NO<sub>2</sub> in the cell

11. Plot your results, for example by

`figure`

`plot(wl_fit, sc.*crs_dif, wl_fit, od_diff)`

`xlabel('wavelength (nm)')`

`ylabel('differential optical depth')`

`legend('scaled NO2 reference', 'measurement')`

`grid`

In your report, please include a plot of one (or all) measured differential optical depth(s) and the scaled differential NO<sub>2</sub> absorption cross-section, and determine the NO<sub>2</sub> concentration in the cell in molec/cm<sup>3</sup> depending on time.

In order to check if atmospheric conditions were stable during your measurements, do the same analysis as for the cell using only the measurements without cell and the very first measurement as I0. How does the NO<sub>2</sub> in the atmosphere change during your measurements? How does this affect your estimate of the NO<sub>2</sub> amount in the cell?

Add a brief error discussion for your results and give some interpretation on the NO<sub>2</sub> time series. Also don't forget to include a printout of the script you used for the data analysis!

### **Off-axis measurements in Bremen**

In principle, this part is very similar to the determination of the NO<sub>2</sub> content in the cell. However, you now use the atmospheric measurements at 1°..15° elevation as I, and the zenith-sky measurement as I0. Compute the NO<sub>2</sub> slant column from these observations and discuss the magnitude, its change with elevation angle and the quality of the agreement between measured differential optical depth and absorption cross-section.

### **Simulated trace gas columns above Bremen**

This last part is again very similar to the determination of the NO<sub>2</sub> content in the cell. However, in this step, you will use two simulated atmospheric measurements taken at different solar zenith angles (TG\_x\_data\_sza1.DAT and TG\_x\_data\_sza2.dat) and 3 different cross-sections TGx\_DIFFXSECTION.DAT, where TGx is O3 (ozone), BrO (bromine monoxide) and HCHO (formaldehyde). The data in these files is given in the units of cm<sup>2</sup>/molec. For the analysis, you should use the wavelength region 336 – 357 nm.

In a first step, find out which of these three trace gases you can identify in the simulated atmospheric spectra. Only one is present! The result of this analysis is the difference of the trace gas slant column measured at two different solar zenith angles on that day. You can convert this to a vertical column by using the airmass factors provided in the files TGx\_AMF.DAT.

In your report, please include a plot of the simulated differential optical depth and the scaled differential trace gas absorption cross-section, and determine the trace gas slant column in molec/cm<sup>2</sup>. Convert the slant column to the vertical column and compare it to "expected" values from the literature. Again, add a brief error discussion.