



Pollutant Type: Gaseous Pollutants

Pollutant Name: Multi-pollutant Species (e.g. Sulphur dioxide, nitrogen dioxide, nitrogen monoxide, ozone, certain volatile organic compounds and inorganic species, several halogen species, water vapor)

Measurement Technology: (Long-Path) Differential Optical Absorption Spectroscopy (LP-DOAS)

A. Measurement Principle

The technique of differential optical absorption spectroscopy (DOAS) is well known for monitoring a wide range of atmospheric trace gas species, including gaseous pollutants. It was developed as a research tool in the 1970's but currently manufactured equipment is available from a number of different manufacturers. The DOAS technique uses the fact that different types of molecules have their own unique optical absorption spectral properties or spectral "fingerprints". The spectral range usually employed is from about 220 nm to 2500 nm (ultraviolet (UV) to near-infrared (IR)). The absorbed radiation as a function of wavelength will thus be based on the electronic transitions of molecules in the ultraviolet and visible spectral regions, and on the absorption in the infrared from molecular vibrational/rotational transitions of generally hetero-nuclear molecules. The optical absorption spectra of many molecules and free radicals of atmospheric interest lie in these broad spectral regions, which allow many such gaseous species to be detected with the DOAS technique, and many of these can be detected simultaneously in the selected optical path. A summary of the DOAS technique can be found at Platt and Stutz 2008.

A large variety of different DOAS techniques exist all applying the same basic principle of molecule absorption in the UV to near IR spectral range. They can be grouped in two main categories. The first group is Passive DOAS techniques, using natural light sources (typically sunlight). They observe the absorption of the sunlight on the way to the instrument. The most famous application is satellite measurements of molecules like nitrogen dioxide or sulfur dioxide. But also a large variety of ground and airborne instruments are extensively used in the scientific community. Such instruments can provide not only concentration of molecules but also vertical concentration profiles, and aerosol optical thickness. These instruments are relative simple and thus cheap. Currently such Passive DOAS techniques are evaluated in different countries for continuous urban pollution monitoring. Due to the requirement of sunlight, they cannot completely replace other observations.

Here it is focused on the second group of DOAS techniques, the Active DOAS principle. These techniques use an own light source, typically xenon arc lamp or LED's. The absorption of the light over distances of view 100m to several km is than observed in the UV to near IR spectral range. To achieve the long absorption path different sub techniques are applied. The most famous one is the Long Path (LP) system directly measuring over such a long distance in the atmosphere. Most commercial DOAS systems apply this principle; therefore this will be the main focus in this document. Other instruments fold the light path with multi reflection systems like a white-cell or a cavity. Thus also in-situ DOAS measurements are possible.

The LP-DOAS system involves using a beam of optical radiation generated by a broad optical bandwidth (multi-continuous wavelength) optical source. This is usually a high intensity xenon lamp (or LED's), which is collimated and directed over a chosen path of several 100m to km in the atmosphere. This light is then directed onto a reflector and send back to the instrument. In older systems without reflector, a

separate optical telescope acts as a receiver. In the receiving unit, all broad spectral radiation is collected, and then directed in turn onto an optical spectrometer with high spectral resolution. The spectrometer is employed to analyze the intensity of the radiation as a function of its wavelength, as outlined in Section C below.

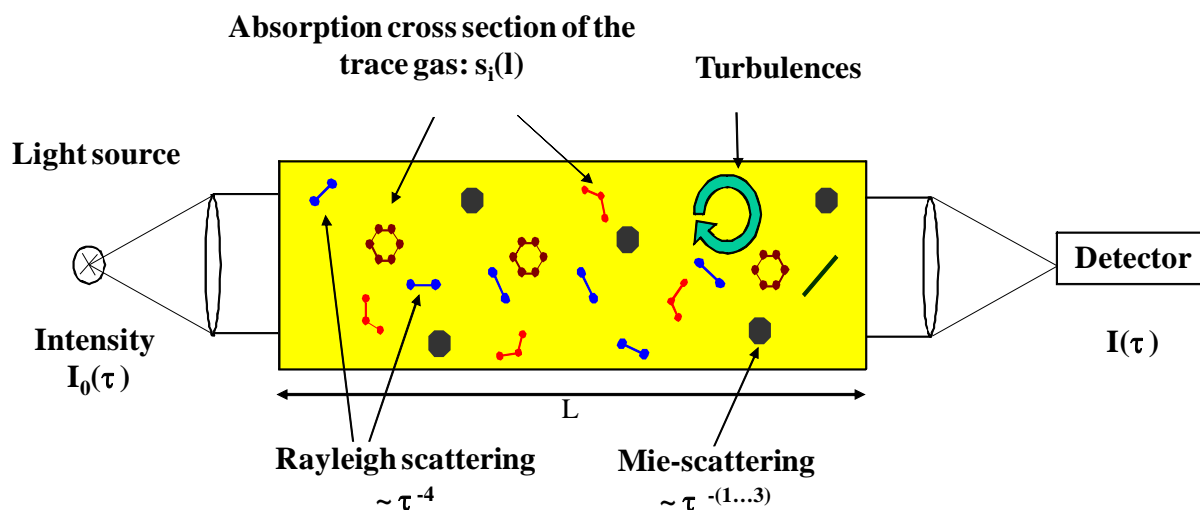


Figure 1: DOAS principle which uses the characteristic differential absorption of molecules over a light path of few meters to several 10km in order to determine its concentration. (reproduced from EN 16253 by permission of CEN-CENELEC)

The method shows good selectivity and sensitivity due to its following combination of technical features:

- The measurement of the intensity of the radiation as a function of wavelength is carried out with high spectral resolution (typically 0.1 nm to 1 nm) over a broad spectral range that comprises numerous vibrational transitions in one or more electronic transitions in the ultraviolet/ visible regions (the main spectral range used in DOAS) or a number of rotational/vibrational transitions in the infrared region. This enables the spectra of the gaseous species present to be readily identified without ambiguity, provided the analyzer is accurately calibrated in wavelength (see below).
- The large number of absorbed wavelengths present for any given gaseous species means that these can be measured with high sensitivity, using de-convolution and nonlinear least squares fitting algorithms, that can be used at optical densities in the absorption spectrum of below 10^{-3} .
- The optical radiation source has a high intensity and is collimated. This means that long optical paths can be established directly through the open atmosphere (typically from 100 metres up to several kilometres for many gaseous species). This increases the detection sensitivities because there are more gaseous molecules in the total optical path for a given average concentration.
- Other optical processes, beside the molecule absorption, absorb the light of the transmitted optical beam quasi-continuous across the measured spectrum. This uniform attenuation of the radiation over this broad spectral region, contains no narrow band absorption features like the detectable molecules and will therefore not affect the results. These processes for example are from absorption and scattering by particulates, aerosols, and droplets, and from the Rayleigh scattering arising from atmospheric species (e.g. nitrogen) particularly in the UV spectral region.

- The DOAS technique is in principle inherent calibrated. Each instrument requires an initial calibration which may be done by means of calibration gases with accurately known concentrations, or by a complete modeling technique based on a knowledge of the optical spectra of the gaseous target species. This latter is most relevant where it is difficult to prepare known calibration gas mixtures (e.g. for unstable species and atmospheric radicals). It also provides the possibility to completely calibrate without calibration gases, what is state of the art for scientific applications.
- The DOAS technique with an open path detection is a non contact measurement method, what means that the observed molecules were not in contact with a surface or inlet which may lead to a change of the concentration due to surface reactions.
- DOAS is a real time measurement and possible to apply for remote sensing.
- The DOAS technique lends itself to a wide range of diverse applications. The LP-DOAS technique is less practical directly to implement in-situ point monitoring stations, as it requires an optical path of few hundred meters (e.g. see EN 16235 Annex F). Modern LP-DOAS systems require only one instrument for transmitting and receiving the light and a reflector. This significantly simplifies the setup, as the instrument can be located at the point monitoring station, and the reflector on any building or pole. New developments of multi-reflection systems which fit in the dimensions of classical in-situ instrument housings come up in the recent years. They combine the advantages of DOAS with in-situ observations.
- The LP-DOAS measurement averages the concentration over a few hundred meter path. This is often an advantage if representative concentrations are required, as it is not disturbed by local fluctuations, e.g. a passing car, or very local phenomenon's like a crossing.

B. Configurations of the LP-DOAS Measurement System

LP-DOAS and similar open-path techniques are double-ended as indicated above, and measure the integrated concentration over the defined extended path length that is set up in the open atmosphere as outlined below. The concentration unit is thus expressed as the “(average) concentration x path length” product, and the (average) concentration in the established optical path in the atmosphere is thus derived from this measured value by dividing by the total path length. One of two basic configurations is generally employed for this:

- (i) In a bi-static configuration (Figure 1), the optical transmitter (xenon lamp or similar) and the detection unit are located separately at the two opposite ends of the open atmospheric optical path. This requires separate power supplies to both ends and also requires a suitable orientation mechanism for aligning the optical beam from the radiation source onto the detection unit, and for co-aligning the detection unit with this source beam, as indicated in Figure 1.
- (ii) A mono-static configuration, similar to the above figure but where the optical source together with its collimating telescope, and a detection unit together with its collecting telescope, are all located at one end of the open atmospheric path as a single unit, and there is a (passive) retro-reflector at the other end of the open atmospheric path. This retro-reflector is generally made up of a two-dimensional array of 90-degree cube-corner reflectors, and it is large enough to reflect most of the transmitted radiation back along an identical path to that received from the transmitter. This has the advantage that electrical power is only required at one end of the open atmospheric path, not both. Another advantage is that the optical radiation is transmitted twice over the open atmospheric path, thereby doubling the path length and increasing the detection sensitivity. A further advantage is that it is somewhat easier to calibrate than the bi-static system (see below). It also allows for simple reference measurement of the light source and background light which improve the measurement

quality. A former disadvantage is that the combined source and receiving system is more complex to engineer and to set up. Newer mono-static systems apply fibre optics which overcome this problem and are simple to adjust.

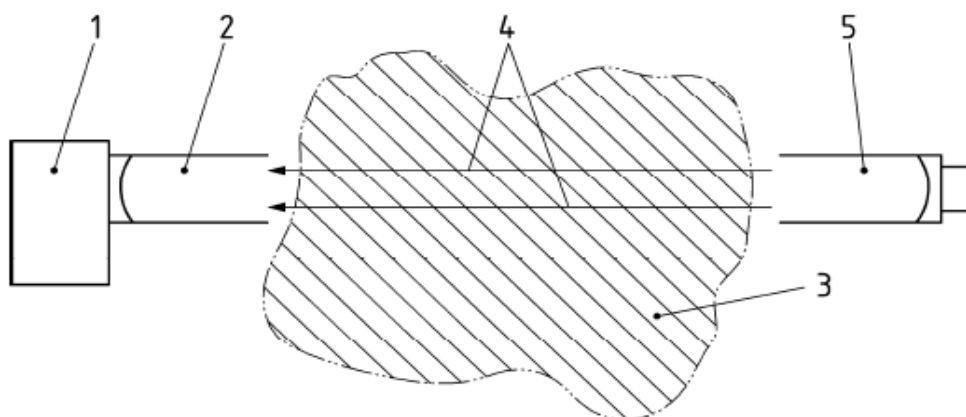


Figure 1 bi-static DOAS configuration (reproduced from EN 16253 by permission of CEN-CENELEC); key

- 1 DOAS spectrometer with high spectral resolution
- 2. Optical telescope for collection of the radiation from the source
- 3. Ambient air containing pollutant gases
- 4. Open atmosphere monitoring path
- 5. Optical radiation source with collimating telescope

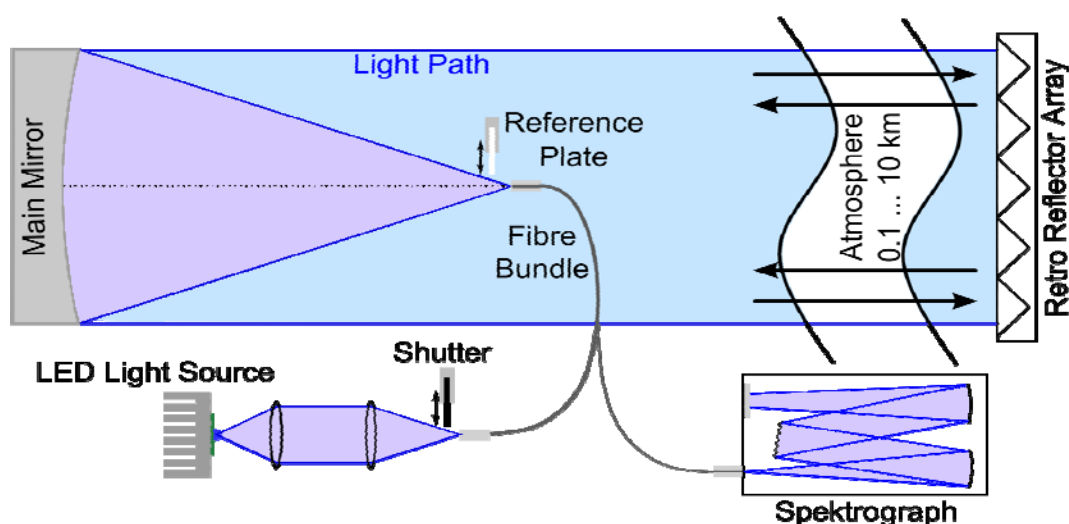


Figure 2: Principle of a mono static set-up with a new type of fiber optics which simplifies the adjustment and operation. The light is coupled through a fibre into the telescope. This transmits a parallel light beam through the atmosphere and is reflected back by the reflector. The light is then transmitted with a fibre to the spectrometer. Reprint by courtesy of D. Pöhler, University of Heidelberg

A high intensity collimated source (as noted above - usually a continuous xenon lamp, high power LED's or similar) is used that has a very broad spectral coverage ideally across the spectrum from the ultraviolet (~260, nm or in certain applications 220 nm) to the infrared (~2500 nm). In practice the system has only to cover the spectral range where molecules of interest feature strong absorption structures. In addition, if the requirement is to monitor nitrogen monoxide, this requires an ultraviolet source at wavelengths around 226 nm, which requires a special xenon lamp that has a fused silica window that transmits well at these wavelengths. In this case, in addition, there is also a limitation on the optical path length that can be used, due to atmospheric absorption, which in turn limits the detection sensitivity of the DOAS technique for nitrogen monoxide. There may also be a requirement for improved transmission of this fused silica window of the optical transmitter in the infrared for some applications.

It is also possible to make measurements over a relatively short open atmospheric path length, but to increase their sensitivity by means of a multiple reflection system at either end of the path. This is more complex to implement but has been carried out in research studies (e.g. to monitor pollutants in a road tunnel (Kurtenbach et al 2002) where a range of aromatic hydrocarbons were monitored using a base path of 15 m with a total folded atmospheric path length of 720 m)

Also several other DOAS configurations exist, for example applying multi-reflection systems (e.g. White-system) to achieve a long absorption path in a relative compact setup. Recently also Cavity Enhanced systems are used which achieve an absorption path of several km in a few ten cm long setup. Several of these systems are used in science and may become commercially available in the next years.

It is possible to operate the DOAS technique without any active light source such as that described above. Instead the receiving telescope and detection system measures scattered UV/visible radiation from the sun or other sources (e.g. moon), and thus this method is called "Passive DOAS". There are a large variety of Passive DOAS applications from ground based, mobile, airborne and satellite depending on the required application. For example a vertically up into the atmosphere pointed ground passed telescope can determine an effective total column concentration of, for example, nitrogen dioxide in the atmosphere above the DOAS system, and then by moving the system upwind and downwind of a local source the emissions from that source may be determined. This has been demonstrated to produce satisfactory results (Johansson et al 2008), but this is not the normal configuration of the technique for monitoring gaseous species close to the ground, as required by EC directives. The most common Passive-DOAS configuration is the Multi Axis (MAX-DOAS) which observes the scattered sunlight from different elevation angles. It allows in combination with radiative models to derive not only vertical columns, but complete vertical profiles of aerosols and molecules from ground level up to several kilometers. Currently studies are performed how such mostly scientific measurements can also be used for monitored pollutants. The main disadvantage of Passive DOAS techniques is that it requires daylight.

C. Detection Systems

As indicated above, one of the advantages of the DOAS technique is that it allows for the measurement of the concentrations of a range of atmospheric species simultaneously. A list of the usual gaseous trace species that may be monitored using the DOAS technique is given in Table 1. It can be seen that this is a large list covering both hydrocarbons and other species, and it may be noted that this covers all the gaseous pollutants that are required to be monitored by EU Directive 2008/50/EC. The spectra of these regulated species are covered with the ultraviolet/visible spectral regions and thus they are typically all monitored using one instrument.

The DOAS technique requires that the detection system has the capability to resolve all the wavelengths necessary to determine the concentration of a given gaseous pollutant species. There are several methods for doing this in practice, including:

(a) By the use of a spectrometer as shown as an example in Figure 2 below. The grating resolves the source spectrum that has been transmitted through the atmosphere, which is then either:

- Focused on a multi array photo-detector (e.g. CMOS PDAs, or CCD arrays) that may be used to determine the spectrum. This is today the most common way.
Older versions used a large diameter detector with the spectrum dispersed across this, and a mechanical slit is then scanned across the detector so that the spectrum is measured as a function of where the slit is across the detector. The spectrum was produced as a function of the time/position of the slit as it is scanned across the detector;
- Other older versions employed scanning of the spectrum from the diffraction grating across a detector that was small. This provided the dispersed spectrum wavelength as a function of the position of the scanned grating;

(b) By replacing the usual grating spectrometer and its multi-array detection system with a fourier-transform (FT) spectrometer. The optical radiation received at the collection telescope is directed into the input optics of the FT spectrometer and a scanned mirror (usually a cube-corner) within the FTIR spectrometer provides the dispersion of the wavelengths of the optical source. This requires sufficient movement of the scanned FTIR mirror to provide the requisite spectral resolution.

This type of detection system is generally used when the DOAS technique is often employed to measure gaseous pollutants that have absorption spectra in the infrared spectral region (usually also at wavelengths less than or equal to 2500nm), and their measurement is not practical in the ultraviolet and/or visible. In this case it is clearly necessary for the FT spectrometer to operate in the correct region of the infrared, with an appropriate infrared detector.

(c) It is also possible to replace the broad spectral bandwidth optical source with one which has much less spectral coverage (e.g. by using one or more lasers), and then other detection techniques are more practical. However, this reduces considerably the multi-species monitoring capability that is one of the strengths of the DOAS technique, and this configuration therefore is usually applied to very specialized trace gas monitoring (e.g. for atmospheric radical measurements), and it is not usually applicable to the monitoring of pollutant species that are regulated by means of the EU ambient air Directive.

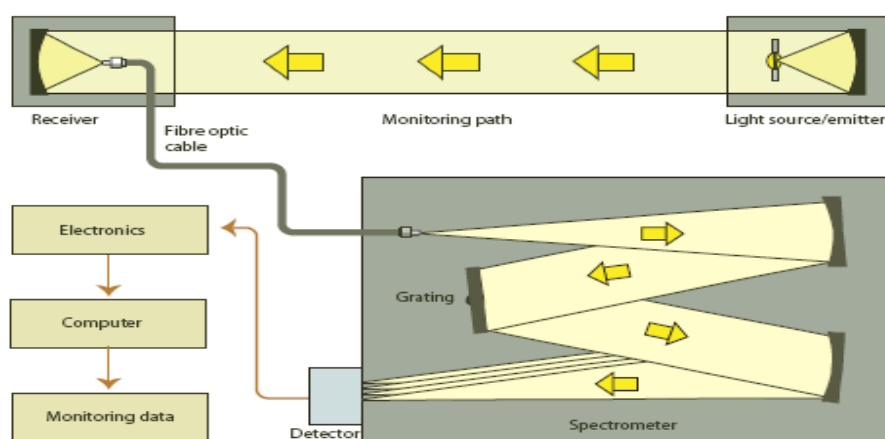


Figure 2: Schematic of a bi-static DOAS system operated using a grating spectrometer in the ultraviolet/visible spectral region (reproduced from EN 16253 by permission of CEN-CENELEC)

D. Practical Limitations of the DOAS Technique

There are a number of limitations in practice in the operation of the DOAS technique if accurate results are to be obtained for selected gaseous trace species in the atmosphere. Examples of these are:

- (a) As noted previously, the DOAS technique actually measures the product of the concentration of gaseous species in the atmospheric path and its path length. It produces, for example, the same absorption signal and hence the same result with a uniform concentration of atmospheric gas species over the entire selected atmospheric path as it will for a much higher concentration localized at some point in this open atmospheric path, with the same product concentration. Thus there is no range resolution of the gaseous species in the path and the “average” concentration is presented, by knowing the open path length. Spatial fluctuations of the gas concentrations within the fixed optical path are only detectable as fluctuations in this average concentration. This has advantages including the fact that the results could be considered more representative of the wider area. A disadvantage is that they do not mimic well the large fluctuations that may occur locally at a point location such as the human breathing zone.
- (b) A European (CEN) standard has been published that covers the LP-DOAS technique (EN 16235). However, the DOAS technique is not specified as a reference method for use in monitoring the pollutants specified in the EC’s ambient air regulation (Directive 2008/50/EC), even if it is in many countries outside the EU. This means that the DOAS technique has not been taken up for use with EC regulatory ambient air monitoring purposes to any significant extent. It is of course possible for any ambient air monitoring technique to be used for these purposes once it has been demonstrated as “equivalent” within the requirements of the EC document “ Guide to the Demonstration of Equivalence of ambient Air Monitoring Methods”. However, this procedure entails operating any method that is seeking to become equivalent alongside the relevant reference method given in the DIRECTIVE, Annex IV. This would mean comparisons of the results obtained from a point-monitoring reference method with those obtained from the open atmospheric path LP-DOAS technique, with its open atmospheric path averaging of the ambient air concentrations. In these circumstances it is unlikely that the two data sets would agree consistently, within the specifications given in the current version of the Guideline (GUIDE), unless the tests were carried out at a remote site where there are insignificant local fluctuations of the gaseous pollutants. Tests of this have been carried out, for example for ozone and nitrogen dioxide. Thus there are few instruments which prove these agreements and are in principle allowed for monitoring regulated pollutants. However such regulations of comparison, which make no sense from scientific point of view, should be updated. In principle EC’s regulation should be updated to allow new measurement techniques. For the DOAS technique it becomes obvious that there is a large gap between EC’s ambient air regulation and scientific ambient air measurements, where DOAS is reliably applied since decades.
- (e) DOAS spectroscopy requires like most spectroscopic principles a precise wavelength calibration, which should be checked regularly. A shift of the wavelength calibration (e.g. due to temperature variations of the spectrometer) may result in an incorrect spectral information for the data analysis. A known example of this is when monitoring low concentrations of benzene in the atmosphere in the presence of (higher) concentrations of aromatic hydrocarbons (e.g. toluene) that have spectral features that are adjacent to benzene in the ultraviolet region. Then, if the wavelength axis of the spectrometer is not accurately calibrated, it is possible to misidentify benzene in the atmosphere as

another aromatic - with consequential incorrect results. It should be noted, however, that the DOAS technique generally is equipped with some regular checking of the wavelength axis to reduce problems with this. This is carried out by utilizing certain spectral absorption features that are generally present – for example the xenon spectral line from the source lamp, and absorption that occurs from oxygen in the atmosphere itself. Other emission or absorption features may be used - depending on the application (e.g. wavelength calibration lamps). To avoid problems with spectral shifts many instruments apply additional methods like temperature stabilizing the spectrometer.

Table 1: Gaseous species that may be monitored using the DOAS technique operating in the infrared and ultraviolet/visible spectral regions (regulated species in bold letters)

| Hydrocarbons | Non-hydrocarbons |
|------------------------------------|---|
| ethyne C_2H_2 | bromine Br_2 |
| ethene C_2H_4 | chlorine Cl_2 |
| ethane C_2H_6 | chlorine dioxide ClO_2 |
| acetaldehyde C_2H_4O | carbon monoxide CO |
| formaldehyde $HCHO$ | carbon dioxide CO_2 |
| propane C_3H_8 | phosgene $COCl_2$ |
| trimethylbenzene $C_6H_3(CH_3)_3$ | carbon disulphide CS_2 |
| o-,m-,p-xylene, $C_6H_4(CH_3)_2$ | water vapour H_2O |
| ethylbenzene $C_6H_5C_2H_5$ | hydrogen sulphide H_2S |
| styrene $C_6H_5CH=CH_2$ | hydrogen bromide HBr |
| phenol C_6H_5OH | hydrogen chloride HCl |
| benzene C_6H_6 | hydrogen cyanide HCN |
| toluene C_7H_8 | hydrogen fluoride HF |
| o-,m-,p-cresol $CH_3C_2H_4OH$ | mercury Hg |
| methane CH_4 | nitrous acid HNO_2 |
| ethanol C_2H_6O | nitrous oxide N_2O |
| methanol CH_4O | ammonia NH_3 |
| naphthalene $C_{10}H_8$ | nitrogen monoxide NO |
| glyoxal $CHOCHO$ | nitrogen dioxide NO_2 |
| | nitrate radical NO_3 |
| | oxygen O_2 |
| | ozone O_3 |
| | sulphur dioxide SO_2 |
| | sulphur trioxide SO_3 . |

NOTE: the detection sensitivities of the DOAS technique for the above listed species vary enormously; The spectral wavelength ranges that are suitable for measuring some of these gaseous species, and their estimated detection sensitivities achievable, are listed in Table 2.

Table 2: Wavelength intervals and typical detection limits achievable with DOAS (From Platt and Stulz 2008.)

| Species | Wavelength interval in nm | Detection limit ^a in ppt |
|--|------------------------------|--|
| SO ₂ | 200 – 230 | 62 |
| | 290 – 310 | 700 |
| CS ₂ | 320 – 340 | 10000 |
| NO | 200 – 230 | 167 |
| NO ₂ | 330 – 500 | 1600 |
| NO ₃ | 600 – 670 | 20 |
| NH ₃ | 200 – 230 | 22 |
| HNO ₂ | 330 – 380 | 780 |
| O ₃ | 300 – 330 | 40000 |
| H ₂ O | above 430 | 1,33·10 ⁵ |
| CH ₂ O | 300 – 360 | 8300 |
| ClO | 260 – 300 | 110 |
| OCIO | 300 – 440 | 35 |
| BrO | 300 – 360 | 40 |
| OBRO | 400 – 600 | 35 |
| I ₂ | 500 – 630 | 220 |
| IO | 400 – 470 | 20 |
| OIO | 480 – 600 | 36 |
| Benzene | 240 – 270 | 180 |
| Toluene | 250 – 280 | 310 |
| Xylene (o/m/p) | 250 – 280 | 2000/650/210 |
| Phenol | 260 – 290 | 20 |
| Cresol (o/m/p) | 250 – 280 | 200/135/50 |
| Benzaldehyde | 280 – 290 | 90 |
| Glyoxal | 400 – 480 | 400 |
| ^a Most of the values were calculated for an optical path length of 5000 m. For this table they were referred to an optical path length of 500 m using the conversion factor 10. | | |

E. References

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