SLOVENSKI STANDARD
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Kakovost zraka - Prizemne meritve zunanjega zraka z diferencialno optično absorbcijsko spektroskopijo (DOAS) - Meritve zunanjega zraka in razpršenih emisij

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

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

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

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English Version

Air quality - Atmospheric measurements near ground with 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

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Foreword

This document (prEN 16253:2011) has been prepared by Technical Committee CEN/TC 264 "Air quality", the secretariat of which is held by DIN.

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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, 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.

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1 Scope

This document describes the operation of *active* DOAS measuring systems with continuous radiation source, the calibration procedures and applications in determining gaseous constituents (e.g., NO_2, SO_2, O_3, 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 lamp switched off

NOTE   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 wavenumber 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 the root mean square noise

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 (approx. 250 nm to 2500 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 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 ca. 800 m, 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 Figures 1 and 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.
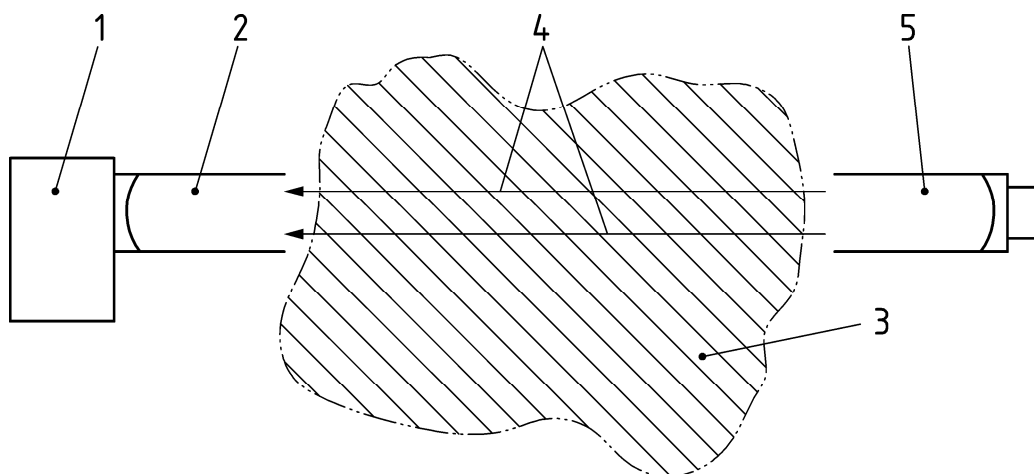
Key
1   DOAS spectrometer
2   telescope for radiation collection
3   ambient air
4   monitoring path
5   radiation source with collimating optics

Figure 1 — Bistatic arrangement for DOAS remote sensing
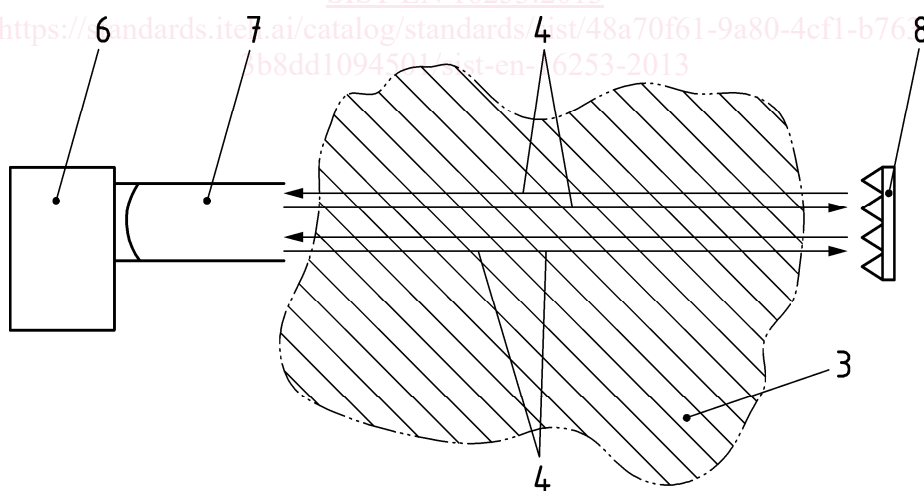
Key
3   ambient air
4   monitoring path
6   DOAS spectrometer including radiation source
7   telescope for transmission and collection of radiation
8   retro-reflector

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:

$$I(\lambda, l) = I_0(\lambda) \cdot \exp\left(- a(\lambda) \cdot c \cdot l\right) \tag{1}$$

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 $(\mu g/m^3)^{-1} \cdot m^{-1}$;

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

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. As a general rule, the rotational bands are not resolved, so what is measured essentially is the vibrational structure of the electronic transitions [1].

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

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

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

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

NOTE   The term *extinction* is also widely used for $D(\lambda)$. The quotient $\dfrac{I(\lambda)}{I_0(\lambda)}$ 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:

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

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 $(\mu g/m^3)^{-1} \cdot m^{-1}$;

c_{LM} is the density of the ambient air in $\mu g/m^3$;

$a_M(\lambda)$ is the Mie scattering coefficient in $(\mu g/m^3)^{-1} \cdot m^{-1}$;

c_{AE} is the aerosol concentration in $\mu g/m^3$;

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 $(\mu g/m^3)^{-1} \cdot m^{-1}$;

c_i is the concentration of constituent i in $\mu g/m^3$;

$S(\lambda)$ 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 $x_i = n_i/n_{tot} = V_i/V_{tot}$ in ppm or ppb 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 $\mu g/m^3$ (or mg/m^3)
x_i is the mixing ratio of constituent i in ppb (or ppm)
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 (= 8,3145 J/(mol·K))

Reference conditions (pressure, temperature) for ambient air measurements are usually 1013 hPa and 20 °C.

Equation (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:

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

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).

Equation (4) can then be modified as follows:

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

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 Equation (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, Equation (6) can be modified as follows:

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

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 $D'(\lambda)$:

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

This procedure ensures that DOAS spectra can be properly analyzed, 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 $I(\lambda)$, $I_0(\lambda)$, $I'_0(\lambda)$.
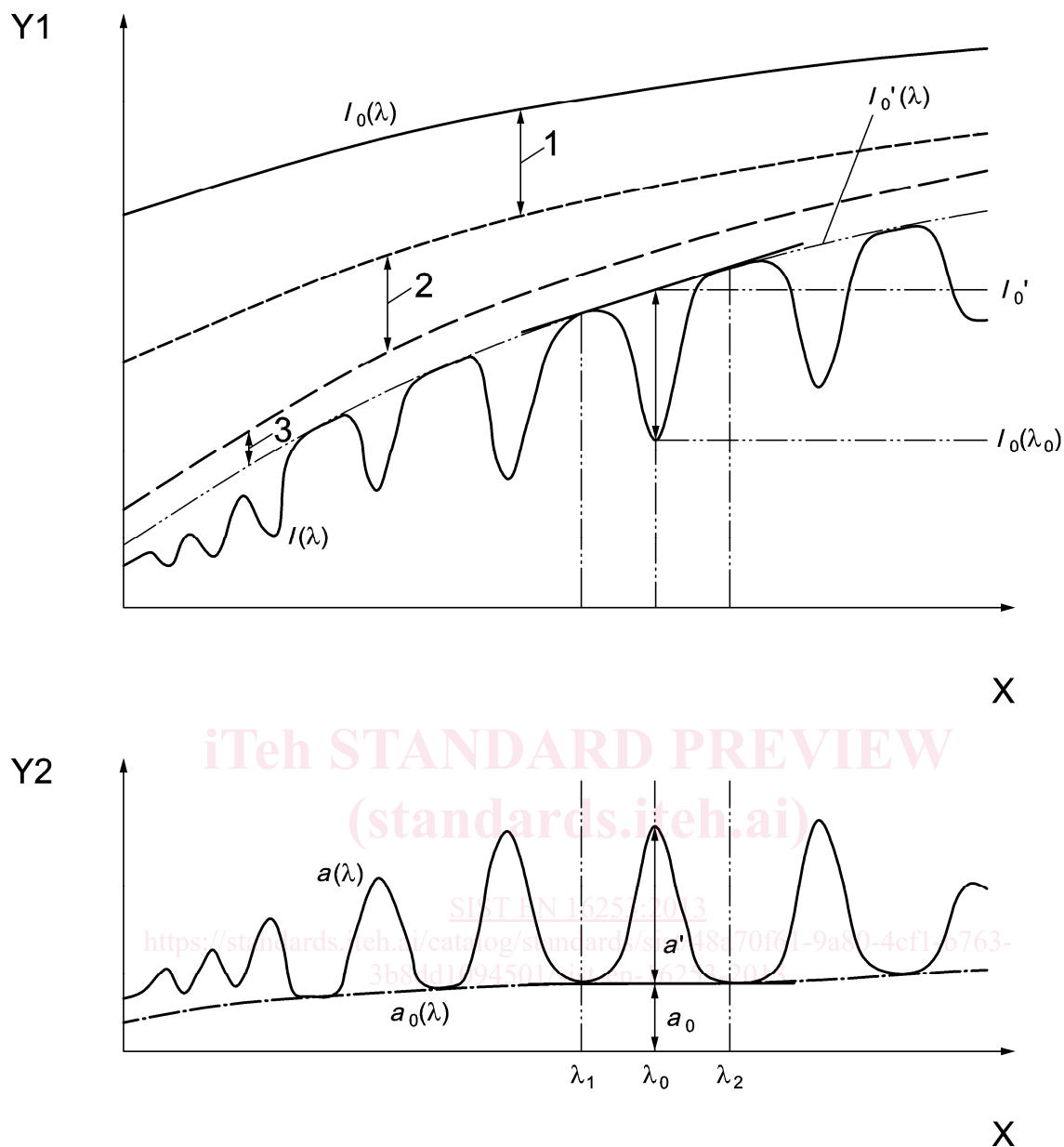
Key
1   Mie extinction
2   Rayleigh extinction
3   continuous absorption component
X   wavelength
Y1   intensity
Y2   absorption coefficient

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 Equation (9).

$$D'(\lambda) = \ln\frac{I_0'(\lambda)}{I(\lambda)} = \ln\left(I(\lambda_1) + \left(I(\lambda_2) - I(\lambda_1) \right) \cdot \frac{\lambda_0 - \lambda_1}{\lambda_2 - \lambda_1} \right) - \ln I(\lambda_0) \qquad (9)$$

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 minimizing the deviation between $I(\lambda)$ and $I_{mod}(\lambda)$, where $I_{mod}(\lambda)$ is the modelled intensity as a function of wavelength (i.e., a modelled spectrum).

$$I_{mod}(\lambda) = P(\lambda) \cdot \exp - \left(\sum_i a_i'(\lambda) \cdot c_i \cdot l \right) \tag{10}$$

$P(\lambda)$ describes the combined influences of all influencing variables which vary little with wavelength, such as $\tau(\lambda)$ or broadband absorbers (cf. Equation (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:

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

e.g., a 5th order polynomial [1]) or a low-pass filtered spectrum of $I(\lambda)$ (e.g., with the aid of a Bessel filter [2]), see Figure 4.

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

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

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 (Equation (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 [3].