Introduction to Measurement Techniques in Environmental Physics

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Differential Optical Absorption Spectroscopy (DOAS)

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Overview

- What is Differential Optical Absorption Spectroscopy?
- What is it being used for (in this lab experiment)?

- How does the DOAS method work?
  - Spectral retrieval
  - Light path

- How does a DOAS instrument work?

- Example of measurements
- Summary

1: Introduction to DOAS

Differential

Optical

Absorption

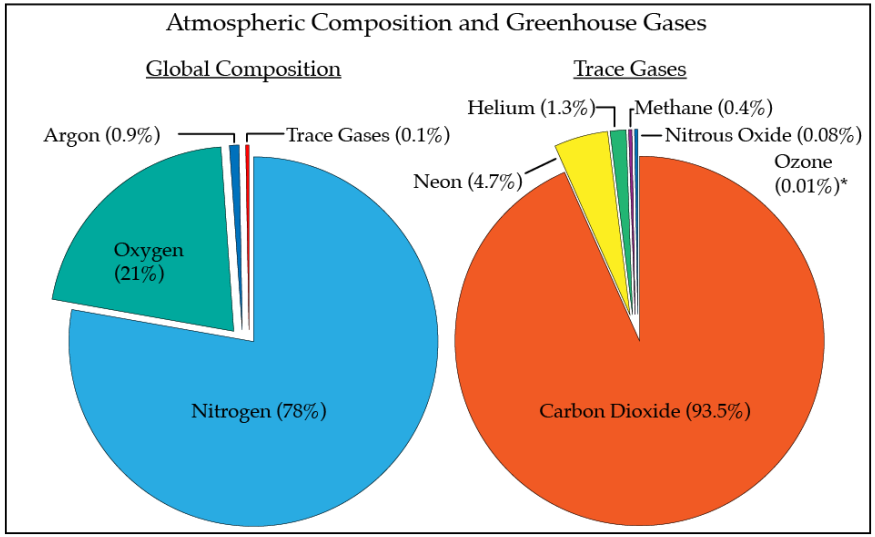
Spectroscopy

Basic ideas of DOAS measurements

- **Remote sensing** measurement of atmospheric trace gases in the atmosphere
- Measurement is based on **absorption spectroscopy** in the UV and visible wavelength range
- Detection of **trace gases** is based on their specific wavelength dependent absorption characteristics
- Effect of atmospheric scattering is removed by treating only signals **varying rapidly with wavelength** (thus the *differential in DOAS*)
- **Light sources** can be strong lamps, the sun or moon, or scattered sunlight
- The longer the **light path**, the larger the signal
- DOAS **instruments** are relatively simple and automated
- Instruments can be operated from all kind of **platforms** (ground, aircraft, balloons, satellites,…

Trace gases

- Most of the atmosphere consists of a small number of stable molecules (N_2, O_2, Ar)
- Water vapour plays a special role because of its varying concentrations and phase changes
- In addition there is a large number of trace gases present in small or even tiny amounts but governing
  - Atmospheric chemistry
  - The greenhouse effect
  - Filtering of sun‘s UV radiation
  - Pollution



https://climateaware.org/greenhouse-gases/

Constituent	*Chemical Formula*	*Volume Mixing Ratio in Dry Air*	*Major Sources and Remarks*
Nitrogen	N_2	78.084%	Biological
Oxygen	O_2	20.948%	Biological
Argon	Ar	0.934%	Inert
Carbon dioxide	CO_2	360 ppmv	Combustion, ocean, biosphere
Neon	Ne	18.18 ppmv	Inert
Helium	He	5.24 ppmv	Inert
Methane	CH_4	1.7 ppmv	Biogenic and anthropogenic
Hydrogen	H_2	0.55 ppmv	Biogenic, anthropogenic, and photochemical
Nitrous oxide	N_2O	0.31 ppmv	Biogenic and anthropogenic
Carbon monoxide	CO	50-200 ppbv	Photochemical and anthropogenic
Ozone (troposphere)	O_3	10-500 ppbv	Photochemical
Ozone (stratosphere)	O_3	0.5-10 ppm	Photochemical
Nonmethane hydrocarbons		5-20 ppbv	Biogenic and anthropogenic
Halocarbons (as chlorine)		3.8 ppbv	85% anthropogenic
Nitrogen species	NO_y	10 ppt-1 ppm	Soils, lightning, anthropogenic
Ammonia	NH_3	10 ppt-1 ppb	Biogenic
Particulate nitrate	NO_3^-	1 ppt-10 ppb	Photochemical, anthropogenic
Particulate ammonium	NH_4^+	10 ppt-10 ppb	Photochemical, anthropogenic
Hydroxyl	OH	0.1 ppt-10 ppt	Photochemical
Peroxyl	HO_2	0.1 ppt-10 ppt	Photochemical
Hydrogen peroxide	H_2O_2	0.1 ppb-10ppb	Photochemical
Formaldehyde	CH_2O	0.1-1 ppb	Photochemical
Sulfur dioxide	SO_2	10 ppt-1 ppb	Photochemical, volcanic, anthropogenic
Dimethyl sulfide	CH_3SCH_3	10 ppt-100 ppt	Biogenic
Carbon disulfide	CS_2	1 ppt-300 ppt	Biogenic, anthropogenic
Carbonyl sulfide	OCS	500 pptv	Biogenic, volcanic, anthropogenic
Hydrogen sulfide	H_2S	5 ppt 500 ppt	Biogenic, volcanic
Particulate sulfate	SO_4^{2-}	10 ppt-10 ppb	Photochemical, anthropogenic

Nitrogen oxides $NO_x = NO_2 + NO$

In the troposphere:

- Emitted mostly in the form of NO from
  - Natural sources such as fires, lightning, soil emissions
  - Anthropogenic sources such as energy production, transportation, industry, agriculture
- Relevant for
  - Health
  - Background ozone chemistry
  - Ozone smog formation (together with VOCs)
  - Aerosol formation
- **Leighton equilibrium**:

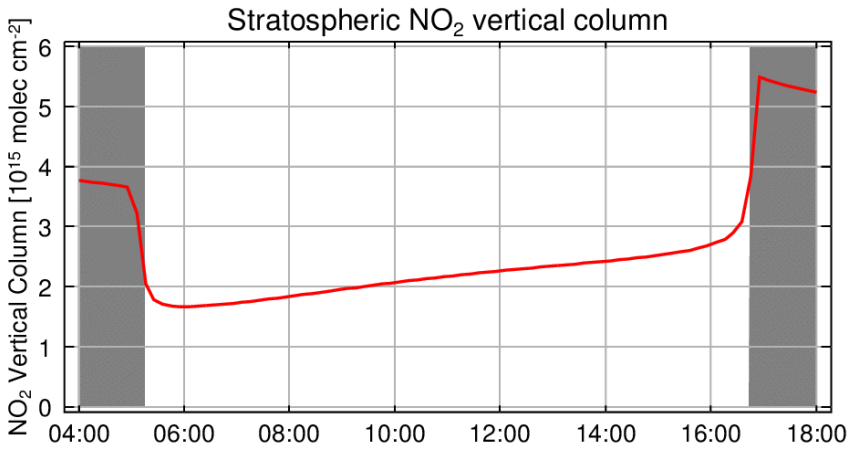
$$NO_2 + h\nu \rightarrow NO + O$$
$$O + O_2 + M \rightarrow O_3 + M$$
$$NO + O_3 \rightarrow NO_2 + O_2$$

- Removal mainly through HNO_3 formation and wet & dry deposition

Nitrogen oxides $NO_x = NO_2 + NO$

In the stratosphere:

- Produced from natural N_2O
- Involved in
  - Catalytic ozone destruction (NOx cycle)
  - Formation of halogen reservoirs ($ClONO_2$, $BrONO_2$, …)
- Strong diurnal cycle because of NO_2 photolysis and formation and photolysis of reservoir species such as N_2O_5 and HNO_3



Summary Introduction

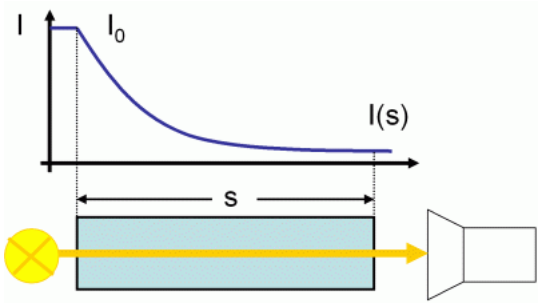
- DOAS is a remote sensing technique used to measure trace gases in the atmosphere
- Trace gases are present at tiny concentrations but play many important roles in Atmospheric Chemistry
- NO_2 (together with NO) is a particularly interesting trace gas which is present in both the stratosphere and the troposphere
- It is involved in ozone chemistry, aerosol formation and determines the lifetime of other trace gases
- NO_2 can well be measured with DOAS and this will be the focus of your DOAS lab experiment.

Things to review:

- Sources and sinks of NO_x in the atmosphere
- NO_2 chemistry in the troposphere
- NO_2 chemistry in the stratosphere

2: How does the DOAS method work?

Lambert Beer‘s law



- Within a uniform medium, the decrease in light intensity in a thin layer ds is proportional to
  - The concentration of absorbing molecules ρ_A
  - Their ability to absorb light, the absorption cross-section σ_A
  - The intensity I

$$dI = -\rho_A \, \sigma_A \, I \, ds$$

- When integrated, this leads to an exponential decrease of the initial intensity I_0 along the light path s (**Lambert Beer’s law**)

$$I(s) = I_0 \exp\{-\sigma_A \, \rho_A \, s\}$$

Absorption and scattering

- In the atmosphere, there is not only absorption but also scattering
  - Rayleigh scattering on particles small relative to the wavelength
  - Mie scattering on particles large relative to the wavelength
- Light extinction by scattering can be treated in a similar way as absorption using the scattering cross-sections σ_{Ray} and σ_{Mie}
- The wavelength (λ) dependence of scattering is smooth and can be approximated by polynomials:
  - $\sigma_{Ray} \sim \lambda^{-4}$
  - $\sigma_{Mie} \sim \lambda^{-1..+1}$

- Combining absorption and scattering we have

$$I(s) = I_0 \exp\{-\sigma_A \rho_A s - \sigma_{Ray} \rho_{Ray} s - \sigma_{Mie} \rho_{Mie} s\}$$

Rayleigh scattering cross-section

Concentration of Rayleigh scatterers

Multiple Species

- In reality, there is not only one absorber but several of them
- The absorption of different species just adds up
- Each molecule has a characteristic absorption spectrum with different strength and specific wavelength dependence

- Including several (N) absorbers and explicitly showing the wavelength dependence we get

$$I(s,\lambda) = I_0(\lambda)\exp\left\{-\sum_{i=1}^{N}\sigma_{A_i}(\lambda)\rho_{A_i}s - \sigma_{Ray}(\lambda)\,\rho_{Ray}\,s - \sigma_{Mie}(\lambda)\,\rho_{Mie}\,s\right\}$$

Sum over all *N* absorbing species

Concentrations changing along light path

- So far, we assumed a homogeneous medium, but the atmosphere is not homogeneous
- Absorber concentrations vary strongly with altitude and also horizontally
- We thus introduce a quantity called **Slant Column SC** which is defined as the absorber concentration integrated along the light path

Top **O**f **A**tmosphere, assuming instrument is on the ground

$$SC_i = \int_0^{TOA} \rho_{A_i} ds$$

- Introducing this into the equation we get

$$I(s,\lambda) = I_0(\lambda)\exp\left\{-\sum_{i=1}^{N} \sigma_{A_i}(\lambda) SC_i - \sigma_{Ray}(\lambda) SC_{Ray} - \sigma_{Mie}(\lambda)\, SC_{Mie}\right\}$$

Slant Column of absorber i

Approximating Scattering

- As noted before, the scattering cross-sections are proportional to polynomials in wavelength and can therefore be approximated by a polynomial

$$\sigma_{Ray}(\lambda)SC_{Ray} + \sigma_{Mie}(\lambda)SC_{Mie} = \sum_{j=0}^{M} p_j \lambda^j$$

- Introducing this into the equation we get

$$I(s,\lambda) = I_0(\lambda)\exp\left\{-\sum_{i=1}^{N}\sigma_{A_i}(\lambda)SC_i - \sum_{j=0}^{M} p_j\lambda^j\right\}$$

Polynomial in wavelength approximating extinction by scattering

The DOAS equation

- This equation can be converted to a linear equation by taking the logarithm on both sides resulting in the **DOAS equation**

known from literature

$$\ln \frac{I(\lambda)}{I_0(\lambda)} = -\sum_{i=1}^{N} \sigma_{A_i}(\lambda)\, SC_i + \sum_{j=0}^{M} p_j \lambda^j$$

these are the measurements

what we want to determine

also needs to be determined but is not our main interest

Comments:

- We need two measurements I and I_0, one with and one without absorption
- We can only determine the integral of the absorber amount along the light path (the slant columns SC_i)
- We have one equation but $N + M + 1$ unknowns…

Using wavelength information

- As the DOAS equation must hold for all wavelengths, measuring at many discrete wavelengths λ_1 ... λ_k provides many equations for the same SC_i and p_j:

$$\ln\frac{I(\lambda_1)}{I_0(\lambda_1)} = -\sum_i \sigma_i(\lambda_1)SC_i + \sum_j p_j\lambda_1^j$$

$$\ln\frac{I(\lambda_2)}{I_0(\lambda_2)} = -\sum_i \sigma_i(\lambda_2)SC_i + \sum_j p_j\lambda_2^j$$

$$\vdots$$

$$\ln\frac{I(\lambda_k)}{I_0(\lambda_k)} = -\sum_i \sigma_i(\lambda_k)SC_i + \sum_j p_j\lambda_k^j$$

- If k is large enough, this is an overdetermined set of linear equations which can be solved using a standard linear least squares fit

Wait a minute …

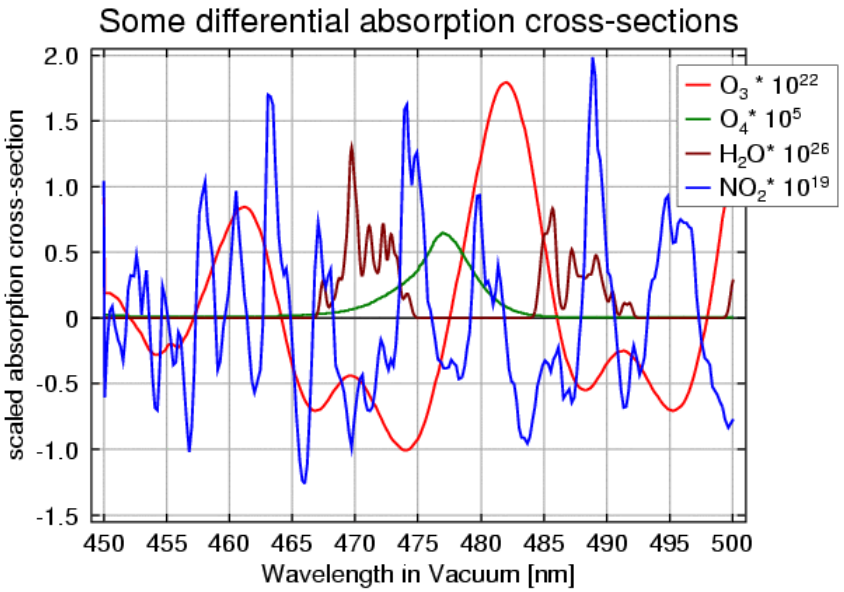
$$\ln\frac{I(\lambda_1)}{I_0(\lambda_1)} = -\sum_i \sigma_i(\lambda_1)SC_i + \sum_j p_j\lambda_1^j$$

$$\ln\frac{I(\lambda_2)}{I_0(\lambda_2)} = -\sum_i \sigma_i(\lambda_2)SC_i + \sum_j p_j\lambda_2^j$$

$$\vdots$$

$$\ln\frac{I(\lambda_k)}{I_0(\lambda_k)} = -\sum_i \sigma_i(\lambda_k)SC_i + \sum_j p_j\lambda_k^j$$

- Sounds good – but are all these equations independent?



- This is only the case if the absorption cross-sections are sufficiently different as a function of wavelength, and in only these cases we will get an unambiguous result
- Luckily, the NO_2 cross-section is a very good candidate…

But then …

- One always needs two measurements, one $I(\lambda)$ with, and one $I_0(\lambda)$ without absorber. In the lab, this may be possible, but in the atmosphere, we cannot remove the absorber!
- Luckily, it is enough to have two measurements with different light paths to solve this problem:

$$\ln\frac{I_1(\lambda)}{I_0(\lambda)} = -\sum_i \sigma_i(\lambda) SC_{1,i} + \sum_j p_j \lambda^j \qquad \ln\frac{I_2(\lambda)}{I_0(\lambda)} = -\sum_i \sigma_i(\lambda) SC_{2,i} + \sum_j p_j \lambda^j$$

- Taking the difference removes $I_0(\lambda)$!

$$\ln\frac{I_1(\lambda)}{I_2(\lambda)} = -\sum_i \sigma_i(\lambda)\left(SC_{1,i} - SC_{2,i}\right) + \sum_j p_j^* \lambda^j$$

← Polynomial changes, but we don‘t care

- Note that this will only yield the difference ΔSC_i of the two Slant Columns.

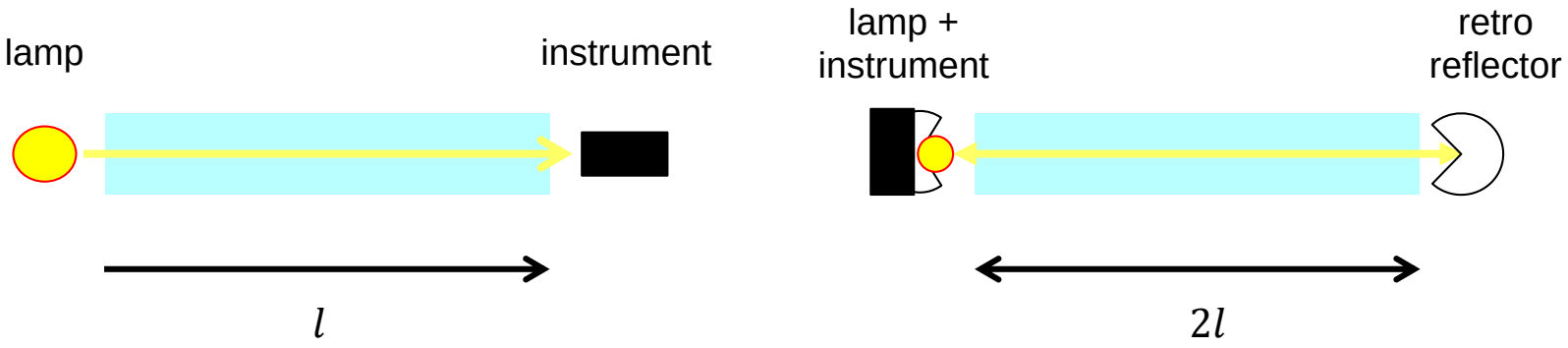
Summary DOAS method

- DOAS is based on Lambert Beer's law
- Trace gases are identified using the characteristic wavelength dependence of their absorption spectra
- In order to measure multiple trace gases at the same time, measurements at many wavelengths are needed
- Trace gas amounts are determined using the magnitude of the absorption
- Extinction by scattering is accounted for using a closure polynomial
- Only the total amount of a trace gas, integrated along the light path can be determined
- There are always two measurements needed for a DOAS analysis: the current measurement and a reference measurement

Things to review:
- Lambert Beer's law
- Rayleigh scattering
- Mie scattering

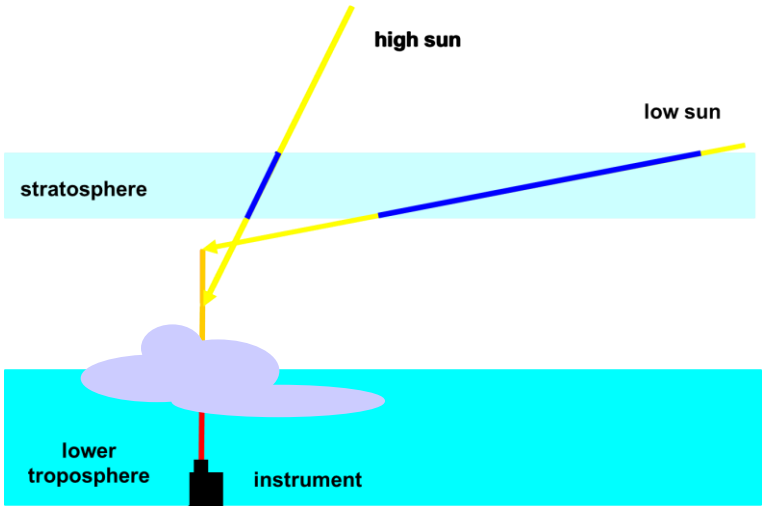
3: What is the light path in the atmosphere?

Active DOAS



- Light path is simple geometric distance
- Light path length is limited by strength of lamp and size of collecting telescope
- Usually, light path is duplicated by putting a retro reflector at one side and combining light source and light collection into one telescope
- Typical light paths are of the order of a few kilometres

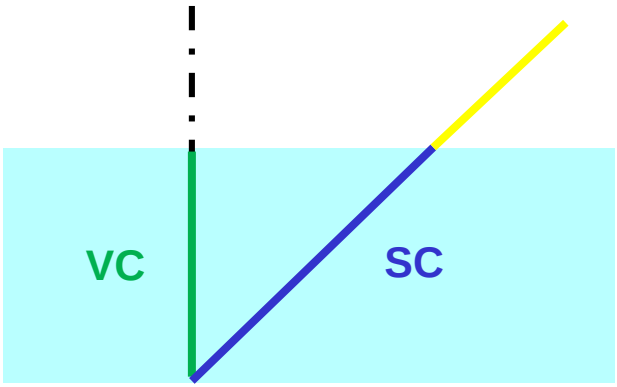
Zenith-sky DOAS



- Light is scattered high above the instrument
- Short light path through the troposphere
- Long light path through the stratosphere
- Very long light path through the stratosphere at low sun
- Clouds don’t change the light path in the stratosphere

=> zenith-sky measurements at twilight are good for stratospheric absorbers

Air Mass Factor



- Now we can try to estimate the light path
- We have introduced the **Slant Column**

$$SC_i = \int_0^{TOA} \rho_{A_i} ds$$

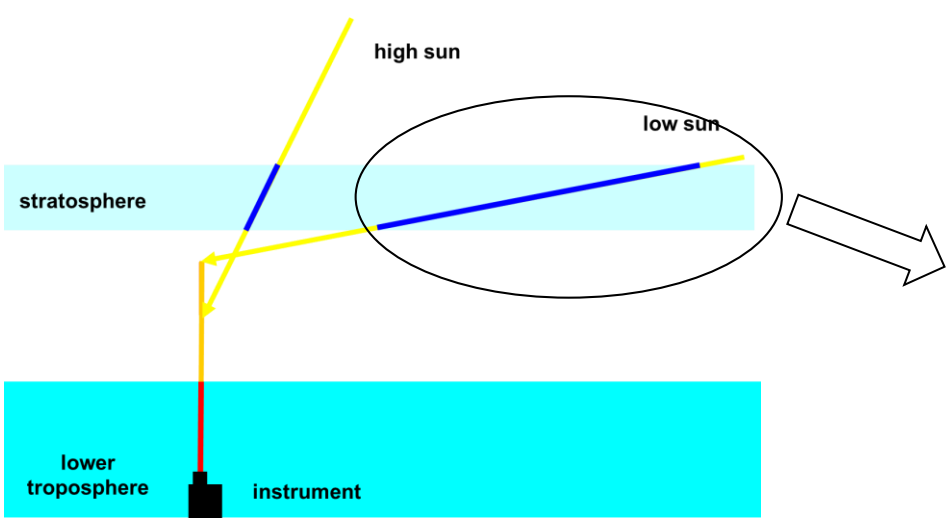
  which depends on light path
- A better quantity would be the **Vertical Column**

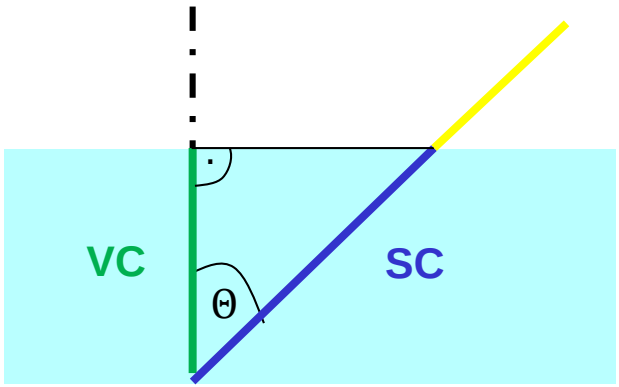
$$\mathrm{VC_i} = \int_0^{TOA} \rho_{A_i} dz$$

  which is integrated vertically in the atmosphere and does not depend on light path
- The ratio between the two is called **Air Mass Factor**

$$AMF \equiv \frac{SC}{VC}$$

Air Mass Factor zenith-sky

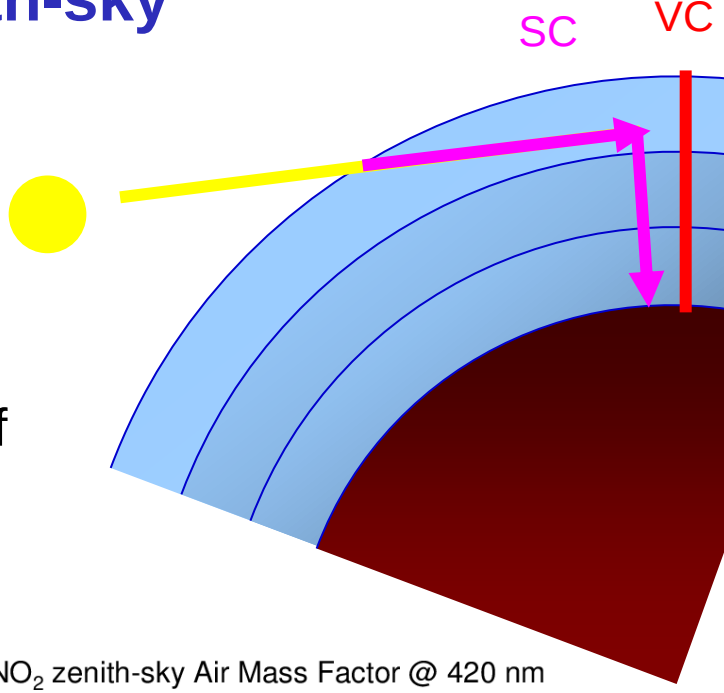




$$AMF \equiv \frac{SC}{VC} = \frac{1}{\cos(\Theta)}$$

- In first approximation, the AMF can be determined as function of the **Solar Zenith Angle** (SZA) by $1/\cos(\Theta)$
- However, at $SZA = 90°$ the AMF becomes infinity which can‘t be correct
- Something is not quite right with this approximation at large SZA…

Air Mass Factor zenith-sky

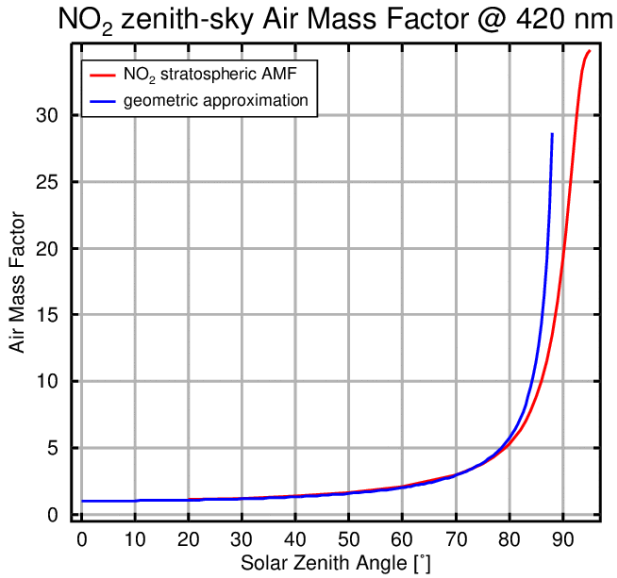


So what is missing?

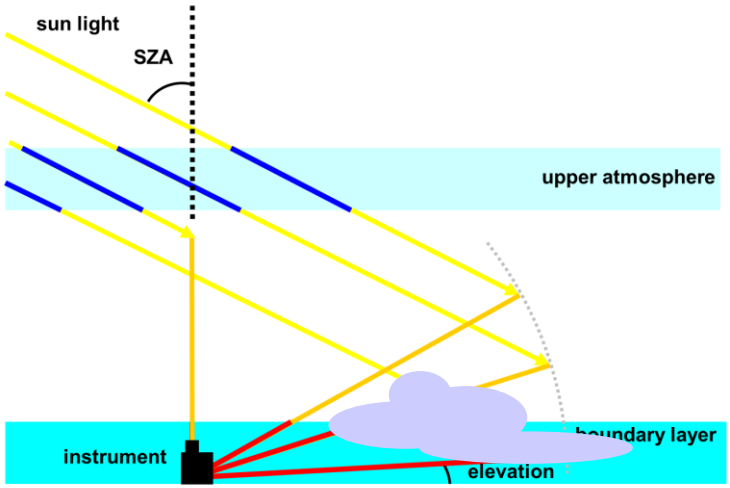
1. Earth is not flat, and in a spherical atmosphere, light paths are limited
2. scattering can take place at any altitude, and what we see is a weighted average of all possible light paths

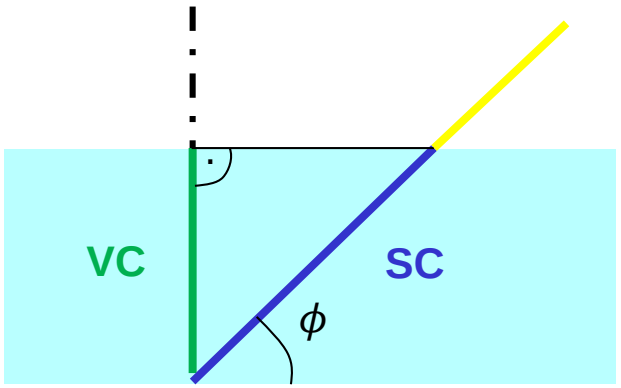
⇒ more complex calculations are needed, usually performed with radiative transfer models

⇒ AMF also depends on wavelength and vertical distribution of absorber



Off-Axis DOAS





$$AMF \equiv \frac{SC}{VC} = \frac{1}{\sin(\phi)}$$

- long light path through the lower troposphere
- constant light path through the stratosphere
- the lower the measurement is pointed, the longer the light path gets
- small dependence on sun position
- AMF can be approximated as function of the **Elevation Angle** by $1/\sin(\phi)$
- clouds strongly change light path

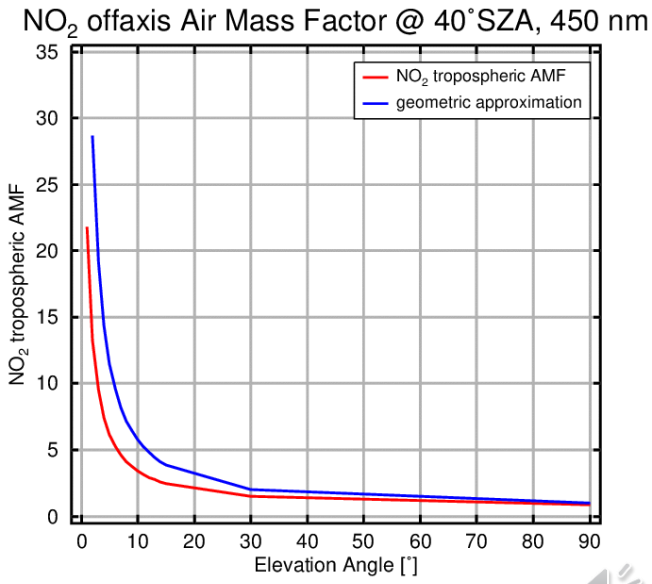
=> off-axis measurements are good for tropospheric absorbers

Air Mass Factor off-axis

- As for zenith-sky, the geometric approximation fails as ϕ approaches 0°
- Reasons are
  - Spherical nature of the atmosphere
  - Scattering limits possible path length
  - In particular aerosol scattering can strongly reduce path length

$\Rightarrow$ more complex calculations needed

$\Rightarrow$ AMF also depends on wavelength and vertical distribution of absorber



Selection of background spectrum I_0

What is a good background spectrum I_0?

$$\ln\frac{I(\lambda)}{I_0(\lambda)} = -\sum_i \rho_i(\lambda)(SC_i - SC_{0,i}) + \sum_j p_j^* \lambda^j$$

- Active DOAS, lab measurements:
  - A measurement of the lamp without atmosphere
- Zenith-sky DOAS:
  - A measurement at high sun when the light path through the stratosphere is short
  - $\Delta SC = SC(\Theta) - SC(\Theta_0)$
- Off-axis DOAS:
  - A measurement in the zenith direction for which the light path through the troposphere is short
  - $\Delta SC = SC(\phi) - SC(\phi = 90°)$
- Satellite DOAS:
  - A measurement of the sun without the atmosphere

Computation of vertical columns

How can vertical columns be computed from ΔSC?

Assumption:
VC remains constant!

$$VC = \frac{SC}{AMF}$$

$$\begin{aligned}\Delta SC &= SC(\Theta) - SC(\Theta_0) \\ &= VC \cdot AMF(\Theta) - VC \cdot AMF(\Theta_0)\end{aligned}$$

$$VC_{zenith} = \frac{\Delta SC}{AMF(\Theta) - AMF(\Theta_0)}$$

In the case of off-axis DOAS

$$VC_{offaxis} = \frac{\Delta SC}{AMF(\phi) - AMF(\phi = 90°)}$$

Summary Light Paths

- Zenith-sky measurements have very long light paths in the stratosphere at twilight
  => good for stratospheric absorbers
- Off-axis measurements have very long light paths in the boundary layer if pointing at small elevation angle
  => good for tropospheric absorbers
- Geometric approximations can be used to estimate light path lengths but they have limited validity range
- More accurate results are obtained when using Air Mass Factors calculated with radiative transfer models
- Clouds have a negligible impact on stratospheric measurements but strongly affect tropospheric measurements

Things to review:
- Lambert Beer's law
- Rayleigh scattering
- Mie scattering

4: What does a DOAS instrument look like?

The (MAX)DOAS instrument

- Need to collect light from the zenith and from different directions above the horizon
  => **telescope** to collect light

- Telescope is outdoors, instrument is indoors
  => **fibre optics** to bring light from telescope to lab

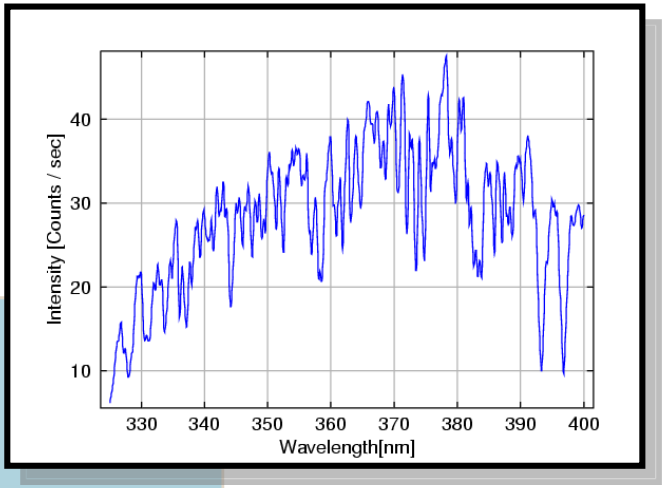
- Need to measure light at different wavelengths
  => **spectrometer** to create spectrum

- Need for automated and quantitative measurement
  => **detector** to record spectrum

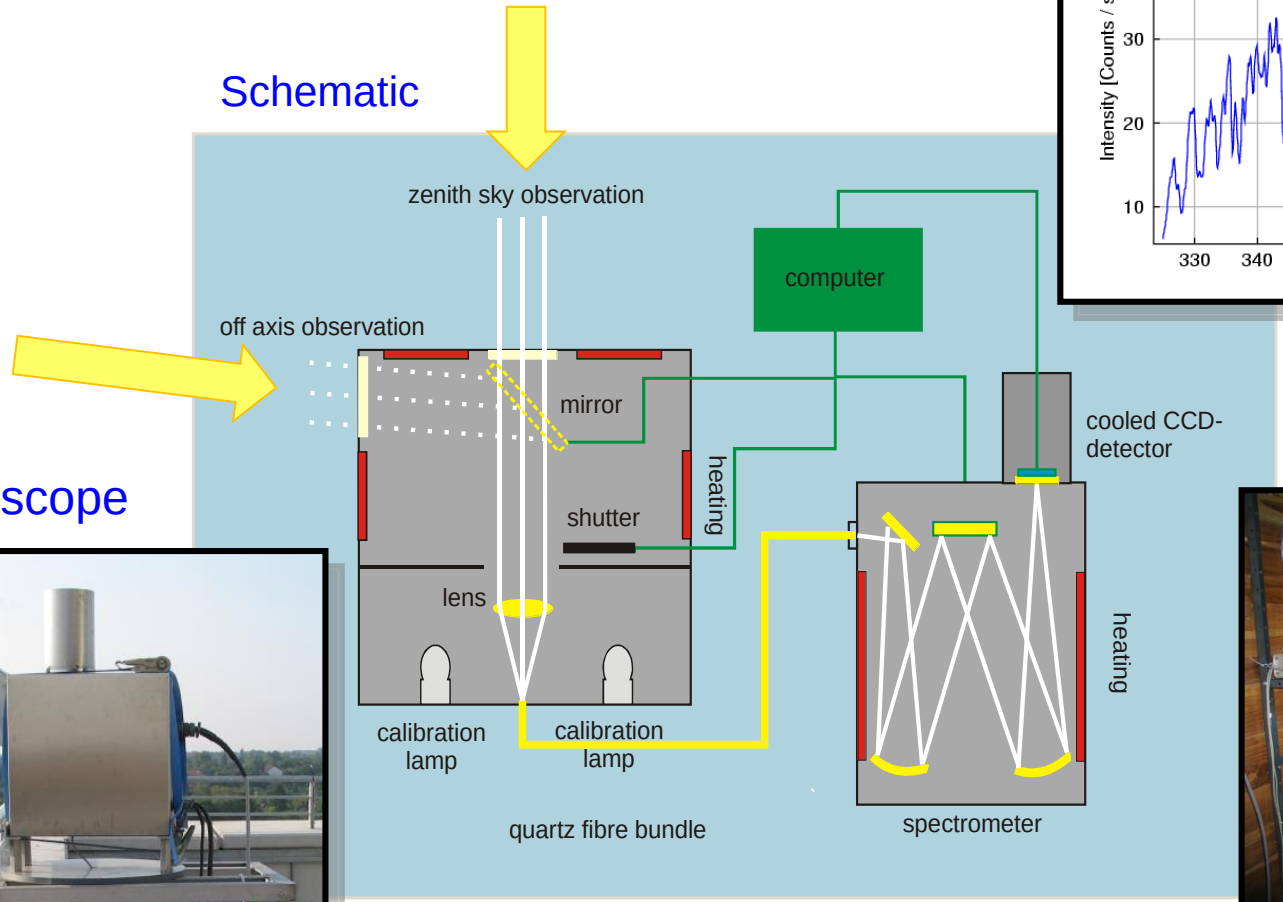
The MAXDOAS instrument

MAXDOAS = Multi Axis Differential Optical Absorption Spectroscopy

Measured Spectrum

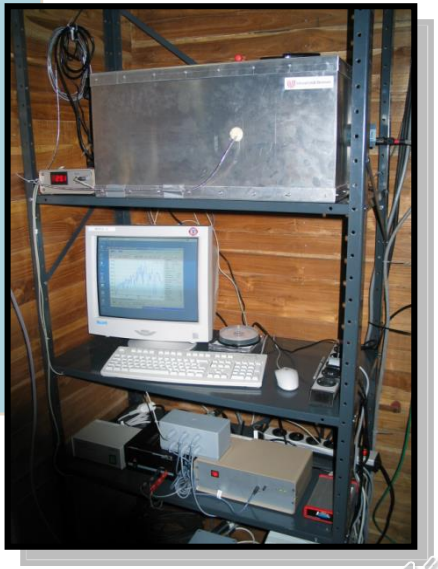


Schematic

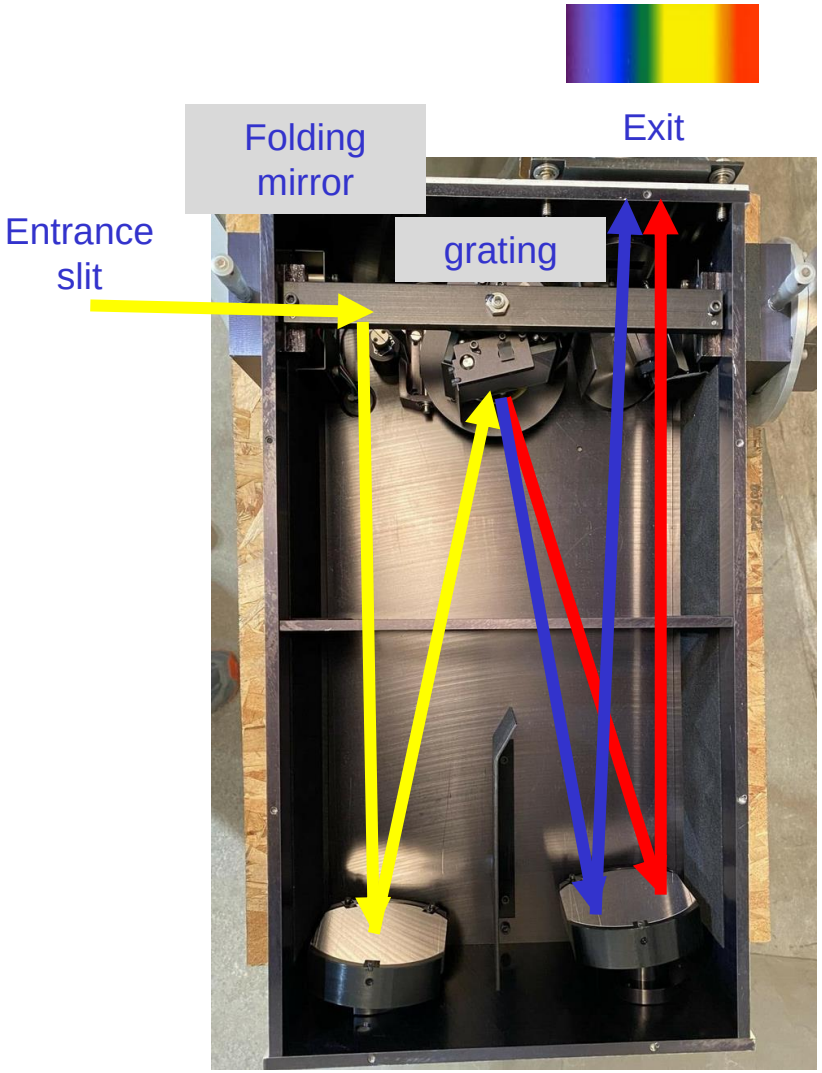


Telescope

Instrument



The (MAX)DOAS instrument: Czerny Turner Spectrometer

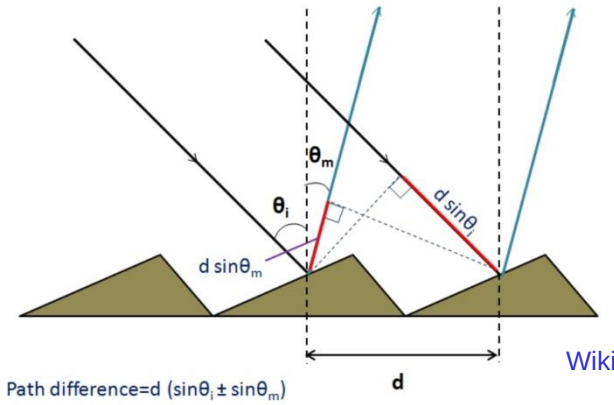


Reflective Grating:

- Multi beam interference
- Maximum intensity under wavelength dependent angle
- **Grating equation**:

$$d(\sin\Theta_i - \sin\Theta_m) = m\lambda$$

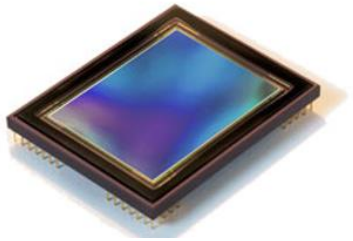
m is order of maximum

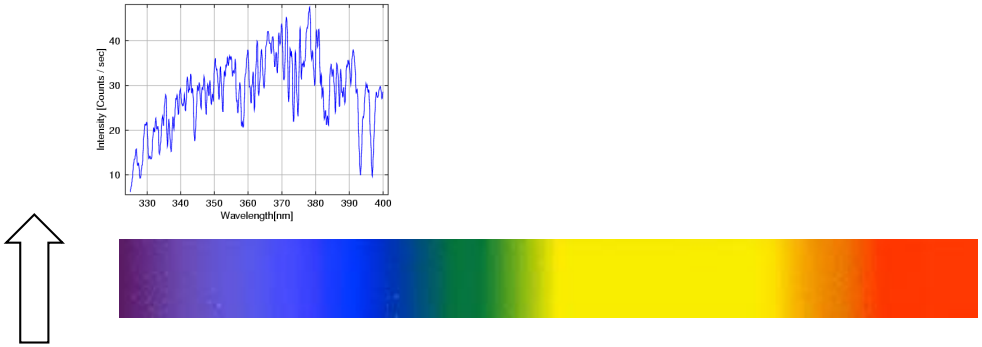


The (MAX)DOAS instrument: Detector

CCD detector

- Charge-coupled device
- 2-d detector converting light into electrical charge
- Image is read out sequentially by moving charge from one pixel to the next
- Cooled to reduce noise and dark signal
- Evacuated to avoid condensation
- Here: integrated vertically as only one direction (wavelength) is of interest

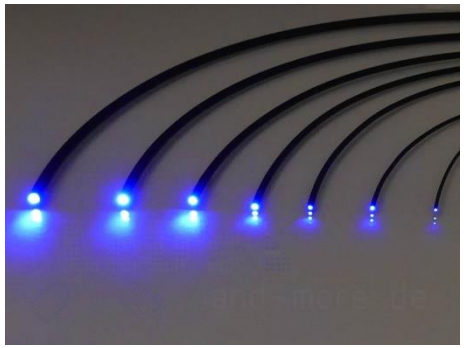


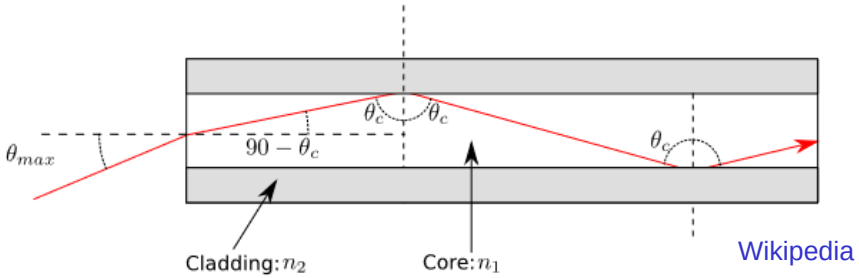


The (MAX)DOAS instrument: Quartz fibre

Quartz fibre bundle

- Fibres are used to bring light from telescope to spectrometer
- Flexible, low losses
- Quartz is being used for UV transmittance
- Many thin fibres are used to convert from round entrance at telescope to rectangular entrance at spectrometer slit





Wikipedia

- **Total reflection** in fibre at boundary between materials with different refractive indices $n_1 > n_2$
- Only light with entrance angle smaller than Θ_{max} will stay in fibre

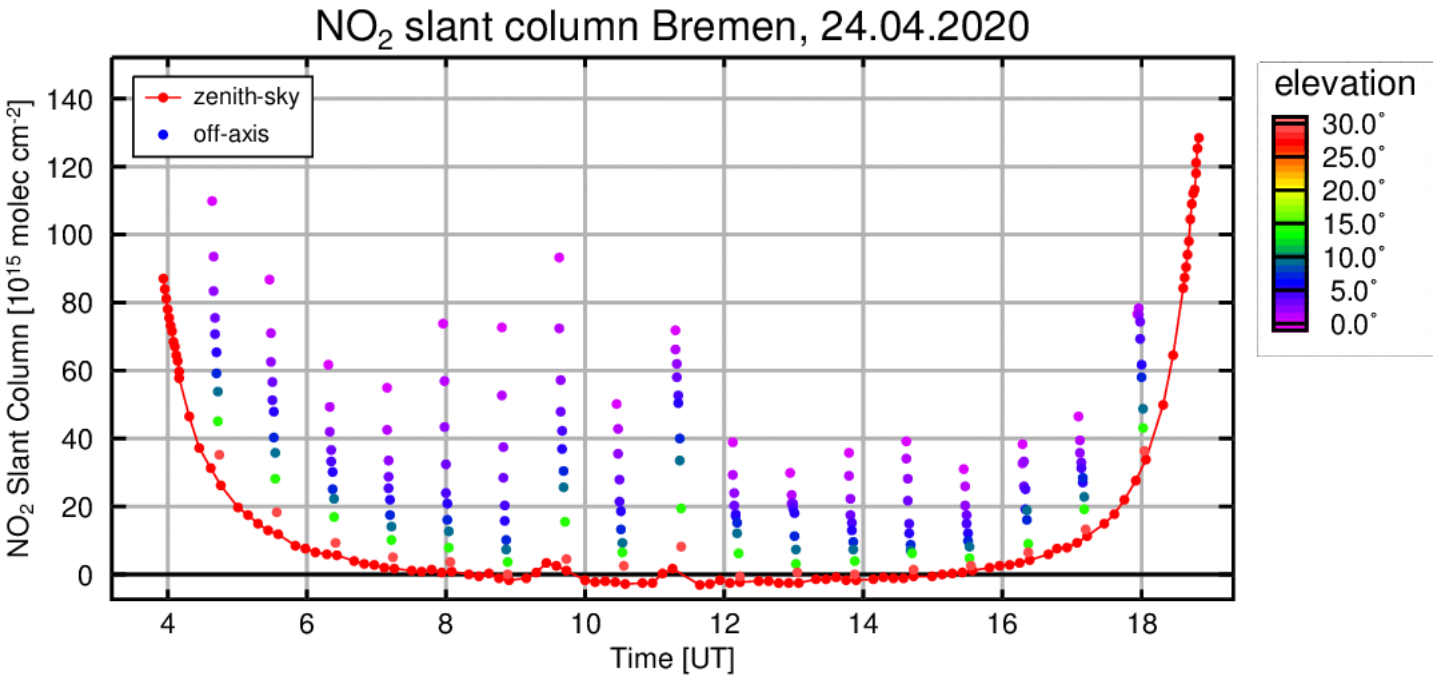
Summary: MAXDOAS instrument

- A typical MAXDOAS instrument consists of
  - Telescope
  - Fibre bundle
  - Grating spectrometer
  - CCD detector

Things to review:
- Spectrometers
- Diffraction grating
- CCD detector
- Total reflection

5: Example of Measurements

MAXDOAS measurements in Bremen



- U-shaped zenith-sky diurnal variation because of longer light paths at low sun
- Higher PM than AM values because of stratospheric chemistry
- Off-axis measurements increase with decreasing elevation angle because of longer light path in the pollution layer
- Pollution varies over the day

Summary

- DOAS measurements use absorption spectroscopy to detect trace gases in the atmosphere
- the method is based on Lambert Beer's law
- only the "differential" part, i.e. the high frequency component is used to separate molecular absorption from extinction by scattering
- as light source, the sun (or moon or stars), scattered light or a lamp can be used
- for scattered light applications, computation of the light path through the atmosphere is the most difficult part of the data analysis
- the instruments used are grating spectrometers with CCD detectors connected to a telescope
- DOAS instruments can be operated from all kind of platforms including satellites