7. New generation of UV-Vis instruments

Multi-Axis Differential Optical Absorption Spectroscopy (MAX-DOAS)

Courtesy Michel Van Roozendael et al.
Differential Optical Absorption Spectroscopy (DOAS): the idea

- Use **differences** of intensities at different wavelengths
- Record the intensity in **many** (typically over 100) wavelength channels
- **High-pass filtering** of spectra (→ remove continuum)
- **Fit** laboratory **reference spectra** of trace gases → make use of full spectral information to **identify** molecules and **quantify** their abundance
Absorption cross-sections of atmospheric molecules
DOAS retrieval (1)

- Analysis of spectra based on the **Lambert-Beer law** which describes the attenuation of light in the atmosphere:

\[
I(\lambda) = I_0(\lambda) \cdot e^{- \int \left( \sigma(\lambda) \cdot \rho(s) + k_r(s) + k_m(s) \right) \cdot ds}
\]

- Basic quantity measured by DOAS is the **slant column density** (SCD) of an absorber:

\[
S = \int \rho(s) \cdot ds
\]

or the corresponding **optical depth**:

\[
\tau(\lambda) = \sigma(\lambda) \cdot S
\]
DOAS retrieval (2)

- After linearization of the Lambert-Beer equation and accounting for the smooth (unstructured) contribution from Rayleigh and Mie scattering using a polynomial $P$, one obtains the DOAS equation:

$$\ln I(\lambda) = \ln I_0(\lambda) - P(\lambda) - \sum_i \sigma_i(\lambda) \cdot S_i$$

- The DOAS equation can be solved for the slant column densities $S_i$ and the coefficients of the polynomial $P(l)$ using a linear least-squares minimization technique.

- Note that in practice the problem is often made non-linear due to the need to correct for spectral shifts as part of the inversion.
Advantages of DOAS

✓ Overlapping absorption structures due to different species can be separated
✓ Species not anticipated can be measured
✓ Warning against unexpected absorbers (residual)
✓ Immune against continuous (broad band) extinction due to e.g. aerosol or molecules
✓ High sensitivity, since many trace gas lines (bands) are used.
Example of a DOAS Evaluation

A: Sample atmospheric spectrum from April 16, 2001

B: Ozone absorption spectrum

C: BrO absorption spectrum

D: Residual (noise+unknown absorbers)

Black lines: measurement
Red lines: fit result

\[
\begin{align*}
\text{[O}_3\text{]} & = 6.6 \times 10^{11} \text{ molec/cm}^3 [24 \text{ ppb}] \\
\text{[BrO]} & = 3.8 \times 10^8 \text{ molec/cm}^3 [13 \text{ ppt}]
\end{align*}
\]
The Principle of Multi-Axis (MAX)-DOAS

- The most likely altitude of scattering for visible and near-UV light is 5 – 8 km or below depending on wavelength and visibility
- Slant column density (SCD) for stratospheric gases only depends on the solar zenith angle $\vartheta$
- In first approximation, SCD of tropospheric gases depend on viewing elevation angle $\alpha$

$$SCD = \frac{VCD_T}{\sin \alpha} + \frac{VCD_S}{\cos \vartheta}$$

- Vertical column density (VCD) of tropospheric gases can be determined from simultaneous measurements at low elevation angle ($\alpha=1^\circ$) and at the zenith ($\alpha=90^\circ$)
MAXDOAS in the field

zenith

Off-axis

Cabauw, NL – Sep. 2006
MAXDOAS technique for tropospheric trace gases profile inversion
MAXDOAS air mass factors (AMFs)

AMFs represent the geometrical amplification of the measurement and can be calculated using modern multiple scattering RT codes (e.g. DISORT, LIDORT, SCIATRAN)

- MAXDOAS AMFs are largest in the lower troposphere
- MAXDOAS AMFs depend on aerosol content and surface albedo
Trace gases profile inversion from MAXDOAS observations

Step 1: Spectral evaluation using DOAS method $\rightarrow$ slant columns of target trace gases + O$_4$

Step 2: Use O$_4$ measurements to constrain radiative transfer settings (aerosols)
- O$_4$ has known concentration profile $\rightarrow$ simulate O$_4$ slant columns (vertical column is known) and vary aerosol scenario and surface albedo until closure for all lines of sight and also solar zenith angles is obtained

Step 3: Use information from different lines of sight to derive profile information for the absorber of interest:
- simulate absorber’s slant column using aerosol and albedo settings from O$_4$ retrieval and vary profile until good agreement with retrieved slant columns is reached for all directions.
Example 1: O₄ retrieval in a clean tropical site (Reunion Island)

(a) Calculation assuming a visibility of 40 km
(b) Calculation assuming a visibility of 80 km
Example 2: HCHO profile retrieval during FORMAT campaign (Po Valley, 2002)

→ On a clear and stable day (ideal situation), one vertical profile and one set of aerosol settings brings all line of sights on the same value

Courtesy of Folkard Wittrock, IUP Bremen, Germany
Advantages of MAX-DOAS

✓ Separation of stratospheric and tropospheric trace gas absorptions.

✓ High sensitivity for tropospheric trace gases owing to the long optical path length (> 5 km) at low elevation angles.

✓ Simple experimental setup and the capability to automatically operate over long intervals of time.

✓ Validation of radiative transfer through the simultaneously measured absorptions of O₂, O₄, and H₂O. Recognition of clouds, fog, and aerosol is possible.

✓ Advanced evaluation methods (currently under development and testing) allow for vertical trace gas profiling of gases and aerosol
MAXDOAS applications

- Detection of volcanic plumes (SO$_2$, BrO)
- Monitoring of pollutants (NO$_2$, SO$_2$, HCHO, glyoxal)
- Study of polar and marine boundary layer (BrO, IO)
- Retrieval of tropospheric aerosol properties
- Satellite validation (NO$_2$, BrO, HCHO, …)
- Tomography of pollutant/volcanic plumes

... a few examples
Polar BrO plumes seen from satellite

GOME and SCIAMACHY Arctic BrO Columns in March

http://www.temis.nl
MAX-DOAS BrO Measurement Results, Alert

elevation angles
- 5°
- 10°
- 20°
- 90°

Date: April / May 2000 [GMT]
Free-tropospheric BrO detection and satellite validation

MAXDOAS BrO fit at Reunion Island

- Time-series of total and tropospheric BrO columns, and comparison with SCIAMACHY measurements

Theys et al., to be submitted to ACP
Tropospheric NO$_2$ and satellite validation (1)

DANDELIONS campaign in Cabauw, NL

SCIAMACHY NO$_2$ columns: May 2005

OMI tropospheric NO$_2$ columns

MAXDOAS NO$_2$ slant columns

A. Richter, IUP Bremen, Germany
Tropospheric NO$_2$ and satellite validation (2)

Cloud free data

**Tropospheric NO$_2$ during DANDELIONS - satellite cloud Free**

NO$_2$ tropospheric vertical columns:
- IASB MAX-DOAS: geometrical approximation
- Satellites: closest pixels within 200 km over Cabauw and cloud selection
MAXDOAS: a new technique to derive information on atmospheric aerosols

**Principle:**
- MAX-DOAS measurements of a trace gas with a known vertical profile ($O_4$):
  - Contain information on the light path through the atmosphere
  - Allow to gain information on atmospheric aerosols
- Numerous absorption bands, easy to detect with DOAS
- $O_4$ concentration proportional to the square of the $O_2$ concentration
- Scale height of $O_4$ profile: ~4km
- Aerosol inversion uses Optimal Estimation technique
Aerosol extinction profile retrieval
Capability of the technique explored using simulated spectra

Friess et al., JGR, 2006
Thank you very much for your attention