Kakovost zunanjega zraka - Prizemne meritve zunanjega zraka s FTIR spektroskopijo

Ambient air quality - Atmospheric measurements near ground with FTIR spectroscopy

Luftqualität - Messungen in der bodennahen Atmosphäre mit FTIR-Spektroskopie

Qualité de l'air ambiant - Mesurages de l'air ambiant à proximité du sol par spectrométrie à transformée Fourier (FTIR)

iTeh STANDARD PREVIEW
(standards.iteh.ai)

Ta slovenski standard je istoveten z: **EN 15483:2008**

ICS:

13.040.20	Kakovost okoljskega zraka	Ambient atmospheres

SIST EN 15483:2009 **en,fr,de**

iTeh STANDARD PREVIEW

(standards.iteh.ai)

EUROPEAN STANDARD

NORME EUROPÉENNE

EUROPÄISCHE NORM

EN 15483

November 2008

ICS 13.040.20

English Version

Ambient air quality - Atmospheric measurements near ground with FTIR spectroscopy

Qualité de l'air ambiant - Mesurages de l'air ambiant à proximité du sol par spectroscopie à transformée de Fourier (FTIR)

Luftqualität - Messungen in der bodennahen Atmosphäre mit FTIR-Spektroskopie

This European Standard was approved by CEN on 11 October 2008.

CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration. Up-to-date lists and bibliographical references concerning such national standards may be obtained on application to the CEN Management Centre or to any CEN member.

This European Standard exists in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the CEN Management Centre has the same status as the official versions.

CEN members are the national standards bodies of Austria, Belgium, Bulgaria, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland and United Kingdom.

EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

Management Centre: rue de Stassart, 36   B-1050 Brussels

Ref. No. EN 15483:2008: E

EN 15483:2008 (E)

Contents

Page

Foreword

This document (EN 15483:2008) 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 May 2009, and conflicting national standards shall be withdrawn at the latest by May 2009.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. CEN [and/or CENELEC] shall not be held responsible for identifying any or all such patent rights.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Bulgaria, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland and the United Kingdom.

Introduction

Fourier transform infrared spectroscopy (FTIR spectroscopy) has been successfully developed from an established laboratory analytical method to a versatile remote sensing method for atmospheric gases.

In this method, the long-path absorption of IR radiation by gaseous air pollutants is measured over an open path between an artificial IR source and an IR spectrometer and used to calculate the integrated concentration over the monitoring path. Since IR radiation is used for remote sensing, the measurements can be made without contact, that is to say without direct sampling, and can be made in various directions. These measurements include monitoring diffuse emissions from large-area sources, for example landfills, road traffic routes, sewage treatment plants, areas used for industrial or agricultural purposes, and in addition the minimization of production losses by tracing leaks in plant sections or piping systems. FTIR spectroscopy is thus suitable for a great number of analytical tasks which cannot adequately be performed using in-situ methods that make point measurements.

Generally, using a suitable measuring arrangement, an overview of the local air pollution may be obtained on site in a short time. This also includes measurements in areas to which access is difficult or impossible, or where the direct presence of staff or set-up of instruments is dangerous. FTIR spectroscopy can be used to determine different compounds at the same time.

This European Standard presents the function and performance of FTIR analytical systems. At the same time, operational notes are given, so that reproducible and valid measurements can be obtained. In addition, questions of measurement planning are discussed and the appendices give a selection of typical applications.

In some circumstances (e. g. CO) the method might be applicable for measurement of air quality as required by European legislation [1].

EN 15483:2008 (E)

1 Scope

This European Standard is applicable to open-path absorption measurements of 'concentration $\times$ path length' product using the Fourier transform infrared (FTIR) technique with an artificial radiation source. It is applicable to the continuous measurement of infrared active organic and inorganic compounds in the gaseous state in ambient air using fixed tropospheric open paths up to approximately 1 km in length and provides a spatial average.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

EN ISO 6142, *Gas analysis - Preparation of calibration gas mixtures - Gravimetric method (ISO 6142:2001)*

EN ISO 6144, *Gas analysis - Preparation of calibration gas mixtures - Static volumetric method (ISO 6144:2003)*

EN ISO 9169, *Air quality - Definition and determination of performance characteristics of an automatic measuring system (ISO 9169:2006)*

ISO 6145 (all parts), *Gas analysis – Preparation of calibration gas mixtures using dynamic volumetric methods*

3 Terms and definitions

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

3.1
absorbance
the negative logarithm of the transmission, $A(v) = -\lg(I(v)/I_0(v))$, where $I(v)$ is the spectral transmitted intensity of the radiation and $I_0(v)$ is the incident spectral intensity

NOTE $\lg = \log_{10}$

3.2
apodisation
application of a weighting function to interferogram data to alter the instrument's response function

3.3
background spectrum
with all other conditions being equal, that spectrum taken in the absence of the particular absorbing species of interest

3.4
instrument line shape (ILS)
mathematical function which describes the effect of the instrument's response on a monochromatic line.

3.5
intensity
radiant power per unit solid angle (non-collimated beam) or per unit area (collimated beam)

3.6
interferogram
effects of interference that are detected and recorded by a two-beam interferometer

4

3.7
interferogram acquisition time
time to acquire a single interferogram

3.8
monitoring path
actual path in space over which the pollutant concentration is measured and averaged

3.9
open-path measurement
measurement which is performed in the open atmosphere

3.10
path length
distance that the radiation travels in the open atmosphere

3.11
reference spectrum
spectrum of the absorbance versus wavenumber for a pure gaseous sample under defined measurement conditions and known and traceable concentrations

3.12
signal-to-noise ratio
ratio between the signal strength and the RMS (root mean square) noise

3.13
spectral acquisition time
time to acquire and co-add interferograms to achieve required signal-to-noise ratio, including the Fourier transform processing

3.14
spectral intensity
radiant power per unit solid angle per wave number (non-collimated beam) or per unit area per wave number (collimated beam)

3.15
synthetic background spectrum
spectrum that is derived from a field spectrum by choosing points along the baseline and connecting them with a high-order polynomial or short, straight lines

4 Symbols and abbreviations

$a(\widetilde{\nu})$ specific (decadic) absorption coefficient;

$a_i(\widetilde{\nu})$ specific (decadic) absorption coefficient of the ith compound;

$a(\widetilde{\nu})_{\mathrm{IV}}$ specific absorption coefficient of the interfering variable;

$a(\widetilde{\nu})_{\mathrm{MV}}$ specific absorption coefficient of the measured variable;

$a'(\widetilde{\nu})$ specific (natural) absorption coefficient ($=a(\widetilde{\nu})/\mathrm{lg}(e)$);

c concentration;

c_i concentration of the ith compound;

EN 15483:2008 (E)

c_{IV} concentration of the interfering variable;

c_{MV} concentration of the measured variable;

$I(\widetilde{v})$ spectral intensity incident on the receiver (also abbreviated I);

$I_0(\widetilde{v})$ spectral intensity of radiation emitted by the transmitter (also abbreviated to I_0);

IV index for interfering variable;

l length of the monitoring path;

MV index for measured variable ;

n number of measured values;

$\widetilde{v}$ wave number in cm^{-1};

$\Delta\widetilde{v}$ unapodised spectral resolution;

s_{max} maximum optical path difference;

σ standard deviation;

t student factor (for a statistical confidence of 95%).

iTeh STANDARD PREVIEW

(standards.iteh.ai)

5 Principle

5.1 General

In infrared (IR) absorption spectroscopy, IR radiation is passed through a sample to a detector and the detected radiation is analysed to determine the spectral intensity which is received. Comparison of the transmitted intensity versus non-attenuated intensity shows at which wavelengths species present in the sample have absorbed radiation. Absorption takes place as a result of rotational and vibrational excitation of the absorbing species, and the wavelengths at which the radiation is absorbed are therefore characteristic of the molecular structure. The infrared absorption spectrum is therefore able to provide a basis for identification and quantification of the absorbing species present. For further information on the fundamental principles of IR spectroscopy, a number of suitable texts are available [e. g. 2; 3].

The FTIR technique measures the interferogram, for example using the Michelson interferometer technique, of the broadband IR radiation intensity. By performing a Fourier transform of this interferogram across a wide range of wavelengths a spectrum is obtained containing information about the absorption features of gases within the monitoring path. In principle it is then possible to analyse these absorption features to determine the total concentration of a wide range of species. The FTIR system is capable of making simultaneous measurements of multiple species.

5.2 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 total 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 [4].

In the bistatic system (Figure 1) the transmitter and the detector are separated at the two ends of the optical beam. 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.
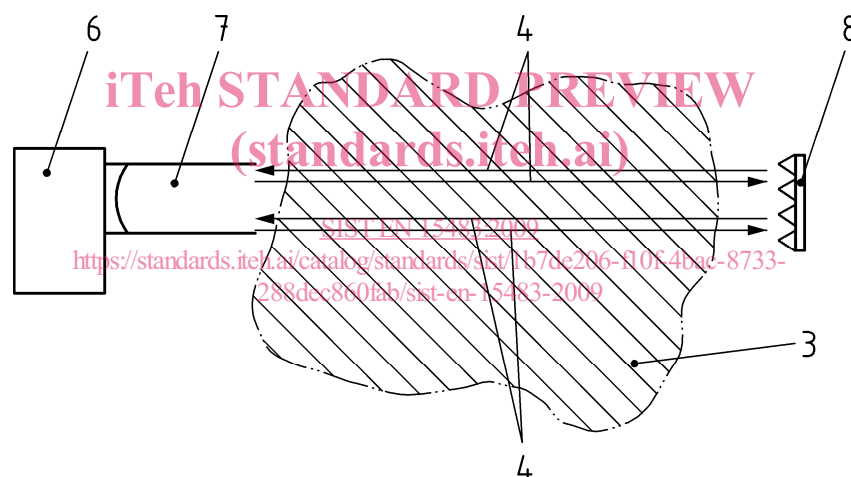
iTeh STANDARD PREVIEW
(standards.iteh.ai)
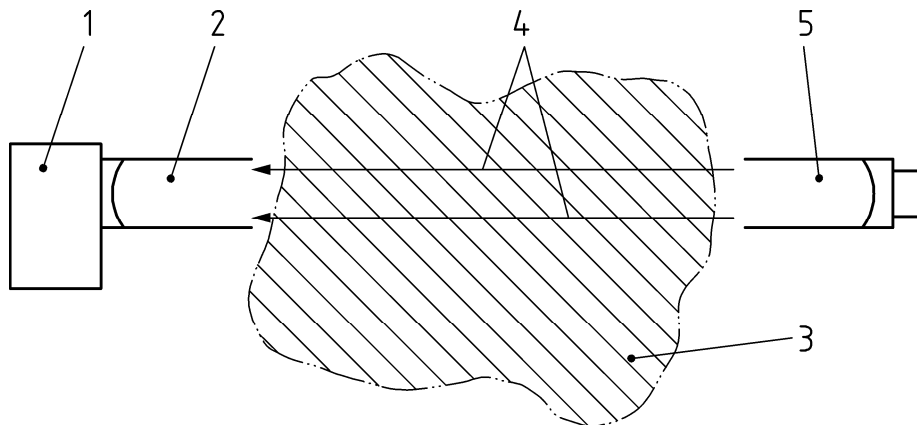
Key
1   FTIR spectrometer
2   telescope for radiation collection
3   ambient air
4   monitoring path
5   IR radiation source with collimating optics

Figure 1 – Bistatic arrangement for FTIR remote sensing

Key
1   FTIR spectrometer
2   telescope for radiation collection
3   ambient air
4   monitoring path
5   IR radiation source with collimating optics
6   FTIR spectrometer including radiation source
7   telescope for transmission and collection of IR radiation
8   retroreflector

Figure 2 – Monostatic arrangement for FTIR remote sensing

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

For a monostatic measurement set-up, transmitting and receiving optics are an integral part of the FTIR spectrometer (6), which also includes the IR radiation source and a beam splitter serving to separate the received and transmitted beams. By means of a retroreflector (8) the IR beam passes twice through the

measurement volume. The monitoring path length in this case is defined by twice the distance between the transmitter/receiver and the retroreflector optics. Monostatic systems have the advantage that the transmitted radiation can be modulated to reduce the effect of background emission interference.

5.3 The Beer-Lambert law

The basis for the quantitative evaluation of transmission measurements for the determination of concentrations of gases is the Beer-Lambert law. This relates the frequency-specific absorption of the emitted infrared radiation by the gases present in the monitoring path between source and FTIR spectrometer and their concentrations.

The Beer-Lambert law, for the special case of only *one* absorbing gas mixed homogeneously in the monitoring path has the following form:

$$\frac{I(\widetilde{v})}{I_0(\widetilde{v})} = e^{-(a'(\widetilde{v}) \cdot c \cdot l)} \tag{1}$$

With the relationship

$$a(\widetilde{v}) = \lg(e) \cdot a'(\widetilde{v})$$

the following applies

$$T(\widetilde{v}) = \frac{I(\widetilde{v})}{I_0(\widetilde{v})} = 10^{-(a(\widetilde{v}) \cdot c \cdot l)} \tag{2}$$

where

$T(\widetilde{v})$ transmittance;

$I_0(\widetilde{v})$ intensity of radiation emitted by the transmitter (also abbreviated to I_0 below);

$I(\widetilde{v})$ intensity incident on the receiver (also termed I below);

$a'(\widetilde{v})$ specific (natural) absorption coefficient of the gas, based on Equation (1);

$a(\widetilde{v})$ specific (decadic) absorption coefficient of the gas, based on Equation (2), for example in $(mg/m^3)^{-1} \cdot m^{-1}$ or converted into $ppm^{-1} \cdot m^{-1}$;

c gas concentration, e. g. in mg/m^3, or converted from concentration into mixing ratio in ppm or ppb;

l length of the monitoring path, in m.

NOTE 1   The Beer-Lambert law is commonly used in the form of Equation (2).

NOTE 2   The Beer-Lambert law is valid for monochromatic radiation. It is an excellent approximation of the measured transmittance if high spectral resolution is applied. For low spectral resolutions, an apparent deviation from the law is observed (see 8.1.2). However, this deviation is caused by the instrument line shape, which is well characterized in the case of a Fourier transform spectrometer. Thus the apparent deviation can be modelled and the effect of the deviation on the quantification can be removed (see 8.1.3).

The transmittance is a direct measure of the attenuation of I_0 caused by the gas.

EN 15483:2008 (E)

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 FTIR spectrometer

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 Scan speed

Where it is possible to select scan speed, the scan speed shall be selected such that it is as fast as possible within the limits imposed by the detector hardware. The maximum rate at which the detector system can acquire and digitise data points shall not be exceeded in selecting the scan speed.

6.2.3 Spectral acquisition time

The spectral acquisition time shall be selected in order to make quantitative measurements with the required signal-to-noise ratio using the coaddition of interferograms. In such circumstances the spectral acquisition time shall be determined in the field (see Clause 7) as part of the operational setup.

NOTE 1   The measurement requirements will identify the measurement uncertainty necessary for the purpose of the measurement. From this may be derived the signal-to-noise ratio which must be achieved in order for the processing which is performed on the spectral data to produce results with the defined measurement uncertainty.

NOTE 2   The interferogram acquisition time should be shorter than the expected timescales for major concentration changes. If fast concentration changes occur significantly during acquisition of a single interferogram, then interferogram shape distortion causing loss of spectral resolution will result. Peak height changes will also occur. Use of a faster scan speed combined with coaddition of interferograms achieves the same spectral acquisition time in preference to slower acquisition of a single interferogram. In this way the same signal-to-noise ratio is obtained however the peak shape distortion is avoided.

6.2.4 Path length

The path length shall be selected in order to optimise the signal-to-noise of the 'concentration $\times$ path length' product, taking into account the constraints imposed by the location in which measurements are to be made and the measurement requirements.

NOTE 1   At high 'concentration $\times$ path length' products non-linearity (apparent nonlinearity in the absorbance spectrum at low spectral resolutions) or even saturation might occur. These apparent nonlinearities are not present if the modeling approach as described in 8.1.3 is applied.

NOTE 2   If the spatial distribution of gases to be measured is non-localized, longer path lengths will give better signal-to-noise ratios, so long as scattering effects and the efficiency of the optical arrangement allow sufficient radiation to reach the detector. Where the spatial distribution of species of interest is localized and interfering species (typical examples H_2O or CO_2) are homogeneous, selecting a shorter path length may give rise to an optimum 'concentration $\times$ path length' product for the species of interest, relative to the 'concentration $\times$ path length' product for the interfering species.

10

6.2.5 Spectral range

The selected spectral range for the measurement shall include the spectral features to be measured for the species of interest.

NOTE 1   The maximum spectral range of the measured data is related to the data point interval of the interferogram. In order to avoid the effect of aliasing, the upper limit of the sampling interval Δs is given by the sampling theorem: $\Delta s <$ $1/(2 \cdot \sigma_{max})$, where σ_{max} is the maximum wavenumber that causes a detector signal. For real measurements in the field the selected spectral range is a trade-off between storage capacity, data acquisition times and the dynamic range of the spectral lines.

NOTE 2   Spectral filters may be used to improve the signal to noise ratio by limiting the spectral range to the region of interest.

6.2.6 Apodisation

Where the spectrometer allows selection of apodisation functions, the same apodisation function shall be maintained throughout the measurement procedure, applying to all sample, reference or background interferograms.

NOTE 1   Selection of apodisation function will affect the signal-to-noise ratio, spectral resolution and linearity of response with respect to concentration.

NOTE 2   There are various types of weighting functions; the most common are boxcar, triangular, Happ-Genzel, Beer-Norton and Blackman-Harris functions.

6.2.7 Spectral resolution

The spectral resolution is specified by the width of the instrument line shape. For perfectly collimated radiation and if no apodisation function is applied, the full width at half maximum of the instrument line shape is approximately $1{,}2/(2 \cdot s_{max})$ where s_{max} is the maximum optical path difference between the two interferometer paths. However, due to the finite solid angle subtended by the source of radiation and other effects such as misalignment and nonlinear movement of the mirrors, the instrument line shape is broadened. Moreover, the application of an apodisation function results in additional broadening. Thus, in order to include these effects, the spectral resolution is specified by the reciprocal of the maximum optical path difference (in centimetres) between the two interferometer paths if no other specification is explicitly stated. The spectral resolution shall be selected so that quantitative measurements of the species of interest can be made.

NOTE   The spectral resolution should be chosen to avoid broadening of the peaks of interest in the spectrum such that they are not resolved from other interfering species. Lower resolutions offer a signal-to-noise ratio advantage [5], and therefore an optimum is sought. It is recommended to identify and use the lowest spectral resolution which is consistent with the measurement requirements (trade-off between scan rate and spectral resolution). It is essential to take into account the linewidths of the spectral features to be measured when considering the selection of spectral resolution [6].

6.2.8 Concentration range

The method shall only be used within the range of the 'concentration $\times$ path length' product over which the system has been calibrated (see 6.2.4, Note 1).

6.2.9 Source intensity

The source intensity should have a level that the signal-to-noise ratio enables significant measurement results above the limit of detection. Stability of the source intensity over the experimental measurement period shall be sufficient to allow measurements in accordance with the measurement requirements.

6.2.10 Wavelength range of optical components

Where selection of the detector and the beam splitter is possible these shall be selected so that quantitative measurements of the species of interest can be made.

EN 15483:2008 (E)

NOTE   As radiation intensity increases, detectors operate in a linear, then non linear, then saturated regime. Operation when saturated is to be avoided. Operating in the non-linear region is possible if suitably corrected. The choice of detector type determines the operational wavelength range. The detector should be chosen such that sufficient sensitivity to make quantitative measurements exists at the wavelengths of the spectral features of interest.

7   Measurement procedure

7.1   Initial set-up

In addition to the proper selection of the monitoring path and the positioning of the equipment, the following requirements shall be met:

—   The path length shall be determined based on the objectives of the measurement, the performance of the system and the meteorological conditions.

—   Sufficient heating up times for FTIR spectrometer and IR radiation source must be taken into account. Causes of fluctuations in radiation source power shall be minimised. If the detector element requires a reduced working temperature (for example an MCT photo-detector), sufficient time for detector cooling is required.

—   The atmospheric monitoring path length shall be determined precisely because its uncertainty affects the uncertainty of the measured concentration.

—   Obstructions, which block the IR beam for a significant part of the measuring time (more than approx. 10 %), shall be avoided. Partial obstructions, which affect the signal intensity, shall be taken into account when carrying out preliminary measurements.

—   Significant interferences from IR radiation from other sources (e. g. hot gases, ambient black body radiation, solar radiation) shall be excluded, either by baffles or by choice of path geometry.

7.2   Preliminary measurements

After the system has been set up, and before commencing routine measurements, preliminary measurements shall be made with regard to the following requirements; these will provide assurance that the system is functioning correctly and enable the optimum selection/ verification of system parameters:

—   The optical components in mono- and bistatic systems shall be optimally aligned to maximise the intensity of the returned signal. During the measurement period care shall be taken to minimise influences on the stability of the alignment of the transmitting and receiving optics.

—   The FTIR spectrometer measurement time shall be optimised to achieve spectral signal-to-noise ratios sufficient for quantitative spectral analysis.

—   Saturation of the detector shall be avoided.

NOTE 1   Saturation is potentially a problem when operating with short monitoring paths.

NOTE 2   Non-zero intensities below the detector cut-off wavelength indicate detector non-linearity. Detector saturation or ADC overflow will result in deformed single-beam spectra when compared to routine measurements. In such cases corrective actions may be e. g.
• a smaller aperture
• use of a mesh
• application of a detector nonlinearity correction method [7]
• reduce the source intensity

7.3   Measurements to be made

During the measuring period all transmission data and interferograms, if available, should be recorded and stored to allow for subsequent re-analysis and quality assurance.

—   Full information on instrument parameters should be recorded as defined in 7.2.

—   Parallel to the spectroscopic measurements, meteorological parameters such as pressure, temperature, humidity, wind speed and wind direction shall be monitored close to the measurement site and at a similar height to the monitoring path because they might be important for the interpretation of the data. The time resolution of wind measurement should be of the same order of magnitude as the FTIR spectrometer measuring time.

—   For calculating the absorbance spectra which are the basis for the IR spectroscopic quantitative trace gas analysis the following information shall be recorded:

  - a background reference spectrum (see 9.3), which is typical for the measurement site. If humidity changes significantly, a new background reference spectrum shall be recorded for compounds which show spectroscopic overlap with water vapour spectral features;

  - a spectrum of the ambient black body emission radiation three times per day if the evaluation of spectral data is carried out in a range from detector cut-off to approx. 1500 cm^{-1} (FTIR spectrometer with non-modulated IR radiation as found for bistatic FTIR spectrometer systems; see 10.3.6);

  - a spectrum of the internal stray radiation once after turning on the instrument, once per week during continuous operation (FTIR spectrometer with modulated IR radiation as found for monostatic FTIR spectrometer systems; see 10.3.6).

—   In addition the following information shall be available:

  - reference spectra for the compounds to be measured including compounds which have cross-sensitivities (see 10.3.2);

—   The user shall ensure that either the components to be measured are free from cross-sensitivities to interfering gases or that interfering compounds are known and properly taken into account within the evaluation procedure.

For every measurement with a non-modulated signal, at least at the beginning and the end of a series of measurements a background radiation spectrum shall be recorded. For relatively long series of measurements the background radiation spectrum may vary greatly. Changes in the background radiation spectrum will affect measurement uncertainty. The frequency of measurements of the background shall be chosen to meet the required measurement uncertainty. The measured spectra shall then be corrected using the recorded spectra of the natural background radiation. This applies particularly with meteorological conditions which change rapidly.

7.4 Information to be recorded

Documentation of the measurements variables shall include:

—   scan speed;

—   spectral acquisition time and number of co-added interferograms;

—   path length;

—   spectral range;