Master Thesis

Characterization of a Miniaturized DOAS Instrument for Automobile Applications

Submitted by:

Mohammad Ikramul Haque Matr. No.-2589996 Date of Birth-02.01.1987 15th of July, 2014

1st Examiner : Prof. Dr. John. P. Burrows
 2nd Examiner : Dr. Annette Ladstätter-Weißenmayer
 Supervisor : Dr. Andreas Richter

Postgraduate Program in Environmental Physics (PEP) Institute of Environmental Physics (IUP) University of Bremen Universität Bremen



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Abstract

Nitrogen dioxide is one of the most important pollutants which is emitted from cars and power generation. It is involved in photochemical ozone smog formation, acid rain, and also global warming. Anthropogenic pollution in the troposphere affects most large cities, both in the industrialized and the developing world. Measurements of NO₂ can be performed by different methods. The Differential Optical Absorption Spectroscopy (DOAS) is a well-known method based on absorption spectroscopy of scattered sun-light using observations under different elevation angles in the atmosphere. For better characterization of the NO₂ distribution, measurements should be taken in different places and at high frequency.

A small and battery powered spectrometer such as the Avantes spectrometer (AvaSpec-ULS2048x16-USB2) is needed for taking measurements from mobile platforms. It is important to know the properties and the performance of the instrument well for DOAS applications; aside the information's given by the manufacturers. In this Master Thesis work, an AvaSpec-instrument is characterized for dark signal, noise, and non-linearity as well as temporal stability. The calibration procedures have been done in the laboratory at IUP-Bremen. The spectrometer was then used for taking atmospheric measurements which were compared to results from a standard MAX-DOAS instrument and very good agreement was found.

In my Master Thesis paper, I described the scientific background and the first phase of the work done with the Avantes instrument in laboratory as well outside of the laboratory to check the performance and stability of this instrument. The Avantes instrument was also used for taking some test measurements within and around city of Bremen including power plants from a car and from a bicycle.

Chapter 1: Introduction

In the atmosphere, nitrogen Dioxide (NO₂) is an important trace gas but it is also an important constituent of air pollution. It plays an important role in the chemistry of the atmosphere. The oxides of N (NO, NO₂), have an important role in atmospheric chemistry in the determination of earth's ozone distribution. In my Master thesis paper, I have discussed about the sources and sinks for NO₂ in the atmosphere with some short details on NOx health effects. I have presented a short introduction to DOAS (Differential Optical Absorption Spectroscopy) which is now one of the most commonly used spectroscopic methods to measure atmospheric trace gases.

In my work, I have used a new DOAS instrument (AvaSpec-ULS2048x64) with a wavelength range of 300 - 550 nm and plan to operate it on a car. The reasons to choose this instrument are its small size, robustness, light weight (850 grams) and relatively low price. Afterwards some general information about car MAX-DOAS, its advantages and disadvantages are described. I have also included some work and results from earlier studies using car MAX-DOAS instruments. The new instrument has been characterized first and tested. Dark measurements have been taken in different conditions e.g. dark signal as a function of exposure time on different days, dark signal temperature dependence at constant exposure time. Dark signal shows some variations with time and temperature. Then line lamp measurements were done to determine the changes in spectral calibration in response to temperature change and have found temperature dependence of spectral calibration is small. Slit function is Gaussian, stable with temperature and nearly constant with wavelength. Afterwards, linearity measurements were taken to investigate the size and behaviour of non-linearity of the instrument by investigating the ratio of measurements at different exposure time. A clear non-linearity was found but this can be corrected. Then comparison between the large DOAS instrument and Avantes was done. For NO₂ columns, the agreement between the large (and expensive) MAX-DOAS instrument and the Avantes instrument was found well up to 92° SZA.

Finally, the Avantes instrument was used for taking some test measurements within and around city of Bremen including power plants from a car and from a bicycle. Some variability of NO_2 was observed but more measurements will be needed to better characterize the pollution levels in Bremen.

Overall, the results what I have found are very satisfactory and also it can be said that the Avantes instrument is suitable and performs adequately in the characterization. This instrument also shows very good agreement with the regular DOAS instrument result and performed well during measurements from mobile platforms. Indeed it might be interesting and is considered as a possible activity for the future measurements for other trace gases (e.g. SO_2 etc.) with this Avantes spectrometer.

Chapter 2: Nitrogen Oxides in the Atmosphere

2.1 Nitrogen Oxides in Troposphere

The atmosphere that surrounds the Earth's surface is a mixture of gases and suspended particles. The Earth's atmosphere has a vital role in absorbing harmful radiation coming from the Sun and it consists of different regions, the lowest of which is up to 10-15 km and called Troposphere. It contains around 75% of the atmosphere's mass. The following Figure 1.1 shows the temperature profile in different regions of the Earth's atmosphere. In the Troposphere, air masses are well mixed and temperature decreases with altitude. This happens primarily because Earth's atmosphere is heated upward from the lowest level (earth surface). This is the case although the sun light comes from the top to the bottom of the atmosphere. The reason is that the troposphere's gases absorb very little of the incoming solar radiation. Instead, the earth ground absorbs this radiation more and then warms up the tropospheric air by conduction and convection. Since this heating is most effective near the ground, the temperature in the troposphere gradually decreases with increasing altitude until the tropopause is reached.

The atmospheric gas commonly used in breathing and photosynthesis is air. By volume, dry air contains about 78.09% nitrogen, 20.95% oxygen, 0.93% argon, 0.039% carbon dioxide and small amounts of other gases (called traces gases). The most important forms of reactive nitrogen (78.09%) in the air are nitrogen dioxide (NO₂) and nitrogen monoxide (NO). Together, NO and NO₂ are referred to as NOx. These highly reactive gases are mainly formed from the breakdown of nitrogen molecules (N₂). Very high temperature is needed to break the bond of the nitrogen atoms in NO. Also a few bacteria have developed special mechanisms to do this.



Figure 2.1: Vertical profile in average global atmospheric temperature with different altitude. Variations are due to changes in the chemical and physical characteristics of the atmosphere with altitude (source: http://www.physicalgeography.net/fundamentals/7b.html).

The oxides of N (NO, NO₂), have an important role in atmospheric chemistry in the determination of earth's ozone distribution. Mainly nitric oxides are formed by the oxidation of nitrous oxide (N₂O) in the stratosphere. Nitrogen dioxide is a strong oxidizing agent which reacts in the air to form nitric acid, as well as toxic organic nitrates (Wayne R.P.; 2000).

In the atmosphere, NO and NO₂ are rapidly converted into each other and are therefore combined to NO_x. The ratio [NO] / [NO_x] is about 0.2 at the surface but increases towards higher altitudes (red line in Figure 1.2). Close to the surface the atmospheric lifetime of NO_x is short (some hours) but at higher altitudes lifetime is a few days (blue line). Lifetime changes with seasonal variation as for NOx, it is longer in winter than in summer because of lower [OH] in the atmosphere. The short lifetime results in little transport, both vertically and horizontally, at least in the form of $NO_{x.}$



Figure 2.2: Atmospheric lifetime and distribution of NOx in the Troposphere (Ehhalt D.H. et al., 1992).

2.2 Sources and Sinks of Nitrogen Oxides

The sources of nitrogen oxides in the troposphere are both natural and anthropogenic processes. Fossil fuel combustion, biomass burning and lightning constitute major sources. Lightning storms, emission from soils by microbes in nitrification and de-nitrification processes, are the natural sources of NOx in the atmosphere. Natural sources of nitrogen oxides produce globally 15 - 31 million tons of nitrogen fixed as NOx per year (Platt and Stutz; 2007). Aircraft emissions and stratospheric input are also to be considered as small sources of nitrogen oxides.

<u>**Table-2.1**</u>: Different sources of NOx and their uncertainties in tons of fixed nitrogen dioxides per year in the atmosphere and contribution to global emission in percentage terms. Numbers in brackets are the range of different estimates (Delmas et al.; 1997).

NOx Sources	x Sources Magnitude (TgN/yr)						
Surface sources							
Fossil fuel combustion	22(15-29)	100% anthropogenic					
Biomass burning	6.7(3-10.4)	95% anthropogenic					
Biogenic soil emission	5.5(3.3-7.7)	40% anthropogenic					
Tropospheric sources							
Lightning	2(1-4)	Natural					
Stratospheric injection	0.5(0.4-0.6)	10% anthropogenic					
Aircrafts	0.55(0.5-0.6)	100% anthropogenic					
Ammonia oxidation	1.0(0.5-1.5)	60% anthropogenic					



As stated above, the emission of NOx has both natural and anthropogenic causes. The largest emissions are in cities and from power plants. The US Environmental Protection Agency (EPA) has derived air quality trends for NO_2 , using a nationwide network of monitoring sites. Since 1980, the average NO_2 concentrations in the US have decreased substantially over the years.

Reductions in NO_2 are explained by the fact that the emission rate of NOx in the US, Europe and Japan is decreasing. The main reasons are that these countries have switched from coal and oil to natural gas use and have started use of catalytic converters. In tropical regions and industrial areas, the NOx emission rate is more or less constant. The rate is increasing in developing

countries mainly in Asia because of rapid economic growth. Most megacities in China, India, and the Middle East show increasing NO₂ columns of +5 to 10 % yr⁻¹ (Hilboll et al., 2013). In addition, heavy industries have been shifted to developing countries from developed countries. Satellite data show that NO_x emissions from China increased by 13% in between 1994 - 2000 (Richter et al., 2005). The main reasons for the growth of anthropogenic NOx emissions in China are increasing power consumption, traffic, and industrial and domestic heating sources.



Figure 2.3: Air Quality in selected cities in the US. (source: http://www.epa.gov/airtrends/nitrogen.html)

The main sink for NOx gases is oxidation in the atmosphere. Significant amounts of NOx arising from soil can also be used up in the tree canopy before they escape to the troposphere. Another pathway for NOx in the atmosphere is dry deposition back to the land. Nitric acid (HNO_3) is an important sink of NOx which is rained out from the atmosphere to the surface and is incidentally a component of acid rain.

2.3 Global Distribution of NO₂

Measurements from the Global Ozone Monitoring Experiment (GOME) have been analyzed for tropospheric NO_2 using the Differential Optical Absorption method. The GOME instrument was

launched on the European ERS-2 satellite in April 1995 and has been operational since July of that year. The GOME is a grating pseudo double monochromator covering the spectral range of 240 to 790 nm (Burrows et al.; 1999). It has a spectral resolution of 0.2 - 0.4 nm with a ground-pixel size of 320 X 40 km². The GOME observes light scattered back from the atmosphere and reflected from the ground in near a nadir viewing geometry.



GOME-2b tropospheric NO₂ 2013

Figure 2.4: Tropospheric excess NO₂ over the world from GOME-2 for 2013.

From GOME measurements, NO_2 columns can be retrieved applying the DOAS method in the 425-450 nm regions. As an example, the Figure 2.2 shows tropospheric excess NO_2 from GOME-2 for 2013. From the overlook on the above figure, we can see that there is a strong enhancement of NO_2 columns over the industrialized parts of the world and in regions with large biomass burning and fossil fuel combustion. Strong emission of NO_x is found in the eastern part to China and northern Europe because of heavy traffic and increasing power consumption. There is also some indication of NO_2 from lightning over Africa and Australia and for transport from the US, Asia and Africa to the Oceans. It should, however, be considered that the natural NOx sources are much more equally distributed over the surface of the earth than the anthropogenic sources.

The Ozone Monitoring Instrument (OMI) project is a co-operation between the Netherlands Agency for Aerospace Programmes (NIVR), the Finnish Meteorological Institute (FMI) and the National Aeronautics and Space Agency (NASA) (http://www.nasa.gov). It is a nadir-viewing wide-field-imaging spectrometer giving daily global coverage. OMI has the smallest pixel size of all satellite instruments so far (13 x 24 km² in nadir) but still the pixels are larger than a city like Bremen. Therefore, validation at one point is difficult as a local measurement cannot be compared directly to an integrated measurement. This is the reason why it makes sense to put sensors on cars – to get the spatial distribution of NO₂ locally but also at the scale for satellite pixels.



Figure 2.5: Zoomed picture of Germany from OMI satellite image for tropospheric NO_2 which shows a good spatial resolution.

2.4 Chemistry of Nitrogen Oxides

Nitrogen oxides react with OH to form nitric acid (HNO_3), which is a major contributor to acid rain. HNO_3 can be formed in several ways and its deposition is one of the main sinks of nitrogen oxides (Wayne R. P.; 2000).

$$NO_2 + OH + M \rightarrow HONO_2 + M$$
 (2.1)

$$N_2O_{5(g)} + H_2O_{(g,l)} \rightarrow 2HNO_{3(g,aq)}$$
(2.2)

$$NO_{3(aq)} + H_2O_{(I)} \longrightarrow HNO_{3(aq)} + OH_{(aq)}$$
(2.3)

$$NO_3 + RH \rightarrow HNO_{3(g)} + R$$
 (2.4)

In the upper troposphere, HNO_3 is recycled back to NOx by the reaction with OH or by photolysis. In the troposphere, NOx reacts with volatile organic compounds (VOC's) and carbon monoxide, to produce ground level O_3 . The global transport of NOx that occurs in the atmosphere is shown in figure 2.6. Peroxyacetyl nitrate (CH₃C(O)OONO₂) [PAN] is produced by the photo oxidation of hydrocarbons in the presence of NOx.



Figure 2.6: Transport of NOx, HNO_3 and $CH_3C(O)OONO_2$ (PAN) from urban centers to the clean troposphere. PAN has a long lifetime in the middle and upper troposphere and may deliver NOx in the warmer lower troposphere at large distances from the urban centers in which PAN has initially formed (Crutzen P. J.; 1979).

2.5 Nitrogen Oxides in The Background Atmosphere

Photolysis of NO_2 is the only known way to produce O_3 in the troposphere. Tropospheric ozone is primarily produced through the photolysis of NO_2 at wavelengths less than 430 nm. The concentration of tropospheric ozone in the presence of nitrogen oxides can be determined by the equation named the Leighton relationship.

$$NO_2 + hv (\lambda < 240 \text{ nm}) \rightarrow NO + O (^{3}P)$$
(2.5)

$$O(^{3}P) + O_{2} + M \rightarrow O_{3} + M$$
 (2.6)

$$NO + O_3 \rightarrow NO_2 + O_2$$
 (2.7)

$$\frac{[O_3][NO_2]}{[NO]} = \frac{[J_{NO2}]}{[K_{O3+NO}]}$$
(2.8)

The above Leighton relationship, named after Philip Leighton, shows how production of ozone is directly related to the solar intensity. In general, the Leighton relationship is expected to hold when reactions (2.5) and (2.6) are the major loss processes for NO_2 and O_3 (Finlayson-Pitts B.J.; 2000).

2.6 NOx in The Polluted Troposphere

About half of the ozone is supplied to the troposphere by transport from the stratosphere; the other half is formed photochemically. In the presence of nitric oxide and nitrogen dioxide, the oxidation of carbon monoxide (CO) is the simplest scheme of ozone formation in the troposphere. The following reactions take place in the atmosphere (Crutzen P.J; 1979).

$$CO + OH \rightarrow H + CO_2$$
 (2.9)

$$H + O_2 + M \rightarrow HO_2 + M$$
(2.10)

$$HO_2 + NO \rightarrow HO + NO_2$$
 (2.11)

 $NO_2 + hv \rightarrow NO + O$ (2.12)

 $O + O_2 + M \rightarrow O_3 + M$ (2.13)

Net:
$$CO + 2O_2 \rightarrow CO_2 + O_3$$
 (2.14)

If NO is oxidized to NO₂ by HO₂ or RO₂ instead of ozone, O₃ is catalytically formed by NO. However the amounts of CO, CH₄ and other hydrocarbons have also an impact on how much O₃ can be formed in the presence of NOx. If NOx has very high concentration, O₃ levels are reduced by reaction with NO and NO₂ in particular at night (titration).

The following schematic (Figure 2.7) shows the gas-phase O_3 chemistry in the troposphere emphasizing the coupling between the cycles of O_3 , HOx, and NOx. Ozone is supplied to the troposphere by transport from the stratosphere, is removed by deposition to the surface, and is produced and consumed chemically within the troposphere. Chemical production and loss are the dominant terms in most of the troposphere.



Figure 2.7: Schematic of tropospheric O_3 chemistry illustrating the coupling between the chemical cycles of ozone, HO*x* and NO*x*. RO₂ refers to the ensemble of organic peroxy radicals (Jacob, D.; 2000).

2.7 Environmental Effects of NOx

The increase of NO_2 in the atmosphere can have long lasting direct or indirect effects on living beings and also on the environment. NO_2 can enter into our bodies through the skin and by inhalation. It can damage capillaries and increase risk of inflammation, which is much like sunburn on the skin. NO_2 can create other problems like headache, coughing and pain when taking deep breaths. It is also more harmful for asthma patients. Long inhalation of NO_2 may cause bronchitis (EPA-2013).

Reaction of NO_2 with OH creates HNO_3 which is easily dissolved in droplets and together with H_2SO_4 leads to acid rain. Because of the acid rain there is a decrease in the pH value of water i.e. ground and surface water on the Earth. This acidification of ground and surface water leads to harmful effects on ecosystems. Acid rain can also damage and reduce the longevity of structures and buildings. In fact there are also several environmental effects that can be more risky due to the presence of NO_2 or NOx in the atmosphere. It can reduce forest growth and crop yields and potentially impact on the diversity of our ecosystems (EPA-2013).

In addition, there are three climate effects of NOx:

- a) Direct warming through light absorption by NO_2 .
- b) Indirect effects through the formation of O₃ which is a greenhouse gas.
- c) Indirect influence on the OH concentration which determines the lifetime of greenhouse gases like methane (CH₄).

Chapter 3: Differential Optical Absorption Spectroscopy*

Absorption spectroscopy is a well-established tool for the analysis of the chemical composition of the atmosphere. DOAS (Differential Optical Absorption Spectroscopy) is now one of the most commonly used spectroscopic methods to measure atmospheric trace gases.

DOAS is the process where trace-species concentrations are derived from measurements of electromagnetic radiation. These measurements are observed at limited spectral intervals so that we can separate different trace species. DOAS measurements are based on absorption spectroscopy in the UV and visible spectral ranges. Spectroscopic NO_2 measurements were made as early as 1973. The first analysis of scattered light measurements was performed by Noxon (1975) in the field of differential optical absorption spectroscopy. The name DOAS was first used by Platt and Stutz (2008).

3.1 Principle of DOAS

When the solar radiation passes through the atmosphere, some part of energy is absorbed by the atmosphere. The different molecules in the atmosphere absorb radiation of different wavelengths. By observing on the absorption spectrum, we can extract information about the abundance of different species in the atmosphere.

The following scheme in Figure 3.1 shows an experimental set up to measure trace gas absorptions in the open atmosphere with an active DOAS system. From a suitable spectral broadband source light is emitted and passes through a volume with absorbers (here open atmosphere) with an intensity $I_0(\lambda)$. There is a detector at the end of the light path to collect the reduced intensity I (λ). As we know if light travels through the atmosphere, absorption happens due to specific trace gases and the intensity of light reduces. However, it also undergoes extinction because of absorption by other trace gases and scattering by air molecules and aerosol particles in the atmosphere. The transmissivity of the instrument (mirrors, grating, retroreflectors etc.) might also influences to reduce the intensity of light as the light beam being

^{*}This chapter is based on the book 'Differential Optical Absorption Spectroscopy' by Platt, U., Stutz, J. and Measurements Techniques notes by Richter, A.

widened by turbulence. By expanding Beer -Lambert's law and considering the respective components that have an influence on the light intensity by an equation which contains variables like the absorption of different trace gases with concentration c_j and absorption cross-sections $\sigma_j(\lambda)$, Rayleigh and Mie extinction, $\sigma_e^{Rayleigh}(\lambda)$ and $\sigma_e^{Mie}(\lambda)$ respectively.



Figure 3.1: Sketch of an experiment to measure trace gas absorptions in the open Atmosphere (Adapted from U. Platt and J. Stutz).

As mentioned earlier, the absorption phenomenon can also be explained by the well-known Beer -Lambert's law, which is used in the DOAS technique. Light travelling through the atmosphere is partly absorbed by trace species along the way following Lambert Beer's law of absorption:

$$I(\lambda, l) = I_o \exp(-\sigma(\lambda)\rho l)$$
(3.1)

Where I_0 is the initial intensity, I (λ , s) is the measured intensity, $\sigma(\lambda)$ is the absorption cross section of the substance, ρ is the number density of the absorber in the medium and I is the path length.



Figure 3.2: Sketch explanation of Lambert Beer's law. (http://www.doas-bremen.de/doas_tutorial.htm).

In the atmosphere solar radiation can be deflected by the molecules or particles. This deflection of radiation is called scattering. Mie scattering is an important type of scattering in the atmosphere. It is an analytical solution of Maxwell's equations. Mie scattering or Mie theory is named after its developer German physicist Gustav Mie. This is elastic scattering because the wavelength (λ) of incoming radiation does not change but the only thing varied is the angular distribution. This type of scattering happens in the atmosphere due to the presence of some particles like aerosols, dust etc. We can also say that Mie scattering is dominant when the size of the particle is greater than the wavelength of a radiation. It produces white glare. The crosssection in Mie scattering is proportional to σ_s^{Mie} (λ) ~ $\lambda^{-1} \rightarrow \lambda^{-1.5}$. Figure 3.3 shows Mie scattering and some of its properties.

The most dominant part of atmospheric scattering is Rayleigh scattering. The Rayleigh scattering is the scattering of light by particles which are small compared with the wavelength of the light. The phenomenon is named after the English physicist Lord Rayleigh. Because of the presence of gas molecules in the atmosphere this type of scattering occurs. In Rayleigh scattering the wavelength (λ) of incoming radiation does not change but only the angular distribution change. The results of Rayleigh scattering in the atmosphere are blueness of sky and haze in photography. The cross-section in Rayleigh scattering is proportional to $\sigma_s^{Rayleigh}$ (λ) ~ λ^{-4} . If the scattering angle is θ , then the intensity of scattered radiation is proportional to (1+cos2 θ). It depends strongly on the polarizability of the molecules. In Rayleigh scattering, there is more forward and backward scattering as shown in the Figure 3.3.



Figure 3.3: Mie scattering & Rayleigh scattering description (Source: www.hyperphysics.phy-astr.gsu.edu (modified)).

In the atmosphere, radiation can undergo numerous processes like absorption and scattering. In DOAS only those signals are analyzed that are changing rapidly with wavelengths. This is expressed by the term 'differential' in DOAS. This method can be applied from different platforms. We can investigate different species simultaneously. From DOAS, target species that can be retrieved are H_2O , HONO, HCHO, CHOCHO, O_3 , NO_2 , NO_3 , BrO etc. Some differential absorption cross-sections are shown in the following Figure 3.4.



Figure 3.4: Differential absorption cross-sections of different species (source: Richter. A.; measurement techniques, 2006)

3.2 DOAS Equations

In principle, it is important to measure all other factors that affect the light intensity before the determination of the concentration of a particular trace gas. In the laboratory if we just remove the absorber from the light path, we will get the value of concentration for the trace gas. However, in the atmosphere this is impossible. Because multiple factors are present in the atmosphere that have an influence on the intensity of light and create a dilemma. Differential optical absorption spectroscopy (DOAS) overcomes this challenge by using the fact that the effect of turbulence and many trace gas absorptions show very broad or even smooth spectral characteristics (Platt et al.; 2007). Even so, there are some trace gases which show narrowband absorption structures. The principal of DOAS is thus to separate the broadband and narrowband spectral structures in an absorption spectrum so that these narrow trace gas absorptions can be separated. Then the broad spectrum is used as a new intensity spectrum and the Beer-Lambert's law can be applied again to the narrowband trace gas absorptions.

As stated before, in the atmosphere many absorbing trace species are present that are not homogeneously distributed along the path length. The modified form of Lambert's Beer Law for such a case is given as follows:

$$I(\lambda) = I_o(\lambda) \exp(-\int \sum \sigma_i(\lambda) l dl)$$
(3.2)

The basic idea of DOAS analysis is to identify absorbers using characteristic variations in their absorption cross-section. The measured quantity is the zenith-sky brightness $I(\lambda)$ at different solar zenith angles θ . In the data analysis, the abundance of the absorber along the light path is determined with the differential spectroscopy method. The next step is to compute of the average light path with a radiative transfer model. Lambert-Beer's law is used for finding the slant column, accounting for the extinction by molecular absorption of different trace species, Mie and Raleigh scattering. Now by approximating both types of scattering, we have to include their cross-sections i.e. $\sigma_s^{Rayleigh}$, σ_s^{Mie} into the equation 3.2. After that putting the contribution of Rayleigh scattering and Mie scattering, we get the following equation 3.3:

$$I(\lambda,\theta) = \boldsymbol{a} \ (\lambda,\theta) \ \boldsymbol{I}_{\boldsymbol{o}}(\lambda) \ \exp(-\int \left(\sum_{i} \boldsymbol{\sigma}_{i} \ (\lambda) \boldsymbol{\rho}_{i}(l) + \boldsymbol{\sigma}_{s}^{Rayleigh}(\lambda) \boldsymbol{\rho}_{Ray}(l) + \boldsymbol{\sigma}_{s}^{Mie}(\lambda) \boldsymbol{\rho}_{Mie}(l) dl\right)$$
(3.3)

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Here $\mathbf{a}(\lambda, \theta)$ represents the scattering efficiency. If the variation of absorption cross-section is not significant along the light path then we can introduce the integral of the absorber column which called Slant Column Density (SCD) as shown below:

$$SCD = \int \rho(l) dl$$

Therefore, using slant column density in equation 3.3, we find the following relation:

$$I(\lambda, \theta) = \boldsymbol{a} \ (\lambda, \theta) \ \boldsymbol{I}_{\boldsymbol{o}}(\lambda) \ \exp[-\sum_{i} \boldsymbol{\sigma}_{i} \ SCD + \ \boldsymbol{\sigma}_{s}^{Rayleigh}(\lambda) SCD_{Ray} + \boldsymbol{\sigma}_{s}^{Mie}(\lambda) SCD_{Mie}]$$
(3.4)

The cross section of absorbing species has two components, one changing slowly with the wavelength (combined with Rayleigh and Mie scattering and approximated with a low order polynomial) and the other one varies rapidly.

$$I(\lambda,\theta) = a(\lambda,\theta) I_{o}(\lambda) \exp[-\sum_{i} \sigma'_{i}(\lambda) SCD_{i} + \sum_{p} b_{p} \lambda^{p}]$$
(3.5)

In equation 3.5, $\sigma'(\lambda)$ is the rapidly varying part of the cross section of absorbing species. Finally, the logarithm is taken and $\ln a(\lambda, \theta)$ included in the polynomial. The result is a linear equation between the optical depth, a polynomial and the slant columns of the absorbers (Richter A.; 2006).

$$ln(\frac{I(\lambda,\theta)}{I_o(\lambda)}) = -\sum_{j=1}^{J} \sigma'_j(\lambda) SCD_j + \sum_p b_p^* \lambda^p]$$
(3.6)

Where, $I_o(\lambda)$ is the reference measurement, $I(\lambda, \theta)$ is the intensity with absorption and $\sigma'_j(\lambda)$ are the different measured differential absorption cross-sections. Finally this equation is solved for many wavelengths in a linear least squares analysis with the slant column densities SCD_j and the polynomial coefficients b_p^* as parameters.

The DOAS algorithm is useful to retrieve column densities of various trace gases. In order to derive vertical column densities from the measured slant column densities using DOAS, the Air Mass Factor (AMF) has to be determined which depends on solar zenith angle, geometry, absorber altitude and wavelength.

3.3 Zenith-sky and Off-axis Measurements

The most common DOAS geometry is a ground-based instrument, which is pointed at the zenith sky. The effective path along which the light travels is determined by the solar zenith angle (SZA). During sunrise and sunset, the path length in the stratosphere varies by an order of magnitude. The reference spectrum is usually obtained around noon for solar zenith angles less than 80° and the retrieval is performed on spectra obtained at larger solar zenith angles, typically $88-95^{\circ}$ (Solomon et al.; 1987). These observations have the highest sensitivity for stratospheric absorbers. For measurements of tropospheric species, the zenith-sky geometry provides low sensitivity and therefore usually is employed to provide the background measurement.

During off-axis measurements, lights scatter from the source are measured to the horizon direction not to the zenith. These measurements were first used in stratospheric research, but now-s-days mainly using for tropospheric measurements. The basic idea is that the viewing directions have a very long light path in the lowest tropospheric layers with small elevation angles whilst the light path in the upper troposphere and stratosphere does not depend strongly on the viewing direction.

3.4 MAX-DOAS

From Multi-Axis- Differential Optical Absorption Spectroscopy (MAX-DOAS) observations, we can get information on tropospheric trace gases close to the surface and up to the free troposphere. Normally, MAX-DOAS observations are performed at fixed locations; however, they can also be performed from mobile platforms like cars, aircrafts or ships. The diurnal variation of tropospheric species can be retrieved from MAX-DOAS observations at a fixed location. Then, in addition to the vertical (and temporal) distribution, also the horizontal variation of tropospheric trace gases can be measured. Such information is important for the quantitative comparison with model simulations, the study of transport processes, and for the validation of tropospheric trace gas products from satellite observations (Wagner et al.; 2010).

Multi axis Differential Optical Absorption Spectroscopy (MAX-DOAS) uses measurements in the zenith and in several viewing directions close to the horizon. It separates tropospheric and stratospheric absorptions and can be used to retrieve profiles in the lower troposphere. The measurements are either taken sequentially by rotating the whole telescope or by using a mirror or simultaneously by employing an imaging spectrometer and an imaging telescope or an array of small telescopes pointing in different directions.

The MAX-DOAS instrument uses the horizon viewing measurement directions for tropospheric observations. As shown in Figure 3.2, the light path through the upper atmosphere (dark blue, above the scattering point) does not depend on viewing direction, while in the lowest atmospheric layers, the light path (red) increases as the viewing direction approaches the horizon.



Figure 3.5: Tropospheric observations at different layers with different light paths. (http://www.doas-bremen.de/maxdoas_instrument.htm).

The light path's length in the lowest layer depends on geometry (the elevation angle used) but also on the mean free path of the photons. In the above Figure 3.2, the dotted line indicates the scattering point on the circle. When the scattering point is above the surface layer then by using geometry the light path can be determined. An important boundary condition for the interpretation of the measurements is the assumption, that horizontal gradients can be neglected. In real measurements, this is not always the case and results can become uncertain with respect to a signal variation, which might be because of vertical or horizontal changes.

The tropospheric column is often important for satellite validation. It can be determined either by integrating the retrieved profile or by using a viewing direction of 30° or 45° elevation where the last scattering point is almost always above the layer with high concentrations.

3.4.1 Instrumental Design

To optimize the instrumental design certain features were taken into consideration in the choice of type of instrument. DOAS measurements are done in the ultraviolet / visible (UV / Vis) spectral regions and grating instruments are ideal for this region. Spectrometer, Quartz fibre, CCD detector, telescope etc. are the main components of a DOAS instrument. In Figure 3.5, a schematic of the instrumental set up of Bremen Max-DOAS is shown.



Figure 3.5: Schematic features of the instrumental set-up of Bremen MAX-DOAS instrument (source: Richter, A., 2006)

A spectrometer is an optical instrument that is used in spectroscopic analysis to measure light intensity of electromagnetic spectrum as a function of wavelength. Its vast use in spectroscopy makes it an important instrument for investigation of electromagnetic spectrum. The Czerny-Turner type grating spectrometer used in Bremen MAX-DOAS instruments is composed of two convex mirrors to create parallel light and to focus the outgoing radiation and a plane diffraction grating which is used as the dispersive element. In the spectrometer there is an entrance slit and an optical fibre that can be attached there. The light entered into spectrometer via optical fibre through entrance slit and it is pointed at a collimating mirror. The purpose of the collimating mirror is to produce a parallel beam on the grating. This dispersed light is then transferred towards the focusing mirror. The mirror focuses this radiation towards the entrance of the CCD detector.



Figure 3.6: Regular MAX-DOAS instrument in DOAS laboratory, IUP, Bremen.

Detectors are a key area of consideration. The qualification for this has almost always being linked to low noise and high sensitivity. CCDs (Charged Coupled Devices) are often used as detectors in DOAS instruments. The main advantages of these detectors are their very low dark signal, particularly when cooled. Another reason is the option to retrieve the 2-dimensional distribution of the intensity. Low dark signal facilitates measurements at low intensities and improves signal to noise.

In DOAS systems, telescopes are used for two purposes: to collect light from (natural or artificial light) sources and in active DOAS applications, to transmit a collimated beam of radiation from

the light source through the open atmosphere. The telescope, which collects the scattered light from the atmosphere, is sealed well to prevent contamination and condensation of water on the interior optics. Stainless steel is used to build the telescope body and sealed with UV-transmitting quartz windows (both zenith sky and horizon directions). It is designed in such a way to prevent water, snow etc. from accumulating in front of the telescope. Figure 3.7 shows the telescope mounted on the roof - top of IUP, Bremen with closed and opened door displaying the internal features.



Figure 3.7: Roof top mounted telescope at IUP, Bremen.

3.5 Air Mass Factor

The calculation of path average trace gas concentrations from slant column density measurements using direct sunlight or active DOAS arrangements is straightforward. For analyzing and interpreting of DOAS measurements using scattered sunlight, where the radiation can travel along multiple paths, it is important to describe the radiative transfer in the atmosphere accurately, because the radiation can travel along multiple paths (Rozanov et al.; 2002).

The concept of air mass factors has been used for interpreting zenith scattered light DOAS observations for many years (e.g. Solomon et al.; 1987; Perliski and Solomon, 1993). The air mass factor (AMF) establishes the relation between the slant column (SC) and vertical column (VC).

$$AMF = SC/VC \tag{3.7}$$

The vertical column is defined as the absorber amount, which is integrated vertically through the atmosphere.

$$VC_{j} = \int \rho_{j}(z) dz$$
(3.8)

The AMF depends on a variety of parameters such as geometry (viewing geometry of the detection system), wavelength, vertical distribution of the species and boundary conditions such as surface albedo and clouds. The AMF strongly increases with solar zenith angle (SZA) for ground-based, airborne and satellite measurements.

4.1 MAX-DOAS Instruments

A typical MAX-DOAS (Multi-Axis Differential Optical Absorption Spectroscopy) instrument has a spectral resolution of 0.4 - 1.5 nm and a spectral range from 300 - 700 nm depending on target species. The Bremen MAX-DOAS instrument consists of a grating spectrometer equipped with a cooled CCD detector and a separate telescope unit connected to the main instrument via a quartz fiber bundle. Charged Coupled Devices (CCD) are often used as detectors in DOAS instruments. A disadvantage of CCD's are their relatively small full well capacity, which needs frequent read out of the detector and the long time it takes to read out the detector. In most DOAS instruments, a quartz fiber bundle is used to connect the spectrometer with the telescope. The reason for using quartz fiber is that light is efficiently depolarized when leaving the bundle; it also provides flexibility for instrument set-up. The spectrometer is temperature stabilized to avoid wavelength drifts. Although the CCD used is a 2-dimensional detector, it is operated in full vertical binning for optimal signal to noise.

4.2 Avantes Spectrometer

In this work, a different instrument (AvaSpec-ULS2048x64) is used. This instrument is small in size (175 x110 x 44 mm), robust, light weight (850 grams) and not too expensive. It does not need any external power supply, just an USB connector (450 mA) and is easy to move. However, it has no temperature stabilization and no cooling of the detector. Therefore, characterization is needed, and testing if good DOAS retrievals are possible with this instrument. Finally, it will be tested in a car for mobile measurements.



Figure 4.1: Avantes spectrometer AvaSpec-ULS2048x64 (A) and a set-up with a laptop before dark measurements have been taken at IUP, Bremen laboratory (B).

4.3 Avantes Technical Data

In the following Table 4.1, some technical information is given about AvaSpec-ULS2048x64 which is retrieved from http://www.avantes.com/products/spectrometers/sensline/item/817-avaspec-uls2048x64 on 16.12.2013.

Optical Bench	Symmetrical Czerny-Turner, 75 mm focal length
Wavelength range	300 – 550 nm
Resolution	0.65 nm
Stray light	< 0.3%
Sensitivity	250,000 counts/ μ W per ms int. time
Quantum efficiency @ peak	78% (600nm)
Detector	Back-thinned CCD image sensor 2048x16 pixels
Signal/Noise	450:1
AD converter	16 bit, 1.33 MHz

Table 4.1: Some technical data about AvaSpec-ULS2048x64 instrument.

A small and battery powered spectrometer (such as the Avantes AvaSpec-ULS2048x16-USB2) was used for taking calibration measurements. It is important to know well enough about the properties and the performances of the overall instrument aside the information's given by the manufacturers. In my work, an AvaSpec-instrument was characterized for dark signal, noise, slit function, and non-linearity as well as temporal stability. The details below give the results of the tests performed in the laboratory of the DOAS group within IUP, Bremen. Three different measurements were carried out during the calibration measurements of this work as described in the following sections namely: dark signal, line lamp measurements (temperature dependence of spectral calibration, slit function) and linearity measurements respectively.

5.1 Dark Signal Measurements

Dark measurements are used for characterizing the detector readout noise and dark current (leakage of charges into the pixel) as a function of integration time and detector temperature. In a dark signal measurement, the total signal observed in a measurement, is without light source. Some dark measurements have been taken using AvaSpec-ULS2048x64 spectrometer which has a back-thinned CCD image sensor 2048x64 pixels detector. Measurements at different exposure time starting from 0.005s to 5s have been recorded on four different days. The number of measurements was 500 for each exposure time.

5.1.1 Avantes Dark Signal

During the dark signal measurements, one head of the quartz fiber was connected to the Avantes spectrometer and the other head was kept closed with a cap. While taking dark signal measurement as function of exposure time, the room was air conditioned and had a constant temperature of around 18^{0} Celsius.

After taking measurements, dark signal as function of exposure time have been drawn as shown in figure 5.1. A straight line was fitted and observed that there was a little fluctuation at some points. The straight line, which we have found is linear as expected because dark signal has a dependence on exposure time. The fluctuation happens because of small temperature differences. From the result, we can say that this instrument has really smaller dark signals than other instruments. From the linear fit: $S_{dark}(\tau) = S_0 + \alpha . \tau$; where $\alpha = 678.68$ is the offset, $S_0 = 678$ counts / sec is the slope, $\tau = 0.005$ s to 4.995s is the exposure time.



Figure 5.1: Mean dark counts versus exposure time. The red line is the linear fit through the data.

Temperature and the difference (measurement - straight line) was plotted as shown in figure 5.2. In figure 5.2, it is observed that at the starting stage temperature increases and after some time it starts decreasing (below the starting temperature). From this plot, it can be seen that at the highest temperature we get the largest difference between measurement and straight line. At low temperature the difference is small. From this measurement, we can say that one should be aware about the instrument temperature. Because even a small variation in temperature can result in a visible change in dark signal. One important thing is that the temperature shown is taken somewhere in the instrument electronics, not at the CCD. The temperature of the instrument varied from 25.39 to 25.68° Celsius.



Figure 5.2: The difference between the measurement and a straight line. Also shown is the instrument temperature (green curve).

5.1.2 Dark Signal Reproducibility

The same measurement dark signal as function of exposure time was done on three different days (different color in plot indicates different days). In each case, a straight line was fitted to the data and it was observed that the lines are different (Figure 5.3). Each measurement set was found to behave linearly, but different slopes and offsets are found each day. We should take notice that it varies day to day and that's why we need daily dark measurements. These differences in lines are because of different instrument temperatures on each day. It should be noted that the absolute changes in dark signal are small at short integration times (< 1s) usually applied during DOAS measurements.



Figure 5.3: Mean dark counts versus exposure time on three different days (08th, 11th and 12th November, 2013).

5.1.3 Dark Signal Temperature Dependence

Then another measurement was taken, dark signal as a function of temperature while keeping fixed exposure time (3.2 seconds). As stated, this instrument does not have any temperature stabilizer. Therefore we want to see how it varies with temperature. This measurement was taken at IUP, Bremen roof top room by opening and closing the window in order to change the temperature.

In Figure 5.4, the dark signal as a function of temperature is shown. At the beginning, the temperature was around 23^{0} Celsius and then we started cooling the Avantes instrument by putting it outside the window. After 2 hours, when it was fully cooled, it was put back into the room and brought it to warm temperature by turning on the room heater. From Figure 5.4, we see that the cooling and heating line are not the same because while changing temperature, the part of the instrument where the temperature detector is located and the CCD do not change their temperature at the same time, creating a hysteresis. We observed an exponential curve with

rapidly increasing dark signal with increasing temperature as expected. The highest and lowest temperature recorded were 14.60° C and 31.06° C respectively. From the overlook on Figure 5.4, we see that dark signal can become large at high temperature. In a car, the temperature will be higher during summer and this will effect on our measurements. Hence we need to measure dark current after time to time.



Figure 5.4: Dark signal versus instrument temperature at an exposure time of 3.2 seconds.

5.2 Line Lamp Measurements

5.2.1 Temperature Dependence of Spectral Calibration

The line lamp measurement was taken in the DOAS lab, IUP, Bremen. This measurement was done to see the impact of temperature changes on the spectral calibration by measuring the change of emission line positions with temperature. During measurements integration time was 3.2 seconds. After measurements, some figures (see below, Figure 5.5) were plotted with peak position of the spectrum as a function of instrument temperature.



Figure 5.5: Schematic representation of the set-up for line lamp measurements with HgCd lamp in the laboratory of IUP, Bremen

In the following figures, the line lamp peak position as a function of temperature is shown. At the beginning, the temperature was around 26^{0} Celsius and then started cooling as the Avantes instrument was put outside the window. Around 2 hours later, when it was fully cooled, it was put back into the room and brought it to warm temperature by turning on the room heater. From Figure 5.7, we see that again the cooling and heating lines are not the same because the temperature changes in the instrument are not instantaneous and temperature measurement is not located directly at the CCD. During measurements, the spectrometer was moved from one place to another leading to small movements of the quartz fibre and that's why we get few points outside of the trend.



Figure 5.6: A HgCd lamp spectrum during line lamp measurements.

The highest and lowest temperatures recorded were around 13.80° C and 37.40° C respectively. From the overlook on Figure 5.7, we see that peak position does not vary too much (~0.6 pixels) with changing of temperature, which is a good output of the instrument.

Table 5.1:	List of some	peak r	ositions v	with their	overall ra	ange of s	shifts on Hg	gCd lamp	spectrum.
						<u> </u>			

Peak position (pixels)	Overall range of shift (pixels)
381	0.7
426	0.7
532	0.7
561	0.7
855	0.6
1093	0.4
1345	0.3
1442	0.3
1678	0.3
1998	0.3

In Figure 5.7, some plots have been drawn at different peak positions from 380 to 2000 pixels and how they change with increasing pixels as a function of temperature. It is observed that with increasing of peak positions, the amount of line shift with temperature changes and the values are listed in Table 5.1. The temperature induced changes at the left side of 1093 pixels spectrum, have prevalence around 0.7 pixels. The smaller change at the right side of the spectrum indicates that the spectrum is stretched rather than shifted by temperature changes.





Figure 5.7: Avantes line lamp measurement as a function of temperature at different peak positions.

5.2.2 Slit Function

The slit function is the instrument transmission with wavelength function. It is obtained by measuring the spectrum of a line lamp (HgCd lamp) with the spectrometer (AvaSpec-ULS2048x64) and choosing a line that is sharp and free from overlap with surrounding lines. For a particular spectrometer, it is important to know about the slit function before a convolution of cross sections. Convolution is a useful process because it describes precisely the effects that might occur in the spectrometer such as the shape of the spectrum. Here this slit function is needed to convolute the cross-section for the DOAS retrieval.

In this experiment, the spectrum of a HgCd emission line lamp was measured. Before starting the measurement, the HgCd lamp was switched on and allowed to warm up for around 5-10 minutes to become fully charged and have stable brightness. This measurement was done to determine the slit function of the Avantes instrument at different wavelengths and different temperatures. During the measurement, a teflon foil was used as a diffuser to get uniform illumination of the quartz fibre. The measurements were averaged over 100 measurements and an estimate of the dark signal was subtracted from the measurement. Interpolation was done to 1/100 of a detector pixels and the maximum of each interpolated line shifted to 0.

After taking the measurement, the normalized intensity as a function of pixels have been drawn as shown in Figure 5.8. Different color in the Figure 5.8 stands for measurements at different peak positions.



Figure 5.8: Spectrum of the HgCd lamp obtained on the chip of Avantes Spectrometer with slit width of 100 nm.

It has observed that the width of the spectrum increases with increasing pixels values. From Figure 5.8, we see that the full width half maximum is 5 - 6 pixels or 0.6 to 0.7 nm. Therefore, the spectrum is wider in one side and narrower on the other side. Each spectrometer has a little bit of this effect. Temperature might have also an influence of getting different shapes of spectrum.

<u>Table 5.2</u> :	List of some	peak positions	with their	FWHM	values	both in pixels	and nanometer	on HgCd
lamp spectru	um.							

Peak position	Values of FWHM	Values of FWHM
(pixels)	(pixels)	(nm)
426	5.1	0.658
856	5.3	0.683
1093	5.5	0.701
1444	5.7	0.734
1678	6.0	0.774
1998	6.4	0.826

The same measurement was done on three different emission lines and different peak positions 426 pixels, 1093 pixels and 1998 pixels respectively. During the measurement, temperature changed from around 14 ^oC to 37 ^oC. Therefore, at three different temperatures such as coldest temperature 14.32 ^oC, room temperature 25.37 ^oC and warmest temperature 37.15 ^oC, the analysis was repeated at 426, 1093 and 1998 pixels. Different color in plot indicates different temperatures. It was observed that there is a very small dependence on temperatures at different emission lines (Figure 5.8, Figure 5.9 and Figure 5.10). Each plot was found almost same, but different value of full width half maximum (increases with increases pixels).



Figure 5.9: Spectrum of the HgCd lamp obtained on the chip of Avantes Spectrometer at 426 pixels in three different (\sim 25°C, \sim 14 °C and \sim 37 °C) temperatures at 1 emission line.



Avantes slit function at 1093 pixels

Figure 5.10: Spectrum of the HgCd lamp obtained on the chip of Avantes Spectrometer at 1093 pixels in three different ($\sim 25^{\circ}$ C, $\sim 14^{\circ}$ C and $\sim 37^{\circ}$ C) temperatures at 1635 emission line.



Figure 5.11: Spectrum of the HgCd lamp obtained on the chip of Avantes Spectrometer at 1998 pixels in three different (~25°C,~14 °C and ~37 °C) temperatures at 3102 emission line.

The results show that the slit function looks like a Gaussian and is quite symmetric, with a little bit of an asymmetry on the right side of the spectrum. The FWHM (Full Wave Half Maximum) of the slit function of the instrument as we operate it is about 6 pixels and has a small dependence on wavelength (or position on the CCD). The FWHM shows nearly no change with temperature. Finally, these properties of the slit function make the Avantes instrument well suited for DOAS applications.

7.3 Linearity Measurements

The linearity measurements were done using a halogen lamp with the spectrometer (AvaSpec-ULS2048x64) in the DOAS lab, IUP, Bremen.



Figure 5.12: Schematic representation of the set-up for linearity measurements with Halogen lamp in the laboratory of IUP, Bremen.

In this experiment, the spectrum of a halogen lamp at different exposure times was measured, repeating a measurement at 0.2 s exposure time to check the stability of the measurements and the lamp output. Then the ratio of measurements taken at different exposure times was investigated. As we know CCDs (Charged Coupled Devices) which are often used as detectors in DOAS instruments for showing nonlinearities at large signals. The Avantes manufacturer reports such non-linearities (www.avantes.com). This experiment was done to investigate the size and behavior of the non-linearities and see how they can be corrected.



Figure 5.13: A Halogen lamp spectrum during linearity measurements.

Before starting the measurement, the halogen lamp was switched on and allowed to warm for about 10-15 minutes to become fully stable. The laboratory was kept dark and blocked of all possible external light sources. The position of the lamp was maintained fixed throughout the measurement to ensure nearly constant intensity. During the measurement, a Teflon foil was used as a diffuser to get uniform illumination of the quartz fibre. The measurements were averaged over 100 measurements and the dark signal was subtracted from the measurement. Exposure time was changed between 0.1 to 0.8 seconds, always repeating the 0.2 seconds before taking each new measurement to check for possible drifts in lamp or instrument. First, ratios of all 0.2 seconds measurements were taken to observe the stability of the instrument. Then ratios between measurements with varying exposure time (0.1s to 0.8 s) and the reference measurement (0.2 s) were taken to investigate the linearity. The measurements were performed at around 27 0 C instrument temperature.

No. of	Exposure time (s)		
measurements			
01.	0.2		
02.	0.1		
03.	0.2		
04.	0.3		
05.	0.2		
06.	0.4		
07.	0.2		
08.	0.5		
09.	0.2		
10.	0.6		
11.	0.2		
12.	0.7		
13.	0.2		
14.	0.8		
15.	0.2		

Table 5.3: Different measurements at different exposure time for lamp measurement.

After taking the measurements, the ratio of all 0.2 s measurements as a function of pixel number were plotted as shown in Figure 5.14. As mentioned earlier, for each measurement dark signal was subtracted. Different color lines in Figure 1 stand for measurements at different times. It was observed that the variation range is very low, around $\pm 1\%$, which is a good output of the instrument. Ideally the line should be straight at 1.0. But from Figure 5.14, we see that at the beginning, there is some noise and then lines go on as a straight line with a little bit tilt. The larger fluctuations at small pixel numbers are explained by the low output of the lamp at UV wavelengths. In Figure 5.14, the lines for different ratios are not the same. This might happen because of temperature variations. During the measurement, temperature was always changing which can have an effect on lamp output. As seen in the dark measurements (Chapter 5.1), temperature changes also affect the dark signal of the Avantes instrument. In summary we can

say that the stability of lamp and instrument over the measurement series were good with the exception of the shortest wavelengths.



Avantes lamp measurement

Figure 5.14: Lamp measurements with Avantes spectrometer for the ratio of 0.2 s measurements (see Table 5.3) with one lamp at different time as a function of pixels number.

The ratio of measurements taken at different exposure times (longer exposure time divided by shorter exposure time) as function of the intensity of the measurements is shown in Figure 5.15. The intensity range was limited to 10000 to 60000 counts to avoid the noise at small intensities in the UV. The ratio was divided by the ratio expected from the relation of the exposure times. Ideally, the output signal should be equal to the input signal multiplied by a proportionality constant i.e. Signal_(output) = C* Signal_(input). In Figure 7.15, we therefore expected a straight line which should go through 1. However, it is observed that there is a smooth deviation for each of the lines from the expected line. Different color lines in Figure 5.15 stand for different ratios of exposure times with reference exposure time (0.2s).



Figure 5.15: Linearity measurements with Avantes spectrometer for the ratios of 0.1 s to 0.8 s with 0.2 s exposure time as a function of intensity of the measurement having the longer exposure time.

From Figure 5.14, we can say that the stability of the measurements and lamp at 0.2 seconds exposure time is better than 1% over the full time series and probably better between individual measurements. In Figure 5.15, the ratios of measurements taken at different exposure times deviate from the expected values at larger intensities. As observed, the deviation is smooth and increases to larger intensities, the largest values being about 4% at 60000 counts. The result shows that the ratios are similar in all cases but increase as the difference in exposure times increases.

5.3.1 Correction Polynomial

Polynomial fits are used in DOAS applications for two purposes. First reason is- they remove the varying contribution of scattering to the extinction of the signal that can be approximated by a polynomial of low order. The second reason is by using a polynomial in the DOAS fit is the separation of low frequency and high frequency parts of the absorption cross sections. While this helps to separate different absorbers in the spectra. That's why I used polynomial and tried to fit

a polynomial to the ratio 0.8 / 0.2 seconds. The polynomial provides a correction factor for all measurements as a function of the measured intensity. Table 5.4 shows the values for the coefficients of the polynomial.

Table 5.4: Different values for the coefficients of the polynomial.

Ratios of	Coefficients of	Coefficients of	Coefficients of	Coefficients of
measurements	Х	\mathbf{X}^2	X ³	\mathbf{X}^{4}
0.8 / 0.2	-0.0112	0.0830	- 0.1609	1.0488

Then this linearity correction was applied to all measurements and then the same ratios were calculated as for Figure 5.15. The results are shown in Figure 5.16. Clearly, most of the non-linearity is removed, the remaining small (< 0.5%) effect indicating that the correction is slightly too small.



Figure 5.16: Avantes corrected linearity measurements for the ratios of 0.1 s to 0.8 s with 0.2s exposure time as a function of intensity of the measurement having the longer exposure time.

In conclusion, we can say that the Avantes instrument shows a clear non-linearity with decreasing output at large intensities. In this case the effect is up to 4%. The effect in these measurements increases to larger differences in exposure time and thus signals. This is to be expected as also the reference measurement taken at shorter exposure time is already affected by the non-linearity. Therefore, the best measurement is the one with the largest difference in exposure times. From Figure 5.16, we can see that with the correction, there is little evidence for non-linearity. Finally, as the non-linearity is smooth and reproducible, it can be corrected by a multiplicative polynomial based on the intensity. Thus, this correction should be applied also for the DOAS measurement data.

Chapter 6: DOAS Results and Comparisions

6.1 DOAS Analysis

For DOAS data analysis, it is important to get an accurate wavelength assignment from the raw signal which is measured on the detector. The basic idea behind this is that a linear regression between detector number and wavelength for a known spectrum for example a line lamp provides dispersion. During data analysis, one can face some problems because emission lines are not evenly distributed and also the dispersion is not necessarily linear. We can use higher order polynomials as calibration function to overcome these problems.

Besides the trace gas column density calculated from the spectra, some additional information is required so that we can use the data in an orderly way. This information includes:

- Detailed information about the site of measurement (i.e. geolocation, typically latitude and longitude of the measurement). Obviously, this information will always be required for measurements from mobile platforms. In our measurements, we use a GPS connected to the computer for this information.
- Time and date of measurements.
- Viewing direction (for off-axis DOAS measurements), azimuth and elevation Solar Zenith Angle (SZA).
- Some technical information, including number of pixels per spectrum, type of spectrometer, grating used, type of detector, optical filter, wavelength, etc.

6.2 Avantes DOAS Measurements

For taking measurements with the MAX-DOAS telescope and Avantes spectrometer, a quartz fibre was used to connect them. Measurements at different elevation angels were taken to observe NO_2 colume in Bremen on 3rd June, 2014. The telescope was faced towards Radio Bremen Tower, Bremen city at different elevation angels (e.g. 1°, 2°,.... 15°, 30° and zenith) during measurements.



Figure 6.1: Schematic representation of the set-up for Avantes DOAS measurements with telescope connection in the IUP, Bremen.

For comparison, data from the normal Bremen instrument were used. The actual MAX-DOAS instrument that we have in the laboratory has two channels, one in the UV (220-400 nm) and one in the visible (400-740 nm). This instrument has temperature stabilised grating spectrometers to guarantee high stability. Cooled CCD detectors, which are used in this instrument is to minimize the noise and provide simultaneous measurements at all wavelengths.

For the DOAS analysis of the Avantes data, a fitting window of 425 - 497 nm was used. The cross-sections for O₃, NO₂, O₄, H₂O and Ring effect were included and a polynomial of degree 4. The background (I₀) measurement used is a zenith-sky measurement around noon. During my measurements the integration time was 20 seconds in each direction. DOAS retrievals were performed on data for all directions. NO₂ slant columns for some viewing directions relative to noon zenith columns are shown in Figure 6.2. Here, the local time means local solar time when the sun has its highest point at 12:00. This is not local time on our watch herein Bremen due to our time zone and daylight saving time. When the sun is low (morning and evening) we get long light path and short light path is found during high sun (zenith).



Figure 6.2: Avantes NO₂ measurements in Bremen, June 3, 2014.

From the above Figure 6.2, we see that early morning at low elevation angel (1°) high NO₂ column are found indicating that there is large NO₂ concentrations in the lower troposphere. After some time the values are almost same at different elevation angels. Overall no visible noise is observed. There is a clear separation of viewing directions as expected for polluted site. The zenith-sky measurements with the Avantes instrument show a Stratospheric "U-shape" and expected higher PM than AM values at twilight. We also found larger pollution in the morning than in the evening on June 3rd.



Figure 6.3: Avantes and Bremen MAX-DOAS NO₂ results for zenith sky 3rd June, 2014.

In Figure 6.3, solid blue line shows the Avantes results and magenta colored dot shows Bremen MAX-DOAS results. The Bremen instrument was oriented in the same direction and also used integration of 20 seconds, The NO₂ DOAS analysis was performed in the same way as for the Avantes instrument. As can be seen from Figure 8.3, the agreement between the zenith NO₂ columns of the large (and expensive) MAX-DOAS instrument and the Avantes (around 10 times cheaper than MAX-DOAS) instrument is very good up to 92° SZA. The results shown here are both for zenith viewing direction. The instrument can thus be used for NO₂ measurements, both for the stratosphere during twilight and for pollution measurements during the day.

6.3 Effect of Linearity-correction

During linearity measurements in laboratory (section 5.3), I found a non-linearity of the instrument. Then I derived a correction polynomial and now want to see what the effect on the DOAS retrieval is if I apply the correction to the spectra before running the analysis. The following Figure 6.3 shows the improvement in RMS from linearity correction on June 3rd, 2014. The ratio shown here is for a DOAS retrieval on uncorrected spectra divided by the RMS of the fit for the corrected spectra. In the following figure, the values larger than 1 indicate improved fit. From the overlook on Figure 6.4, we can see that the correction works fine in the morning and evening but less good around at noon, probably because of rapid intensity changes from clouds. We have also found the effect on NO₂ columns is surprisingly small.



Chapter 7: Avantes Car Measurements

7.1 Introduction of Car MAX-DOAS Measurements

For car MAX-DOAS observation, a MAX–DOAS instrument is mounted on a car. Then the car is driven at different locations and observes scattered sun light under different elevation angels (e.g. 45^{0} , 90^{0}). Normally the car MAX-DOAS instrument is automated and light weighted. It is covered by a box (normally aluminum) containing an entrance for quartz fiber and some other electronics to control the instrument. Sometimes a stepper motor is also attached outside of the box and helps the instrument to move at different viewing angles. These instruments are powered by the car battery. Using car MAX-DOAS instrument normally traces gases such as NO₂ or SO₂ are measured.

Usually for car MAX-DOAS observation, the route is mapped by putting a polluted city, industrial area or power plant at the center and then the car is driven in a circle way for measurements. Using data on wind direction and speed, the emission from the sources within the circle can be estimated.

The choice of the route around the investigated area has to satisfy two important criteria. Firstly the route should be comparatively free of traffic jams, otherwise the measurements could be distracted several times and also the pollution from the traffic would cause a systematic background error in the NO_2 measurement. Secondly the route should not be very large so that it would be far from the investigated area. Sometime this large route would take more time for only one measurement and also the wind direction might change before finishing one complete cycle (Shaiganfar et al.; 2011).

7.1.1 Previous Work By Others

A car MAX-DOAS observation for the determination of the total NOx emissions from the Mannheim/Ludwigshafen industrial and urban area has been done by Ibrahim et al (2010). Their method is similar to that introduced by Johansson et al. (2008), but instead of measuring

scattered sun light from zenith sky observations, they measure under different angles with a MAX-DOAS instrument mounted on top of a car. On August 2006, their measurements were carried out around the Mannheim-Ludwigshafen industrial/urban area. The sequence of elevation angles was chosen to: 45^0 , 45^0 , 45^0 , 45^0 , 90^0 and the duration of an individual measurement was about 20–25 seconds. Both cities were surrounded in four successive circles with approximate extensions of 26 km in north-south direction and 18 km in east-west direction. During these circles, a repeating pattern with high and low tropospheric NO₂ VCDs was found. From their measurements , the determined total emissions for those 4 circles range from 4.9×10^{24} to 9.2×10^{24} molec/s with an average value of $(7.4 \pm 1.8) \times 10^{24}$ molec/s.

On September, 2006, some measurements were carried out on the road between Brussels (Belgium) and Heidelberg (Germany) by Wagner et al (2010). The distance between the two cities is about 350 km. The sequence of elevation angles was chosen to: 22^{0} , 22^{0} , 22^{0} , 22^{0} , 40^{0} , 90^{0} and the duration of an individual measurement was about 20–25 seconds which contained between a few tens and more than 200 individual scans. From their measurements, they retrieved the distribution of the tropospheric NO₂ VCD along the driving route with a spatial resolution of about 1 km. The results were consistent for all three used elevation angles (22^{0} , 40^{0} and 90^{0}) indicating that in their case the geometrical approximation was appropriate. The comparison with OMI (Ozone Monitoring Instrument) satellite observations yields rather fair agreement (satellite observations are 25 to 100% larger than the AUTO-MAX-DOAS observations) (Wagner et al.; 2010).

7.1.2 Advantages And Disadvantages

Car MAX-DOAS provides a better spatial resolution then that of satellites. It enables encircling pollution sources with measurements (e.g. power plants, industrial areas). The set up for car MAX-DOAS can be easily installed on a car-top or out of a window. It is also much cheaper in its operation than airborne and satellite instrument. However, such measurements have also some problems. Clouds and obstacles along the road can impact on the light path. If the instrument is not pointing to the zenith, frequent changes of the viewing direction relative to the sun complicates radiative transfer calculations, lack of good knowledge about wind speed and direction may cause errors during data analysis. In addition, chemical transformations between

the emission sources and the location of the measurement might affect the result. These errors can be reduced by collecting detailed information on the meteorological condition and chemical composition at the location where measurements will take place (Ibrahim et al.; 2010).

7.2 Avantes Car Measurements

Car measurements were performed with the Avantes spectrometer for some test measurements on 17^{th} June, 2014 at 14:00 local time for around 2 hours. The temperature was ~ 22 °C and weather was partly cloudy. The road map is shown in Figure 7.2. Slant columns are shown color coded in the figure 7.2. Instrumental set up was as before, this time quartz fibre was pointed in zenith-sky direction. Measurements were averaged over intervals of 1 minute. A GPS device was used for registration of position during measurements. DOAS fit performed for NO₂ as shown in chapter 6, Figure 6.3. Figure 7.3 shows time evolution of measured NO₂ around the Bremen city. Here I₀ was one of the last measurements close to IUP. Negative values mean less NO₂ than at IUP.



Figure 7.1: Instrumental set up during Avantes Car and bicycle measurements (photo courtesy: Richter, A. and Wittrock, F.).



Figure 7.2: Road map during car measurements on 17th June, 2014 around Bremen city.

From the over-view in figure 7.2, we see that there is a large variability observed in NO_2 SC and that there are some hotspots in the vicinity of highways and crossings, also in the city center, Bremen. Lower values are found in the North compared to the South by observing the road map. Variations in NO_2 are different from differences in local pollution levels but could also result from measurements uncertainties:

- Over the time of measurements (2 hours), stratospheric NO₂ might have changed this could lead to small error as observations at the end of the trip see slightly larger stratospheric NO₂ columns. There is however no indication in the data for a systematic NO₂ increases during the observations.
- Weather was partially cloudy so some effect of light path enhancement in clouds cannot be excluded. As the instrument was pointing to the zenith, the light path in the lower troposphere is not much affected by clouds, unless they are very low. However, if there is

 NO_2 inside a cloud, a large increase in signal can be obtained. However, comparison of NO_2 values and measured intensity showed no correlation.

- There were also some problems in general: clouds, trees and choice of good background spectrums during car measurements. With shading of the observations by trees, bridges and buildings. In these situations, the light path and the signal are very different from the normal situation and should be excluded. Therefore, for future measurements, data at high temporal resolution will be saved and bad or suspicious measurements removed before averaging.
- The choice of background spectrum introduces some uncertainty as only differences in NO_2 column amounts relative to I_0 are retrieved. If these measurements (in our case the last measurements close to IUP, Bremen) have a large NO_2 content, all other NO_2 columns are too low.



Figure 7.3: Time evolution of measured NO₂ around the Bremen city.

7.2.1 Stability Of The Avantes Instrument

To observe the stability of the Avantes instrument, another plot (spectral shift versus time) was drawn. The spatial distribution of NO_2 on that day is shown in Figure 7.4. The spectral shift needed in the fit is shown in the Figure 7.4 below and is smaller than 2 thousands of a nanometer. This is a very small shift, indicating the very good stability of this Avantes instrument in spite of temperature changes in the car.



Figure 7.4: The spatial distribution of NO_2 on 17^{th} June, 2014 in Bremen City.

A similar measurement was done by bicycle on 4th July, 2014 at around 11:30 am local time (40 minutes ride). Figure 7.5 shows the road map while the measurements were taken in Bremen City. Both the instrument and the computer were carried in a normal backpack with the quartz fiber attached to the side and pointing to the zenith. During these measurements, data were saved every 0.5 seconds and observations with low intensity removed before averaging over 20 seconds. As many cycling paths in Bremen are below trees, this data selection is essential for bicycle measurements.

On that day, temperature was around 27 $^{\circ}$ C and cloud cover over Bremen city was 20% (www.accuweather.com). The variation in NO₂ was really small in during my trip and this was all close to the detection limit. From Figure 9.5, we can see that lower values were close to University and in the part south of the Bürgerpark and higher values were in the city.

During the measurements from the bicycle, there were repeated problems with the connection between computer and Avantes instrument being lost. As a result, data from the second half of the bicycle trip were lost. The most probable source of this failure are USB connector problems and the strong vibrations and shocks that happen during a bicycle ride in a city. For a routine application, the connection needs to be improved. Also, it would be good to have some means of online monitoring of instrument operation.



Figure 7.5: The road map while taking bicycle measurements from University to City center, Bremen on 04th July, 2014.

Chapter 8: Summary and Conclusion

In my master thesis paper, I described the fundamentals of the tropospheric chemistry of nitrogen oxides (NO_2 , NO), the DOAS principle and formulation and the detailed characterization of a new Avantes spectrometer in the lab. Then a comparison between data of the regular DOAS instrument (IUP, Bremen) and those from the Avantes spectrometer was done. Finally, some very first test measurements from a car and from a bicycle were performed in Bremen and surroundings.

Nitrogen oxides (NO₂, NO) have a vital role in tropospheric chemistry as well as stratospheric chemistry. NO₂ is a toxic gas with reddish-brown colour which is a key species in tropospheric ozone and aerosol formation. In the troposphere, NO and NO₂ are rapidly converted into each other and are therefore combined to $NO_x = NO + NO_2$. The gas phase of O₃ chemistry in the troposphere emphasizing the coupling between the cycles of O₃, HO_x, NO_x, where NO_x acts as a catalyst. Chemical production and loss are the dominant term in most of the troposphere. The emission trend of NOx is decreasing in Europe, USA and Japan. On the other side in Asia and Middle East, this trend is widening rapidly. We are concern about NOx because it has bad impact on living beings, environment and agriculture as also on climate system.

A low cost (compared with existing DOAS instrument in DOAS lab, IUP, Bremen) Avantes spectrometer was calibrated in the laboratory. It is important to know the properties and the performance of the instrument well for DOAS applications; aside the information's given by the manufacturers.

My first characterization of the Avantes instrument was dark measurements. Dark signal showed some variations with time and temperature. Linear behaviour was observed as expected because dark signal has a dependence on exposure time. At larger temperature, the dark signal increases as expected for an uncooled CCD.

It is noticed that slit function is Gaussian, stable with temperature and nearly constant with wavelength. The full wave half maximum (FWHM) have found about 5 - 6 pixels or 0.6 to 0.7 nm. The temperature dependence of spectral calibration was found to be small during line lamp measurements.

While taking linearity measurements, it was seen that the ratio of observations at different exposure time deviate from the expected factor at larger intensities. A clear non-linearity was found but this can be approximated by a polynomial and be corrected.

Parallel measurements were also done with existing DOAS instrument and very good agreement in NO_2 results have observed. The zenith-sky measurements with the Avantes instrument showed a stratospheric "U-shape" and expected higher PM than AM values at twilight. We also found larger pollution in the morning than in the evening on measurement's day (3rd June, 2014) in Bremen. The instrument appears to be a good choice for mobile DOAS measurements.

Finally, the Avantes instrument was used for taking some test measurements within and around city of Bremen including power plants from a car and from a bicycle. Some variability of NO_2 was observed with lower values in the North and high values close to highways and some busy crossings, but more measurements will be needed to better characterize the pollution levels in Bremen.

Overall, it can be concluded that the results are very satisfactory, that the Avantes instrument is suitable and performs adequately in the characterization. This instrument also shows very good agreement with the regular DOAS instrument result and performed well during measurements from mobile platforms. Indeed it might be interesting and is considered as a possible activity for the future measurements for other trace gases (e.g. SO_2 etc.) with this Avantes spectrometer.

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