

Differential Optical Absorption Spectroscopy

-How does it work and what can it measure?

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1 Introduction

Differential Optical Absorption Spectroscopy, or DOAS, is a widely used method to determine concentrations of atmospheric species. The technique was first used by U. Platt and D Perner in the late 70s, [6]. It has been used for groundbased applications as well as satellite measurements, for both active and passive instruments [5]. In general, the DOAS technique, is about analysing broadband spectra, in the UV and visible region, that has been transmitted through a long open path. Different atmospheric species will leave their absorption fingerprints in the spectra from which concentrations could be retrieved. The theoretical parts will be derived in section 2.

2 Method

The basic equation of absorption spectroscopy, describing pure absorption of a single species in a homogeneous media, is Beer-Lamberts Law, equation 1.

$$I(\lambda) = I_0(\lambda)e^{-L\sigma(\lambda)n} \quad (1)$$

where $I(\lambda)$ is the measured intensities, $I_0(\lambda)$ the unattended reference intensities, L the pathlength [cm], $\sigma(\lambda)$ the wavelength dependent absorption cross sections [$\text{cm}^2 \text{ molecule}^{-1}$] and n the number density of the species [$\text{molecules}/\text{cm}^3$]. The dimensionless quantity $L \cdot \sigma \cdot n$ is often referred to as the optical depth, denoted τ .

In atmospheric conditions Rayleigh and Mie scattering also contribute to the radiation extinction. By scattering light away from the line of sight these phenomena acts like absorption processes, although they are actually not. Adding Rayleigh and Mie scattering to equation 1 gives;

$$\tau(\lambda) = \ln \frac{I_0(\lambda)}{I(\lambda)} = L (\sigma(\lambda)n + \varepsilon^R(\lambda) + \varepsilon^M(\lambda)), \quad (2)$$

where $\varepsilon^R(\lambda)$ is the Rayleigh extinction coefficient which is the product of the Rayleigh cross section, $\sigma^R(\lambda)$, and the number density of air, n_{air} . Similarly, the Mie extinction coefficient, $\varepsilon^M(\lambda)$, corresponds to $\sigma^M(\lambda)n_{air}$.

Several atmospheric species that have significant absorption cross sections in the studied wavelength interval must be included and Beer-Lamberts law must be further extended. As long as the atmosphere is optically thin, $\tau \ll 1$, the different species can just be added. In addition the attenuation function, $A(\lambda)$, which describes the attenuation of the instrument optics should be included and equation 2 becomes.

$$\tau(\lambda) = L \left(\sum_i \sigma_i(\lambda)n_i + \varepsilon^R(\lambda) + \varepsilon^M(\lambda) \right) A(\lambda), \quad (3)$$

where i denotes atmospheric species, for example: O_3 , NO_2 or SO_2 .

Cross sections for a specific species can be separated in two components, one slowly varying with wavelength, $\sigma_i^s(\lambda)$, and other rapidly varying, $\sigma_i^r(\lambda)$, see figure 1. This rapidly varying cross section is also called differential cross section. The total cross section, $\sigma_i(\lambda)$, is simply the sum of the two components;

$$\sigma_i(\lambda) = \sigma_i^s(\lambda) + \sigma_i^r(\lambda) \quad (4)$$

The slowly varying component, describes the general slope, and the differential cross section corresponds to the difference between the slope and the

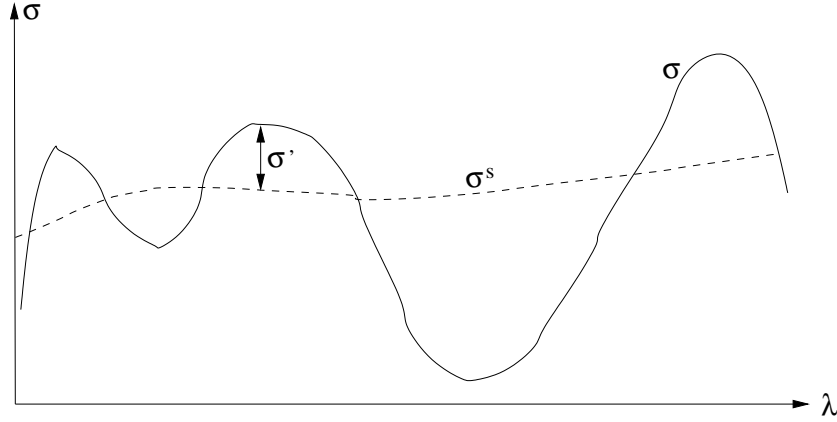


Figure 1: The differential cross section, σ' , is the difference between the total cross section, σ and the slowly varying, σ^s .

total cross section. σ_i^s , is calculated through a digital smoothing of σ_i . Note that both Rayleigh and Mie scattering as well as the attenuation function are slowly varying with λ , hence they can be referred to a slowly varying component of the optical depth. Inserting 4 into 3 gives:

$$\tau(\lambda) = L \underbrace{\sum_i \sigma'_i(\lambda) n_i}_{\text{rapid}, \tau'} + L \underbrace{\left(\sum_i \sigma_i^s(\lambda) a_i + \varepsilon^R(\lambda) + \varepsilon^M(\lambda) \right)}_{\text{slow}, \tau^s} A(\lambda) \quad (5)$$

Assigning the rapidly varying component, $\tau'(\lambda)$, of the measured optical depth, to the absorption due to differential cross sections, $\sigma'(\lambda)$, makes a separation possible. It's now obvious that by studying differential cross sections and the rapidly varying part of the optical depth, Rayleigh and Mie scattering as well as the attenuation function can be left out.

$$\tau'(\lambda) = \ln \frac{I'_0(\lambda)}{I(\lambda)} = L \sum_i \sigma'_i(\lambda) n_i \quad (6)$$

The intensity of an unattended spectrum, $I_0(\lambda)$, includes simulating an absorbing free atmosphere for the local conditions, which is usually very cumbersome for real measurements. In DOAS, only the differential optical depth, τ' , is important which include the much easier simulation of an atmosphere free from differential absorption, $I'_0(\lambda)$, see figure 2. $I'_0(\lambda)$ could be a polynomial fit of some order n ($\sum a_n \lambda^n$), digital smoothing, or some Fourier transform of $I(\lambda)$.

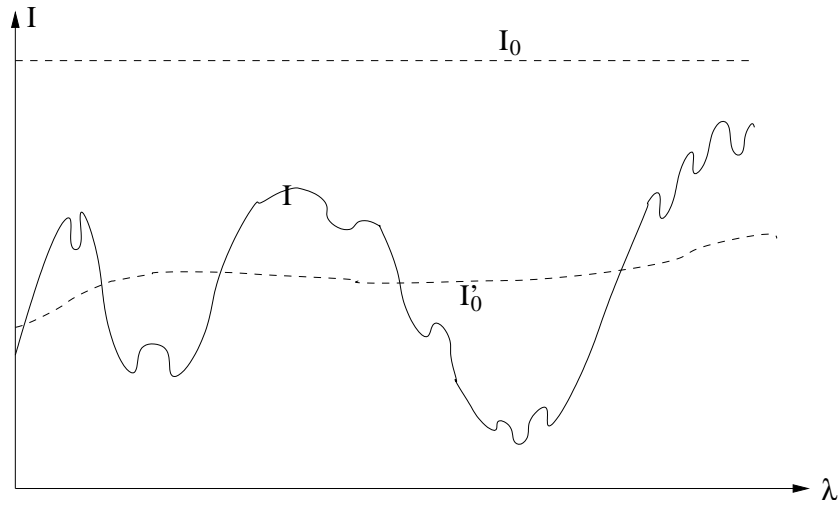


Figure 2: *In DOAS only differential intensities are important, which make the cumbersome calculation of I_0 unnecessary.*

Finally, the number densities for each species are calculated through a least square fit of equation 6

In order to correctly determine the number densities in equation 6, cross sections of the atmospheric species have to be convolved to the wavelength resolution of the instrument. Another way of dealing with this problem would be to measure cross sections with the instrument in a controlled environment with known concentrations.

3 DOAS instruments

The DOAS technique can be used in both passive and active instrumentation, figure 3. In fact both cases need some kind of light source, but the passive technique is referred to extraterrestrial sources.

- Active
 - Thermal light sources. Give a smoothed broadband spectrum, but the divergence could be a problem.
 - Lasers. Give a very low divergence but only narrow spectral emission.
- Passive
 - Occultation of Sun-, Moon- or Star light.

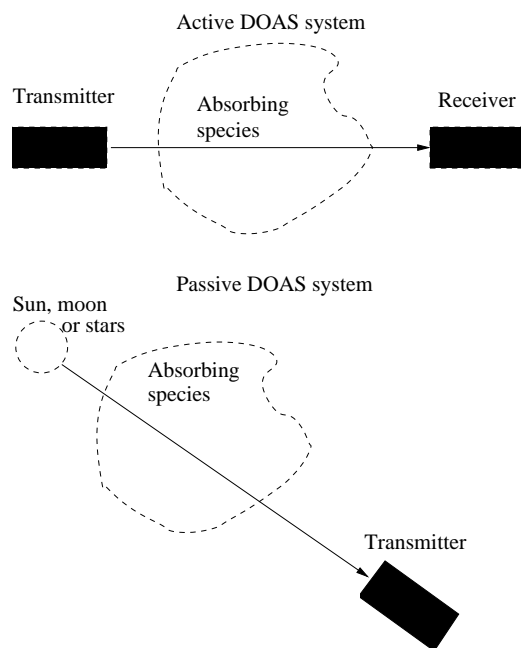


Figure 3: DOAS systems could be both active or passive

- Scattered light from Sun, Moon or Stars.

In the active techniques, I_0 -spectra and pathlengths could be controlled which is favorable for local measurements. Passive techniques are however more commonly used for big scale observations with satellites or ground based measurements of the stratosphere. Power demanding light sources are not favorable here. One big disadvantage about using extra terrestrial light sources are the Fraunhofer lines which could affect the results through inelastic Raman scattering (Ring effect).

In all DOAS measurements, the pathlength has to be long enough to give measurable absorption and short enough to prevent saturation effects of high optical depth. The transmission of the instrument and the spectral response should also be slowly varying with wavelength.

4 Measurable species

To be detectable with DOAS, species must have reasonably narrow electronic transitions in the UV-visible (300-800 nm) region, see figure 4, which strongly limit accessible molecules. Pathlengths of several kilometers is often needed to detect minor species. If the region is stretched further in UV

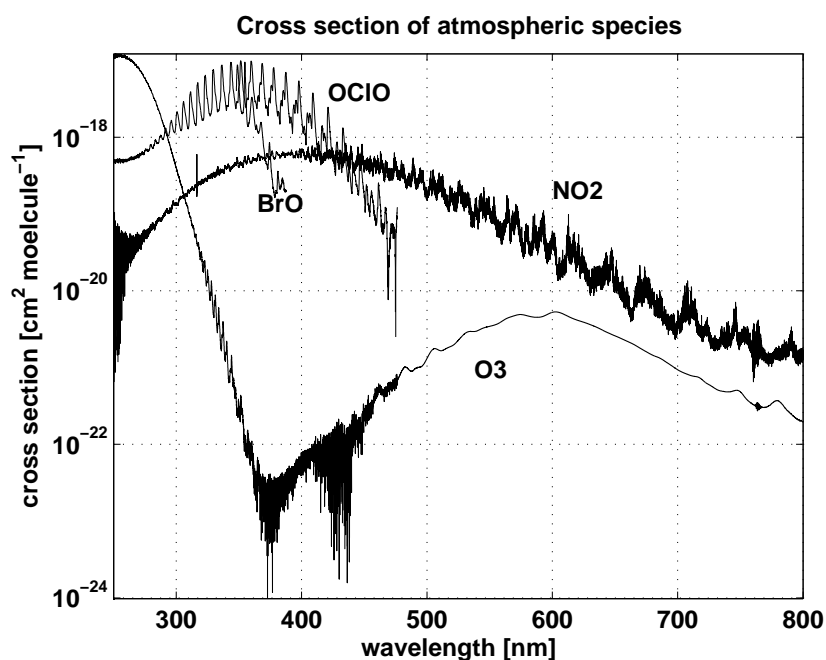


Figure 4: *Cross sections between 250 and 800 nm for some atmospheric species.*

(down to 250 nm), some more species could be retrieved but pathlengths must be reduced due to strong atmospheric attenuation (Rayleigh scattering).

Mainly three categories of compounds could be measured,[1]:

- Photo oxidants: NO_x , O_3 , HNO_2 , CH_2O
- Volatile organic compounds (VOCs) in near UV.
- Radicals: BrO, OClO, IO, and OH

The categories of species including table 4 tells us that DOAS is an important technique for studying ozone depletion and formation.

5 Advantages and disadvantages with DOAS

Advantages:

- Broad band features like Rayleigh and Mie scattering can be omitted.
- No need to estimate I_0 .

Species	Wavelength interval [nm]	Detection limit [ppt]	Pathlength [km]	Reference
SO ₂	290-310	17	0.2	[5]
CS ₂	320-340	500	5	[5]
NO	200-230	240	0.2	[5]
NO ₂	330-500	80	5	[5]
NO ₃	600-670	2	5	[5]
NH ₃	200-230	800	0.2	[5]
HNO ₂	330-380	40	5	[5]
O ₃	300-330	4000	5	[5]
CH ₂ O	300-360	400	0.2	[5]
Benzene	250-290	200	2	[8]
p-Xylene	250-290	100	2	[8]
Benzaldehyde	250-290	46	2	[8]
Ethylbenzene	250-290	560	2	[8]
Styrene	250-290	122	2	[8]
Trimethylbenzen	250-290	600	2	[8]

Table 1: Some atmospheric species that could be detected with DOAS

- High specificity due to broad band spectra.
- High sensitivity due to long pathlengths.
- Possible simultaneous measurements of atmospheric species.

Disadvantages:

- Atmospheric turbulence induce intensity variations in the spectra.
- Only a limited number of molecules have suitable absorptions in UV and visible region.
- Rain, snow, fog and clouds make measurements impossible due to the strong attenuation in the UV-Visible region.

6 Conclusions

DOAS is an highly applicable method for measuring many atmospheric species for local conditions as well as global, with high sensitivity. It has been used to a wide range of purposes as, monitor urban emissions [2], measure ammonia from a dairy [4], observe NO₃ in arctic winter using moonlight [9], supervise volcanic eruptions [7], study stratospheric ozone depletion with satellite [3].

References

- [1] B. Galle, *Development and application of methods based on DOAS and FTIR absorption spectroscopy for atmospheric research*, Ph.D. thesis, Dep. of Experimental Physics, Chalmers university of technology, Sweden, 1999.
- [2] K. Kourtidis, I. Ziomas, C. Zerefos, A. Gousopoulos, D. Balis, and P.Tzoumaka, *Benzene and toluene levels measured with a commercial DOAS system in thessaloniki,greece*, *Atm. Env.* **34** (2000), 1471–1480.
- [3] I. McDade, K. Strong, C. Haley, J. Stegman, D. Murtagh, and E. Llewellyn, *A method for recovering stratospheric minor species densities from the Odin/OSIRIS scattered-sunlight measurement*, to appear in *Can. J. Phys.* (2001).
- [4] G. Mount, B. Rumberg, J. Havig, B. Lamb, H. Westberg, D. Yonge K. Johnson, and R. Kincaid, *Measurement of atmospheric ammonia at a dairy using differential optical absorption spectroscopy in the mid-ultraviolet*, *Atm. Env.* **36** (2002), 1799–1810.
- [5] U. Platt, *Differential optical absorption spectroscopy (DOAS)*, Air monitoring by Spectroscopic Techniques (M. Sigrist, ed.), John Wiley & Sons, Inc., 1994, pp. 27–84.
- [6] U. Platt, D. Perner, and H. W. Pätz, *Simultaneous measurements of atmospheric CH₂, O₃ and NO₂ by differential optical absorption*, *J. Geophys. Res.* **84** (1979), 6329–6335.
- [7] S. Svanberg, *Geophysical gas monitoring using optical techniques:volcanoes, geothermal fields and mines*, *Optics and Lasers in Engineering* **37** (2002), 246–266.
- [8] R. Volkamer, T. Etkorn, A. Geyer, and U. Platt, *Correction of the oxygen interference with uv spectroscopic (DOAS) measurements of monocyclic aromatic hydrocarbons in the atmosphere*, *Atm. Env.* **32** (1998), 3731–3747.
- [9] T. Wagner, C. Otten, K. Pfeilsticker, I. Pundt, and U. Platt, *Doas moonlight observation of atmospheric NO₃ in the arctic winter*, *Geophys. Res. Lett.* **27** (2000), 3441–3444.