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Air quality — Atmospheric measurements near ground with active Differential Optical Absorption Spectroscopy (DOAS) — Ambient air and diffuse emission measurements

National foreword

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English Version

**Air quality - Atmospheric measurements near ground with active
Differential Optical Absorption Spectroscopy (DOAS) - Ambient
air and diffuse emission measurements**

Qualité de l'air - Mesurages atmosphériques à proximité du
sol par Spectroscopie d'Absorption Optique Différentielle
(DOAS) - Mesurages de l'air ambiant et des émissions
diffuses

Luftqualität - Messungen in der bodennahen Atmosphäre
mit der aktiven Differentiellen Optischen
Absorptionsspektroskopie (DOAS) - Immissionsmessungen
und Messungen von diffusen Emissionen

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Foreword

This document (EN 16253:2013) has been prepared by Technical Committee CEN/TC 264 “Air quality”, the secretariat of which is held by DIN.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by January 2014, and conflicting national standards shall be withdrawn at the latest by January 2014.

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Introduction

Differential Optical Absorption Spectroscopy (DOAS) has been successfully progressed, starting in the late 1970s, from a laboratory based method to a versatile remote sensing technique for atmospheric trace gases. In the DOAS measuring process, the absorption of radiation in the ultraviolet, visible or infrared spectral range by gaseous constituents is measured along an open monitoring path between a radiation source and a spectrometer, and the integral concentration over the monitoring path is determined.

DOAS systems support direct multi-constituent measurements. They provide alternative measuring techniques in that they can handle a large number of measuring tasks which cannot be adequately addressed by in situ techniques based on point measurements. Examples of such tasks include the monitoring of diffuse emissions from area sources such as urban settlements [1], traffic routes, sewage treatment plants and industrially or agriculturally used surface areas; the minimisation of production losses through a detection of leaks in equipment zones or pipeline systems; or ambient air monitoring in any of the above-mentioned applications.

With an appropriate measuring set-up, the local air pollution can usually be assessed very quickly. Measurements can be taken effectively even in areas which are difficult or impossible to access, or where the direct presence of personnel or equipment would be hazardous. The measurement in the open atmosphere eliminates potential losses by sample handling. An overview on the DOAS measurement technique can be found in [2].

1 Scope

This European Standard describes the operation of *active* DOAS measuring systems with continuous radiation source, the calibration procedures and applications in determining gaseous constituents (e.g. NO₂, SO₂, O₃, BTX, Hg) in ambient air or in diffuse emissions.

2 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

2.1

active DOAS

DOAS with artificial radiation source

2.2

background spectrum

spectrum taken by the DOAS system with the light beam blocked or the lamp switched off

Note 1 to entry: The background spectrum results mainly from scattered sunlight.

2.3

complete spectral modelling

process of using synthetic spectra to match with observed experimental spectra

2.4

dark spectrum

spectrum which identifies the thermal effects of the detector when no radiation is admitted to the detector

2.5

electronic offset spectrum

spectrum which identifies the electronic effects of the detector when no radiation is admitted to the detector

2.6

instrument line shape

ILS

mathematical function which describes the effect of the instrument's response on a monochromatic line

2.7

intensity

radiant power per unit solid angle (non-collimated beam) or per unit area (collimated beam)

2.8

lamp spectrum

spectrum which is achieved by admitting direct light from the lamp to the spectrometer

2.9

monitoring path

actual path in space over which the pollutant concentration is measured and averaged

2.10

open-path measurement

measurement which is performed in the open atmosphere

2.11

path length

distance that the radiation travels in the open atmosphere

2.12

reference spectrum

spectrum of the absorbance versus wavelength for a pure gaseous sample under defined measurement conditions and known and traceable concentrations

2.13

signal-to-noise ratio

ratio between the signal strength and its standard deviation

3 Symbols and abbreviations

3.1 Symbols

$a(\lambda)$	specific absorption coefficient at wavelength λ
$a_i(\lambda)$	specific absorption coefficient of constituent i at wavelength λ
$a_{0i}(\lambda)$	portion of the specific absorption coefficient which varies little with the wavelength
$a'_i(\lambda)$	portion of the specific absorption coefficient which varies strongly with the wavelength
a_M	Mie scattering coefficient
a_R	Rayleigh scattering coefficient
c	mass concentration
c_{AE}	aerosol mass concentration
c_i	mass concentration of constituent i
c_{LM}	density of air
d_j	coefficient j of a polynomial
$D(\lambda)$	optical density
$D'(\lambda)$	differential optical density
i	index number
$I(\lambda, l)$	intensity of received radiation of wavelength λ after a path-length l
$I_0(\lambda)$	intensity of emitted radiation of wavelength λ
$I'_0(\lambda, l)$	differential initial intensity
$I_{mod}(\lambda)$	modelled intensity
l	length of the monitoring path
M_i	molar mass of component i

p	atmospheric pressure
R	molar gas constant (= 8,3145 J/(mol·K))
$S(\lambda)$	intensity of scattered solar radiation of wavelength λ
T	ambient temperature
x_i	mixing ratio of component i
$\tau(\lambda)$	attenuation factor of the optical system

3.2 Abbreviations

DOAS	Differential Optical Absorption Spectroscopy
IR	Infrared
UV	Ultraviolet
UV/VIS	Ultraviolet/Visible

4 Principle

4.1 General

The DOAS measurement is based on the principle whereby the atmospheric concentration of gaseous constituents is quantified on the basis of their characteristic absorption of radiation. The radiation spectrum examined for this purpose ranges from near ultraviolet to near infrared (approximately 250 nm to 2 500 nm). Accordingly, the analysed absorption of radiation will be based on electronic transitions in molecules and, possibly, atoms and in the near infrared on molecular vibrational transitions.

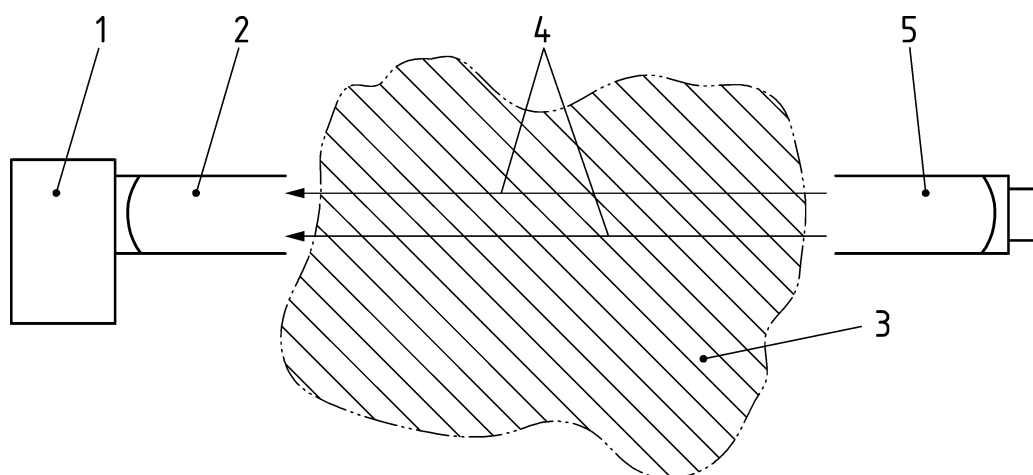
The method shows high selectivity and sensitivity due to the following combination of features:

- The measurement of radiation intensities is conducted with a high spectral resolution (0,1 nm to 1 nm) over a broad spectral range comprising numerous vibrational and/or rotational bands of one or more electronic transition(s).
- Reference spectra are fitted to the measured spectra by the least squares method. Thus, the characteristic absorption structures of the target compounds are employed to identify the measured compounds. Superimposed absorption structures of other constituents may be separated.
- Since the structured spectral absorption is analysed, unusually low optical densities (in some cases below 10^{-3}) can be identified. This fact, in conjunction with the long monitoring paths (usually from ca. 100 m to several kilometres, depending on the compounds to be measured) in the open atmosphere, yields low limits of detection for the trace gases.
- Quasi-continuous absorptions resulting from absorption processes by particles and droplets (e.g. radiation attenuation due to aerosol dispersion or decreasing transmittance of the optical system) as well as moderate fluctuations of the radiation intensity will not affect the result over a wide measurement range because in this technique differential absorption is used rather than the absolute absorption.

4.2 Configuration of the measurement system

Open-path techniques measure the 'concentration $\times$ path-length' product of one or more species in the atmosphere within a defined, extended optical path. The concentration of the species is derived from this measurement value. Two of the basic configurations for an open-path monitoring system are given in Figure 1 and Figure 2.

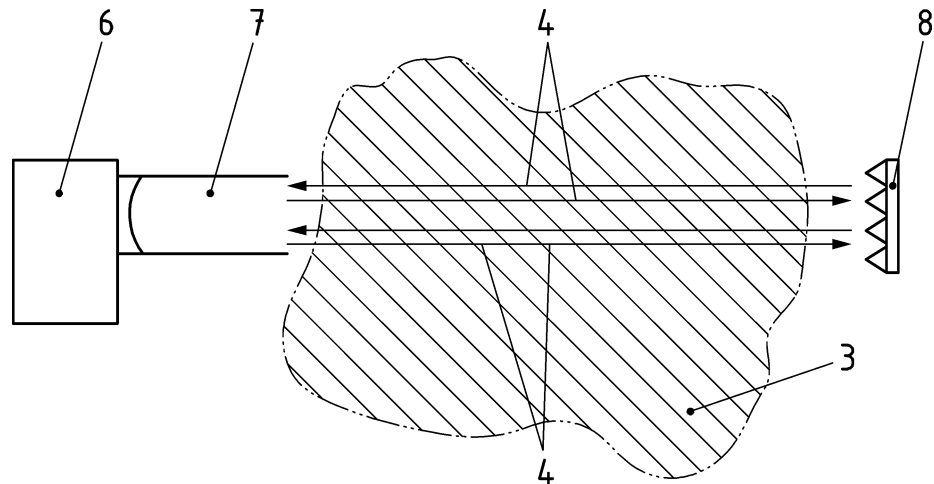
In the bistatic system (Figure 1) the transmitter and the detector are separated at the two ends of the optical path. The monostatic system (Figure 2) operates by transmitting the optical beam into the atmosphere to a passive retroreflector which returns the beam to the detector.



Key

- 1 DOAS spectrometer
- 2 Telescope for radiation collection
- 3 Ambient air
- 4 Monitoring path
- 5 Radiation source with collimating optics

Figure 1 — Bistatic arrangement for DOAS remote sensing



Key

- 3 Ambient air
- 4 Monitoring path
- 6 DOAS spectrometer including radiation source
- 7 Telescope for transmission and collection of radiation
- 8 Retro-reflector

Figure 2 — Monostatic arrangement for DOAS remote sensing

In the bistatic measurement set-up, the radiation source (5) and the DOAS spectrometer (1) are spatially separated. The two instrumental parts are oriented in such a way that the radiation emitted from the radiation source and collimated by a parabolic mirror is collected by the DOAS spectrometer telescope (2). The monitoring path length is the distance between collimating and receiving optics.

For a monostatic measurement set-up, transmitting and receiving optics are an integral part of the DOAS spectrometer (6), which also includes the radiation source and a beam splitter serving to separate the received and transmitted beams. By means of a retroreflector (8) the radiation beam passes twice through the measurement volume. The monitoring path length in this case is twice the distance between the transmitter/receiver and the retroreflector optics.

4.3 The Beer-Lambert law

When radiation passes through a medium, e.g. the atmosphere, it undergoes a change in intensity that can be expressed by means of the Beer-Lambert law:

$$I(\lambda, l) = I_0(\lambda) \cdot \exp(-a(\lambda) \cdot c \cdot l) \quad (1)$$

where

$I(\lambda, l)$ is the intensity of the radiation of wavelength λ incident on the receiver after passing the atmosphere along the monitoring path l ;

$I_0(\lambda)$ is the intensity of the radiation of wavelength λ emitted by the radiation source;

$a(\lambda)$ is the specific absorption coefficient of the medium at wavelength λ in $(\mu\text{g}/\text{m}^3)^{-1} \cdot \text{m}^{-1}$;

c is the concentration of the measured constituent in $\mu\text{g}/\text{m}^3$;

l is the length of the monitoring path in m.

The radiation absorption produces changes in the energy state of the absorbing gaseous species. In the UV/VIS range considered here, this implies a change in the rotational and vibrational state of the gaseous species, in addition to the change in their electronic state. In general, the rotational bands are not resolved, so what is measured essentially is the vibrational structure of the electronic transitions [3].

By introducing the optical density $D(\lambda)$

$$D(\lambda) = \ln \left(\frac{I_0(\lambda)}{I(\lambda)} \right) \quad (2)$$

and from Formula (1), the concentration c of the absorbing gaseous species is:

$$c = \frac{D(\lambda)}{a(\lambda) \cdot l} \quad (3)$$

NOTE The term *extinction* is also widely used for $D(\lambda)$. The quotient $\frac{I(\lambda)}{I_0(\lambda)}$ is defined as the transmittance.

4.4 Extended Beer-Lambert law

In atmospheric measurements, radiation is attenuated not merely by molecular absorption effects. It also disappears from the monitoring path due to scattering by air molecules (Rayleigh scattering) and to absorption and scattering by aerosol particles (Mie scattering). Apart from these attenuation effects, Rayleigh scattering of solar radiation leads to an increase in the radiation intensity incident on the detector. This additional contribution shall be determined and taken into account, as appropriate (see Annex B). Considering all these effects the absorption law (1) takes the following form:

$$I(\lambda, l) = I_0(\lambda) \cdot \exp \left((-a_R(\lambda) \cdot c_{LM} - a_M(\lambda) \cdot c_{AE}) \cdot l + \sum_i -a_i(\lambda) \cdot c_i \cdot l \right) + S(\lambda) \quad (4)$$

where

- $I(\lambda, l)$ is the intensity of the radiation of wavelength λ incident on the receiver after passing the atmosphere along the monitoring path l ;
- $I_0(\lambda)$ is the intensity of the radiation of wavelength λ emitted by the radiation source;
- $a_R(\lambda)$ is the Rayleigh scattering coefficient in $(\mu\text{g}/\text{m}^3)^{-1} \cdot \text{m}^{-1}$;
- c_{LM} is the density of the ambient air in $\mu\text{g}/\text{m}^3$;
- $a_M(\lambda)$ is the Mie scattering coefficient in $(\mu\text{g}/\text{m}^3)^{-1} \cdot \text{m}^{-1}$;
- c_{AE} is the aerosol concentration in $\mu\text{g}/\text{m}^3$;
- l is the length of the monitoring path in m;
- $a_i(\lambda)$ is the specific absorption coefficient of constituent i at wavelength λ in $(\mu\text{g}/\text{m}^3)^{-1} \cdot \text{m}^{-1}$;
- c_i is the concentration of constituent i in $\mu\text{g}/\text{m}^3$;
- $S(\lambda)$ is the intensity of scattered solar radiation.

NOTE The concentration of the constituent i in a mixed medium is expressed as a mass concentration ($c_i = m_i/V$). It can also be expressed as a mixing ratio $x_i = n_i/n_{\text{tot}} = N_i/N_{\text{tot}} = V_i/V_{\text{tot}}$ (n is the number of molecules, N is the number of moles, $N = n/N_L$, N_L being the Loschmidt constant) in $\mu\text{mol/mol}$ or nmol/mol using the following conversion formula:

$$c_i = x_i \cdot \frac{p \cdot M_i}{T \cdot R}$$

where

c_i is the mass concentration of constituent i in $\mu\text{g/m}^3$ (or mg/m^3);

x_i is the mixing ratio of constituent i in nmol/mol (or $\mu\text{mol/mol}$);

p is the atmospheric pressure in Pa;

T is the ambient temperature in K;

M_i is the molar mass of component i in kg/mol ;

R is the molar gas constant ($= 8,314 \text{ J/(mol}\cdot\text{K)}$).

Reference conditions (pressure, temperature) for ambient air measurements are usually 1 013 hPa and 20 °C.

Formula (4) does not yet allow an analysable correlation between $I(\lambda, l)$ and $I_0(\lambda)$ to be established, i.e. determining a concentration averaged over the monitoring path. This is due to the difficulty of determining the intensity $I_0(\lambda)$ incident on the absorber and to the variability of light scattering effects in the atmosphere as expressed by $a_R(\lambda)$ and $a_M(\lambda)$.

4.5 Differential optical density

The DOAS method relies only on the high-frequency (narrowband) part of the absorption structure. For this purpose, the absorption coefficient $a_i(\lambda)$ is considered the sum of two components as shown in Figure 3:

$$a_i(\lambda) = a_{0i}(\lambda) + a'_i(\lambda) \quad (5)$$

where

$a_{0i}(\lambda)$ is the portion of the specific absorption coefficient which varies little with the wavelength;

$a'_i(\lambda)$ is the portion of the specific absorption coefficient which varies strongly with the wavelength.

The parameters $a_{0i}(\lambda)$ and $a'_i(\lambda)$ denote the low-frequency and high-frequency portion of the absorption coefficient of the gaseous component i (see Figure 3).

Formula (4) can then be modified as follows:

$$I(\lambda, l) = I_0(\lambda) \cdot \exp\left((-a_R(\lambda) \cdot c_{LM} - a_M(\lambda) \cdot c_{AE}) \cdot l + \sum_i -a_{0i}(\lambda) \cdot c_i \cdot l\right) \cdot \exp\left(\sum_i -a'_i(\lambda) \cdot c_i \cdot l\right) + S(\lambda) \quad (6)$$

The differentiation with respect to the absorption coefficient $a_i(\lambda)$ permits definition of the differential initial intensity $I'_0(\lambda)$ which corresponds to the initial intensity $I_0(\lambda)$ after attenuation through Rayleigh and Mie scattering and through the continuous portion of the component-related absorption. Furthermore it is assumed that the intensity of the scattered solar radiation $S(\lambda)$ (see Formula (4)) will be determined and subtracted. Additionally, the attenuation factor $\tau(\lambda)$ is introduced which allows for the broad wavelength-dependent

transmission of the entire optical system (radiation source, telescopes, spectrometer (cf. Annex A)), including the spectral sensitivity of the detector. Thus, Formula (6) can be modified as follows:

$$I'_0(\lambda) = I_0(\lambda) \cdot \exp\left(\left(-a_R(\lambda) \cdot c_{LM} - a_M(\lambda) \cdot c_{AE}\right) \cdot l + \sum_i -a_{0i}(\lambda) \cdot c_i \cdot l\right) \cdot \tau(\lambda) \quad (7)$$

where

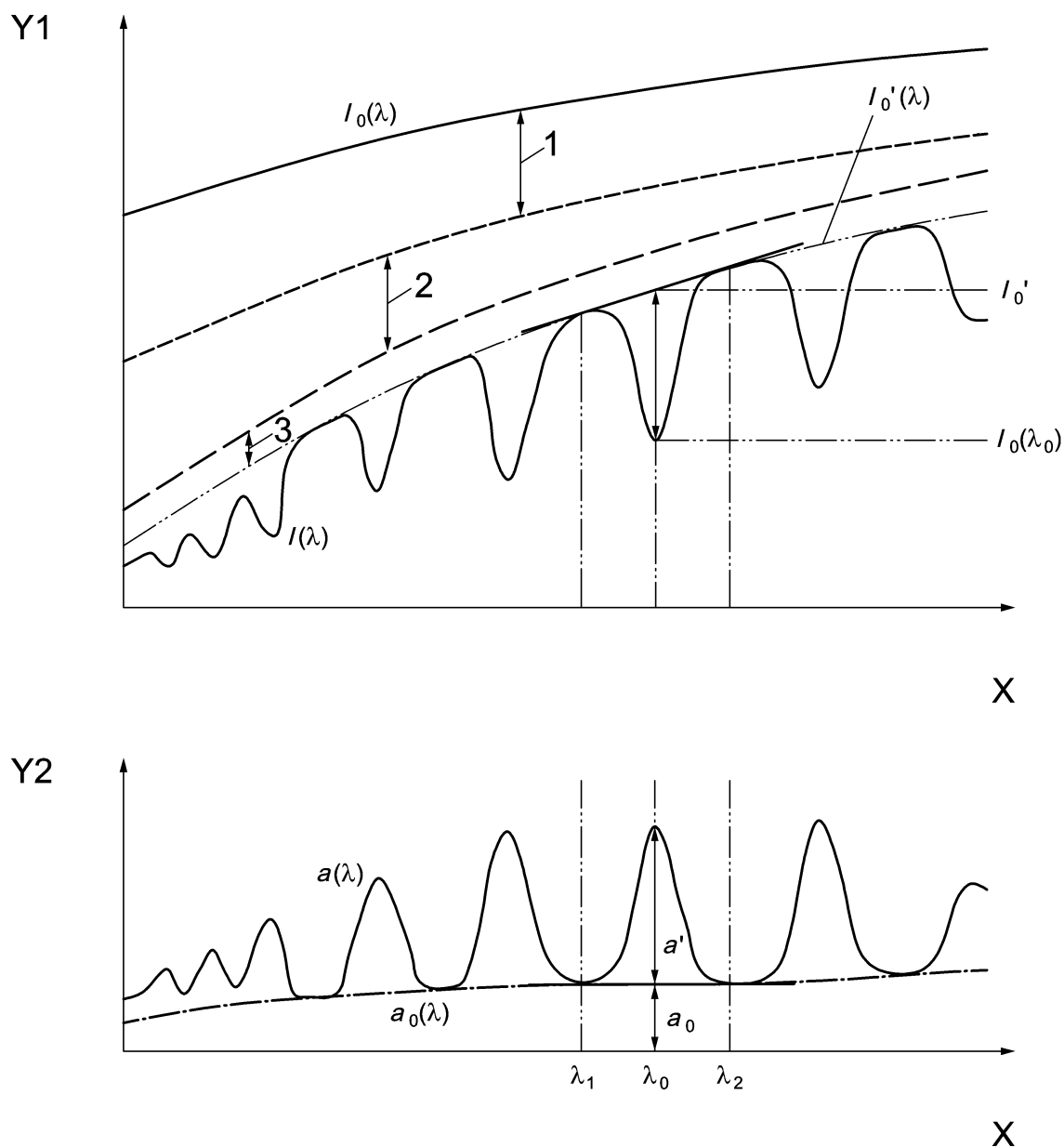
$I'_0(\lambda)$ is the differential initial intensity;

$\tau(\lambda)$ is the attenuation factor of the optical system.

The optical density determined on the basis of the differential initial intensity $I'_0(\lambda)$ is referred to as the differential optical density $D'(\lambda)$:

$$D'(\lambda) = \ln \frac{I'_0(\lambda)}{I(\lambda)} = \sum a'_i(\lambda) \cdot c_i \cdot l \quad (8)$$

This procedure ensures that DOAS spectra can be properly analysed, as the optical density definition is expanded by taking into account the influence of the continuous absorption structures, i.e. those which do not vary much with the wavelength. By relying on the concept of differential initial intensity $I'_0(\lambda)$, DOAS solves the problem that the intensity of initial radiation $I_0(\lambda)$ emitted by a radiation source is impossible to determined from a measured spectrum due to absorption and scattering effects. Figure 3 illustrates the difference between the intensities $I(\lambda)$, $I_0(\lambda)$, $I'_0(\lambda)$.



Key

- 1 Mie extinction
- 2 Rayleigh extinction
- 3 Continuous absorption component
- X Wavelength
- Y1 Intensity
- Y2 Absorption coefficient

Figure 3 — Intensities $I(\lambda)$, $I_0(\lambda)$ and $I'_0(\lambda)$ in an absorption spectrum (upper panel) and associated absorption coefficients $a(\lambda)$, $a_0(\lambda)$ and $a'(\lambda)$ (lower panel)

$I'_0(\lambda)$ can be determined by interpolation between the shoulder values $I(\lambda_1)$ and $I(\lambda_2)$. $D'(\lambda)$ is then obtained from the quotient of the intensities $I'_0(\lambda)$ (centre of band) and $I(\lambda)$ according to Formula (9).

$$D'(\lambda) = \ln \frac{I'_0(\lambda)}{I(\lambda)} = \ln \left(I(\lambda_1) + (I(\lambda_2) - I(\lambda_1)) \cdot \frac{\lambda_0 - \lambda_1}{\lambda_2 - \lambda_1} \right) - \ln I(\lambda_0) \quad (9)$$

However, this method is used only in simple cases (one single strong, dominant absorber). Usually, the analysis is conducted by mathematical modelling of $I(\lambda)$ with the aim of minimising the deviation between $I(\lambda)$ and $I_{\text{mod}}(\lambda)$, where $I_{\text{mod}}(\lambda)$ is the modelled intensity as a function of wavelength (i.e. a modelled spectrum).

$$I_{\text{mod}}(\lambda) = P(\lambda) \cdot \exp - \left(\sum_i a'_i(\lambda) \cdot c_i \cdot l \right) \quad (10)$$

$P(\lambda)$ describes the combined influences of all influencing variables which vary little with wavelength, such as $\tau(\lambda)$ or broadband absorbers (cf. Formula (7)), where it is not necessary to determine all coefficients. It suffices to approximate $P(\lambda)$ to the wavelength using a suitable smooth function, e.g. a higher-order polynomial:

$$P(\lambda) \approx \sum_{j=0}^k d_j \cdot \lambda^j \quad (11)$$

e.g. a 5th order polynomial [3]) or a low-pass filtered spectrum of $I(\lambda)$ (e.g. with the aid of a Bessel filter [4]), see Figure 4 (SO₂ measurement).

The deviation between $I(\lambda)$ and $I_{\text{mod}}(\lambda)$ is usually minimised by the least squares method:

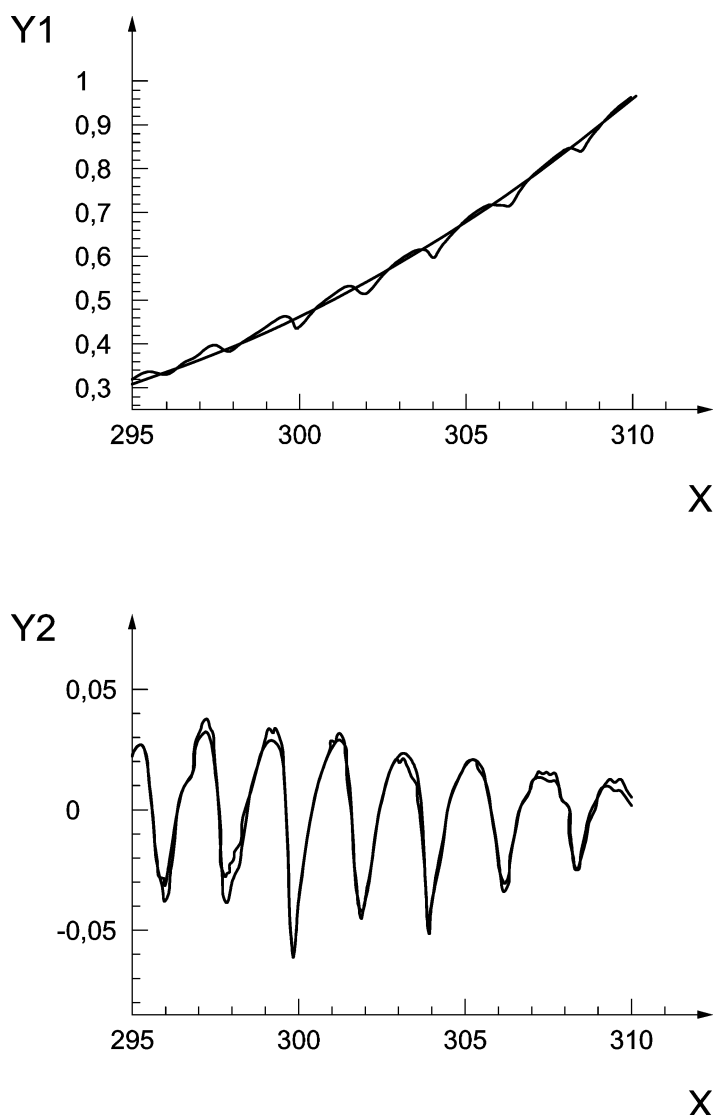
$$\chi^2 = (I_{\text{mod}}(\lambda) - I(\lambda))^2 = \text{minimal} \quad (12)$$

Thus the desired concentrations c_i of the absorbing constituents averaged over the monitoring path, the coefficients determining $P(\lambda)$ (e.g. the coefficients d_j of the polynomial), and such additional coefficients as may be involved (e.g. those describing wavelength shifts) are obtained.

NOTE The polynomial coefficients d_j (Formula (11)) can be useful for quality control purposes. Major variations of these coefficients during the measurement indicate pronounced changes in atmospheric or system conditions.

The advantage of this analytical procedure is that the differential optical densities of all bands of the given constituents will be taken into account in determining the average concentration across the spectral range selected for the analysis.

A selected spectral range may contain the absorption structures of several constituents. It is possible to distinguish between them and to determine their concentrations c_i independently. In addition, potential shifts in the wavelength scale can be corrected. A detailed description of this method is given in [5].



Key

X Wavelength λ in nm
Y1 Intensity I in relative units
Y2 $\log I_1/I_2$

Figure 4 — Top: Measured raw spectrum and fitted fifth degree polynomial (smoothed line). Bottom: Quotient of raw spectrum and fitted polynomial produces the high-pass filtered spectrum, fitted SO₂ reference spectrum for comparison (smoother line)

5 Measurement procedure

5.1 General

DOAS measurements are based on the principle of recording and analysing absorption bands of the constituents of interest (see Clause 4). In addition, the following parameters shall be measured or recorded:

- monitoring path length, determined, e.g. using a geographical map, a range finder, GPS data or a tape measure (short distances);

- density (temperature and pressure) of the air column, if appropriate (depending on the measurement task), in order to express the results under standard conditions;
- instrument status data (e.g. received relative radiation intensity (e.g. in order to prevent saturation), detector temperature (relevant only for diode laser systems)).

DOAS measuring procedures depend on the instrument type. In addition to the atmospheric raw spectrum, the system shall measure at least the dark spectrum, electronic offset spectrum, lamp spectrum, and, in cases of measurements above 290 nm, the background spectrum due to scattered solar radiation [2]. In order to evaluate the spectra the reference compound spectra shall be known.

5.2 Principle

The general procedure for active long-path DOAS systems is outlined in Figure 5. Depending on the instrument technique not all of these steps and not all of the spectra are necessary.

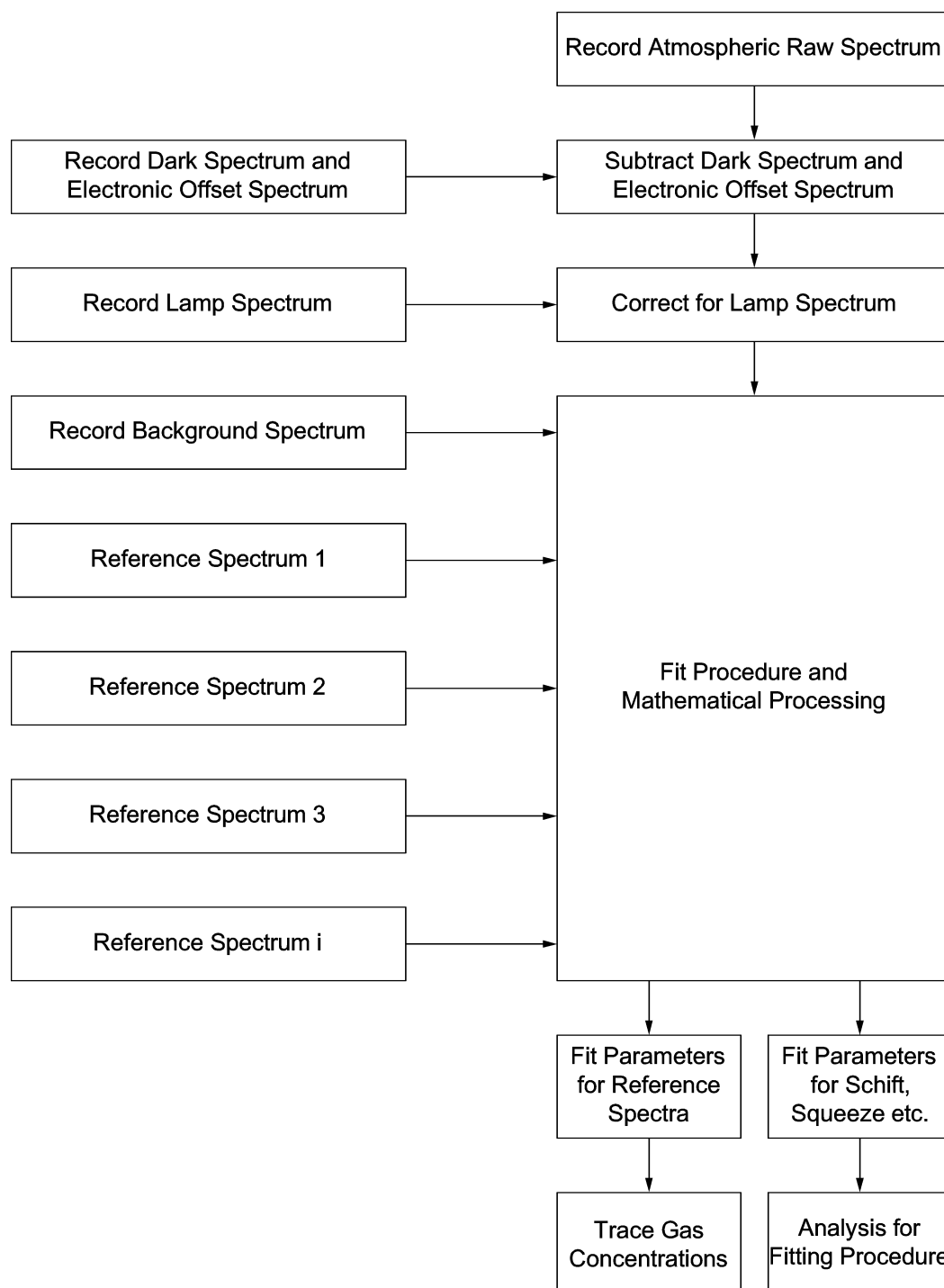


Figure 5 — Flow chart of a DOAS measurement and its evaluation

The true optical density $D'(k)$ is achieved by processing the following spectra:

- the atmospheric raw spectrum $I(k)$, i.e. the spectrum of the lamp with trace gas features and aerosol absorption plus solar scattered light. The standard procedure is to add several (N_M) individual spectra having the integration time (t_M) in each case;

NOTE k numbers the spectral interval covered by an individual detector pixel.

- the dark spectrum $I_D(k)$ (optional), in case of CCD or PDA as detector, with integration time t_D (including electronic offset), wherein the dark spectrum per time base $I_{D1}(k)$ is derived correcting for electronic offset (scan weighted) and integration time ($I_{D1}(k) = (I_D(k) - N_D \cdot I_{Off1}(k)) / t_D$);
- the electronic offset spectrum $I_{Off}(k)$ (optional), in case of CCD or PDA as detector (with negligible dark spectrum due to shortest possible integration time), wherein the electronic offset I_{Off1} for one scan is obtained by dividing with the number of N_{Off} added spectra ($I_{Off1}(k) = I_{Off}(k) / N_{Off}$);
- the lamp spectrum $I_L(k)$, recorded by a direct scan of the lamp radiation excluding the atmosphere;
- the background spectrum $I_B(k)$, for wavelengths above 290 nm with an integration time t_B , since stray solar radiation may interfere with the measurement.

EXAMPLE In a specific DOAS technique the true optical density $D'(k)$ is calculated as follows:

$$D'(k) = -\ln \left[\frac{(I_M(k) - N_M \cdot I_{Off1}(k) - t_M \cdot I_{D1}(k)) - \frac{t_M}{t_B} (I_B(k) - N_B \cdot I_{Off1}(k) - t_B \cdot I_{D1}(k))}{(I_L(k) - N_L \cdot I_{Off1}(k) - t_L \cdot I_{D1}(k))} \right] \quad (13)$$

(N_B and N_L , respectively, indicate the number of background and lamp spectra added up).

As $I_{D1}(k)$ is an averaged dark spectrum, the factors N_M , N_B , N_L are introduced, in order to correlate the correct intensities within this algorithm for the raw atmospheric spectrum, the lamp spectrum, the dark spectrum and the background spectrum. For the same reason the ratio t_M/t_B is introduced, as I_M and I_B might have been recorded with different measurement times.

The true optical density $D'(k)$ can be processed as follows:

- A *least-squares fit* is carried out with a series of reference spectra according to 4.5.
- The resulting fit parameters indicating the optical densities of the respective trace gas are used to calculate the column density of this trace gas (as well as its standard deviation).
- Dividing the column density by the length of the monitoring path gives the trace gas concentration, which can be converted into mixing ratios by using the pressure and temperature of the air column (see Note in 4.4).
- In some cases it is necessary to fit additional parameters describing wavelength shift and/or stretch of the wavelength scale. These are not immediately necessary to calculate the trace gas concentration, but can be used to judge the quality of the spectrometer and provide an indication of error margins ([5], [6]). In this case also a non-linear fit procedure is necessary.

Background spectra need not be recorded in daytime when operating at wavelengths below 290 nm, due to the additionally recorded scattered solar radiation in $I_M(k)$ under these conditions. The lamp spectra shall be determined regularly since they may change due to ageing (i.e. over a span of several days/weeks) depending on instrument design. The use of current lamp spectra improves the data quality as the changes in lamp and also detector characteristics are compensated.

Reference spectra of the respective components can be recorded with the same spectrometer that is used for the atmospheric measurement. An alternative process is to convolute an available high-resolution spectrum (from the literature) with the instrument line shape function of the current spectrometer, which in turn can be obtained in high quality by recording an atomic line spectrum (usually a Hg vapour line spectrum).

Commercial implementations of the DOAS technique are presented in Annex C.

6 Measurement planning

6.1 Definition of the measurement task

In order to interpret and assess the measurement parameters it is necessary to clearly define the measurements to be carried out. This includes the species to be measured, experimental arrangement (field setup), likely interfering species, likely spatial distribution of the gases to be measured, required temporal information. Such limiting conditions shall be clearly defined in the scope of the measurements.

6.2 Selection of measurement parameters of the DOAS system

6.2.1 General

Before beginning the measurement it is necessary to define the relevant measurement parameters with respect to the objectives of measurement.

6.2.2 Monitoring path

The monitoring path (and specifically its length) is determined in accordance with the manufacturer's instructions for the constituents of interest, depending on the optical configuration (monostatic or bistatic). The minimum radiation level needed at the end of the monitoring path may differ, depending on the constituent to be measured. In this context, it is particularly important to take into account the light attenuation due to Mie scattering, as well as any optical filters employed for specific noxious constituents that might reduce the detection limit.

When the monitoring path is installed in public space, potential glare effects caused by the system's radiation source shall be avoided (e.g. accident hazard in the case of traffic-related measurements, health impairment of passers-by).

During installation of the monitoring path, care shall be taken to prevent direct incidence of strong scattered radiation (e.g. solar radiation) into the receiver's optical system.

6.2.3 Time resolution

Suitable averaging periods shall be selected for each constituent. They depend on the detection limits to be achieved, as well as on the spectral properties of the monitoring path. A high time resolution (e.g. short time intervals between the individual measurements) reduces the radiation dose available for each individual measurement and worsens the photo electron statistics. As a result, noise (or the minimum detectable optical density, respectively) will increase, in principle, in proportion to the square root of the radiation dose received. Thus, the detection limit and/or the measuring uncertainty of a DOAS measurement will vary with the square root of the measuring time in many cases (i.e. if photon statistics is applicable). Increasing the time resolution from 10 min (600 s) to 6 s would worsen the measuring error and the detection limit, respectively, by a factor of 10.

NOTE The maximum measurement accuracy for the specific constituent is mainly determined by the instrument characteristics and can be improved only to a certain limit by increasing the number of averaged measurements.

For usual applications, depending on the components to be determined, a time resolution of a few minutes (e.g. 0,5 min to 3 min) is chosen. This parameter may be varied for optimising particular applications.

7 Procedure in the field

7.1 Installation and start-up of the instrument

The following aspects shall be specifically observed during the mechanical installation of the optical components (including a separate analyser unit, where applicable), as well as when setting up and adjusting a monitoring path. The manufacturer's instructions shall be followed.

- a) An adequate, uninterruptible power supply shall be used.
- b) Depending on the measuring system employed, a torsion-resistant stand or sufficiently rugged attachment (wind load!) of the optical components shall be ensured. Particularly when using long measurement paths on systems devoid of automatic adjustment features, a sufficient long-term stability of the measured signal has to be guaranteed. In the case of pronounced ambient air temperature variations or changes in the solar radiation, the de-adjustment (change of alignment) caused by thermal effects needs to be taken into account.
- c) Compliance with the operating conditions defined by the manufacturer (thermal requirements) for both the analyser unit and optical system components shall be ensured. On DOAS measuring systems combining the receiver and analyser unit in a single assembly, meeting these criteria may call for additional measures since the entire system is exposed to ambient conditions. If the optical components and the analyser unit are installed separately, appropriate steps shall be taken (e.g. air conditioning systems, heaters) to guarantee that the manufacturer-specified operating conditions (thermal requirements) will be met, particularly for the spectrometer unit. To optimise the system's availability, all optical components shall be protected against moisture effects (e.g. dew, precipitation).
- d) The adjustment of a monitoring path is started by focussing the radiation source on the receiver's optical system (or, in the case of monostatic systems, on the retro-reflector or mirror element used). The size of the "focus point" shall be selected such that minor system de-adjustments (e.g. due to thermal effects) will not necessarily result in a total signal loss but can be tolerated (typically between 0,5 m to 2 m). These settings will be dependent on the selected monitoring path length and the size of the receiver's optical system; they shall be re-set during every new installation with a view to maximising the signal level.
- e) For some systems adjustments shall preferably be carried out in the dark or in half-light (twilight) conditions since the visible spectral portion of the emitting light source is helpful when adjusting focus settings, optical transfer devices, etc.

NOTE New optical monostatic setups [7] do not require an adjustment at night. They are also simple to adjust at daylight. The adjustment of the light beam and focal point does not require the visibility of the emitting light.

- f) Fibres for the deep UV range (solarisation stabilised) should be used, if working with light sources emitting below 280 nm, to avoid degradation of light transmittance.
- g) If ozone-producing radiation sources are employed, suitable steps shall be taken (e.g. ventilation) to prevent any effects on the measurement and direct exposure to people.
- h) Whenever the system is installed from scratch, its wavelength accuracy shall be re-checked. This can be done, for instance, with the aid of a mercury vapour spectral lamp.
- i) A functional check of the DOAS measuring system shall be carried out before measurements are begun.
- j) Beam alignment and blocking or optical path deflection systems may be necessary, especially for automatic operation. These systems shall be controlled as appropriate.
- k) Once the monitoring path is set up and the optical adjustments have been made, all parameters of the DOAS measuring system which have been set or achieved for this specific monitoring path shall be duly documented so that any drift or de-adjustments can be identified. Where different monitoring paths are

used, all parameters shall be documented for each monitoring path used. These data will include the following:

- 1) overall system signal intensity achieved (a reduction in signal intensity due, e.g. to band pass filtering (to reduce stray light impact for individual constituents), shall be taken into account in this context);
- 2) monitoring path length(s);
- 3) averaging periods for the individual constituents;
- 4) calibration parameters for all constituents (e.g. span, offset, cross-sensitivity correction in the case of gas cell calibration; ILS function; reference spectra in the case of direct calibration);
- 5) pressure and temperature compensation settings.

7.2 Verification of optical properties

When checking the optical or spectral properties of the DOAS measuring system after its installation (but before the start of measurements), the following shall be noted:

- Optical windows and mirrors in the optical transfer devices employed shall be checked regularly for dirt or damage, and shall be cleaned according to the manufacturer's instructions or replaced as appropriate.
- When using external calibration gas cells in conjunction with light guides, care shall be taken to ensure that the light guides are the same as those used in the real-life measurements so as to keep the spectral properties of the overall system constant. Any changes shall be documented.
- When conducting long-term measurements, the limited service life of the radiation sources shall be taken into account (see also A.2.1). When changing lamps or optical parts, observe the precautions defined by the manufacturer.
- All changes made in the course of the system's operation and adjustment of its optical components shall be documented.

7.3 Visibility

Under conditions of extremely poor visibility (e.g. fog or snow), all measurements shall be subjected to a special validation since the visibility has a direct influence on the signal intensity and hence, the measurements.

Particles increase the intensity of atmospheric scatter. Aerosols (mist, fog) or precipitation particles (e.g. rain, sleet, snow, "hydrometeors") can interfere with DOAS measurements. This is attributable to two processes:

- attenuation of the useful radiation intensity, resulting in a deterioration of the signal-to-noise ratio;
- increase in the proportion of scattered solar radiation contributing to the measured signal (depending on time of day, weather, wavelength range).

The type and extent of measurement interferences due to elevated scatter will be evident from the analytical routines. Reduced signal intensities make for inferior photoelectron statistics, however, some compensation for these effects can be made through prolonged measuring times. In extreme cases (dense fog), measurements over a given path length may become altogether impossible. The effects of scattered solar radiation can be eliminated to a large extent with the methods described in Annex B.

8 Calibration methods

8.1 General

The calibration of the measurement system provides the relation between reference materials (reference gases or reference databases) and the measured values. The calibration procedure assures the accuracy of the measurement method.

Two different calibration approaches are applicable to DOAS systems:

- gas cell calibration with and without including the atmosphere using test gases (see 8.2);
- calibration with complete spectral modelling using reference spectra (see 8.3).

The basic calibration of a DOAS system is carried out by the manufacturer and is based on test gases, which shall be traceable to (inter)nationally accepted standards. If such test gases are not available (e.g. for reactive or non-stable compounds) the basic calibration may be based on reference spectra.

The periodic check of the calibration (typically once or twice a year) is carried out by the user according to the manufacturer's instructions and may be based either on test gases or reference spectra.

8.2 Gas cell calibration

8.2.1 Gas cell calibration with exclusion of the atmosphere

This laboratory-based calibration method using gas cells (possibly with different absorption lengths) is carried out under exclusion of the atmosphere. The radiation source should have the same emission characteristics as that which is used in the field measurements. For the calibration, the beam is passed through the gas cells so that any absorption by relevant ambient air constituents is ruled out. This can be achieved by transmitting the output of the radiation source directly through the gas cell using light guides or transfer optics. After transmitting the gas cells the measuring beam is passed directly to the spectrometer. Given the short absorption paths, very high radiation intensities may occur. These may have to be adapted to the level of the subsequent measurements by appropriate attenuation (e.g. de-adjustment, filtering).

One advantage of this calibration method is that it is not affected by atmospheric absorption effects. In addition, it is possible to carry out a calibration under zero gas conditions. Cross-sensitivity surveys can also be made quite easily by using several gas cells arranged in series. Care shall be taken that the background intensity is negligible during the calibration experiment.

8.2.2 Gas cell calibration with inclusion of the atmosphere

This field-based method uses the full optical measurement path in the atmosphere and insertion of a gas cell. The differential optical density D' (see Formula (8)) is given by the gas concentration c in the atmosphere, the path length l , and the differential absorption coefficient a' as follows:

$$D' = a' \cdot c \cdot l \quad (14)$$

It follows that the optical density due to a low concentration over a long optical path is equivalent to the optical density due to a high concentration over a short path.

The insertion of a gas cell of length l_C which contains the measured gas in a concentration c_C into the optical path will raise the total differential optical density D'_{tot} by the contribution D'_C :

$$D'_C = a' \cdot c_C \cdot l_C \quad (15)$$

$$D'_{\text{tot}} = D' + D'_C \quad (16)$$

This permits an incremental calibration, i.e. it allows the calculation of an effective concentration change c_{eff} :

$$c_{\text{eff}} = c_{\text{C}} \cdot \frac{l_{\text{C}}}{l} \quad (17)$$

As regard to the use of the gas cell method, the following limitations apply:

- Not all components which can be analysed by the DOAS method are stable in gas cells (especially under UV irradiation), e.g. NO_3 and other radicals.

NOTE Stable constituents such as SO_2 can be measured in sealed gas cells whereas for such compounds as NO , O_3 and some aromatic hydrocarbons dynamic flow through cells are used. In many cases flow-through gas cells have advantages for calibration purposes compared to sealed gas cells (wall effects).

- It is a necessary condition for the incremental measuring method that the atmospheric concentration of the gas remains constant throughout the measurement.
- In principle, the calibration gas cells shall extend over the entire diameter of the measuring beam. The cell (diameter typically 3 cm to 15 cm, length 3 cm to 10 cm) shall be positioned in the parallel part of the beam.

Gas cells can also be put at other locations in the light path where a parallel light beam is achieved (e.g. between light source and fibre). As the diameter of the light beam is typically much smaller (e.g. 3 cm) the application of cells is simpler and longer gas cells (e.g. up to 1 m) can easily be applied. This increases the calibration accuracy.

8.3 Calibration with complete spectral modelling

In this method an absolute calibration is performed by modelling the overall system and determining all model parameters in the laboratory. Knowledge of the following parameters is required:

- differential absorption coefficient $a'(\lambda)$ of the component for the wavelength used;
- instrument line shape function $H(\lambda)$ of the spectrometer employed;
- length of the monitoring path.

An additional parameter affecting the determination of the limit of detection is the lowest determinable optical density D_{min} . In addition, the calibration may be influenced by:

- stray light in the spectrum;
- non-linearity of the detector characteristic curve;
- apparent saturation of the absorption curve;
- dark current of the detector.

In this method these parameters have to be taken into account. The differential absorption coefficient and the ILS function can also be combined into a specific differential absorption coefficient $a_{\text{H}}'(\lambda)$ for the apparatus at hand. The value of a'_{H} can be determined by the gas cell method according to 8.2.2 for the spectrometer used. However, it will usually be more favourable to determine it by convolution of the ILS function with a high-resolution absorption coefficient spectrum $a_{\text{Ref}}(\lambda)$:

- Absorption coefficient spectra $a_{\text{Ref}}(\lambda)$ established with a high resolution are an optical constant of the molecule considered and can be determined in the laboratory. Appropriate data are available for many constituents of interest (cf. HITRAN database [8]).
- The ILS function $H(\lambda)$ is defined as the spectrometer's response to a spectral distribution of the analysed radiation that is described by a Dirac's delta function or, in other words, as the spectrum produced by the spectrometer for monochromatic radiation. In practice, this intensity distribution can be approximated with high accuracy by means of atomic emission lines.

NOTE 1 The half-width of the mercury emission lines usually exploited is on the order of 10^{-3} nm, that of laser lines is often lower while the spectral resolution of DOAS spectrometers typically varies between 0,1 and 1 nm.

NOTE 2 The mercury lamp can be used for the calibration check.

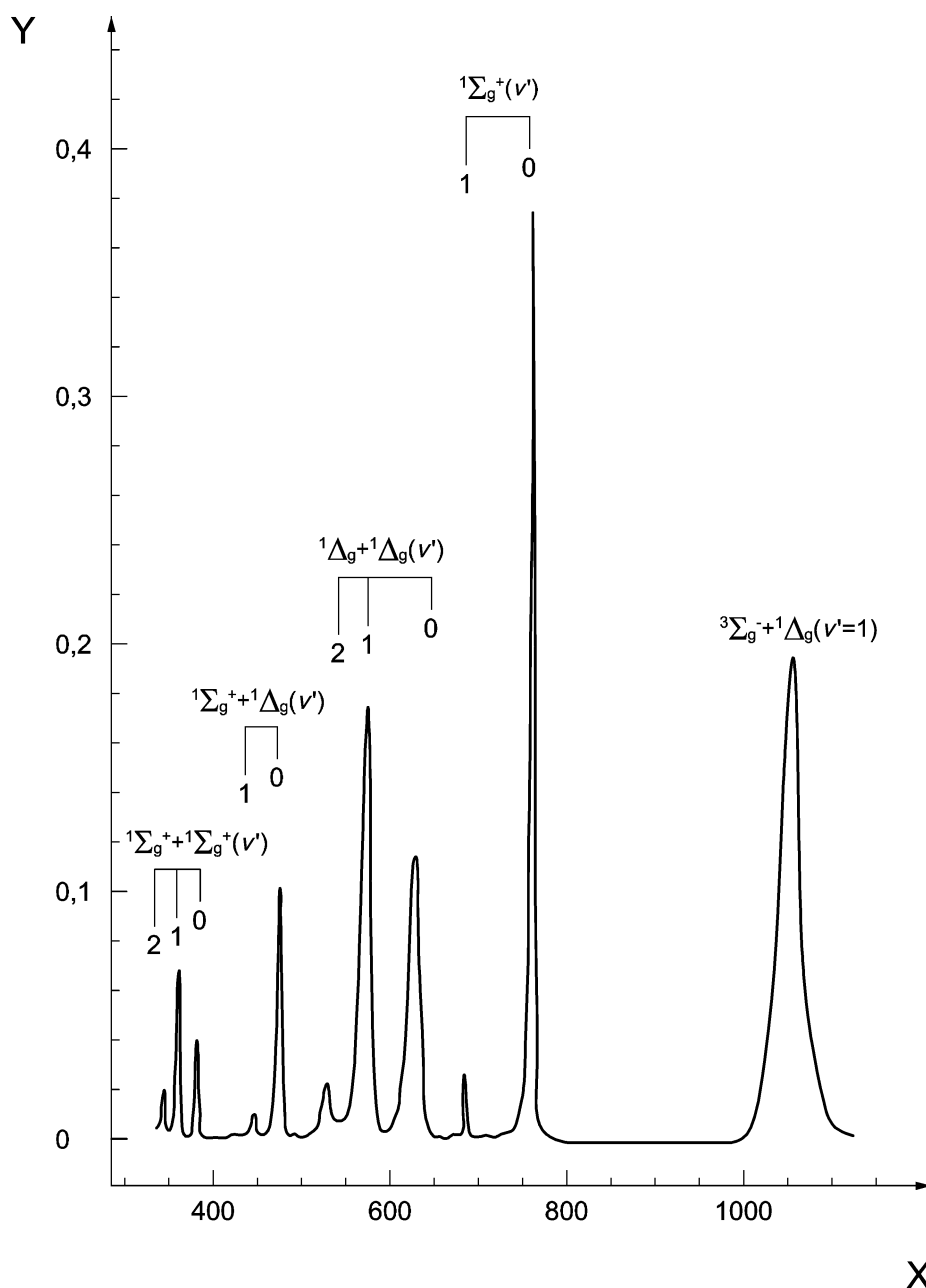
Another possibility is to record high-resolution Fraunhofer structures of solar radiation (cf. WinDOAS [9]).

However, for use as a reference these spectra have to be convolved with the ILS $H(\lambda)$ with the resolution of the spectrometer's detector unit. The reference spectrum $a_{\text{H}}(\lambda)$ or $a'_{\text{H}}(\lambda)$ thus obtained is used to determine the absolute trace substance concentration.

This method yields a reliable calibration of each DOAS system and an accurate determination of the limits of the measuring method [10] while requiring only elementary measurements on the instrument itself.

One potential disadvantage, on the other hand, is the complexity of the calibration procedure; this, however, resides in the necessary calculations rather than in the measurements to be carried out on the apparatus. Care shall therefore be taken while executing this procedure to avoid errors. A method which suggests itself for monitoring and validating the analytical calibration is to determine the line strength of the atmospheric O_4 (oxygen dimer) or, where appropriate, of H_2O or O_2 lines in the atmosphere. The O_4 lines are available within the entire spectral range used in the DOAS method, from near UV to near IR (cf. Figure 6) [11]. The strength of the lines depends only on the air density, which in turn varies only little or can be determined very accurate (via air pressure and temperature). In addition, the error probability can be minimised by automating the measurements (determination of the ILS function) and the analysis (e.g. by integrating the software).

The positions of the most pronounced absorption bands are listed in Table 1.



Key
X Wavelength
Y Absorption

Figure 6 — Spectra of O₄ and O₂

9 Quality assurance

9.1 Measurement procedure

9.1.1 General

As a general rule, a distinction can be made between quality-assurance steps performed before, during and after the measurements. The manufacturer's instructions shall be observed. All quality assurance measures and the changes made in response thereto shall be duly documented.