Winter College on Optics in Environmental Science

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Atmospheric Monitoring, Differential Optical Absorption Spectroscopy

DOAS I, Basics

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Atmospheric Monitoring, Differential Optical Absorption Spectroscopy – DOAS I, Basics

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- The principle of DOAS
- The (many) Variants of DOAS
- Examples
- Sample Results
- (preliminary)Summary
Mixing Ratios of Atmospheric Trace Gases

Noble Gases
- He
- Ar
- Ne
- Kr
- Xe

Other Gases
- CO
- CH₄
- O₂
- N₂
- H₂
- NOₓ
- SO₂
- O₃
- OH
- HO₂
- NM-Hydrocarbons

Concentration Ranges:
- ppt (parts per trillion)
- ppb (parts per billion)
- ppm (parts per million)

No. of different species in conc. range:
- 10-12
- 10-9
- 10-6
- 10-3
- 1

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Requirements for Measurement - Techniques

- **Sensitivity:** Species (like OH, IO) present at mixing ratios of \( \approx 10^{-13} \), (0.1 ppt, about \( 2 \times 10^6 \) molecules/cm\(^3\)) can significantly influence atmospheric chemistry.

- **Specificity:** The result of the measurement of a particular species must not be influenced by any other trace species present in the air.

- **Spatial coverage:** In-situ vs. remote sensing

- **Time resolution**

- **Calibration** should be easy (inherent?), stable, ...

- Further desirable properties:
  - Simplicity of design and use of the instruments based on it.
  - Possibility of unattended operation.
  - Weight, portability, and dependence of the measurement on ambient conditions.
Diversity of Measurement Tasks

Long Term Observations  note ‘operator dilemma’
- Stratospheric ozone trend
- Change of Stratospheric chemistry (NDACC)
- Stratospheric (chlorine) source-gases in the troposphere
- Tropospheric ozone trend (GAW)
- Greenhouse gases

Regional Episodic Events
- Pollution monitoring
- Urban plume evolution
- Continental plumes
- Antarctic Ozone Hole
- Polar boundary-layer ozone loss events

Fast in-situ (Photo)chemistry (process studies)
- Free radical (OH/HO₂) photochemistry

Remember Lectures by Profs. Singh and Wagner ...
Advantages of Spectroscopic Techniques ...

- Direct identification of trace gas molecules
- Remote sensing capability
- Inherent calibration (ideally ...)
- Real time measurements
- Non – contact measurement
  
Remember Lectures by Prof. Svanberg ...
Spectroscopic Measurement of Atmospheric Trace Gases

The Principle

\[ I = I_0 \cdot e^{-\bar{c} \cdot L \cdot \sigma} \]

Lambert-Beer's law

- \( \bar{c} = \text{average trace gas concentration} \)
- \( L = \text{length of light path} \)
- \( \sigma = \text{absorption cross section} \)

(or Bouguer-Lambert law, it was discovered by Pierre Bouguer in 1729, Johann Heinrich Lambert in 1760, and August Beer in 1852)

Gustav Robert Kirchhoff
1824 - 1887
in Heidelberg: 1854 - 1874

Robert Wilhelm Bunsen
1811 - 1899
in Heidelberg: 1852 - 1899
Electromagnetic Radiation

- γ, X-radiation
- ultraviolet
- visible
- Infrared
- radio waves
- microwaves
- electronic
- vibrational
- rotational

Wavelength, m

10^{-9} 10^{-8} 10^{-7} 10^{-6} 10^{-5} 10^{-4} 10^{-3} 10^{-2}

DOAS
Molecules: Electronic – Rotational – Vibrational Spectra

\[ \Delta E = Photon \, Energy = h\nu = \Delta E_{\text{electronic}} + \Delta E_{\text{vibration}} + \Delta E_{\text{rotation}} \]

\[ E_{\text{vibration}} (v) = \left( v + \frac{1}{2} \right) h\nu' \]

\[ \Delta E_v = \left( v' + \frac{1}{2} \right) h\nu'_v - \left( v'' + \frac{1}{2} \right) h\nu'_v \]

\[ \Delta E_{\text{rotation}} (J', J'') = B'J' (J' + 1) - B''J'' (J'' + 1) \]

\[ B = \frac{\hbar^2}{2\Theta} = \frac{\hbar^2}{2r_e^2 \frac{m_1 m_2}{m_1 + m_2}} \]

 Rule
 Atoms: Line Spectra
 Molecules: Band Spectra
Electronic transition associated with absorption/emission of a photon occurs fast compared to the vibrational period.

$$\Delta v = v' - v'' = 4:$$

**Most likely transition in this case**
Problems with ‘Simple’ Absorption Spectroscopy

• How to distinguish extinction due to scattering by aerosol particles (Mie scattering) and by air molecules (Rayleigh scattering) from molecular absorption?

• How can absorptions due to more than one trace gas be separated?

• Effects of degradation of light source, optics, or detector?
How Transparent is the Air?

Extinction Coefficient [km⁻¹]

Wavelength [nm]

- Aerosol-Extinction
- Rayleigh-Scattering
- O₃-Absorption (50 ppb)
- H₂O-Absorption (8600 ppm)
- NO₂-Absorption (20 ppb)

without O₂
Differential Optical Absorption Spectroscopy – The Idea

- Use **differences** of intensities at different wavelengths
- Record the intensity in **many** (typ. several 100) wavelength **channels** (entire spectra)
- **High pass-filtering** of spectra ⇒ remove continuum
- **Fit** reference **spectra** ⇒ Make use of all spectral information
Example: Absorption Cross Section and DOAS – Spectrum of SO$_2$
Differential Optical Absorption Spectroscopy

Lambert-Beer’s Law:

\[ I(\lambda) = I_0(\lambda) \cdot e^{-\sigma(\lambda) \cdot c \cdot L} \]

\[ I(\lambda) = I_0(\lambda) \cdot e^{-\left[\sum \sigma_i^\prime(\lambda) \cdot c_i \cdot L + (\sigma_{\text{bi}} \cdot c_i + \varepsilon_{\text{Ray}}(\lambda) + \varepsilon_{\text{Mie}}(\lambda)) \cdot L\right]} \cdot T(\lambda) \]

Remove by high-pass filtering

narrow-band extinction

Rayleigh scattering \( \sim \lambda^{-4} \)

Trace gas absorption absorption cross section \( \sigma(\lambda) \)

Turbulence

Lamp \( I_0(\lambda) \)

Mie Scattering \( \sim \lambda^{-1\ldots3} \)

Detector \( I(\lambda) \)
From Total Absorption to Differential Absorption

- $I_0(\lambda)\to I_0'(\lambda)$
- $\sigma(\lambda)$
- $\sigma_b(\lambda)$
- $\sigma'\to \sigma_b$
- Continuous gas absorption
- Rayleigh Ext.
- Mie Extinction
Total- and Differential Absorption Cross Sections

Example for the separation of the cross section into its differential and broad-banded parts using an NO$_2$ cross section.

Total cross section (solid line) and broad-band structure (dashed line), derived by interpolating a 3$^{rd}$ order polynomial.

Differential cross section.

From: Frieß 2000
Differential Cross Sections of Atmospheric Molecules
Absorption Cross sections of a Series of Monocyclic Aromatic Hydrocarbons and of O₂ in the Near UV
Deconvolution of NO$_2$ and HONO Spectra
PiPaPo – Campaign, Milano, 1998

A: Atmospheric spectrum

B: NO$_2$ found

C: HONO found

D: HONO reference spectrum

Very weak lines
typ. $<< 1\%$

Lots of photons needed
$>> 10^4$

Note suppressed zero!
Quantitative Evaluation of DOAS Spectra
How is it actually done?

• “Technical correction”
• High pass filtering
• Remove Fraunhofer Spectrum
• Remove “Ring Effect”
• Fit known absorption spectra
• Account for spectral shift
• Account for change in dispersion
• Correct sampling artefacts
• Correct for “I₀ effect”

Passive DOAS only
From Analog Light to Digital Spectrum

- Sufficient sampling?
- Sufficient resolution?
- Log or lin.?
Effect of Spectral Resolution - Key to Absolute Calibration (Example: NO₂)

Spectral Resolution:
- 0.01 nm
- 0.3 nm
- 1.0 nm
- 3.0 nm

Flow Chart of a typical Active DOAS Evaluation
DOAS Evaluation Procedures (1)

\[ I'(\lambda) = I'_0(\lambda) \cdot e^{-L \cdot \sum_j \sigma'_j(\lambda) c_j - L \cdot \left[ \sum_i \sigma_{0j}(\lambda) c_j + \varepsilon_R + \varepsilon_M \right]} \cdot A(\lambda) \]

\[ D'_{\text{meas.}} (\lambda) = \ln \left( \frac{I'_0(\lambda)}{I'(\lambda)} \right) = L \cdot \sum_j \sigma'_j(\lambda) c_j + L \cdot \left[ \sum_j \sigma_{0j}(\lambda) c_j + \varepsilon_R + \varepsilon_M \right] + \ln A(\lambda) \]

- **Differential Part**
- **Continuous Part**

\[ D'_{\text{Fit}} (\lambda) = \sum_j a_j \sigma'_j (\lambda) + \sum_k b_k \lambda^k \]

= ‘Modelled Spektrum’

Determine Coefficients \(a_i, b_i\) such that:

\[ \chi^2 = \sum_i \left[ D'_{\text{Fit}} (\lambda_i) - D'_{\text{meas}} (\lambda_i) \right]^2 = \]

\[ = \sum_i \left[ \sum_j a_j \sigma'_j (\lambda_i) + \sum_k b_k \lambda_i^k - D'_{\text{meas}} (\lambda_i) \right]^2 = \text{min} \]
DOAS Evaluation Procedures (2)

Coefficients $a_j$, $b_j$ for minimum $\chi^2$ can be calculated as long as $D'$ is linear in $a_j, b_k$:

$$\frac{d\chi^2}{da_j} = \sum_i \frac{d}{da_j} \left[ \sum_j a_j \sigma'_j(\lambda_i) + \sum_k b_k \lambda_i^k - D'_{\text{meas}}(\lambda_i) \right]^2 = 0$$

Since $\frac{dx_l}{da_j} = 0$ unless $l = j$

this leads to a system of $N$ linear equations ($N = \text{No. of reference spectra } \sigma_j + \text{degree of polynomial } b^k \lambda_i^k$).

Only if „non-linear“ parameters, like shift in wavelength are included „fitting“ algorithms like Levenberg-Marquardt are required.
Atmospheric Species Measurable by DOAS

Many species can be detected at ppt levels (mix. Ratio of $10^{-12}$) or below
Some DOAS Characteristics

- 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.
Aktive vs. Passive DOAS

Active:
Artificial Light Source (Xe-arc, incandescent lamp, LASER, LED ...)

Advantages:
• Day and night operation
• Wavelengths below 300nm accessible
• Well defined light path (mostly)

Disadvantages:
• Complex set-up (bi-static design)
• 3rd dimension difficult
• Aerosol measurements difficult

Passive:
Natural Light Source (Sun, Moon, Stars, ...)

Advantages:
• Simple set-up (mono-static design)
• 3rd dimension accessible
• Aerosol measurements possible

Disadvantages:
• Daytime only operation
• Only wavelengths above 300nm accessible
• Ill defined light path
Active DOAS Spectroscopy in the Atmosphere

Active DOAS use artificial light source (e.g. Xe-arc)

1) Long-Path DOAS (LP-DOAS)

\[ c = \frac{\ln \frac{I_0}{I}}{\sigma \cdot L} \]

2) Folded-Path DOAS

EUPHORE
SAPHIR
3) Cavity Enhanced DOAS

Intensity entering the cavity: \[ I_{in} = I_L \cdot (1 - R) = I_L \cdot \rho \]
Example: \[ R = 0.9999 \Rightarrow I_{in} = 10^{-4} \cdot I_L \]

Intensity inside the cavity \( I_R \):
\[ I_{in} = I_L \cdot \rho = I_C \cdot N_{refl} \cdot 2\rho \Rightarrow I_C = \frac{I_L}{2} \]

Intensity leaving the cavity, \( I_{out} \):
\[ I_{out} = I_C \cdot \rho = I_L \cdot \frac{\rho}{2} \]
Example: \[ R = 0.9999 \Rightarrow I_{out} = 5 \cdot 10^{-5} \cdot I_L \]

Once in the cavity each photon stays for:
\[ N_{refl} = \frac{1}{1 - R} = \frac{1}{\rho} \] Reflections, Light Path: \[ L_0 = d \cdot N_{refl} = \frac{d}{\rho} \]
Example: \[ R = 0.9999 \Rightarrow N_{refl} = 10^4, \quad L_0 = 10^4 \cdot d \]
4) Tomographic DOAS

Examples:

a) Tomographic indoor validation study (Mettendorf et al. 2005)

b) NO$_2$ Distribution at a Highway near Heidelberg (Pundt et al. 2003)

c) Distribution of trace gases in Heidelberg (Pöhler 2009)
TOMO-DOAS at the Autobahn
Pundt et al. 2003

Crossing light beams
N 40m
S 40m
N 30m
S 30m
N 20m
S 20m
N 10m
S 10m

Parallel light beams
N 40m
S 40m
N 30m
S 30m
N 20m
S 20m
N 10m
S 10m

NO₂ [ppb]

Windspeed [m/s]

Date and time
5/10/2001 06:00 12:00 18:00 00:00 06:00
5/11/2001

Winddirection (°)

Windspeed
Winddirection
Passive DOAS Spectroscopy in the Atmosphere

**Passive DOAS:** Use **natural** light source (sun, moon, stars ...)

5) Zenith Scattered Light (ZSL-DOAS)

6) Multi Axis DOAS (MAX-DOAS)
Passive DOAS Spectroscopy in the Atmosphere

7) Airborne Multi-Axis DOAS (AMAX-DOAS)

8) Balloon-Borne (direct sunlight) DOAS

LPMA/DOAS Gondola + Balloon
Passive DOAS Spectroscopy in the Atmosphere

9) Satellite - Borne DOAS - Nadir Geometry
   GOME, GOME 2
   ILAS
   SCIAMACHY
   OMI, ILAS-2 ...

10) Satellite - Borne DOAS - Scattered Light Limb Geometry
    e.g. SCIAMACHY

11) Satellite - Borne DOAS - Occultation
    e.g. SCIAMACHY
Passive DOAS Spectroscopy in the Atmosphere

12) Imaging DOAS (I-DOAS)

13) Topographic Target Light Scattering - DOAS (ToTaL – DOAS)
14) Determination of the Photon – Pathlength $L$ (in Clouds) ‘inverse DOAS’

$$L = \frac{\ln \frac{I_0}{I}}{\sigma \cdot c}$$

Discoveries of Atmospheric Trace Gases by DOAS

OH (simultaneously with LIF?)
NO$_3$
HONO
O$_4$
OCIO strat.
ClO trop.
BrO strat. and trop.
IO
OIO
$(H_2O)_2$
Schematics of a “Coaxial“ Active DOAS Instrument

Main mirror
ø 20...30cm
f=0.6...1.5m

Injection/extraction mirrors

Fiber to spectrograph

Spectrograph

Retro reflector

Xenon high pressure lamp
150-500W

200m...10km
Components of an Active DOAS Instrument

- Main Mirror
- Retro-reflector array
- Xe-Lamp House
The Fiber-DOAS Instrument
see Kern et al. 2008
Passive DOAS – Direct Radiation

Trace gas layer

Zenith

Spectrometer + Telescope

“Slant“ Column Density $S$: $S = \int_{0}^{\infty} c(s) ds$

Vertical Column Density $V$: $V = \int_{0}^{\infty} c(z) dz$

Airmass Factor $A$: $A = \frac{S}{V}$
Passive DOAS – Scattered Radiation
Multi-AXis DOAS (MAX-DOAS)

\[ S = \int_0^s c(s') ds' = \int_0^s \frac{c(z)}{\cos(\vartheta)} dz = \frac{1}{\cos(\vartheta)} \cdot V \]

\[ S = \int_0^s c(s') ds' = \int_0^s \frac{c(z)}{\sin(\alpha)} dz = \frac{1}{\sin(\alpha)} \cdot V \]

Remember Demonstration by Prof. Wagner ...
Passive DOAS – Scattered Radiation

Radiation scattered into the spectrometer's field of view

Zenith

direct Solar radiation

Weighting function

Spectrometer

$\alpha$

$L_S$
MAX-DOAS: How to Determine Vertical Profiles

\[ h = L_s \cdot \sin(\alpha_0) \]

\[ c_j = \frac{S_j}{h} \]
AMF as a Function of Observation-Elevation and Solar-Zenith Angles

- **P1-P4**: Tropospheric Profiles
- **P5**: $O_4$
- **P6**: Strat. (25Km, 10Km FWHM)

Ground albedo 5%
Vertical Resolution of MAX-DOAS \( \rightarrow \) ‘Poor Man’s LIDAR’


Hönninger and Platt, 2000
Ratios of the modelled $O_4$ and $NO_2$ - Diff. AMF's at different elevation angles → Determine Layer Height

$O_4$-AMF ratio of 2° and 90° elevation angle

Ratios of the modelled $NO_2$ - Diff. AMF's at 2° and 20° elevation angle --> Determine Layer Height

$O_4$-Absorption (Greenblatt et al., 1996)

Ratio of the NO$_2$-DAMFs/DSCD of 2° and 20° elevation angle

Box Height [m]
Slant column densities of NO₂ and O₄ in Heidelberg, July 2003

Reference spectrum of July 6 of at noon
Flow Chart of MAX-DOAS Trace Gas + Aerosol Evaluation Procedure

Sinreich et al. 2005
MAX-DOAS Measurements of NO$_2$ from Polarstern 2000

Leser et al. GRL 2003
doi:10.1029/2002GL015811
Hudson Bay 2001: Comparison of BrO Measurements by active LP-DOAS and passive MAX-DOAS

Hönninger and Platt, Atmos. Environ. 36, 2481-2489, 2002
MAX-DOAS Measurements of NO$_2$ and Glyoxal (CHOCHO) at Cambridge (Mass.), July 26, 2004

Observed Slant Column Densities

- CHOCHO
  - 3° elevation
  - 6° elevation
  - 10° elevation
  - 18° elevation

- NO$_2$

- O$_3$

Derived Mixed-Layer Height and CHOCHO VMR

Sinreich et al., ACPD 2006
Antarctic BrO, MAX-DOAS Observations from RV Polarstern, 2006

BrO slant column densities at 1° elevation

Summary

• UV-Vis Spectroscopy is a basically simple yet very powerful technique for probing the atmosphere

• For many trace gases DOAS allows sub – ppt detection limits

• DOAS is inherently calibrated

• During recent decades many variants of the DOAS technique were developed to solve a large variety of measurement problems ranging from fundamental research to pollution monitoring and satellite applications