Practical Environmental Measurement Techniques:

DOAS Measurements of Atmospheric Species

Last change of document: April 14, 2014
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1 Background of the experiment

The Differential Optical Absorption Spectroscopy (DOAS) instrument at the Institute of Environmental Physics is used for continuous monitoring of atmospheric trace gases such as ozone (O_3), nitrogen dioxide (NO_2), bromine monoxide (BrO) and formaldehyde (HCHO).

One of the scientific questions behind the experiment is stratospheric ozone depletion in mid-latitudes and how dynamics, stratospheric temperatures and changes in chemical constitution of the stratosphere interact in their influence on the ozone layer. In mid-latitudes, ozone columns are mainly determined by transport of ozone from low to high latitudes and by dynamical changes of the tropopause height. The large variability from day to day and year to year makes the determination of reliable ozone trends difficult. However, from long-term measurements at many stations, an ozone reduction of approximately 4 percent per decade has been determined. Mixing of mid-latitude air with ozone depleted air from high latitudes in spring is one possible explanation, but *in situ* ozone destruction and long-term changes in transport patterns have also been proposed as reasons for the observed trend. In the last years, ozone decline has diminished and according to some studies even stopped in some latitudes, as would be expected from the effect of the Montreal protocol on CFC emissions.

Other objectives of the DOAS-measurements at the Institute of Environmental Physics are validation of satellite instruments like GOME, SCIAMACHY, GOME-2 or OMI and the investigation of tropospheric air pollution. In Bremen an important part of air pollution is caused by NO_x (NO + NO_2) emissions of traffic and industry.

With the DOAS method, trace species are identified using their distinct absorption structures in the UV/visible. The 'Differential' in DOAS means that only narrowband structures are analysed whereas the broadband structures - that are e.g. caused by cloud cover or scattering by molecules and aerosols and that are difficult to quantify - are approximated by a polynomial. Therefore, only those species that show significant and structured absorption in the UV/visible wavelength range can be observed, such as O_3, NO_2, BrO, HCHO, CHOCHO, H_2O, OClO or IO. Unlike other techniques such as ozone sondes, LIDAR measurements, or microwave radiometry, DOAS measurements provide only little information on the vertical profile of the absorbers but rather the integrated column in the atmosphere. This disadvantage is compensated by the simplicity of the experiment and the relatively large number of species that can be measured simultaneously. Another option to get some profile information at least for tropospheric absorbers is the analysis of light, scattered from different angles close to the horizon (see e.g. http://www.iup.uni-bremen.de/doas/maxdoas_instrument.htm).

1.1 Recommended reading

Most text books on atmospheric physics and chemistry have chapters dealing with ozone chemistry, both in troposphere and stratosphere and also have an introduction to tropospheric pollution. Some examples are

- Richard P. Wayne, Chemistry of Atmospheres, Oxford Science Publications
- Guy P. Brasseur, John J. Orlando, and Geoffrey S. Tyndall, Atmospheric Chemistry and Global Change, Oxford University Press
- T. E. Graedel, Paul J.Crutzen, Chemie der Atmosphäre, Spektrum Akademischer Verlag

If you are interested to learn more about UV/visible absorption measurements and DOAS, you might find the following books useful:

- The Remote Sensing of Tropospheric Composition from Space, Editors: John P. Burrows, Ulrich Platt, and Peter Borrell, Springer, ISBN 978-3-642-14790-6, online pdf
- Differential Optical Absorption Spectroscopy: Principles and Applications, Ulrich Platt and Jochen Stutz, Springer, ISBN: 978-3-540-21193-8 (Print) 978-3-540-75776-4

2 Experimental set-up

A DOAS instrument usually consists of a grating spectrometer, a CCD detector, a telescope, a quartz fibre bundle between spectrometer and telescope and a computer for data acquisition (see Figure 1).
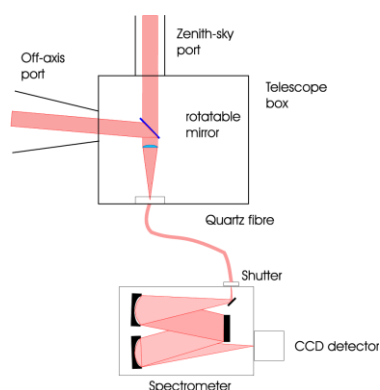

Figure 1: Sketch of the DOAS set-up.

Light scattered from the atmosphere above the instrument is collected by the telescope through the zenith-sky port and fed into the spectrometer via a quartz fibre bundle. The spectrometer used in the practical is of the Czerny-Turner type, has a focal length of 0.275 m and is equipped with a flat ruled grating with 300 lines/mm. The CCD detector has 1024 pixels in the horizontal direction and is 251 pixels high. In the standard operation mode, the signal is integrated vertically resulting in a single spectrum with high signal-to-noise ratio. In automatic operation, the integration time is determined from the measurement taken prior to the measurement itself. In manual operation, the optimal integration time can be determined and set using the menu of the software.

In addition to the zenith pointing port, a second window is located at the side of the telescope to facilitate measurements of light scattered close to the horizon. This is achieved by moving

a computer controlled motorised mirror into the line of sight. Depending on the mirror orientation, measurements at elevation angles between -5° and 30° can be performed. In contrast to zenith-sky observations, this type of measurements is most sensitive towards absorptions in the troposphere.

In the telescope housing, there are also two calibration lamps that are operated automatically during night and are used for the calibration of wavelength and relative radiometric response of the instrument.

3 Data analysis

The basic quantity measured is the sky brightness I as a function of wavelength λ at different solar zenith angles (SZA) Θ. The analysis of the data is divided into two parts. First, the integrated amount of the absorber along the light path (called the *slant column*) is determined using the differential optical absorption spectroscopy method. In a second step, the average light path is computed with a radiative transfer model and used to convert the measured slant column into a vertical column that is the integral of the absorber along the vertical in the atmosphere. In the determination of the slant column, Lambert-Beer's law is used, accounting for extinction by molecular absorption of J species and in addition, Mie and Rayleigh scattering:

$$I(\lambda,\Theta) = a(\lambda,\Theta)I_0(\lambda)\exp\{-\int(\sum_{j=1}^{J}\sigma_j(\lambda)\rho_j(s) + \sigma_{Mie}(\lambda)\rho_{Mie}(s) + \sigma_{Ray}(\lambda)\rho_{Ray}(s))ds\}$$

where σ_j is the absorption cross-section of species j, ρ_x is the density of absorber or scatterer x, I_0 is the radiance outside the atmosphere and the integral is taken along the light path s. The factor a determines the intensity of the scattered light and depends on the density of scatterers and the phase function and is a smooth function of wavelength.

Assuming that the absorption cross-sections do not vary significantly along the light path, the integral of the absorber column along the light path can be taken, leading to the slant columns $SC_j = \int\rho_j(s)ds$. This yields:

$$I(\lambda,\Theta) = a(\lambda,\Theta)I_0(\lambda)\exp\{-\sum_{j=1}^{J}\sigma_j(\lambda)SC_j + \sigma_{Mie}(\lambda)SC_{Mie} + \sigma_{Ray}(\lambda)SC_{Ray}\}$$

The cross-sections for Mie and Rayleigh scattering vary smoothly with wavelength:

$$\sigma_{Ray} \propto \lambda^{-4} \quad \sigma_{Mie} \propto \lambda^{-\kappa} \quad \kappa = 0...2$$

and can be approximated by a polynomial. The basic 'trick' of the DOAS method is that all effects varying smoothly with wavelength are approximated by a low order polynomial including extinction by scattering, the factor a and also low frequency components in the molecular absorption:

$$I(\lambda, \Theta) = a(\lambda, \Theta)I_0(\lambda)\exp\{-\sum_{j=1}^{J}\sigma'_j(\lambda)SC_j + \sum_p b_p\lambda^p\}$$

where σ' is only that part of the absorption cross-section which varies rapidly with wavelength. After taking the natural logarithm and including ln$a$ into the polynomial the DOAS equation reads:

$$\ln(I(\lambda, \Theta)/I_0(\lambda)) = -\sum_{j=1}^{J}\sigma'_j(\lambda)SC_j + \sum_p b_p^*\lambda^p$$

Please note, that all multiplicative factors to I such as instrument sensitivity cancel if I and I_0 are measured with the same instrument. In the final analysis, this equation is solved for many wavelengths in a linear least squares analysis with the slant columns SC_j and the polynomial coefficients b_p^* as parameters.

In the simplified examples analysed in this practical, only one absorber has to be considered (NO_2 or one unknown trace gas respectively) and the polynomial can be subtracted in a first step from both the absorption cross-sections σ and the logarithm of the radiances. The slant column can then be determined by simply scaling the absorption coefficient to the derived differential optical depth: $\tau(\lambda) = -\ln(I(\lambda, \Theta)/I_0(\lambda))$

As a complication, an extraterrestrial spectrum cannot be measured with a ground-based instrument. Therefore, a measurement taken at high sun at a SZA Θ_0 is used as I_0 as then the light path through the atmosphere is short, and only the difference in absorption between the two measurements $\Delta SC_j = SC_j(\Theta) - SC_j(\Theta_0)$ can be determined. This is accounted for in the next step: The conversion from slant to vertical columns. This conversion relies on the concept of airmass factors (AMF). Airmass factors are defined as the ratio between the observed slant column and the searched quantity, the vertical column $VC_j = \int \rho_j(z)dz$ of absorber j:

$$AMF_j(\lambda, \Theta) \equiv SC_j/VC_j$$

In general, airmass factors depend on wavelength, solar zenith angle and vertical profile of the absorber. They are computed with radiative transfer models that simulate the measurement geometry for a standard atmosphere. In the practical, the appropriate airmass factors for O_3, BrO and HCHO are supplied in a file.

As mentioned above, only the difference of slant columns can be determined from ground-based measurements, and some assumptions have to be made for the absorption already contained in the measurement at high sun. The simplest assumption is that the vertical column in the background measurement is the same as in the actual measurement, and the differences are only due to changes in light path. With this assumption, the vertical column can be determined as follows:

$$\Delta SC_j = SC_j(\Theta) - SC_j(\Theta_0)$$

$$= VC_j AMF(\Theta) - VC_j AMF(\Theta_0)$$

$$VC_j = \Delta SC_j/\{AMF(\Theta) - AMF(\Theta_0)\}$$

In the case of NO_2 cell measurements, the background measurement is the measurement without cell, and the light path within the cell is simply given by the length of the cell.

3.1 Recommended reading

There are many papers dealing with the DOAS method and with results obtained with these measurements. Several of them have been published of the Bremen group and are listed on our website www.doas-bremen.de. There is also some general information on the DOAS method and on applications available. A short introduction to the DOAS method can be found here: Lecture Andreas Richter.

4 Experimental procedure and tasks

In the usual operating mode, DOAS measurements taken at twilight are analysed with a spectrum taken at noon as a background. As this takes too much time for a practical, you will be provided with such spectra for analysis. In addition, you will take measurements of NO_2 in a quartz cell and of NO_2 in the troposphere by taking measurements towards the horizon and to the zenith.

4.1 Experiment

4.1.1 NO2 cell measurements

During the practical, you will be introduced to the measurement system, and then take a series of measurements with and without a cell filled with NO_2. By analysing these spectra, you can deduce the amount of NO_2 in the cell. Be careful with the cell and avoid illumination before starting the experiment if possible (why?). In the lab, proceed as follows (a more detailed description is given in a 2nd document provided to you by the supervisor):

1. Familiarise yourself with the instrument and software
2. Take a few test measurements and discuss what you see
3. Switch the instrument to zenith-sky viewing mode
4. Insert the NO_2 cell into the zenith-sky viewing port of the telescope
5. Determine the optimal integration time
6. Take a measurement averaged over 20 individual measurements
7. Save your measurement on USB stick
8. Remove the NO_2 cell.
9. Take a measurement averaged over 20 individual measurements. The two measurements with and without cell should be performed rapidly after each other. (Why?)
10. Save your measurement on a USB stick
11. Repeat the measurement sequence several times for at least 120 minutes.
12. For all exposure times used, take a dark signal measurement and save it to your stick.
13. Don't forget to make notes about the weather, filenames and anything else that might be of importance for the analysis, such as the length of the NO_2 cell.

4.1.2 Horizon measurements

As a second experiment, take one or a few measurements towards the horizon (1° - 15° elevation) and to the zenith (90°). If necessary, also take the dark measurements for the corresponding exposure times. From these data, you can estimate the amount of NO_2 in the boundary layer.

Once you have finished taking measurements, have the supervisor switch the instrument back to automatic operation, collect your USB stick and other things and go to the computer lab or to your own computer.

4.2 Data analysis

The supervisor will provide you with a set of measurement data and some auxiliary files necessary for the analysis. Your task is

1. to determine the concentration of the NO_2 in the cell
2. to determine the NO_2 slant column in the boundary layer as a function of viewing angle
3. to identify a trace gas in one given set of simulated atmospheric spectra and compare the derived vertical trace gas column with satellite measurements (e.g. from GOME-2 or OMI) found in the literature or the internet

A detailed description of the data evaluation will be provided in the 2nd document.

4.3 Special precautions

- The NO_2 cell used in the absorption measurements is made of quartz glass and can break if not handled with care. Please use it carefully. If the cell breaks, leave it alone and get away. If it breaks indoors, leave the room immediately. Alarm your supervisor. **Nitrogen oxides are extremely harmful to human health.**

- The DOAS instrument is used for continuous monitoring of atmospheric constitution. It should therefore never be switched off, reset or moved by you. If any change in the instrument is necessary, the supervisor will take care of it.

- After your experiment, the instrument should be reset to run in automatic measuring mode to ensure continuous data sets. Please ask the supervisor for support.

- The DOAS lab is air conditioned. **Do not open the window and avoid keeping the door open.**

4.4 Prerequisites

For the DOAS practical, in addition to the usual things such as paper and a pocket calculator you will need the following items:

- a USB stick
- a coat (you need to go outside even if it rains)
- it is mandatory to do the practical at least twosome

5 Questions for the preparation

1. What are the basics of stratospheric and tropospheric ozone chemistry? What's the role of NO_2 in this context?
2. What are the main sources of nitrogen oxides in the atmosphere?
3. What is ozone depletion, what is ozone smog?
4. What is the magnitude of ozone columns to be expected in Bremen throughout the year?
5. What mixing ratios do you expect for O_3 and NO_2 in the troposphere in Bremen?
6. What is the basic principle of a grating spectrometer? How is the spectral resolution determined?
7. What is the principle of a light fibre?
8. What are Fraunhofer lines?

9. Why do absorption spectra of molecules show structures in the UV/visible wavelength range?
10. What is a "fitting window"? How is this selected?
11. How does the DOAS algorithm differentiate between extinction by scattering and absorption by molecules?
12. Do you need to know the absolute intensities of the measurements for the DOAS analysis? Why?
13. Is the zenith-sky viewing DOAS instrument sensitive towards absorption in the troposphere? Why?
14. What is the schematic light path for horizon observations?
15. What is the basic quantity we get with the DOAS method?
16. What is the purpose of the "dark measurement"?
17. Why is calibration important in this process?
18. What is an airmass factor?
19. What is a vertical column?