BRITISH STANDARD

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Ambient air quality — Atmospheric measurements near ground with FTIR spectroscopy

ICS 13.040.20

British Standards

National foreword

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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

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

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

Contents

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of an identical text or by endorsement, at the latest by May 2009, and conflicting national standards shall be withdrawn at the latest by May 2009.

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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].

1 Scope

This European Standard is applicable to open-path absorption measurements of 'concentration × 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, $A(\nu) = -\lg(I(\nu)/I_0(\nu))$, where $I(\nu)$ is the spectral transmitted intensity of the radiation and $I_0(\nu)$ 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

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

$a(\tilde{\nu})$	specific (decadic) absorption coefficient;
$a_i(\tilde{\nu})$	specific (decadic) absorption coefficient of the *i*th compound;
$a(\tilde{\nu})_{\mathrm{IV}}$	specific absorption coefficient of the interfering variable;
$a(\tilde{\nu})_{\mathrm{MV}}$	specific absorption coefficient of the measured variable;
$a'(\tilde{\nu})$	specific (natural) absorption coefficient (=$a(\tilde{\nu})$/lg(e));
c	concentration;
c_i	concentration of the *i*th compound;

c_{IV}	concentration of the interfering variable;
c_{MV}	concentration of the measured variable;
$I(\tilde{\nu})$	spectral intensity incident on the receiver (also abbreviated I);
$I_0(\tilde{\nu})$	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;
$\tilde{\nu}$	wave number in cm^{-1};
$\Delta\tilde{\nu}$	unapodised spectral resolution;
$s_{\max}$	maximum optical path difference;
σ	standard deviation;
t	student factor (for a statistical confidence of 95%).

5 Principle

5.1 General

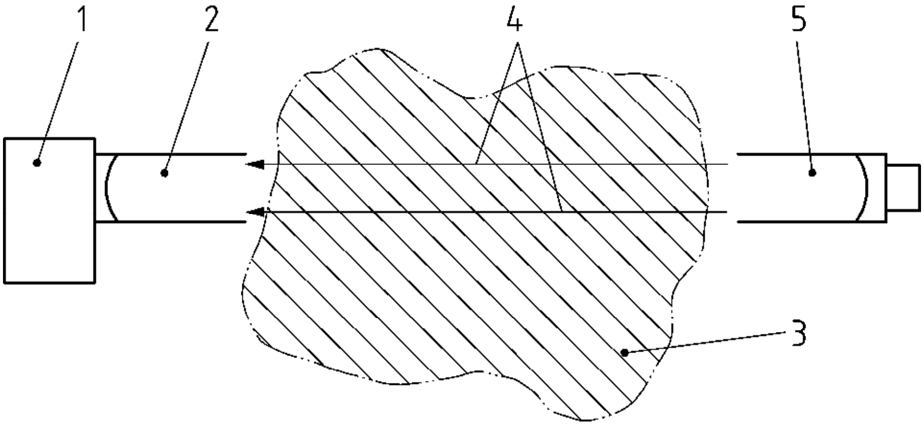
In infrared (IR) absorption spectroscopy, IR radiation is passed through a sample to a detector and the detected radiation is analysed to determine the spectral intensity which is received. Comparison of the transmitted intensity versus non-attenuated intensity shows at which wavelengths species present 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 × 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].

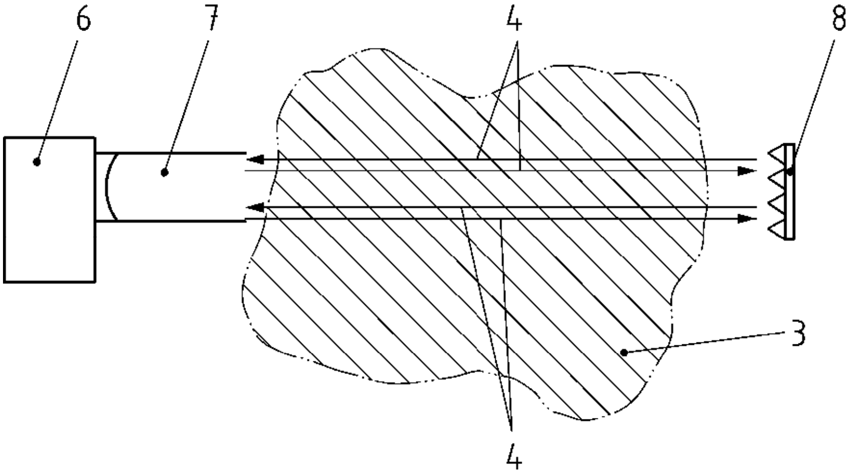
In the bistatic system (Figure 1) the transmitter and the detector are separated at the two ends of the optical beam. The monostatic system (Figure 2) operates by transmitting the optical beam into the atmosphere to a passive retroreflector which returns the beam to the detector.



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:

$$\frac{I(\tilde{\nu})}{I_0(\tilde{\nu})} = e^{-(a'(\tilde{\nu})\cdot c\cdot l)} \qquad (1)$$

With the relationship

$$a(\tilde{\nu}) = \lg(e)\cdot a'(\tilde{\nu})$$

the following applies

$$T(\tilde{\nu}) = \frac{I(\tilde{\nu})}{I_0(\tilde{\nu})} = 10^{-(a(\tilde{\nu})\cdot c\cdot l)} \qquad (2)$$

where

$T(\tilde{\nu})$	transmittance;
$I_0(\tilde{\nu})$	intensity of radiation emitted by the transmitter (also abbreviated to I_0 below);
$I(\tilde{\nu})$	intensity incident on the receiver (also termed I below);
$a'(\tilde{\nu})$	specific (natural) absorption coefficient of the gas, based on Equation (1);
$a(\tilde{\nu})$	specific (decadic) absorption coefficient of the gas, based on Equation (2), for example in $(\text{mg/m}^3)^{-1}\cdot\text{m}^{-1}$ or converted into $\text{ppm}^{-1}\cdot\text{m}^{-1}$;
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.

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 × 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 × 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 × path length' product for the species of interest, relative to the 'concentration × path length' product for the interfering species.

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 $\sigma_{\max}$ 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 × 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.

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;

- apodisation and zero-filling factor;
- spectral resolution;
- concentration range;
- source intensity;
- range of IR detector;
- definition of the measurement objective;
- name of the operator;
- precise measurement location;
- type and uncertainty of the path length measurement;
- return intensity (interferogram maximum or detector ADC output in arbitrary units/counts);
- time of measurements;
- characterization of additional radiation sources in the background (e. g. hot tubes in refineries, engines, motors, hot areas);
- known blockage of the optical path;
- details of the calibration and evaluation method;
- QA/QC checks;
- spectra and/or interferograms;
- electronic gains;
- optical filters;
- electronic filters;
- phase correction information;
- ZPD position;
- parameters of the detector nonlinearity correction procedure;
- meteorological parameters (pressure, temperature, moisture and, if necessary, wind speed, wind direction and turbulence).

Optional:

- position of potential main and minor emitters and any interfering sources of emissions;
- weather details: cloud, precipitation, fog and sunshine conditions.

8 Calibration and quality assurance

8.1 Primary calibration

8.1.1 General

The primary calibration of the 'concentration × path length' product provides the correlation between the concentration of a reference material and the measured signal of the measurement method.

The calibration is only valid over the 'concentration × path length' range which is spanned by the calibration points.

8.1.2 Experimental method

In this method the calibration function is determined experimentally, that is to say the known concentrations of the gas components to be determined are assigned to a value of the measured signal as an expected or forecast value [8; 9; 10].

An IR gas cell of suitable length is placed in the beam path of the FTIR system and is filled with a calibration gas for each component, or an equivalent calibration gas mixture, in at least five concentration levels, which are evenly distributed over the measuring range.

NOTE 1 Use, for example, a gas cell with a length of 10 % of the real monitoring path. Use calibration gas concentrations of, for example, 10 times the expected value to determine the 'concentration × path length' product. If self-broadening effects dominate a longer gas cell should be used. However, in many cases small concentrations are measured and thus the effect of self-broadening is not the dominating broadening effect.

The cell should be filled with buffer gas to 1 bar to ensure line shapes are representative. The different concentration levels are run through in accordance with EN ISO 9169. The test gases are metered into the IR gas cell statically or dynamically in accordance with EN ISO 6142, EN ISO 6144 or ISO 6145. The calibration gases shall be traceable to national standards.

The concentrations c of the test gases used shall be selected so that the product c × l (l is the effective optical length of the IR gas cell) is in the FTIR system working range selected for the respective measurement depending on the objective. It has to be assured that no pressure broadening of the absorption lines through a high partial pressure of the compound occurs.

At each concentration level, the appropriate interferograms are recorded by the FTIR system and the resultant calibration spectra are determined from these.

The evaluation of these spectra provides measured values corresponding to the concentration levels which are used to determine the calibration function with its confidence ranges in accordance with EN ISO 9169.

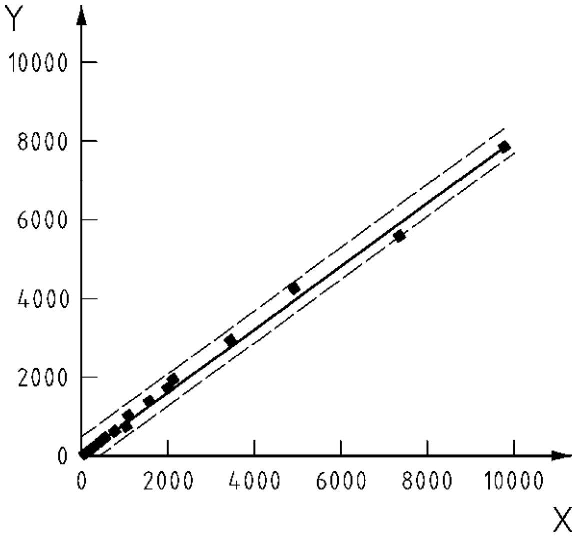
Since the calibration function reflects the correlation between the known test gas concentrations and the measured values determined using the evaluation method, the calibration function also depends on the evaluation method used. This is made clear in the comparison shown in Figure 3 [8]. These diagrams show plots of the calibration functions of the same apparatus at identical concentrations, but using different evaluation methods.

The calibration spectra shall be determined in the primary calibration using the same spectrometer type and the same evaluation method which will also be used later in the field measurements. The primary calibration shall typically be performed at 20 °C. An uncertainty will be introduced if the measurements are not carried out at the same temperature as the calibration.

NOTE 2 Measurements within the range ± 20 K of the calibration temperature are considered permissible.

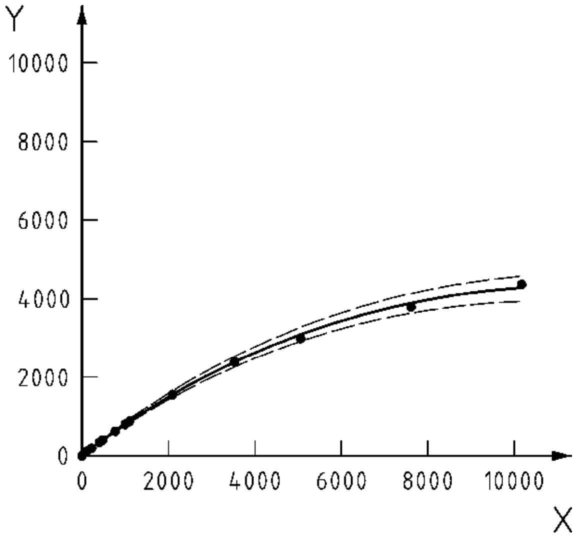
Where traceable measurements are required a five point calibration should be carried out for each instrument and each species measured.

NOTE 3 This is usually the case for regulatory purposes.



Key
X calibration gas mixing ratio × optical path length in ppm·m
Y measurement values in ppm·m

Figure 3a – Plot of a linear calibration function composed of the results of univariate evaluation of absorption bands with different absorption coefficients



Key
X calibration gas mixing ratio × optical path length in ppm·m
Y measurement values in ppm·m

Figure 3b – Plot of a calibration function from multivariate evaluation (uncorrected, no linearization of evaluation results obtained)

The calibration function is used in all following measurements as a basis for correcting values calculated as specified in Clause 9, since otherwise systematic errors, in particular due to apparent nonlinearities (nonlinear relationship between absorbance and concentration) at high concentrations that are caused by the application of a spectral resolution that is significantly lower (width of the instrument line shape significantly larger) than the width of the absorption lines of the species, would arise (see Figure 3b).

NOTE 4 These apparent nonlinearities are not present if the modeling approach as described in 8.1.3 is applied.

The calibration spectra obtained from the primary calibration are stored. This is so that if the evaluation method is changed, the entire calibration experiment need not be repeated, and in principle it should be necessary to apply the changed evaluation method to the calibration spectra already obtained once.

Performance characteristics such as repeatability, detection limit, temperature dependence at zero level, temperature dependence at reference level, drift at zero level, drift at reference level, mains voltage and cross-sensitivity can be addressed in these calibration experiments according to EN ISO 9169. Examples of performance characteristics are given in Annex F.

8.1.3 Calibration with complete spectral modeling

This method is based on the approximation of the measured spectrum by a spectrum that is calculated using a model. The model consists of two sub-models: a radiative transfer model and an instrument line shape function. The radiative transfer calculation is performed using reference spectra of the specific absorption coefficient. The reference spectra are calculated based on molecular line data (compiled in databases such as HITRAN [11] or GEISA [12]) or measured high-resolution spectra are used. The radiative transfer model contains the column density (concentration × path length) of the target gas (or gases) as a parameter. Spectra at the spectral resolution of the measurement are calculated using the result of the radiative transfer calculation and the instrument line shape function. Various methods for the determination of the best-fit parameters are applied in different implementations of the method. Various approaches for this method have been developed [13; 14; 15]. Annex I gives an example.

8.2 Quality assurance

8.2.1 Check of the primary calibration

The calibration spectra determined during the primary calibration remain constant over time for a defined FTIR system and need not be repeated at regular intervals if they have been determined correctly.

Where traceable measurements are required a single point gas cell shall be used to demonstrate that the primary calibration is still valid.

NOTE This is usually the case for regulatory purposes.

8.2.2 Check of the proper operation of the FTIR system

8.2.2.1 Determination of atmospheric N_2O and CH_4

A required quality assurance method for checking the proper operation of the FTIR system is, on each day of measurement, to determine the N_2O and CH_4 concentration in the ambient air. The N_2O mixing ratio is slightly above 300 ppb and the CH_4 mixing ratio is only rarely less than 1,7 ppm (see Figure 4 [16] and [17]). If relatively high deviations in the N_2O mixing ratio occur or if the measured values of the CH_4 mixing ratio fall below 1,7 ppm, the FTIR system shall be checked.

NOTE The exceptional methane concentration drop on 26/27 is due to the rapid transport of fresh polar air to the measurement site by a thunderstorm.

8.2.2.2 Determination of atmospheric water vapour

A recommended quality assurance method is the determination of the atmospheric water vapour content from the measured spectra and comparing them with the values from independent air humidity measurements [18] (see Figure 5). Note here that the water vapour content, which is determined by evaluating the spectra, represents the absolute water vapour concentration, whereas most commercial humidity meters determine the relative humidity. Convert the measurements appropriately using the atmospheric pressure and temperature.

On each day of measurement check the position of characteristic water lines in the measured spectra, for example at wavenumbers 1009 cm^{-1}, 1014 cm^{-1} and 1017 cm^{-1} [4; 19] or 1101,5 cm^{-1} and 2023 cm^{-1}. In the event of differences with respect to the reference spectra, shift the measured spectra to their correct wavenumber on the wavenumber axis.

NOTE In principle these water vapour lines serve as transfer standards.

8.2.2.3 Determination of the baseline noise

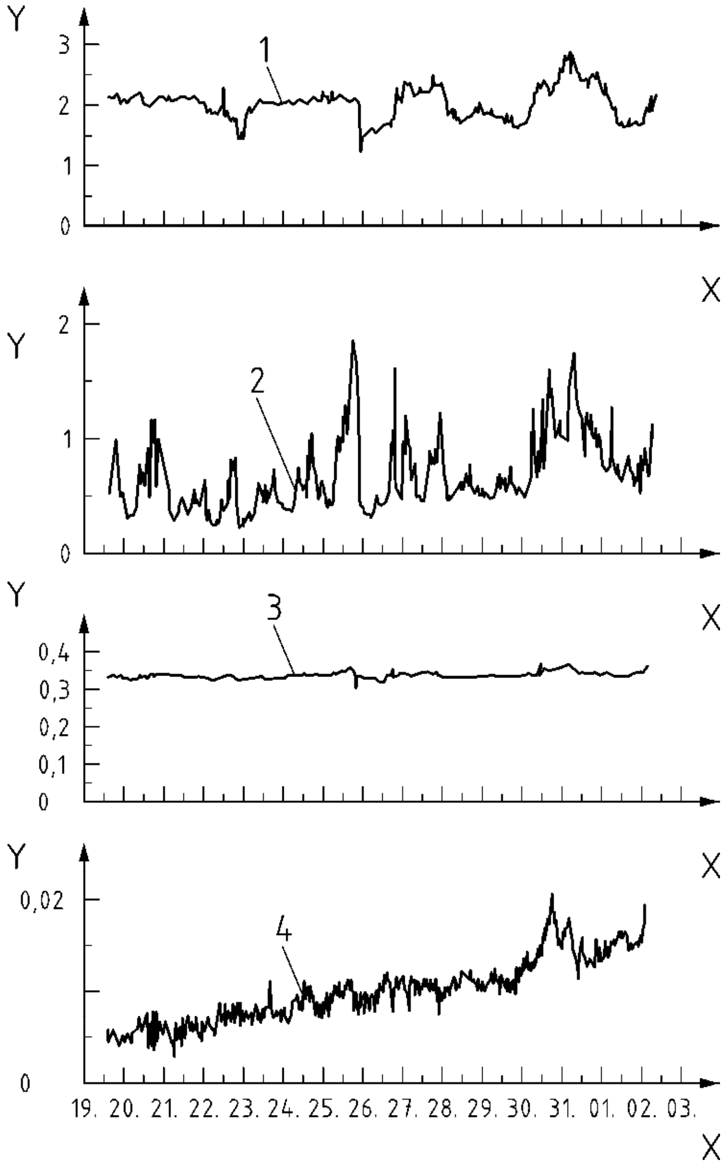
An optional quality assurance measure is the determination of the baseline noise in three spectral regions. A precondition of the method described below is that the concentration of the compounds which absorb in the specified ranges remains essentially constant over the time taken for two sequential measurements. Carry out the method as follows:

1. Calculate an absorbance spectrum from two spectra measured immediately one after the other. During this time, the composition of the atmosphere should not change significantly.

2. From the wavenumbers e. g. $\tilde{\nu}_1$ = 960 cm^{-1}, $\tilde{\nu}_2$ = 2480 cm^{-1} and $\tilde{\nu}_3$ = 4380 cm^{-1} determine the standard deviation of the following 98 data points. Use this standard deviation as a measure for the baseline noise. The 98 data points correspond to a range of about 47 cm^{-1} for an instrument with a resolution of 1 cm^{-1}, for a system with a resolution of 0,2 cm^{-1} these data points correspond to a range of 9 cm^{-1}.

3. Form the ratios of the standard deviations from the ranges at $\tilde{\nu}_1$ to $\tilde{\nu}_2$ and the ranges $\tilde{\nu}_2$ to $\tilde{\nu}_3$.

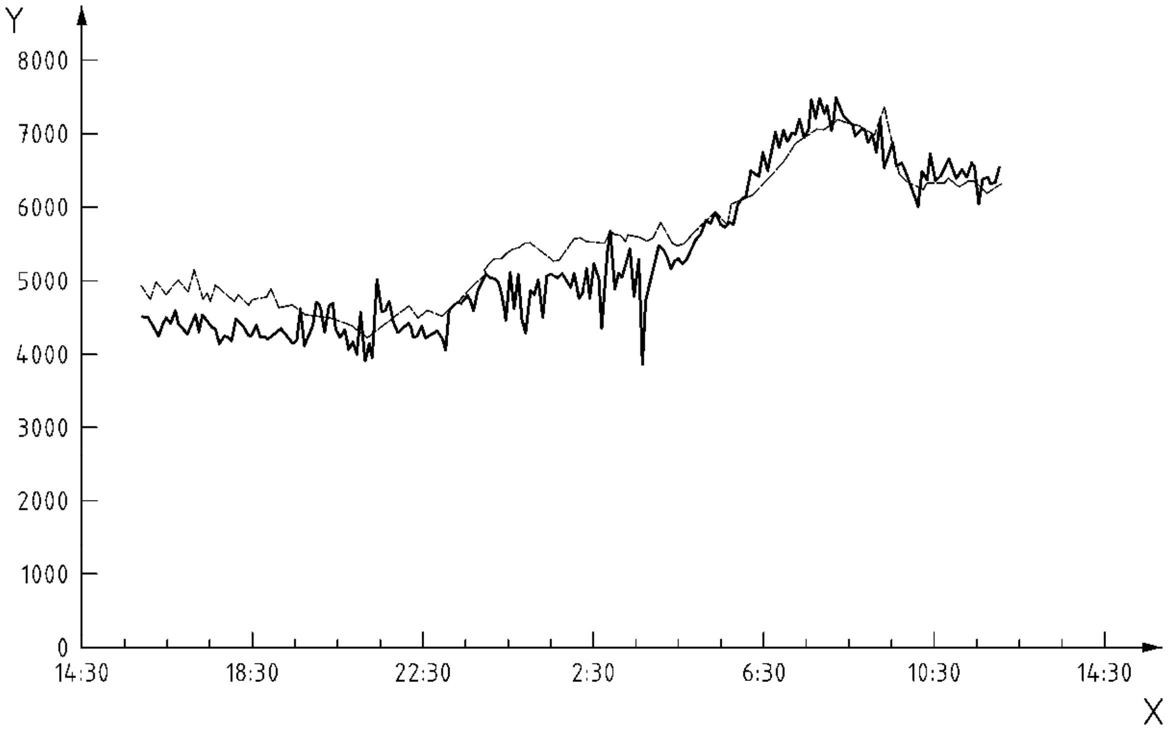
These ratios are typical of the spectrometer and should not change greatly over the operating time [20]. However, if this is the case, common reasons for this may be meteorological effects, for example fog; dirt on the optics; blockage of the monitoring path or a degradation of the alignment. In these cases check whether the measurement results are adversely affected and whether this can be compensated by appropriate measures (for instance appropriate background reference spectra). The baseline noise at $\tilde{\nu}_2$ and the two ratios shall be determined at suitable time intervals and documented.



Key

1 methane
2 carbon monoxide
3 dinitrogen monoxide
4 ammonia
X date
Y mean mixing ratio in ppm

Figure 4 – Measurement of atmospheric trace gases by FTIR spectrometer over a relatively long period



Key

X time

Y water vapour mixing ratio in ppm

Figure 5 – Comparison between FTIR spectrometer (continuous line) and standard humidity meter (hair hygrometer; dotted line)

8.3 Control measurements

For continued operation of the system at a fixed site and line of sight, control measurements shall be recorded at a fixed concentration using a gas cell which is representative for the concentration of the pollutant. The gas cell should be installed in the measurement beam, internal or external to the measurement system. At a fixed installation a control measurement in a weekly period should be performed. The time period of this measurement should be based on the experience of the behaviour of the system and this procedure should be carried after maintenance, modification of the system or change of position. If there are significant changes compared to the primary calibration (see 8.1) and regarding the permissible uncertainty a complete recalibration of the system shall be carried out. If a change can be regarded as significant depends on the specific measurement task. For example the changes should be not greater than the maximum uncertainties for that measurement task according to the relevant EU Directives.

9 Data processing

9.1 General

The knowledge of the specific absorption coefficient $a(\tilde{\nu})$ for the species being measured is a precondition for quantitative analysis. It is determined from reference spectra or calibration spectra which were produced from measurements made on a sample of a traceable concentration (see Clause 8).

The specific absorption coefficient is a function of:

— wavenumber;

— gas temperature;

— absolute pressure of the medium studied.

The apparent specific absorption coefficient, i.e. the specific absorption coefficient that is calculated by dividing a measured absorbance spectrum (known column density) by the column density, is also influenced by the FTIR spectrometer parameters (especially the spectral resolution and apodisation function). These parameters shall be identical during calibration and measurement.

By taking logarithms and subsequent transformation, Equation (2) may be solved for *c*:

$$c = \frac{-lg\,\frac{I}{I_0}}{a(\tilde{\nu})\cdot l} \tag{3}$$

The parameter $-\lg(I/I_0)$ is the absorbance and is a linear function of concentration, the specific absorption coefficient and the length of the monitoring path. The corresponding spectra are called absorption spectra.

The Lambert-Beer law also applies to the analysis of mixtures. In this case, the law has the following form:

$$-\lg\frac{I(\tilde{\nu})}{I_0(\tilde{\nu})} = l\cdot\sum a_i(\tilde{\nu})\cdot c_i \tag{4}$$

where

$a_i(\tilde{\nu})$ specific absorption coefficient of the *i*th gas;

c_i concentration of the *i*th gas;

Σ sum over all gases present.

Equation (4) implies that the total absorbance at any specific wavelength is composed linearly from the absorbances of the individual compounds. When numerous compounds occur in the spectrum, their patterns can superimpose. This superposition may cause cross-sensitivities if the interfering species are not taken into account.

NOTE 1 H_2O and CO_2 are the key cross-interferences in FTIR measurements in the atmosphere.

NOTE 2 Where the instrument software includes the analysis procedure it should be designed in accordance with the requirements of this standard.

NOTE 3 Equations (3) and (4) and the implications are only valid for high spectral resolutions (i.e. width of the instrument line shape smaller than the width of the spectral lines). If lower spectral resolutions are applied, calibration procedures (see 8.1.2) or a modelling approach (see 8.1.3) should be applied.

9.2 The quantities $I_0(\tilde{\nu})$ and $I(\tilde{\nu})$

To determine concentrations, the two quantities *I* and I_0 are required, see Equation (3). Whereas *I* can be measured directly, this is not possible for I_0. Between the transmitter and receiver is the monitoring path along which I_0 is attenuated by absorptions due to the gases to be analyzed and by additional effects (for example interfering gases, particles in the monitoring path or measurement system optics). Equation (2) can therefore also be written in the following form:

$$I(\tilde{\nu}) = I_0(\tilde{\nu})\cdot 10^{-a(\tilde{\nu})_{IV}\cdot c_{IV}\cdot l}\cdot 10^{-a(\tilde{\nu})_{MV}\cdot c_{MV}\cdot l} \tag{5}$$

where

$I_0(\tilde{\nu})$ intensity of radiation emitted by the transmitter;

$I(\tilde{\nu})$ intensity incident on the receiver;

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

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

c_{IV} concentration of the interfering variable;

c_{MV} concentration of the measured variable;

l length of the monitoring path.

Instead of I_0, the product $I_0 \cdot 10^{-IV}$ can be used as a reference variable in the Beer-Lambert law. The interfering variable here can also comprise the absorbance of compounds which are not to be analyzed in the actual measurement objective, for example water vapour or CO_2. The product $I_0 \cdot 10^{-IV}$ is determined from a suitable background reference spectrum (see 9.3).

9.3 The background reference spectrum

9.3.1 General

A background reference spectrum can be generated in three different ways:

- measurement off to one side;
- synthetic background spectrum;
- measurement with short monitoring path.

9.3.2 Measurement over equivalent path without the target compounds

9.3.2.1 Measurements off to one side

These are measurements in which detectable occurrence of the measurand can be excluded. When measurements are made off to one side, care shall be taken to ensure that the metrological and meteorological conditions substantially correspond to those when the compound is determined (see Figure B.1). If the measurand cannot be definitely excluded, one of the other methods shall be applied.

9.3.2.2 Upwind/downwind measurements

An important special case is the upwind/downwind method, which is particularly suitable for measuring diffuse emissions from industrial plants, landfills, etc. In this method, measurements off to one side are made upwind of the object under study, and in contrast the pollutant measurements are made on the downwind side (see Figure B.1). As a result, the air pollutants which do not originate from the source under study may be eliminated if they are present in both upwind and downwind measurements. When this type of measurements is carried out, care shall be taken to ensure that the metrological and meteorological conditions substantially correspond to those when the compound is determined.

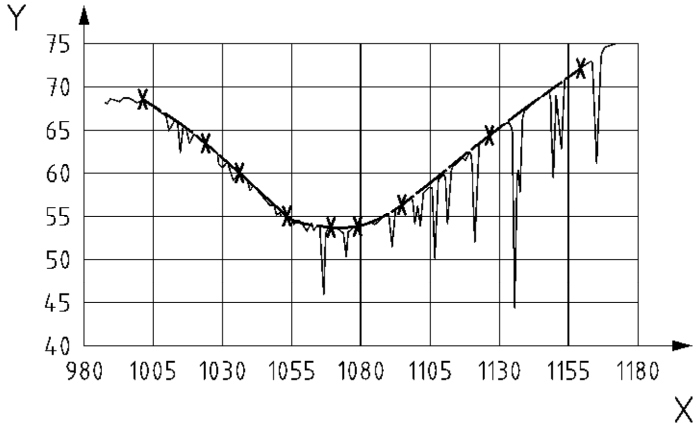
9.3.3 Synthetic background spectrum

In this case, only the measured spectral intensity is used for the evaluation, and there is no need for a separate background reference spectrum. I_0 is generated at the points in the spectrum required for analysis (support points) in a synthetic background spectrum by appropriate interpolation between wavenumber ranges where there are absorptions due to gases present in the measuring path which are to be excluded (Figure 6)

[21]. It can be checked by comparison with independent measurement methods if the synthetic background spectrum has been taken properly with respect to the required uncertainty of the given measurement task.

9.3.4 Measurement with short monitoring path

In this – least common – method, to determine I_0, the IR source or the retroreflector is positioned immediately in front of the FTIR spectrometer and then a spectrum is recorded. However, this method is only practicable for long-path measurements if appropriate attenuators (e. g. meshes, filters) are available which can be introduced into the optical path to avoid saturation of the detector.



Key
X wave number in cm^{-1}
Y intensity (relative unit)

continuous line: original spectrum
dashed line: synthetic (interpolated) spectrum
crosses: support points for the interpolated spectrum

Figure 6 – Outline of the procedure for preparation of a synthetic background spectrum

9.4 Quantitative analysis

9.4.1 General

Calibration of the wavenumber axes of all spectra used for the evaluation is a necessary precondition for quantitative analysis. To perform wavenumber calibration for selected spectral lines, their measured positions on the (uncalibrated) wavenumber axis are related to known and sufficiently accurate reference values and used for the calibration. These lines should always be present in the spectra measured and in addition should cover the entire wavenumber range relevant to the analysis. Water vapour spectra are particularly highly suitable for the wavenumber calibration (see also 6.2).

For quantitative analysis, concentration values shall be assigned to the measured spectral profiles of the identified compounds (in qualitative analysis). For this purpose calibration or reference spectra are required (see Clause 6).

As measured parameter and comparison parameter from the reference spectra, customarily the absorbance is evaluated (see 9.1) which is generally calculated using the regression method. When cross-sensitivities can be excluded the evaluation can be carried out via peak height determination.

9.4.2 Multivariate regression method

NOTE This method is not detailed here as it is a basic analytical technique.

In contrast to the determination of peak height, in the multivariate regression method entire wavenumber ranges are used for the evaluation. Cross-sensitivities can thus be taken into account considerably more readily, since generally each compound has a unique absorption spectrum. In this method an attempt is made to bring the absorbances from the measurement spectrum and reference spectrum to coincide as closely as possible via a regression calculation, the concentration values of the relevant compounds being the regression variables.

Different analytical methods are used for this (see, for example, [22; 23]). In any case the quantitative analytical procedure shall be validated using the calibration experiment.

In cases where the cross-sensitivity to other compounds can be neglected in a restricted wavelength range and if only one compound is of interest, the univariate regression fitting of a single or multiple peaks is applicable.

9.4.3 Peak height determination

This procedure can only be used when cross-sensitivities with other compounds which have profiles of the same wavenumber can be excluded, because due to the small amount of spectral information used, analytical errors occur if the interfering components are not taken into account or not completely. For the determination of peak height, I and I_0 are evaluated at those wavenumbers in the spectrum at which the absorption of the gas under test is maximal. From the parameters I and I_0 thus determined, the transmittance is obtained directly and from this the absorbance. The peaks which are used for the evaluation shall not be in the saturation regime of the detector.

In the simplest case of the analysis of a single compound without cross-sensitivity to other components and a linear relationship between concentration and absorbance, the following is obtained for concentration of the gas in question:

$$c = \frac{-lg \frac{I}{I_0}}{a'(\tilde{\nu}) \cdot l} \tag{6}$$

In the event of departure from linear behaviour, calibration curves shall be determined and Equation (6) shall be correspondingly modified.

10 Sources of uncertainty

10.1 General

Various influences can affect the performance characteristics (see Annex F). These influences may be classified into three groups:

- instrument-specific influence;
- evaluation-specific influence and cross-sensitivities;
- influence on the measurement due to meteorological conditions: for example changing wind conditions, large changes in temperature and atmospheric pressure, visual conditions, scattering by aerosols and fog, beam interruptions, dew formation;
- interaction of non-ideal instrument and sample properties (for open-path monitoring, black body emission can play a role with certain spectrometer configurations affecting the photometric accuracy significantly).

These errors are described in more detail e. g. in [24].

10.2 Sources of uncertainty within the instrument

This includes all influences which have an adverse effect on the correct functioning of the spectrometer. This can result from, for example: wavenumber stability, intensity stability, resolution stability, optical alignment stability, stray radiation, concentrations of internal interfering gases, saturation of the detector etc. These influences should be minimized by the manufacturer in advance and during measurement by the quality assurance measures described in 8.2.

The effect of temperature variation on FTIR spectrometer stability has been demonstrated by MacBride et al. [25]. The consequences of temperature fluctuation are baseline drift, which however can be compensated by broad spectral range baseline corrections.

A possible wavenumber shift/stretch between sample and reference spectra can cause significant systematic errors in the evaluation. If such a shift occurs, the measured spectrum and the reference spectrum have to be aligned (i. e., shifted and stretched) before evaluation. Exemplary results for 0,2 cm^{-1} spectral resolution spectra with most appropriate spectral interval chosen for quantitative analysis were reported up to 5 % for a spectral shift of 0,1 cm^{-1} [26]. However, modern evaluation software can correct the line shifts properly (0,001 cm^{-1} as residual maximum line shift after software correction are reported).

In the case of analytical systems operating with closed instrument casings, care shall be taken to ensure that gases in the interior of the instrument do not affect measurements due to interfering absorption. If such interference nevertheless occurs, it shall be determined and taken into account. This can be achieved, for example, by measurements made on monitoring paths of different lengths in quick succession [27]. The other way to avoid interferences is to purge the instrument with zero gas.

10.3 Evaluation-specific influence and cross-sensitivities

10.3.1 General

These types of influence relate to all effects which are not specific to the spectrometer and directly affect evaluation of the spectra obtained. This especially includes the superimposition of the spectral signatures of different compounds (cross-sensitivity), but also insufficient compensation of natural background radiation (see 10.3.6) in the case of non-modulated systems or a poorly matched background reference spectrum. Furthermore, it may happen that due to a change in the atmosphere, the background reference spectrum used for the measurement is no longer suitable for the analysis.

10.3.2 Cross-sensitivities

The treatment of cross-sensitivities is described in Clause 9. There it is made clear that a regression method has advantages over simple determination of peak height. Cross-sensitivities in general impair the limit of detection of the analytical system. To minimize these effects the following points shall be taken into account:

The region to be evaluated shall be selected so that firstly there is an absorption structure which is sufficiently strong for the expected concentration range and secondly the number of compounds having cross-sensitivities which is detected is minimal. If cross-sensitivities occur, it shall be ensured that the evaluation region also suitably includes the absorption structure of the interfering compounds and that these are then also included in the evaluation algorithm.

NOTE This can be achieved, for example, automatically by a database expert system which optimizes the evaluation regions. Current developments are moving toward integrating the consideration of cross-sensitivities into the evaluation software.

The effect of cross-sensitivities varies with the target compound and the other compounds being present. An example, how cross-sensitivities are compensated, is given in [28]. If the interfering gases are known, cross-sensitivities have to be taken into account during the calibration experiments.

The effect of background ambient radiation on the measurement does not depend on the length of the monitoring path, but on the atmosphere in the field of view of the spectrometer. Both emission and absorption effects can occur in this case. For an evaluation below the wavenumber of 1500 cm^{-1}, if the natural background radiation is not taken into account errors in the measurement of the order of magnitude up to 30 % can occur.

The choice of background reference spectrum has a significant influence on the measured result. As shown in 9.3, several methods can be used to obtain background spectra. It is important that the effect of water vapour content is sufficiently taken into account, since this is the most important interfering component affecting the measured result. The results shall be checked by plausibility tests. For monostatic systems it shall be checked if internal stray radiation can be neglected.

10.3.3 Uncertainty of calibration parameters

The uncertainty of the concentration of the calibration gas has direct influence on the measurement results. Uncertainties may also arise due to temperature, pressure in the calibration gas cell and path length of the calibration gas cell.

An example of the uncertainty budget of the reference data is given for the NIST Quantitative Infrared database [29]. It is distinguished between Type A uncertainty [30] which is obtained by the linear regression of calibration spectral data. Uncertainties for the linear regression coefficients, i. e., slope and intercept, are given. Furthermore Type B relative uncertainty [30] is calculated, where the relative standard uncertainties are the cell path length, pressure, temperature, FTIR stability, detector non-linearity and sample water content. The uncertainty attributed to the detector non-linearity clearly dominated the Type B relative uncertainties.

The contribution of these possible uncertainties depends on the properties of the target compound (e. g. broad absorption bands or fine absorption structures).

10.3.4 Interpolation/zero filling

Zero filling is a method which increases the number of supporting points in the spectrum. Zero filling does not improve the optical resolution capacity, but does improve the digital representation of the spectrum. In this method, at the ends of the interferogram, zero values are added after which the fast Fourier transform is not carried out [31]. As in the apodisation, all spectra used for the analysis shall have identical zero filling.

10.3.5 Baseline correction

Differences in the spectral sensitivity of the FTIR spectrometer when the measurement and background reference spectra are recorded, can lead to a systematic error in the determination of concentration. This causes the regression function to vary with wavelength and can be modelled in the simplest approach by additional linear baseline terms. This procedure is termed baseline correction.

$$A(\tilde{\nu}) = p + q \cdot \tilde{\nu} + \sum_{i=1}^{m} \left(k_i \cdot a_{Ri}(\tilde{\nu}) + e(\tilde{\nu}) \right) \qquad (7)$$

$$\tilde{\nu} = \tilde{\nu}_1,\ \tilde{\nu}_2 \ldots\ \tilde{\nu}_n$$

The parameters *p* and *q* are varied here.

10.3.6 Ambient background radiation and internal stray radiation from the FTIR spectrometer

In certain FTIR spectrometer applications in which the IR radiation is not modulated by the interferometer prior to its passing through the monitoring path, the ambient background radiation and background radiation of the FTIR spectrometers produce an additional additive term in the equation for $I(\tilde{\nu})$, see Equation (8):

$$I(\tilde{\nu}) = I_E(\tilde{\nu}) + I_0(\tilde{\nu}) \cdot 10^{-a(\tilde{\nu})_{IV} \cdot c_{IV} \cdot l} \cdot 10^{-a(\tilde{\nu})_{MV} \cdot c_{MV} \cdot l} \qquad (8)$$

where $I_E(\tilde{\nu})$ represents this effect. The transmittance shall therefore be determined by subtraction of $I_E(\tilde{\nu})$ in both numerator and denominator:

$$T(\tilde{\nu}) = \frac{I(\tilde{\nu}) - I_E(\tilde{\nu})}{I_0(\tilde{\nu}) - I_E(\tilde{\nu})} \tag{9}$$

The ambient background radiation generally has the form of the Planck radiation and therefore, at typical environmental temperatures, only plays a significant role in the wavenumber range below 1500 cm^{-1}. After blocking switching off and cooling down the IR radiation source (transmitter), with measurement conditions otherwise the same, generally a suitable measurement of the background ambient radiation can be carried out. The problem of determining the background ambient radiation is avoided if the transmitter radiation is modulated.

In the case of instruments having a modulated signal, stray radiation within the instrument can affect the measured result. In these systems a small amount of the modulated IR radiation is then incident on the detector by scattering within the instrument, bypassing the intended beam path and the actual monitoring path, and thus affects the measured signal. This causes lower absorbance values. The internal stray radiation however, is only a problem for measurements at low detected intensities [10]. In contrast to the background ambient radiation, the internal stray radiation is a constant for the instrument and does not change with the monitoring path or the meteorology. The internal stray radiation can be determined simply by measurement without a reflector [10; 18].

10.4 Influence on the measurement due to meteorological conditions

Large changes in temperature (see 8.1.2) and atmospheric pressure, which lead to an interference in the measurement, shall be recorded, and if necessary the measured results shall be corrected by using reference spectra which are suitable for the changed meteorological conditions.

Specific absorption coefficients are temperature-dependent. Appropriate correction factors are already available for selected compounds at various temperatures [32].

10.5 Influences due to accessories

Range finders and instruments for determining meteorological parameters have a direct input on the measurement uncertainty.

11 Servicing

The FTIR spectrometer shall be serviced according to the manufacturer's instructions (see Annex E).

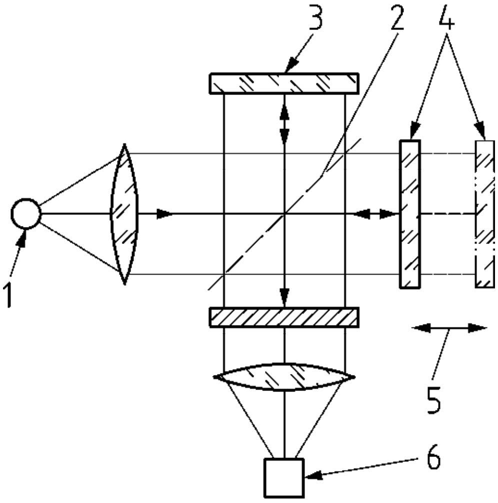
Annex A
(informative)

The classical Fourier transform spectrometer

A.1 Principle

Fourier transform infrared spectroscopy represents one of the most commonly used techniques for obtaining spectrally resolved information about the sample. Derived from the classical principle of the Michelson interferometer, various models of FTIR spectrometers have become widespread as high-performance optical analytical instruments.

The operation of the FTIR spectrometer is based on interferometry. The principle of interferometry is illustrated using the two-beam Michelson interferometer which is shown diagrammatically in Figure A.1.



Key
1 radiation source
2 beamsplitter
3 fixed mirror
4 moving mirror
5 optical path difference (= 2 × mirror displacement)
6 detector unit

Figure A.1 – Schematic of a Michelson Interferometer

Collimated radiation from an infrared source (1) is divided into two beams by a beamsplitter (2). One beam travels a fixed distance, being returned to the beamsplitter by fixed mirror (3) while the other has a path length which is varied by the translation of mirror (4). The difference in distances travelled by the two beams is known as Optical Path Difference (OPD).

The two beams are recombined at the beamsplitter giving rise to a signal on the detector (6) due to interference. The plot of intensity at the detector versus optical path difference is known as interferogram. Interferograms are analysed mathematically by Fourier transformation, which converts intensity versus optical path difference into intensity versus wavenumber. For further information on the implementation of Fourier transforms in FTIR spectrometers, see e. g. [2].

The method is recognised as having a number of major advantages:

- Compared with dispersive spectrometers utilising a single point detector and a grating or prism based monochromator, in the FTIR system all wavelengths are measured simultaneously, making the acquisition of a spectrum with equivalent signal-to-noise ratio much faster. This is known as the Felgett advantage [33]

- Much greater throughput of infrared radiation (etendue) is possible for the same spectral resolution, resulting in a further improvement in signal-to-noise ratio. This is referred to as the Jacquinot advantage [34]

- The reference laser used to provide positional referencing in the interferometer enables very precise recording of optical path differences, so the data points in the interferogram are sampled to a high degree of precision and accuracy and is known as the Connes advantage [35]. This makes the improvement of signal-to-noise ratio by averaging of successive interferograms possible.

- Finally, the FTIR spectrometer can have an intrinsically high spectral bandwidth, principally determined by the optical transmission characteristics of the materials used in the beamsplitter and any windows in the spectrometer, and by the wavelength sensitivity range of the detector. A typical FTIR system bandwidth for remote sensing of air pollutants is the wavenumber range from 600 cm^{-1} to 4200 cm^{-1}.

- Using Fourier transform infrared techniques, numerous gases in the atmosphere can be determined quantitatively, for example:

  - CO, CO_2, NO, N_2O, NH_3, O_3;
  - aromatic hydrocarbons;
  - halogenated hydrocarbons;
  - alkanes, alkenes, alkynes;
  - aldehydes, ketones, alcohols, esters.

Quantitative analysis requires suitable calibration and evaluation methods. Basic procedures for these are dealt with in Clauses 8 and 10.

A.2 Important measurement parameters of the FTIR spectrometer

A.2.1 Spectral resolution and field of view

The unapodised spectral resolution of FTIR spectrometer is correlated with the optical path difference between both interferometer arms (see Figure A.1) as follows:

$$\Delta\tilde{\nu} \approx \frac{1}{s_{max}} \tag{A.1}$$

$\Delta\tilde{\nu}$ unapodised spectral resolution in cm^{-1}

s_{max} maximum optical path difference in a two-beam interferometer, in cm

The spectral resolution might be modified by non ideal collimating of the entering beam.

Changes of the alignment of the IR source might change the spectral resolution and might cause a wavelength shift of the measured spectra. For the ideal interferometer the beam remains collimated when passing through the optics. However, due to the finite size of infrared sources, radiation traverses the interferometer at a finite range of angles. For a circular source of radius *a* and a collimator focal length f, the range of angles traversing the optical system is a/f radians. For a ray entering at the angle Θ, the path (phase) difference can be calculated to be $2s \cdot \cos \Theta$, whereas for the ideal case a value of $2s$ for the optical phase difference exists, i.e. twice the translation distance between the two interferometer mirrors. This gives the Michelson interferometer signal an angular dependence of $\cos \Theta$, resulting in a broadening of the ideal instrument line shape function. The inverse of the resolving power can be shown to be $\Omega/2\pi$, where Ω is the solid angle subtended by the source ($\approx \pi \cdot a^2/f^2$). In addition to the resolution deterioration, a wavenumber shift occurs, since the true wavenumber is measured as $(1 - \Omega/4\pi)$.

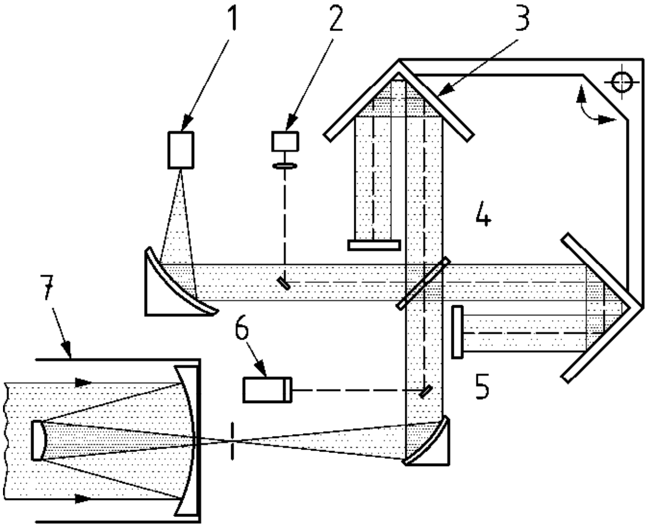
A.2.2 Measurement system designs

A.2.2.1 General

FTIR systems for monitoring air quality in the field may differ with respect to the interferometer module. In addition to systems which are designed according to the classical Michelson principle, instruments which operate according to the double pendulum principle [36; 37] are frequently used in environmental analysis. However, there are also other developments for instruments for field service, for example the system having a rotating retroreflector [38]. When apodised interferograms are used, portable systems typically achieve a spectral resolution of 0,1 cm^{-1} to 4 cm^{-1}. The maximum wavelength range currently extends from 1,3 µm to 28 µm (equivalent to wavenumbers of 7700 cm^{-1} to 350 cm^{-1}).

A.2.2.2 Double pendulum principle interferometers

Figures A.2 and A.3 show the mode of operation and the optical setup of this type of spectrometer.



Key

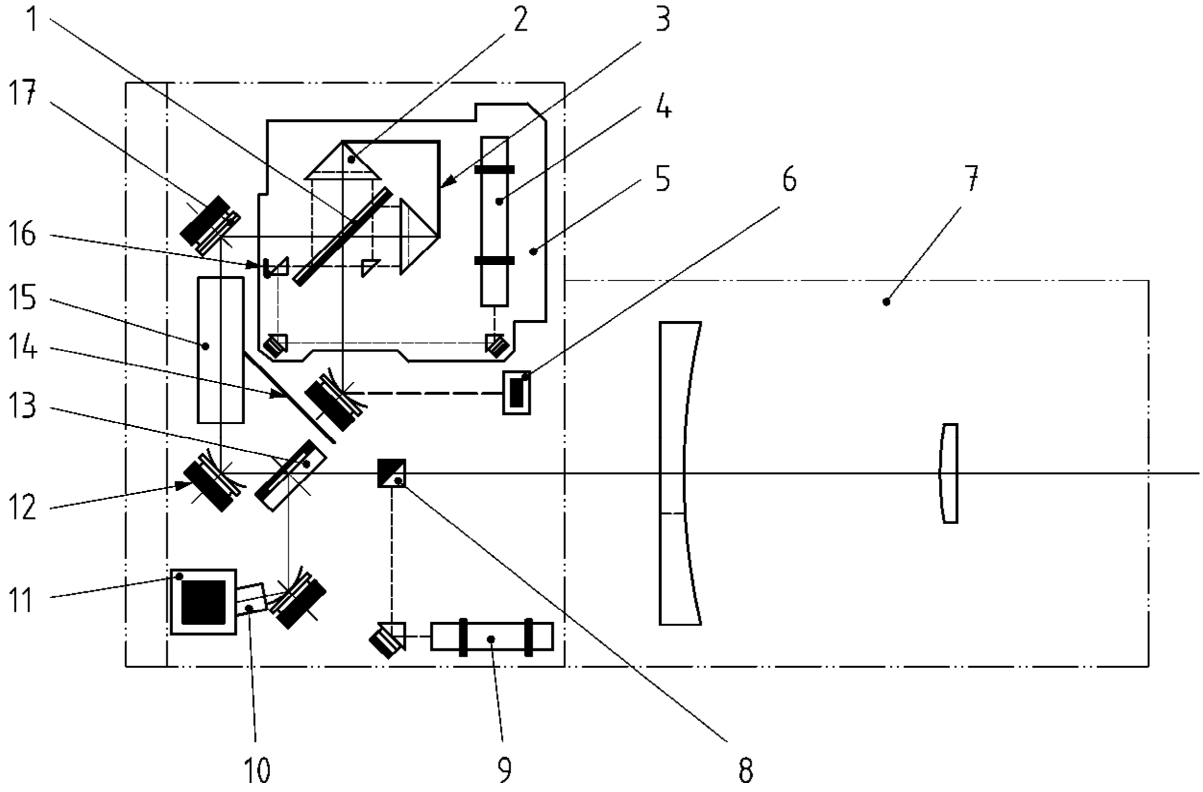
1 infrared detector
2 reference laser detector
3 corner cube reflector
4 beam splitter
5 flat mirror
6 reference laser
7 receiving telescope

Figure A.2 — Michelson double pendulum principle interferometer with folded beam path

In the design shown in Figure A.2, the infrared radiation enters the spectrometer via the receiving telescope and is divided by the beam splitter into the two partial beams. In this specific design, the corner cube reflectors direct the partial beams onto the fixed flat mirror and back again to the beam splitter where the partial beams superpose. This superposition leads to an intensity changing with the movement of the pendulum which is determined by the infrared detector. The laser, combined with the reference detector, makes it possible to assign the detector signal exactly to the pendulum position and thus to the optical path length difference.

The particular design feature of this instrument is the fact that the optical path difference is no longer varied by the linear motion of a mirror element, but by a rotary motion of corner cube reflectors which are fixed to a shared structure (double pendulum) which is mounted in a pivot. Folding the beam path increases the optical path length difference by a factor of four compared with the conventional Michelson interferometer.

In the design for the monostatic configuration shown in Figure A.3, the infrared signal is produced in the spectrometer by a ceramic glower (Globar), then collimated and beamed into the interferometer. The interferometer operates in accordance with the double pendulum principle, but, differing from Figure A.3, without a folded beam path. Thus the optical path length difference compared with the conventional Michelson interferometers is doubled.



Key
1 interferometer beam splitter
2 corner cube reflector
3 double pendulum
4 reference laser
5 interferometer
6 infrared source
7 transmitting/receiving telescope
8 rotating prism
9 adjustment laser
10 infrared detector
11 cooler
12 concave mirror
13 detector beam splitter
14 absorption body
15 gas cuvette
16 reference laser detector
17 flat mirror

Figure A.3 — Optical setup of a spectrometer for a monostatic configuration and modulated beam transmission

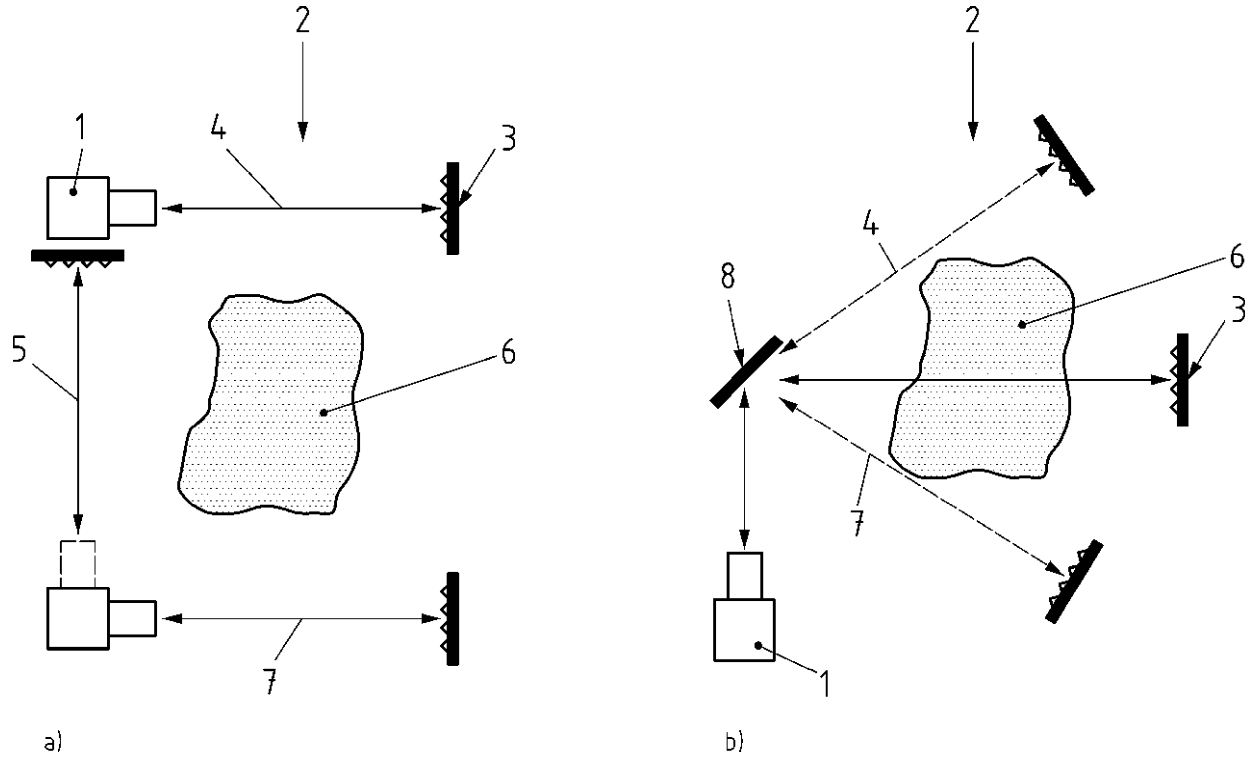
After the superposition signal has left the interferometer, it is deflected by a flat mirror and passed through a cuvette which can be filled from the outside with gases for calibration purposes. After redeflection and focusing, the superposition signal is incident onto a second beam splitter. The reflected part of the signal is deflected onto an absorption body and is lost; the other part exits the casing via an infrared window and is passed via the telescope along the monitoring path to the retroreflector. The retroreflector reflects the superposition signal back along its path, so that the superposition signal passes a second time through the monitoring path. After the superposition signal has been collected again by the telescope and beamed into the casing, it is again incident onto the second beam splitter where one part is deflected via a mirror onto the detector, while the other part returns through the beam splitter and the remaining optical system to the source and is there retransmitted in a highly attenuated form. However, the resultant error is negligible in practice.

The advantage of transmitting the superposition signal over the monitoring path is that the infrared radiation of the environment in practice has no interfering effect on the measurement. However, a disadvantage is the loss of intensity due to the second beam splitter.

Annex B
(informative)

Monitoring configurations

Depending on the measurement task, the monitoring paths are set up differently with respect to the pollutant source (6) and the wind direction (2) (Figure B.1):



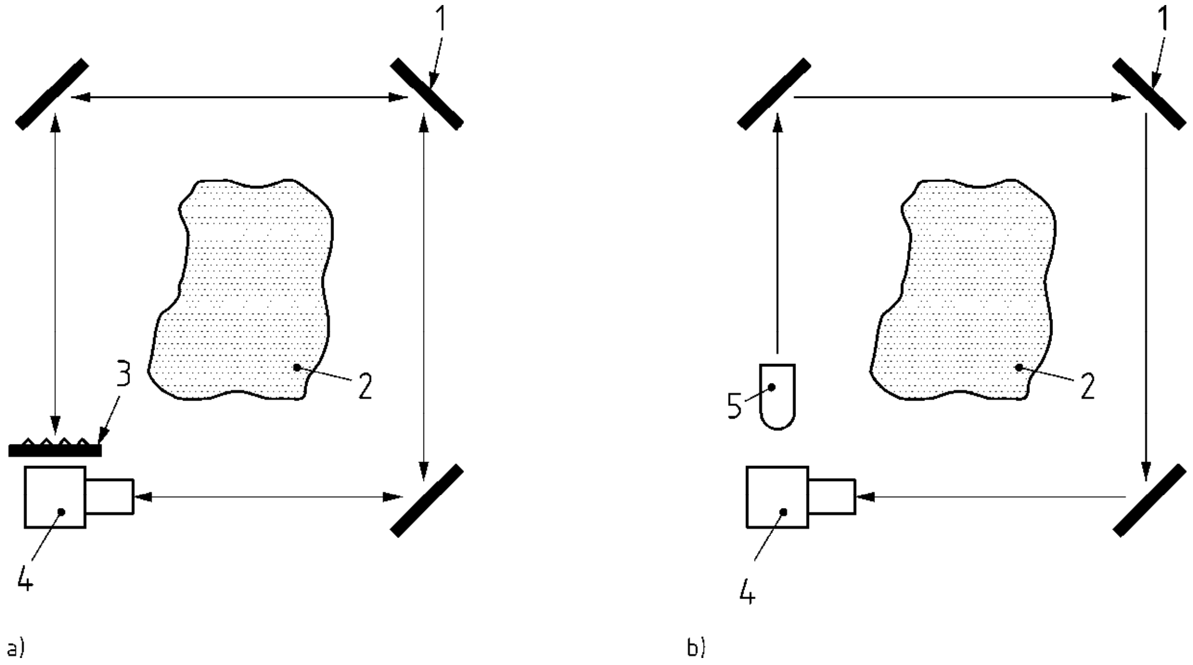
Key

1	FTIR spectrometer
2	prevailing wind direction
3	retroreflector
4	monitoring path (upwind)
5	monitoring path (measurement off to one side)
6	pollutant source
7	monitoring path (downwind)
8	rotary mirror

Figure B.1 — Upwind-downwind measurement: a) conventional, b) using a rotating mirror

Figure B.1a shows an extended or diffuse pollutant source (6) (for example a landfill or industrial plant) with a number of variants for orientating the monitoring paths using a monostatic measuring system as an example. However, the arrangements depicted can also be achieved in analogous form using bistatic systems. The monitoring paths are each built up like a fence at the edge of the pollutant source. Therefore, this measuring arrangement is also frequently called a boundary fence measurement. The monitoring path (7) is downwind of the pollutant source. Measurements along this monitoring path give information on the pollutants which are introduced by the outlined source, but also pollutants which have already been introduced by the wind upstream of the source. If specific statements are to be made about the pollutants which only originate from the source, an additional measurement equivalent to measuring path (4) (upwind measurement), which only contains information on incoming pollutants, is recommended. Comparison between the measurements made on monitoring path (4) and monitoring path (7) then provides information on the pollutants originating from the source alone. Under stable meteorological conditions with only one wind direction it is also possible to set up a monitoring path corresponding to monitoring path (5), as shown in the figure, which can be achieved more quickly. In this case, the use of a second spectrometer is unnecessary.

Figure B.1b shows an arrangement in which different retroreflectors are "sighted" via a rotary scanner. In this manner, under favourable conditions, upwind-downwind measurements can be very simply achieved more rapidly. In addition, an arrangement of this type is of interest if large source areas are to be characterized or industrial plants are to be monitored.



Key
1 flat mirror
2 pollutant source
3 retroreflector
4 FTIR spectrometer
5 IR source

Figure B.2 — Boundary fence measurement with an enclosing monitoring path: a) monostatic arrangement, b) bistatic arrangement

Figure B.2 shows a boundary fence measurement with an enclosing monitoring path for a monostatic configuration and a bistatic configuration. This arrangement is suitable when any possible gaseous emissions from a pollutant source in any direction are to be detected.

Annex C
(informative)

Equipment

C.1 Apparatus

C.1.1 General

The bistatic arrangement (see Figure 1) consists of a

- transmitter;
- receiver;
- control and evaluation computer (usually the same computer performs both tasks).

In the monostatic system (see Figure 2) transmitter and receiver are replaced by

- combined transmitter/receiver unit and
- retroreflector unit.

C.1.2 Transmitter

The transmitter generally comprises

- radiation source; generally this is a heating element (for example Globar, Nernst glower) with a life time of years under normal operation conditions;
- apparatus for collimating the IR radiation in the direction of the receiver (for example parabolic reflector, telescope);
- control unit for stabilizing the desired radiation source temperature.

The source approximates a black-body radiator generating a broadband IR radiation which, if the intensity is sufficient, covers the entire spectral range from approximately 20 µm (500 cm^{-1}) to 1,5 µm (6700 cm^{-1}) which is of importance for using FTIR systems in environmental analysis.

C.1.3 Receiver

The receiver consists of

- FTIR spectrometer and
- telescope for feeding in the radiation.

C.1.4 Combined transmitter/receiver unit

In the monostatic system, transmitter and receiver form one unit. There are two designs:

- radiation source is integrated into the receiving unit. An additional beam splitter divides radiation to be transmitted and to be received.

- transmitter and receiver equipment are designed in the same manner as in the bistatic arrangement. They are however mounted side by side. In this case the retroreflector should be a displacement retroreflector.

C.1.5 Retroreflector unit

The retroreflector consists of

- special mirror design (for example a cube corner matrix) and
- adjustable holder (for example a tripod)

and serves to deflect the beam back to the transmitter/receiver unit.

C.1.6 Control and analysis computer of the Fourier transform spectrometer

- computer performs the following tasks:
- controlling the FTIR spectrometer;
- data acquisition;
- Fourier transformation;
- data processing.

Data can often be evaluated on line even during measurement. However, it is advisable to store the interferogram spectra measured and to analyze these later offline.

C.2 Accessories

To operate an FTIR system, depending on the objective, the following accessories are additionally required:

- Range finder

  This determines the distance between the receiver and transmitter/retroreflector. The distance can be determined, for example, using a laser range finder; it is also possible to use a global positioning system (GPS) for determining the absolute position with respect to the sources. The critical factor in selection of the method used to measure the distance is that the accuracy of the distance measurement shall comply with the accuracy requirements for the concentration measurements.

- Meteorological instruments for determining
  - atmospheric pressure;
  - air temperature;
  - atmospheric humidity, wind direction and wind speed;
  - turbulence, if necessary.
- Sighting telescope

  for mutual orientation of transmitter and receiver or of transmitter/receiver unit and retroreflector

- Mobile stand/turntable, tripods etc.

  Mechanical accessories of this type are useful in mobile measurements for simple adjustment of the entire analytical setup and for mobility of the FTIR spectrometer in the field.

C.3 Supplies

C.3.1 Cooler

Many IR detectors have to be cooled to get an appropriate signal-to-noise ratio. In many FTIR systems the detector is cooled to 77 K, using nitrogen as a refrigerant in gaseous or liquid form:

- liquid

  liquid nitrogen is introduced directly into the detector cooling vessel. Commercially available systems require a refill about every eight hours.

- gaseous

  Joule-Thompson refrigerating system is used which cools gaseous nitrogen to the operating temperature of the detector

There are also FTIR systems having a closed cooling cycle (He Stirling cooling process) which do not need an external supply of operating gases. Cooling temperatures have to be checked regularly and vibrations due to the cooler have to be avoided.

C.3.2 Power supply

The typical power consumption of the individual instruments is as follows:

- transmitter: approximately 30 W to 100 W, depending on design;

- receiver: approximately 50 W to 100 W;

- control and evaluation computer: approximately 30 W to 100 W.

C.3.3 Calibration gases

A set of gases may be required in order to acquire spectra with a cell. This set of gases is intended to allow the operator to determine the uncertainty of the data obtained from the field spectra, but at the present time no procedure using a cell has been developed. The specific gases required are dependent on the particular monitoring program. The gases can be purchased as pure gases, which are then diluted with nitrogen for use or they can be a mixture of gases that are properly mixed. It is recommended to use a basic calibration gas and a dilution system to generate the required concentrations. The required concentrations of the gases are dependent on the anticipated concentration of the target gas in the atmosphere and the ratio of the actual path length used to the length of the cell. Many applications will require that these gases be purchased with certifications traceable to primary national standards.

C.3.4 Attenuation meshes

A set of screens of varying mesh may be required that will be used when determining whether the system is responding linearly. This screening can be regular aluminium window screen or made of other opaque metallic materials. The size of the mesh is not really important, but the screen should be large enough to cover the entire beam. The mesh itself should be chosen so as to change the transmitted intensity by an easily measured amount (on the order of 25 % or more). The screen must not be made of any plastic materials as they transmit infrared energy. This in itself is not a problem but the plastic materials introduce absorbance at specific wave numbers and may not provide the desired result.

Annex D
(informative)

Conditions for measuring emission flux

The measurements made using open-path FTIR techniques give direct information about the line-averaged concentrations of species in the monitoring path. When making open-path measurements of emission flux this may not be directly representative of the concentrations or emission fluxes from the source due to:

- variations in wind-driven transport of the plume;
- concentration variations within the plume;
- turbulent dispersion, leading to short timescale spatial variations.

It is possible to support understanding of the plume dynamics using modelling techniques such as CFD (computational fluid dynamics) but even the complementary use of such techniques offers no guarantee that the measurement data obtained correctly and completely characterises the emission from the source.

Upwind of the emission source(s) being measured, the background concentration can also be measured in order to determine the contribution made by the emission sources of interest.

Maximum lengths and orientations of the monitoring path are determined by:

- objective of the measurement;
- specification of the transmitter and receiver;
- meteorological conditions.

Care shall be taken to ensure that sufficient intensity from the source is incident on the measuring instrument, and the field of view shall be filled as completely as possible. Background and ambient radiation shall be taken into account. With short monitoring paths, saturation of the detector shall be avoided.

Annex E
(informative)

Servicing

E.1 Cleaning the optics

In the infrared region, beams are primarily directed by surface mirrors. The surfaces of the mirror elements are usually coated with gold since this has good reflection properties for IR radiation (> 98 %) and need not be additionally protected against oxidation. The gold surfaces are highly sensitive to mechanical action. They must never be cleaned mechanically (that is to say by wiping or rubbing). To clean them, larger elements of the external optics (for example retroreflectors, larger flat mirrors for beam deflection) are sprayed with a solvent (ethanol, isopropanol) using a strong jet (for example from a commercial hand-operated atomizer pump) until the dirt has dissolved. The relevant safety instructions for handling solvents must be observed. The optics must then be rinsed with distilled water and dried by evaporation. Slight streaking usually does not have any adverse effects. It is necessary to check in advance whether holders, seals or other components may be damaged by the solvent or the water. In this case the equipment must be cleaned by blowing with compressed air (free from oil and grease!) or pure nitrogen. Smaller components are preferably cleaned in an ultrasonic bath. If this is impossible, they must also be cleaned by blowing with compressed air or nitrogen.

Highly hygroscopic components (for example KBr or NaCl beam splitters) are usually used in the interior of an FTIR system. The internal optics are therefore frequently encapsulated and therefore do not need to be cleaned by the user. The FTIR system encapsulation should only be opened by the manufacturer, observing the appropriate safety precautions.

E.2 Purging the casing with pure nitrogen, desiccant cartridges

To avoid concentration of unwanted gases in the interior of an FTIR system, the casing must be regularly purged with pure nitrogen (4,0 or better). By recording spectra during the purge, a check must be made as to whether internal gases affect measurements. If this is the case, the time of the purge must be chosen so that internal gas concentrations remain constant during the actual measurement task [27] (either purge after the measurement or purge during the entire measurement). Alternatively, a check must be made as to whether the FTIR system casing can be evacuated.

Because some of the components are very hygroscopic, desiccant cartridges are frequently used. These must be changed regularly, depending on the design, either by the user or by the manufacturer.

E.3 Detectors

The MCT detectors (mercury/cadmium/telluride semiconductor detector) currently in common use must be cooled to approximately 77 K. A number of cooling systems are available for this:

— liquid-nitrogen cooling using a Dewar;

— helium-Stirling cooling;

— Joule-Thomson cooling.

The cooling systems can usually only be serviced by the manufacturer. The work carried out most frequently is described below:

For liquid-nitrogen cooling, sufficient liquid nitrogen must be provided. Consumption depends on the refrigeration capacity to be provided and the condition of the Dewar. If the periods between refilling shorten markedly, this is generally due to impaired vacuum in the Dewar insulation. This must then be evacuated again; this is usually at yearly intervals.

The helium-Stirling cooler, in contrast, consists of a Stirling compressor using helium as the working medium in a cyclic process. Only electrical power is required for operation. The helium-Stirling cooler, however, is not always designed for continuous operation over several days and weeks, since the high mechanical wear would lead to early destruction of the compressor. In normal operation the helium must be refilled at half-yearly intervals, since it slowly diffuses out. A fall in the helium reservoir can be recognized by significantly prolonged (by a factor of three to five) cooling times. The mechanical damage can be recognized by the marked increase in compressor running noise respectively by significantly prolonged cooling times.

The working medium used by the Joule-Thomson cooler is high-purity nitrogen (99,999 % or better). The cooling is produced by gas expansion. For this purpose, nitrogen must be supplied at a pressure of at least 80×10^5 Pa. Usually, pressurized gas cylinders are used. Consumption depends on the cooling capacity to be provided and is in the order of magnitude of 1,5 kg per day. In principle, the cooler operates in a maintenance-free manner, but icing can occur because of inadequate nitrogen purity. The icing can usually be removed by purging the cooler for half an hour with nitrogen at low pressure. If this is not possible, the gas path is frequently blocked and the cooler must be serviced by the manufacturer.

E.4 Cells and cuvettes

When cells and cuvettes are used for the primary and control calibration, note that polar gases can adsorb to the walls and can be removed only with great difficulty. Usually this is achieved by heating and purging with nitrogen for several days. If the cell can be taken apart, in addition attempts can be made to wash out the interior.

If multiple reflection cells are used, a check should be made of the measuring beam input into the cell. A change in the input geometry can alter the optical path in the cell, which can lead to large errors. A visible laser signal can be observed through the transfer optics and the number of passages within the mirror system thus determined. The check is usually carried out using gases of known concentration.

A check of the optical alignment of the gas cell should be made.

Annex F
(normative)

Performance characteristics

F.1 Limit of detection

F.1.1 General

The limit of detection is defined in accordance with EN ISO 9169 as the smallest value of the parameter which can be distinguished from a zero state at an (agreed) confidence of 95 %. Therefore, if during analysis a measured value of a compound is determined at the limit of detection, there is a 95 % probability that this compound is present in the sample material. However, it is not possible to state the concentration of this compound.

In this standard three methods for the limit of detection (LD) are described.

The first two methods use test gases and cells for the determination of the LD. This has the advantage, that well defined and reproducible conditions can be achieved. Within the first method the LD is determined from the calibration function. In the second method the LD is determined from blank readings from measurements with zero gas. The effort for the second method is less and tends to deliver lower LDs, because only the scatter around zero concentrations is taken into account. However, in both methods using a calibration gas cell for the determination of the LD the influence of the atmosphere within the open monitoring path is omitted.

This is included in the third method. The third method does not use calibration gas cells. Instead of that it makes use of direct measurements within the open atmosphere, simulating "zero gas concentrations" by a special arithmetic evaluation. However, the precondition for the application of this method is that the concentrations of the components present in the atmosphere are constant over the period of measurement.

F.1.2 Determination of the limit of detection from the confidence range of the calibration function

In this method, firstly, confidence ranges of the calibration function are determined from the measured values of the calibration [39; EN ISO 9169]. If the calibration function is not linear, to determine the limit of detection the confidence ranges shall be determined only at low concentrations, that is to say in the linear range [4]. By convention, a measured value at the limit of detection is the upper limit of the confidence range for an expected future individual value at the position of the lowest calibration point [39; EN ISO 9169].

F.1.3 Determination of the limit of detection from blank measurements

If the measurement method is repeatedly successively challenged with zero gas, in accordance with [39; EN ISO 9169], the limit of detection can also be determined using the standard deviation of these blank values.

A "zero gas concentration" can be simulated in the field as follows: various spectra are recorded successively. Each successive spectrum is used as a background reference spectrum for the preceding spectrum. From these pairs of spectra, the respective absorbance is determined, as described in 5.3 [4]. These absorbance spectra then only contain the statistical noise. The absorbance spectra thus produced are then analyzed by a method described in Clause 9 for that component whose limit of detection shall be determined. Not only positive but also negative concentration values arise, the standard deviation *s* of which is determined.

The limit of detection is then given by the following:

$$\mathrm{LD} = t_{(n-1;0,95)} \cdot \sigma \qquad \text{(F.1)}$$

where

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

σ standard deviation

n number of measured values

This method is suitable for use in the open atmosphere only if the concentrations of the components present in the atmosphere are constant over the period of measurement. Alternatively, such measurements can also be carried out in the laboratory with delivery of test gas into a gas cell. In this case the limit of detection which is calculated from the noise might have a significant lower value compared to the limit of detection determined in the open atmosphere. Moreover, the limit of detection calculated from the calibration function tends to higher values than that determined from the noise. Table F.1 compiles the limits of detection for several compounds.

Table F.1 — Examples of limits of detection for FTIR systems

Compound	**Limit of detection ppb**		**Determined via**
	System 1 [a]	**System 2** [b]	
Methane	200	200	calibration function
Ethene	3	4	noise
Propene	4	7	noise
Ethane	23	23	noise
Benzene	18	25	noise [c]
Toluene	44	47	noise
m-Xylene	65	17	noise
p-Xylene	29	55	noise
o-Xylene	45	8	noise
Methanol		7	noise
Ethanol	8		noise
Carbon monoxide	100	87	noise
Nitrous oxide	3	6	noise
Ammonia	1	2	noise
Formaldehyde		11	noise
Isobutene		8	noise
1,3-Butadiene		5	noise

[a] System 1: monostatic arrangement (spectral resolution 1,0 cm^{-1}, optical path length 100 m)

[b] System 2: bistatic arrangement (spectral resolution 0,2 cm^{-1}, optical path length 100 m)

[c] System 2: gas cell method

F.2 Repeatability

The repeatability r is an index of the precision of the measurement method. It is the maximum difference between two randomly selected individual values obtained under repeatability conditions. In this case, repeatability conditions means the same measurement method performed under the same conditions (the same operator, the same instrument, the same laboratory, short period of time).

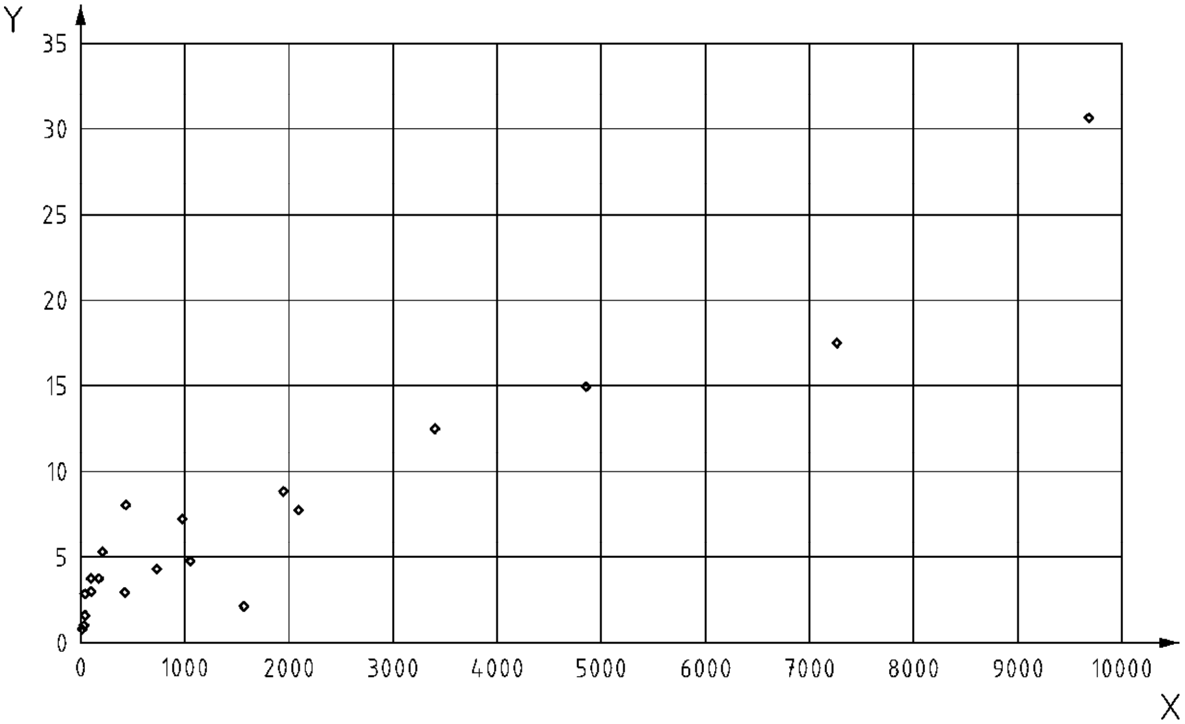
Repeatability is determined by repeated charging of test gas into a gas cell connected to the FTIR system. Using the standard deviation *s* from the corresponding measurement values, the following results:

$$r = t_{(n-1;0,95)} \cdot \sqrt{2} \cdot \sigma \tag{F.2}$$

The repeatability is concentration-dependent (see Figure F.1 [8]). For the FTIR system with a monostatic arrangement, the following were determined as average values (100 m; concentration range: methane 0 to 3000 ppm·m, ethene 0 to 2000 ppm·m.

methane: 100 ppb

ethane: 200 ppb



Key
X mixing ratio × path length in ppm·m
Y repeatability in ppm·m

Figure F.1 — Repeatabilities for the bistatic FTIR system for methane using the CLS analysis

F.3 Linearity

If the readings of the instrument are linearised and these values are used during the measurement, the linearity should be checked.

The linearization can be carried out in the following way: Reference samples (e. g. reference gases in gas cells) which are evenly distributed over the measurement range of interest (e. g. five equidistant concentrations) are applied repeatedly (e. g. 10 times) to the measurement system. A polynomial function is fitted to the uncorrected readings of the instrument using nonlinear regression. The result of the regression is the calibration function. Then the calibration function is inverted. The inverted function is applied to any measured value and thus linearises the instrument readings.

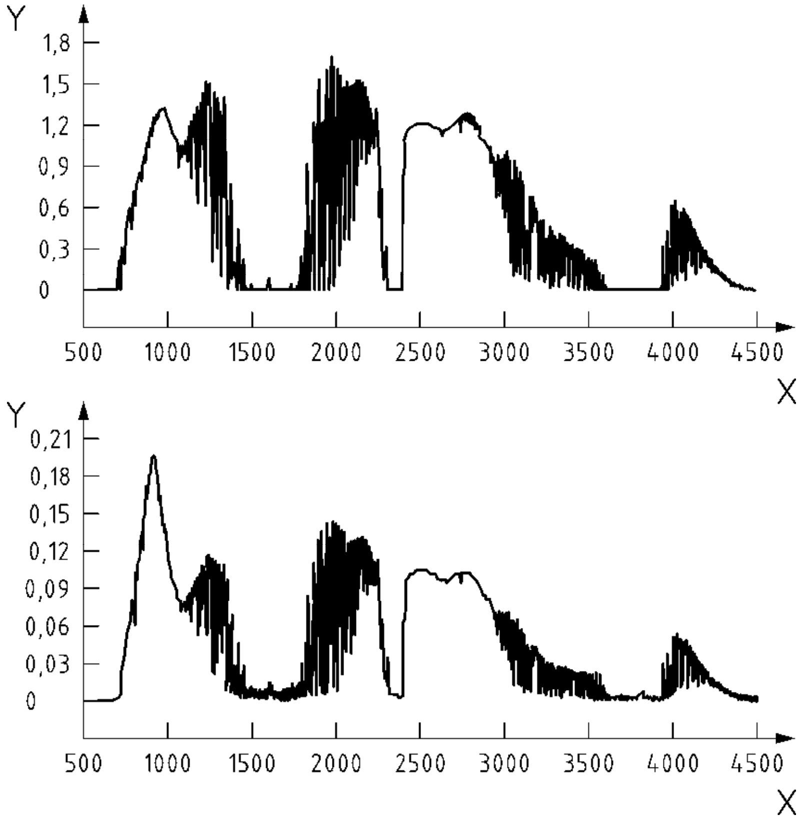
The quality of the linearization can be estimated by calculating the deviation of the mean value of the readings at each reference concentration level from the inverse calibration function. A maximum deviation of 5 % of B1 is achievable in the range between zero and B1 and of 1 % of B2 in the range between zero and B2.

NOTE B1 is twice the annual limit value and B2 is twice the hourly limit value established in Council Directive 1999/30/EC [40].

Annex G
(informative)

Influence of fog on the spectra

Changes in visual conditions due to rain and snowfall have only a minor effect on the measurement. However, the spectra can be changed greatly in fog due to scattering and absorption effects [16]. This results in a change in intensity and also a distortion in the spectra. The distortion can be observed from a change in the behaviour of the baseline noise in various spectral regions [20]. In this case it is necessary to check whether there is any adverse effect on the measured results and whether this can be eliminated using an appropriate correction in the evaluation, for example by specific modification of the background reference spectrum $I_0(\tilde{\nu})$ [16].



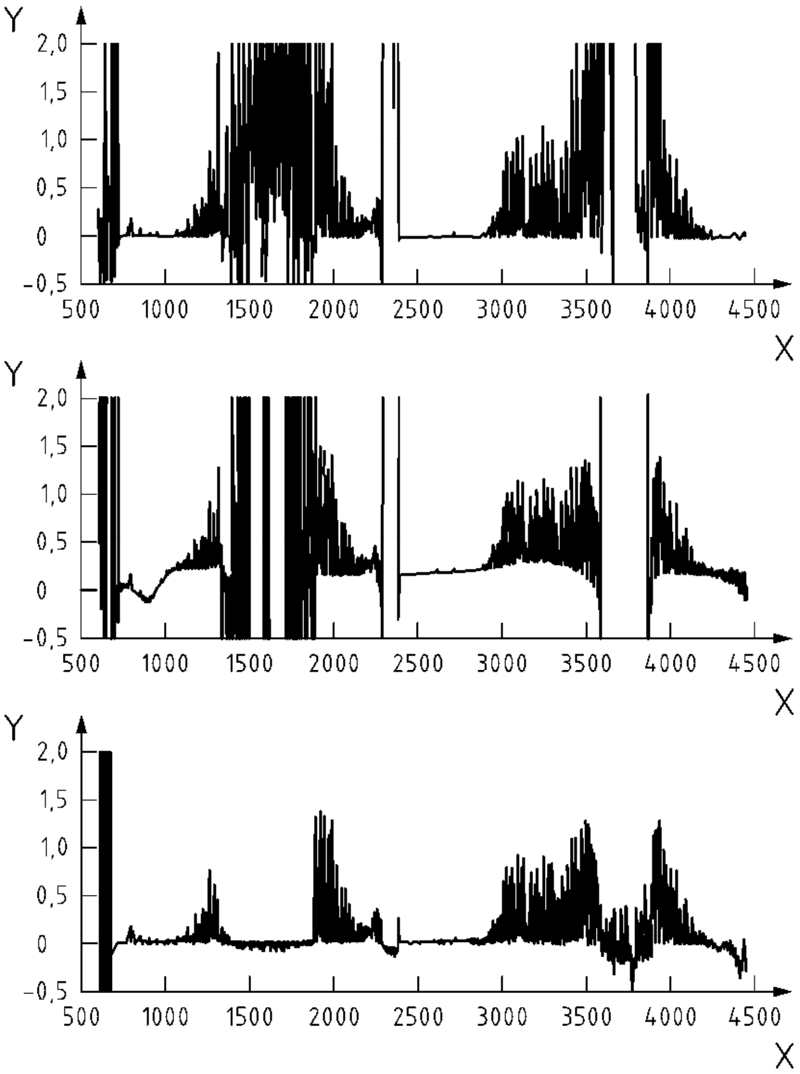
Key

X wave number in cm^{-1}

Y spectral intensity (relative unit)

Figure G.1 — Spectra of a monostatic FTIR system using a modulated signal (monitoring path 128 m, spectral resolution 1,0 cm^{-1}, Globar temperature 1500 K): Top: spectrum with good visibility (without fog), bottom: spectrum in fog with visibility < 350 m

Figure G.1 [16] shows a distortion of the measured spectrum due to fog. The differing attenuation of the spectral intensity at 900 cm^{-1} compared with attenuation at 3000 cm^{-1} may be clearly seen. The resultant interference in absorbance may be seen in Figure G.2 [16].



Key

X wave number in cm^{-1}

Y spectral intensity (relative unit)

Figure G.2 — Absorbance spectra (calculated from the spectra in Figure G.1):

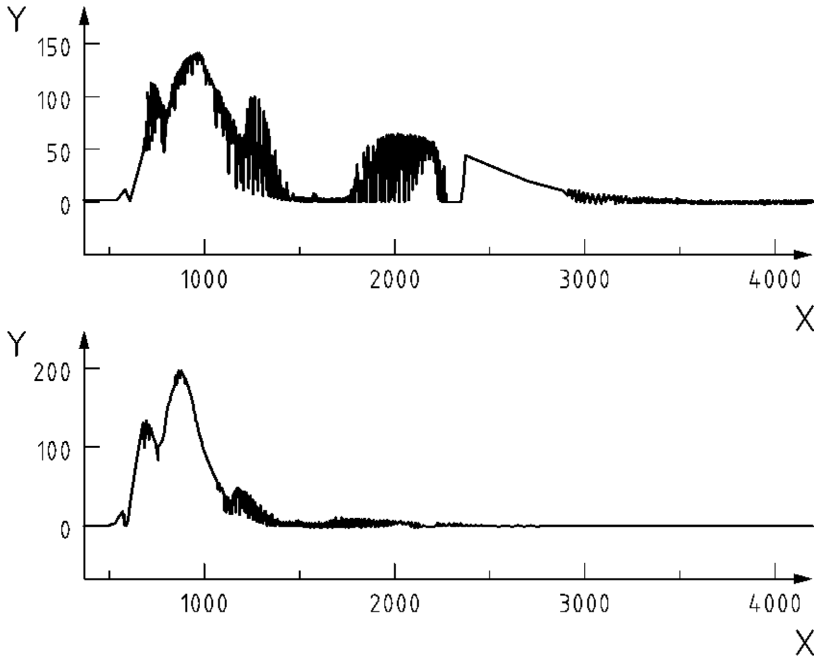
Top: spectrum in good visibility using a standard background reference spectrum

Centre: spectrum in fog using a standard background reference spectrum

Bottom: spectrum in fog using a specially adapted background reference spectrum

The interference in optical density due to fog which can be seen in the middle spectrum (e. g. between ca. 700 cm^{-1} and 1100 cm^{-1}, ca. 1400 cm^{-1} and 1800 cm^{-1}, and ca.3300 cm^{-1} and 4000 cm^{-1}) was compensated for by preparing a specially adapted background reference spectrum.

Figure G.3 shows the change in measured spectra by fog for a bistatic FTIR system and a spectral resolution of 0,2 cm^{-1}.



Key

X wave number in cm^{-1}
Y spectral intensity (relative unit)

Figure G.3 — Spectra of a bistatic FTIR system using a non-modulated signal:
Top: spectrum in good visibility, monitoring path 158 m, spectral resolution 0,2 cm^{-1}, Globar temperature 1500 K
Bottom: spectrum in thick fog, monitoring path 77 m, spectral resolution 0,2 cm^{-1}, Globar temperature 1400 K

Dew formation and fouling or wetting of the mirror systems lead to an additional attenuation of the signal intensity. This shall be avoided by suitable preventive measures, for example encasing and/or heating.

Annex H
(informative)

Sample form for a measurement record

H.1 Measurement objective

○ Measurement to determine the emissions
  ☐ from point source (for example stack outlet)
  ☐ from a line source (for example along a pipeline)
  ☐ from an area source (for example landfill)
  ☐ from a spatially distributed pollutant source (for example exhaust gas plume)

○ Measurement to determine the air pollution
  ☐ in a traffic-related monitoring path
  ☐ in an industrial monitoring path
  ☐ in an area-related monitoring path

○ Other:

____

____

____

____

H.2 Measuring site

1. Position

Radiation source:	**Measuring instrument:**
Address (if available): ____________ ____________ ____________	Address (if available): ____________ ____________ ____________
Coordinate system: ____________	Coordinate system: ____________
Easting: ____________	Easting: ____________
Northing: ____________	Northing: ____________
Height above sea level (in m): ____________	Height above sea level (in m): ____________
Height above ground (in m): ____________	Height above ground (in m): ____________
Distance from nearest emission source (in m): ____________	Distance from nearest emission source (in m): ____________

Length of the monitoring path (type and accuracy of distance measurement):

____

____

2. Description of surroundings

Position:

○ Plane ○ Basin ○ Valley

○ Slope ○ Hill ○ Mountain

○ Inner city ○ Suburb ○ Rural ○ Forest

District use:

○ Industry ○ Trade ○ Commerce ○ Housing

○ Recreation ○ Forestry ○ Agriculture

○ Other

Distance from relevant emission sources (in km):

Industry: ____________ Commerce: ____________ Housing: ____________ Road traffic: ____________

Other: ____

for measurements near traffic (roads closer than 100 m): ______________

Type: ___________ large and broad roads ○

narrow roads ○

”urban canyons“ ○

Traffic density:

very low ○ low ○ ○ medium ○ high

Number of vehicles/day: _____________

3. Site plan

A site plan on a suitable scale (usually 1:1000) shall accompany this record. In addition to an exact representation of the environment, this plan shall include the following elements:

- positions of radiation source or reflector and instrument;
- monitoring path as their connection line;
- relevant emission sources;
- orography;
- obstacles to flow with heights;
- obstacles in the field of view of the instrument;
- prevailing wind direction.

H.3 Measurement conditions

1. Meteorological effects

Characterization of the weather:

____

Meteorological parameters measured:

○ Wind direction
○ Air temperature
○ Global radiation
○ Wind speed
○ Air humidity
○ Visibility
○ Precipitation
○ Atmospheric pressure
○ Other

2. Site-specific influences

○ high aerosol pollution

○ interference with the visual contact between radiation source and instrument varying with time

Characterization of the background of the radiation source:

____

____

3. Instrument-specific parameters

Instrument type: ______________________________
Intensity and temperature of the radiation source: ______________________________
Beam diameter: ______________________________
Measurement of spectral range: ______________________________
Spectral resolution: ______________________________
Scanning time for one scan: ______________________________
Number of scans: ______________________________
Averaging time: ______________________________

Measured components evaluated:

○ NO_2 ○ SO_2 ○ NH_3 ○ HF ○ HCl
○ HCN ○ CO ○ CO_2 ○ O_3 ○ NO
○ N_2O ○ $COCl_2$ ○ AsH_3 ○ SF_6 ○ H_2O
○ Benzene ○ Toluene ○ p,m,o-Xylene ○ Ethylbenzene
○ Methane ○ Ethane ○ Propane ○ Hexane ○ Cyclohexane
○ Ethene ○ Propene ○ Isobutene ○ 1,3 Butadiene ○ Ethyne
○ Formaldehyde ○ Acetone ○ Chloroform
○ Other: ______________________________

4. Particular eventualities

____

H.4 Details of the calibration and evaluation method

a) Type of calibration: primary calibration ○
control calibration ○
operational check ○

b) Calibration method: ____

c) Evaluation method: ____

Background reference spectrum: close measurement ○
measurement off to one side ○
synthetic background spectrum ○

d) Quantitative analysis: regression method ○ CLS method ○
PLS method ○
PCR method ○
peak high determination ○

H.5 Details of performance characteristics and interferences

a) Limit of detection: Determination from the confidence range of the calibration function ○
Determination from blank measurements ○ number of measured values: _______

b) Repeatability: Test gas ____________________________ concentration: _____________
number of measured values: _______

c) Interferences: Instrument-specific interference: ____
____

Evaluation-specific interference: ____
____

Interference due to meteorological conditions: ________________________________
____

H.6 Report of results

Example of a result table

End of the averaging period	Averaging time s	Compound 1 mg·m^3				Compound n mg·m^3
dd.mm.jj hh:mm:ss						

(The meteorological components can/should also be recorded in the presentation of results.)

or reference to an existing file archiving system

H.7 Details of the measuring institute

1. Address and telecommunications connections

---

2. Name of the operator

---

3. Signature

Annex I
(informative)

Calibration by using spectral lines from databases and determination of the instrument line shape (example)

I.1 General

Use of this technique [13] as an alternative to calibration gas mixtures gives advantages in cost, since calibration gas mixtures are expensive and the process of generating a calibration curve is time-consuming.

The spectrum observed when an FTIR spectrum of a gas or gas mixture is recorded is a combination of the ‘true’ gas spectrum and the characteristics of the spectrometer used to make the measurements. If the instrument line shape (ILS) can be evaluated, its removal from the observed spectrum will enable the ‘true’ spectrum to be obtained. This is independent of the instrument used to measure it and therefore enables universal calibration transfer.

I.2 Calculating the theoretical spectrum

The steps involved in calculating the theoretical spectrum of a given sample produced by a given FTIR spectrometer can be summarised as follows:

1. Determine the interferogram in terms of intensity versus path difference

2. Perform the Fourier Transform to express the information in the frequency domain

3. Identify the ILS, taking into account the effect of the apodisation function used to weight the Fourier Transform and the contributions from the geometry of the aperture of the radiation source and the detector used in the spectrometer.

4. Normalise the resulting function to remove slowly-varying factors by dividing by a second measurement similarly processed, but with no sample present.

The accuracy of calculation of the ILS was tested by using low pressure spectra of a variety of gases spanning a wide wavelength range. ‘True’ spectra were recorded on a high-resolution spectrometer or calculated from the line data in Hitran-2000.

I.3 Methods for concentration determination

Two candidate approaches are possible:

1. Determination of the ILS independently followed by use of this ILS to find the set of gas concentrations which best match the measured spectrum

2. To find a set of gas concentrations and parameters describing the ILS simultaneously so as to best match the measured spectrum.

Both approaches have been used successfully. Independent determination of the ILS involves an extra step, but is computationally faster and numerically more stable. The overall method is based on a Bayesian formulation of the probability of a set of gas concentrations and other line shape parameters being true given the measured spectrum, and thus is generic enough to cover both approaches as extreme cases. The problem of determining the ‘system state’, h, which includes the chemical concentrations and lineshape parameters, then reduces to minimising:

$$p(h) = -ln P[h \mid \hat{S}] + (\text{const.}) = \sum_{k,k'} \frac{(\hat{S}_k - \overline{S}_k(h)) C^{-1}_{k,k'} (\hat{S}_{k'} - \overline{S}_{k'}(h))}{2} - ln P[h] \tag{I.1}$$

where

$\hat{S}_k$ measured spectrum at a given point *k*;

$\overline{S}_k(h)$ predicted spectrum, for a specified state *h*, at a given point *k*;

h state of system parameters;

p(h) probability density function for *h*;

$C_{kk'}$ covariance matrix for the spectrum measurement errors at wavenumbers *k* and *k*’.

This approach finds the most probable state *h, i.e.* the solution which maximises this probability, given the measured data. Prior knowledge in *P*[*h*], for example about the line shape, can be included and is beneficial in achieving a successful minimisation.

I.4 Analysis of known gas mixtures

The algorithm developed was used to calculate the concentrations of gases of interest in two known mixtures and four ‘real world’ spectra compared to the conventional Partial Least Squares fir (PLS) method.

Measurand	**Supplier’s mixing ratio ppm**	**Mixing ratio determined by ILS ppm**	**Mixing ratio determined by PLS ppm**
Mix 1			
Carbon monoxide	101 ± 2 %	96	100,5
Nitrogen monoxide	108 ± 2 %	106	111
Mix 2			
Acetone	93,2 ± 2 %	125	140
Methanol	96,6 ± 2 %	80	101
Toluene	92,4 ± 2 %	87	78
Real world 1			
Sulphur dioxide		279	294
Nitrogen monoxide		165	146
Real world 2			
Sulphur dioxide		51	46
Nitrogen monoxide		26	49
Real world 3			
Sulphur dioxide		336	315
Nitrogen monoxide		No value returned	160
Real world 4			
Sulphur dioxide		142	142
Nitrogen monoxide		133	145

Annex J
(informative)

Example applications

J.1 Road traffic

J.1.1 Determination of the CO emission rate on a highway

An example of the determination of vehicle-related emissions is the determination of the CO emission rate on a highway. For this purpose, a measurement campaign was carried out on a highway with virtually constant traffic density (approximately 30 vehicles per minute) [41]. This precondition was necessary, since the measurements had to be carried out sequentially. The surroundings of the highway were flat and there were no other emitters situated here, so that a Gaussian distribution model could be used to determine the emission rate. The measurements were performed with open paths in six different distances to the highway. Table J.1 summarizes all measured and simulated values and the corresponding emission rates. The length of the FTIR monitoring paths was 250 m at all positions P1 to P6 downwind of the highway. Upwind of the highway, the background concentration of CO was measured. The distance x of the absorption paths to the highway varied between 10 m and 500 m. In determination of the emission rate, the proportionality between concentration and emission rate was used and, using a length-integrated concentration c^s simulated for an emission rate of 1 mg/(m^2·s), the emission rate was determined [41]. The measured mean CO emission rates was 160 mg/(m^2·s) which is equivalent to a CO emission of 3,2 g/s.

Table J.1 – CO concentrations and CO emission rates near the highway

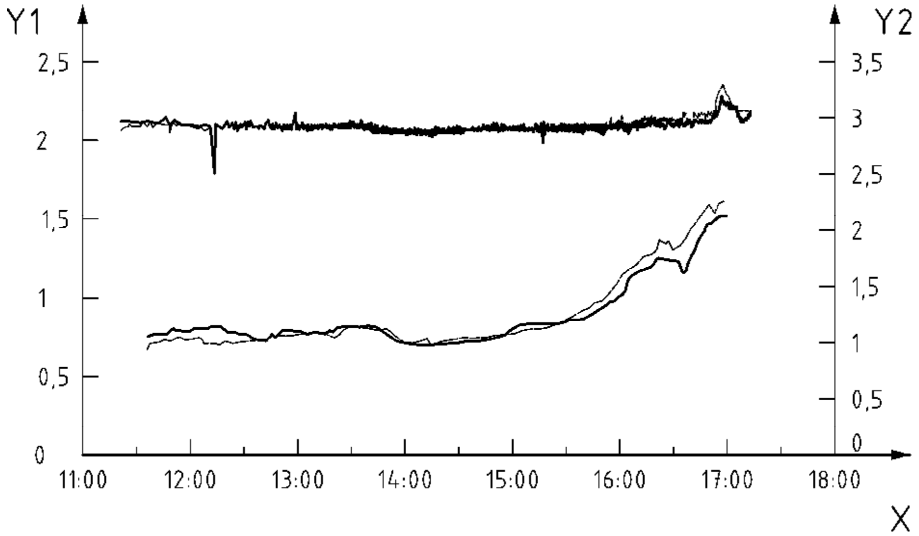
x **position**	**10** **P1**	**30** **P2**	**50** **P3**	**100** **P4**	**200** **P5**	**500** **P6**
u	2,9	3,8	3,6	3,3	2,8	2,6
R	591	3,8	3,6	3,3	2,8	2,6
DQ_{CO}	181	116	89	78	49	30
$c_{\mathrm{CO}}^{\mathrm{M}}$	56,5	36,2	27,8	24,4	15,3	9,4
c^{S}	664,3	239,5	170,3	149,4	104,3	60,8
E_{CO}	85,1	151,3	163,1	163,0	146,8	154,6

x distance in m
u wind speed in m/s
R solar radiation in W/m^2
DQ measured difference in concentration between CO (ppb) and background
c^{M} measured length-integrated concentration in mg/m^2
c^{S} simulated length-integrated concentration in mg/m^2(molecule-independent)
E emission rate in mg/(m^2·s)

At positions P2 to P6, the emission rates found vary between 147 mg/(m^2·s) and 163 mg/(m^2·s), that is by approximately ± 4 %. Thus, for this field of application, the accuracy of the emission rate determination is adequate using the method described. At P1, the air turbulence of the moving vehicles interferes with the spread of the pollutant cloud in the external wind x field and leads to a relatively high dilution in the vicinity of the source, as a result of which $c_{\mathrm{CO}}^{\mathrm{M}}$ is relatively low. Therefore the application of the Gaussian model is not suitable for the determination of the emission rate from concentration measurements close to and at the road.

J.1.2 Determination of CO air pollution due to vehicles in a road

Figure J.1 [42] shows the example of measuring CO air pollution concentrations, caused by vehicles, using the FTIR long-path absorption spectroscopic method along the footpath parallel to a road [42; 43; 36]. The concentration profile is shown here over many hours of a day by sliding half-hourly means (set as mixing ratio in ppm). For comparison with the FTIR long-path absorption method, the diagram additionally shows the CO mixing ratios, as sliding half-hourly means, which were measured at a monitoring station of the North-Rhine Westphalia Landesumweltamt (LUA) [Regional Environmental Agency]. The LUA station was at the start of the FTIR monitoring path. It can be seen that there is good agreement between the two measuring systems for sliding half-hourly means. Slight differences are explained by the different volumes measured. From 15:00 h, both measuring systems record a sharp increase in CO mixing ratio due to the onset of rush-hour traffic. The methane mixing ratio which was measured at the same time in parallel remained substantially constant over the entire period of measurement and corresponds roughly to the background concentration.



Key

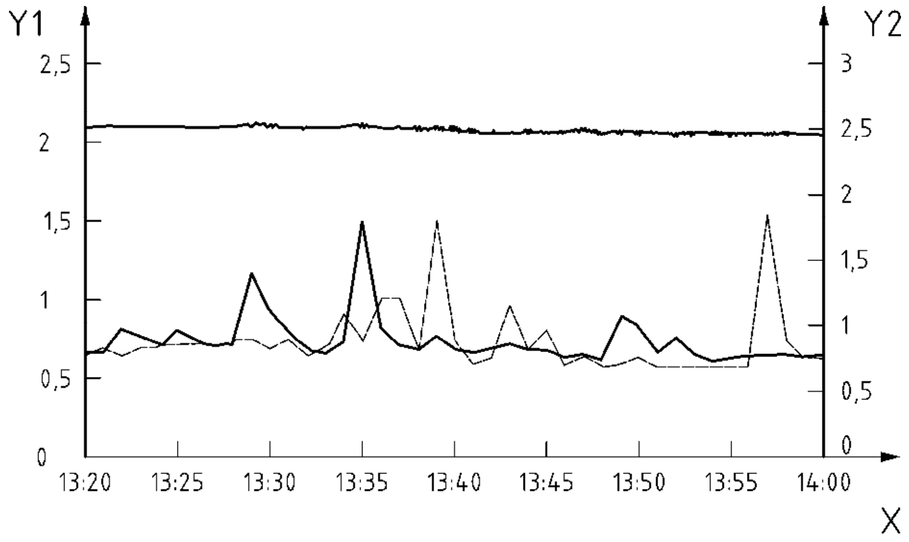
X time

Y1 CH_4 mixing ratio in ppm

Y2 CO mixing ratio in ppm

Figure J.1 — Comparison between point measurements and remote sensing methods, sliding half-hourly means for CH_4 (top) and CO (bottom); continuous line = FTIR measurements, dashed line = monitoring station

Figure J.2 [42] shows that in a comparison between the data from FTIR long-path absorption spectroscopy and those from the point-measurement method, the time average is of great importance. This figure shows an excerpt from the method described above with the corresponding minute values. On this short timescale, differences in the concentrations can clearly be seen. These differences are caused by different volumes being measured by the two measurement methods: the remote-sensing method measures over a distance of 200 m, while the point-measurement method is localized only at the endpoint of the monitoring path. This means that vehicles and groups of vehicles are determined at different times by the two measurement methods. The FTIR long-path method reflects more the pollution along the road, while the measuring station records the pollution at one point. In comparison, Figure J.2 also displays the methane concentration measured in parallel, which was measured with good agreement between the two different methods, since there were no local fluctuations.



Key

X time

Y1 CH_4 mixing ratio in ppm

Y2 CO mixing ratio in ppm

Figure J.2 — Comparison between point measurements and remote-sensing methods, minute values for CH_4 (top) and CO (bottom); continuous line = FTIR measurements, dashed line = monitoring station

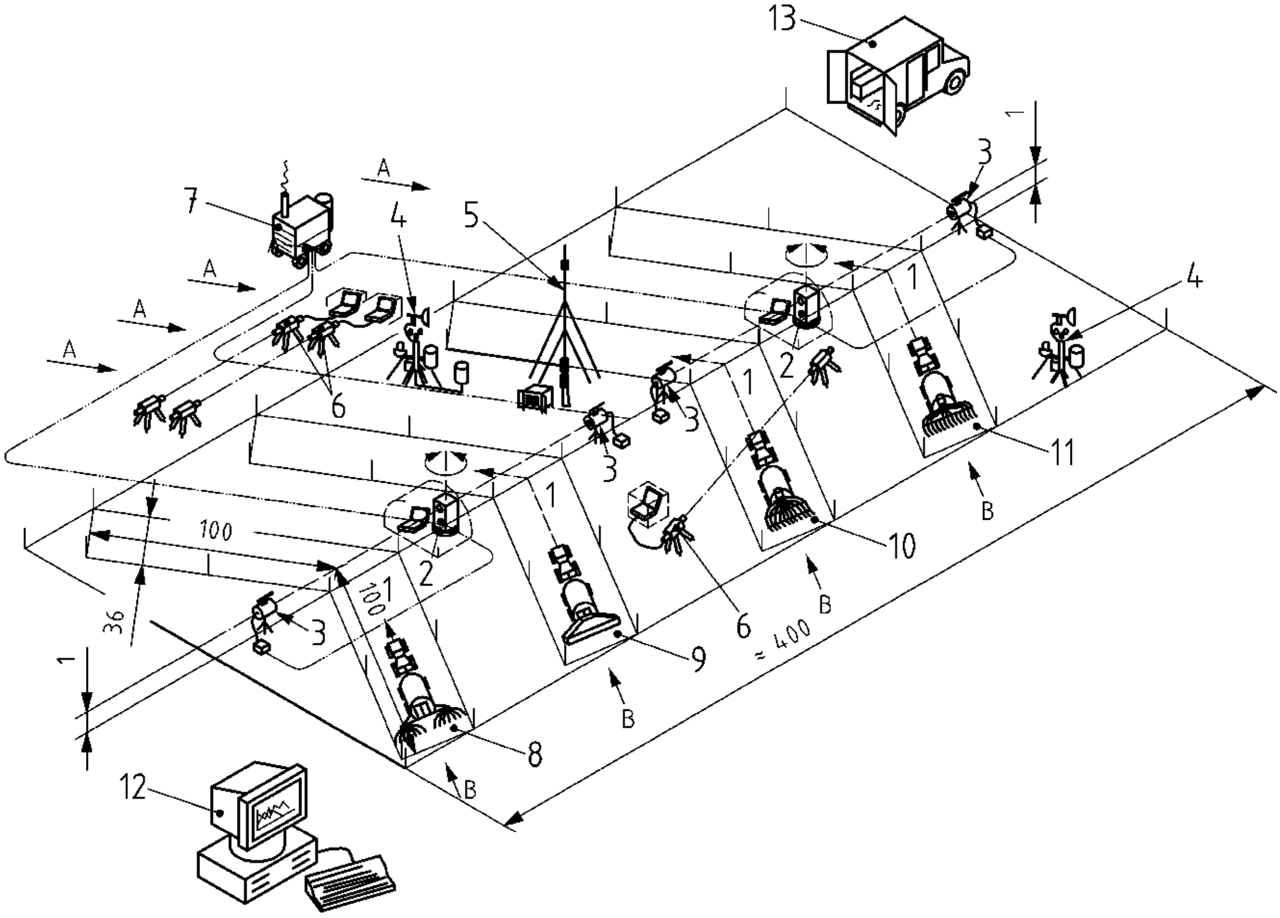
J.2 FTIR measurements and agricultural questions as an example for fugitive emissions

Agricultural emission sources are responsible for more than 90 % of known NH_3 emissions; in the case of CH_4 this is over 30 %, for N_2O approximately 45 %, for CO_2 4 % [44]. All of these components can be measured simultaneously using FTIR spectroscopy.

In agriculture fugitive emissions of varying spatial extent exist, which make up the majority of emissions. These include, for example, freely ventilated animal housing, manure heaps or slurry-treated fields [44]. Measurements over long beam paths are seen as particularly useful here for answering two important questions: How are the immediate surroundings of agricultural production sites affected? And: what quantities of gas are emitted in different types of agricultural processes?

To answer the first question, for example, "optical boundary fences" can be erected at the boundary of housing situated downwind of an installation or at the edge of a forest. Answering the second question assumes that not only gas concentration but also emission rate can be determined by a propagation calculation. As an example, the comparison between different application techniques for liquid manure [44] will be described: in this agricultural cultivation process step, in strong sunshine, up to 90 % of the nitrogen bound in the slurry as ammonium ions can escape as ammonia gas. New application techniques decrease this effect by distributing the slurry not extensively over the entire working width, but depositing in strips.

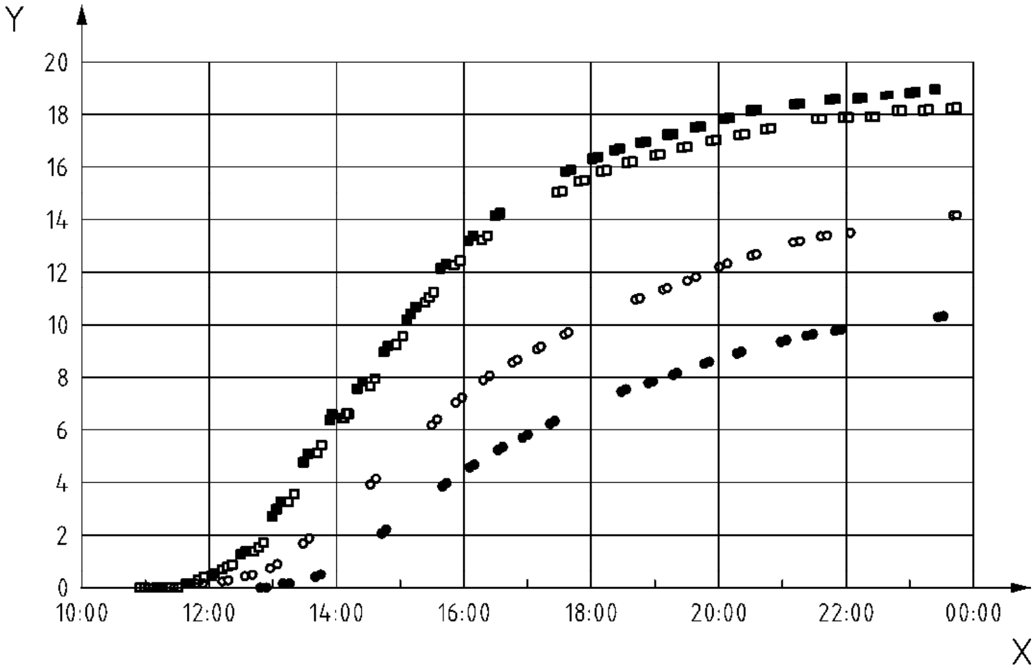
On an experimental field, four different liquid manure application techniques were compared with respect to their emission of ammonia under practical conditions [44]. These were a double broadcasting head spreader, a broadcasting/apron spreader (extensive application), and a towed-hose and towed-shoe spreader (application in strips). The slurry was applied to 36 m wide and 200 m long strips at a sufficient distance from one another. The experimental field was in the upper Bavarian mountain valley, with the strips laid along the valley axis and thus parallel to the two prevailing wind directions. Between every two strips a spectrometer mounted on a rotable table was placed which could be swivelled through 180°. As a result each of its monitoring paths could cover firstly one then the next strip at a height of 1 m. In total, for the four strips, two FTIR systems were used simultaneously. Extensive meteorological measurements were carried out at the same time. These were used together with the measured gas concentrations as input parameters for a propagation calculation, which were used in the determination of emission rates. Figure J.3 shows the analytical setup and Figure J.4 shows the time course of the accumulated emissions. The different application methods differ clearly from one another. The lowest emission is given by the towed-shoe spreader in which the grass is divided using a skid, so that the blade surfaces are not wetted. This further decreases the emitting surface. In this manner, the emission-reducing effect of novel slurry application techniques was verified directly in the field experiment. The non-contact FTIR technique also avoids the problems which occur with the polar gas ammonia due to adsorption to the sampling apparatuses of conventional analytical instruments.



Key

A	wind direction 1
B	wind direction 2
1	slurry-treated partial areas
2	FTIR system (pivotable through 180°)
3	IR source
4	meteorological station
5	differential temperature measurement
6	scintillometer
7	electrical power unit
8	application vehicle with broadcasting head
9	application vehicle with broadcasting apron
10	application vehicle with towed hose
11	application vehicle with towed shoe
12	spread modeling
13	service vehicle

Figure J.3 — Measurement setup for analyzing NH_3-N emissions from different liquid manure application methods



Key

X time

Y emission of NH_3-N in %

■ double broadcasting head

□ broadcasting apron

○towed hose

● towed shoe

Dairy cattle slurry:

pH	TM in %	NT in %	NH_4-N in %
7,2	7,67	0,32	0,15

Application to grassland, experimental site 880 m above sea level, stand height 10 cm, leafy

Averaged weather data over the experimental period:

Relative humidity:	79 %
Temperature 10:00 h to 18:00 h:	10,5 °C
Temperature 18:00 h to 24:00 h:	8,8 °C
Global radiation 10:00 h to 18:00 h:	112,9 $W \cdot m^{-2}$
Global radiation 18:00-24:00 h:	0,9 $W \cdot m^{-2}$
Wind speed:	1,3 $m \cdot s^{-1}$
Total precipitation (from 22:20 h to 24:00 h):	1,7 mm

Figure J.4 — Cumulated emission of NH_3-N from different liquid manure application methods [44]

J.3 Use in the industrial area

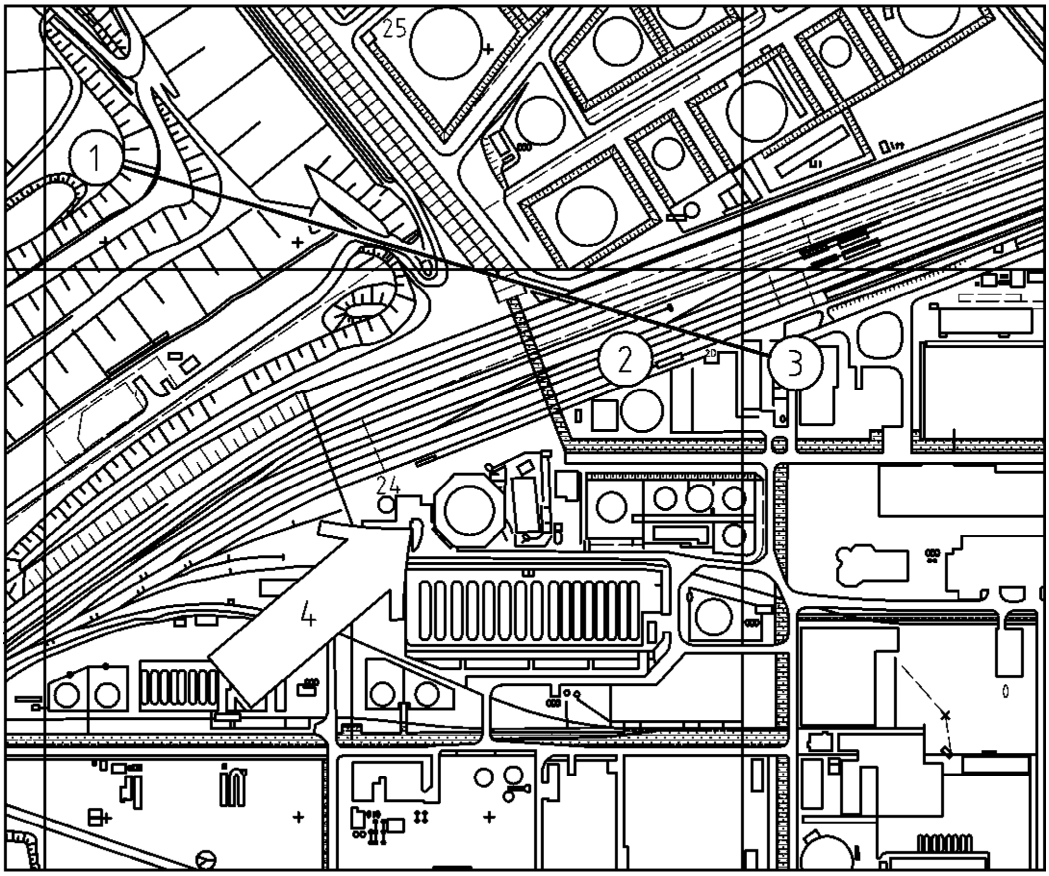
J.3.1 General

Two examples of use in the industrial area are given below. Other industrial applications may be found, for example, in [45 to 48].

J.3.2 Measurements of an industrial ammonia transfer station

In a measurement campaign [43; 49], it was found that, using the FTIR long-path absorption spectroscopy sudden releases of ammonia can be recorded even in an industrial area with a complex topography.

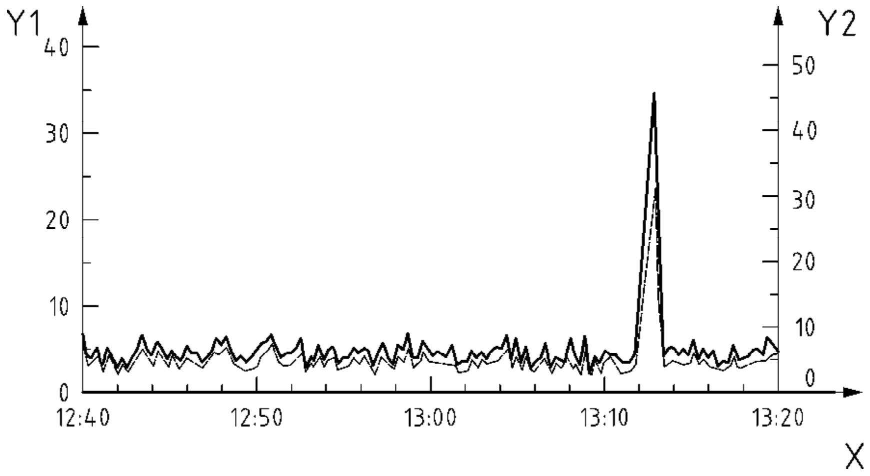
The measurements were carried out using a monostatic instrument. At the measurement site (Figure J.5), railroad tanker trucks were charged with ammonia. In order to be able to record any sudden release of ammonia at the tank-filling station, the spectrometer was positioned remotely on a small hill about 380 m from the tank-filling station. The retroreflector was positioned so that the monitoring path was downwind of the tank-filling station and thus emissions from the station were reliably detected [49].



Key

1 FTIR system position
2 transfer station
3 reflector position, 380 m
4 wind direction

Figure J.5 — Analytical setup for measuring ammonia emissions at an ammonia transfer station



Key
X time
Y1 values in ppm·m
Y2 values in ppb

Figure J.6 — Ammonia released during tank filling, evaluated using two different reference spectra (continuous line: determined with an FTIR system of the same type, dashed line: from a commercial spectral database

At the start of measurements, a virtually constant ammonia concentration was measured (Figure J.6). In the background atmosphere, at the same time, several VOCs were detected. For the evaluation, reference spectra from two different databases were used. This example shows the importance of choosing the reference spectra. More accurate analysis found that the results shown as the continuous line correspond to the actual emission.

As can be seen from Figure J.6, the ammonia concentration increased drastically for a short period. The concentration increase was recorded continuously and is due to the fact that at this point the tank-filling hose was detached from one wagon and ammonia residues escaped from the hose.

The measurements on this facility demonstrate clearly that, in principle, FTIR long-path absorption spectroscopy can be used to detect sudden releases of emissions in an industrial background atmosphere even from a relatively great distance. The method may thus also be used in certain cases for monitoring accidents.

J.3.3 Measurements on an industrial olefin plant

Measurements made on an olefin plant [49] using a monostatic spectrometer demonstrated two things:

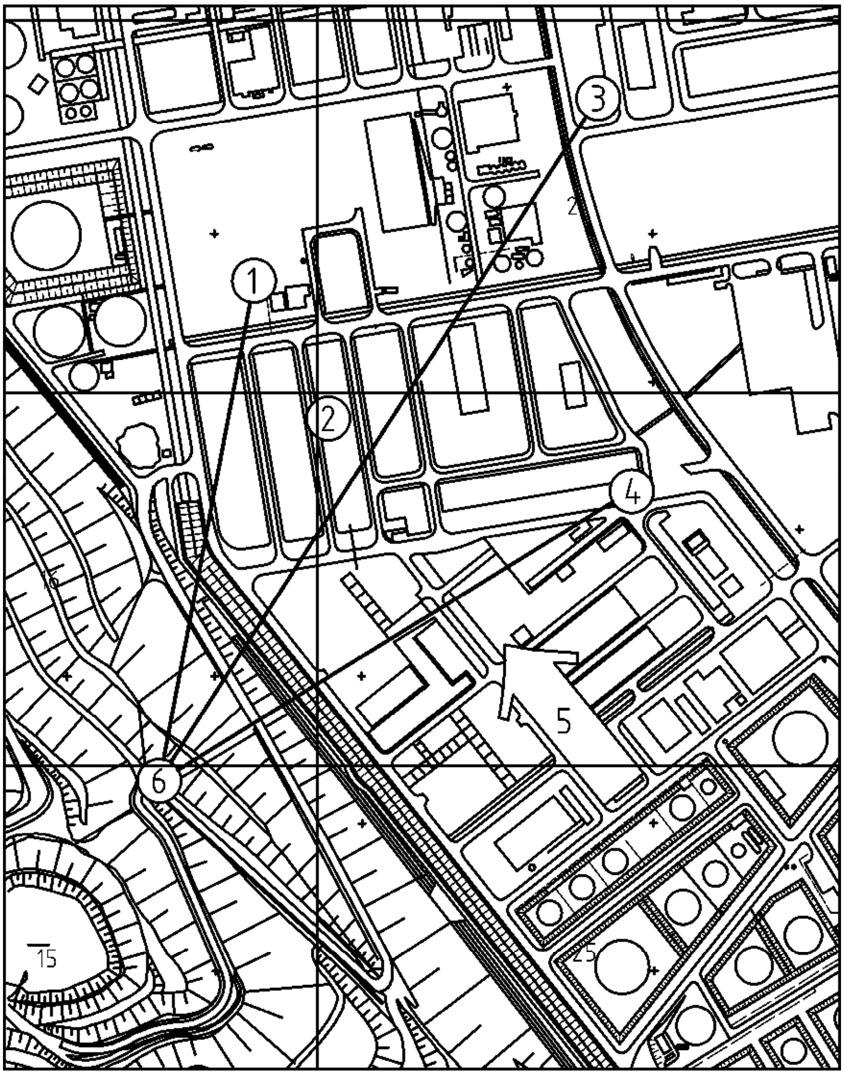
- FTIR long-path absorption spectroscopy can be used to carry out multicomponent measurements of industrially important compounds.
- Measurements can also be made in or above plants which are difficult to reach or unreachable for conventional measuring systems.

For the measurements, the FTIR spectrometer was positioned on a hill. The monitoring paths were arranged so that they were upwind, downwind and above the olefin plant. The olefin plant itself was some tens of meters high. The position of the monitoring paths is shown in Figure J.7.

The results of this FTIR long-path absorption measurement for ethene and propene are shown in Figure J.8. Upwind of the olefin plant, no ethene or propene concentrations were measured, while downwind a marked increase in ethene and propene was observed, which is due to emissions from the plant. A still higher ethene concentration was established using FTIR long-path absorption spectroscopy on the monitoring path above the plant. This shows that, owing to the thermal properties of the plant, a large proportion of the ethene emissions from the plant is carried upward. The propene concentration measured above the plant was lower than in the downwind measurement. The reason for this is that the majority of propene is emitted downwind of the furnace and is not carried to great heights by thermals. The measurement made using the FTIR path above the olefin plant clearly shows that this method also includes possibilities for analysis where conventional measurement can only be carried out with difficulty.

J.4 Measurements on a municipal waste landfill

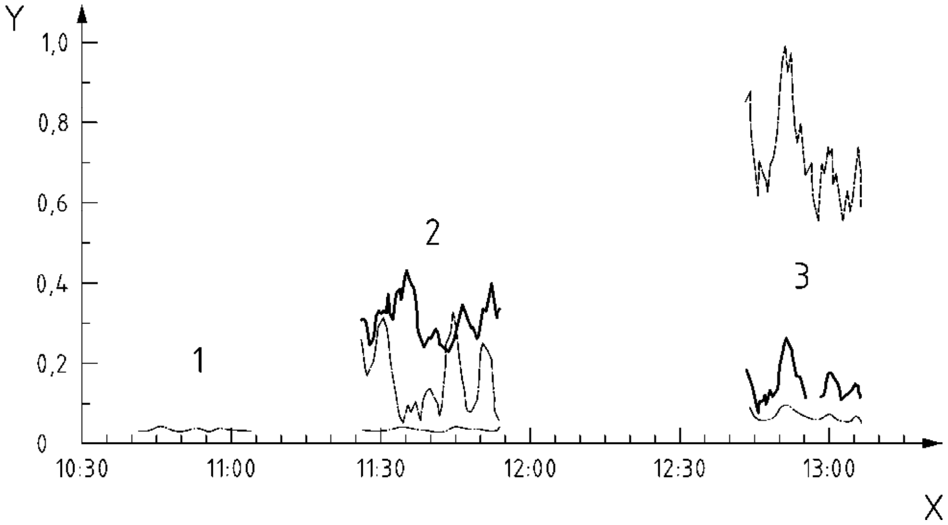
A further useful application for FTIR remote sensing methods may be described using the example of the monitoring of landfill gas emissions from a municipal waste landfill [50]. Other examples may be found, for example, in [51; 52].



Key

1 downwind measurement, 330 m
2 olefin plant
3 measurement above the plant, 540 m
4 upwind measurement, 370 m
5 wind direction
6 FTIR system position

Figure J.7 — Analytical setup for measuring hydrocarbon emissions from an olefin plant



Key

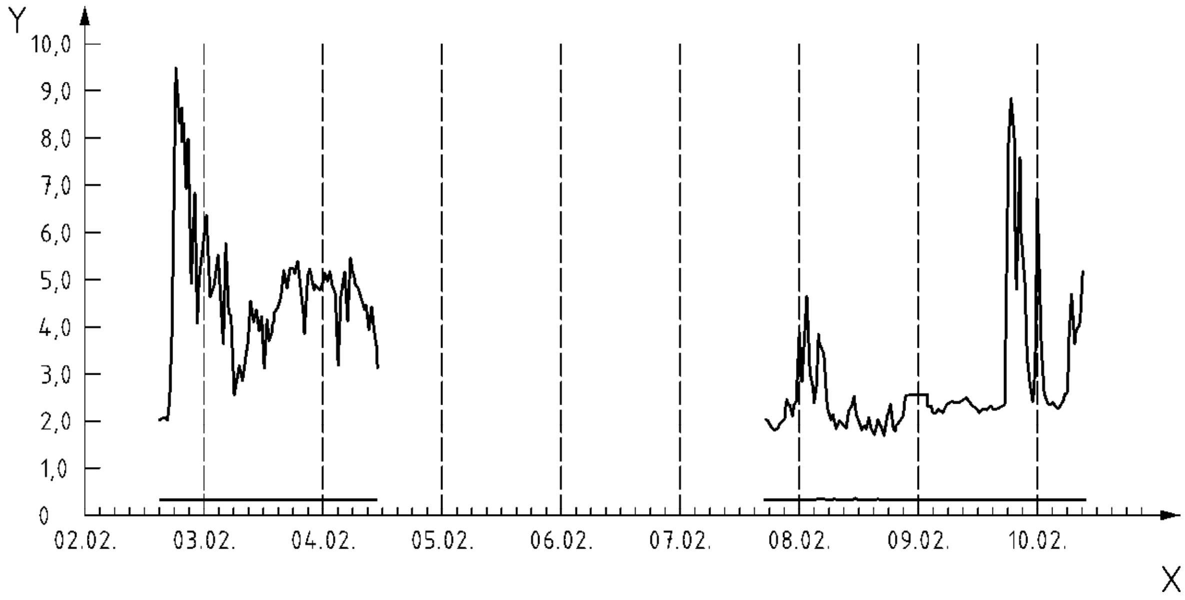
1	upwind measurement
2	downwind measurement
3	measurement above the olefin plant
X	time
Y	mixing ratio in ppm

Figure J.8 — Mixing ratios for ethene and propene at an olefin plant (continuous line: propene, dashed line: ethene, dot-dashed line: error from the remainder of the CLS fitting)

In the immediate vicinity of a waste landfill, when weather conditions with low wind speeds (< 2 m/s) and ground inversion are present, that is to say when relative to the air temperature low ground temperatures are present, odour nuisance occurs due to the emission of landfill gas. To decrease or prevent this cold air flow and the associated odour nuisance, an earth wall several meters high was deposited along the edge of the landfill. During a long-term experiment lasting two times two days, an FTIR remote-sensing system was used to test whether the earth wall can retain the resultant landfill gases and thus prevent the outflow of the lake of cold air.

A monostatic FTIR system was set up on the earth wall along the ridge. The length of the monitoring path was 298 m. Methane, which occurred as the main constituent in the landfill gas at concentrations between 45 % and 65 %, was determined continuously as a guide substance. In addition, as quality assurance of the spectrometer, the concentration of dinitrogen oxide in the atmosphere was recorded.

Figure J.9 shows the methane and dinitrogen oxide mixing ratios measured during the two measuring periods. It can clearly be seen that, compared with the typical atmospheric background mixing ratio (approximately 1,8 ppm of CH_4), at times markedly increased methane values were recorded at the measurement site. In particular, in the late hours of the evening of February 9, a very sudden overflow of the lake of cold air was observed, which led to mixing ratio peaks of over 8 ppm of methane. The N_2O mixing ratio, in contrast, remained constant for the entire measuring period at about 300 ppb. The studies clearly establish that under the prevailing meteorological conditions, the earth wall installed is not sufficient to prevent a flow of cold air of the resultant landfill gas emissions into the immediate vicinity.



Key
X date
Y mixing ratio in ppm

Figure J.9 — Mixing ratios of CH_4 (top) and N_2O (bottom) on the ridge of an earth wall between a municipal waste landfill and a housing estate

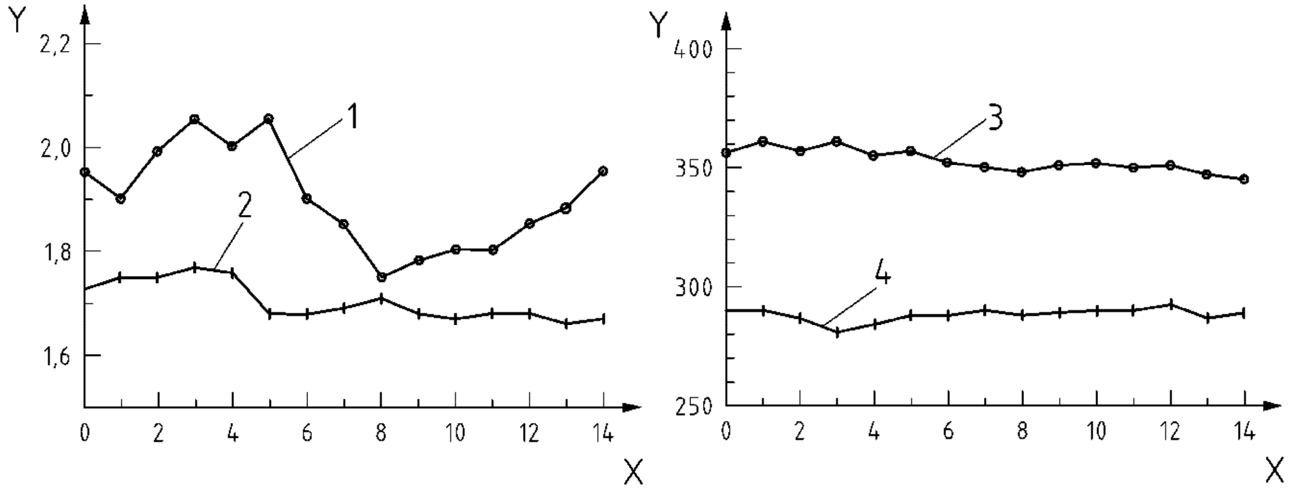
This measurement again documents the advantage of FTIR long-path absorption spectroscopy compared with the use of point measurements in dealing with analytical problems in which continuous determination of concentration of gases is necessary with high time resolution over a relatively long path length.

J.5 Gases of climatic relevance (greenhouse gases)

To measure the concentrations as air pollutants of the important gases of climatic relevance (CO_2, CH_4, N_2O, CO, H_2O) [53], a number of measurement campaigns have already been carried out.

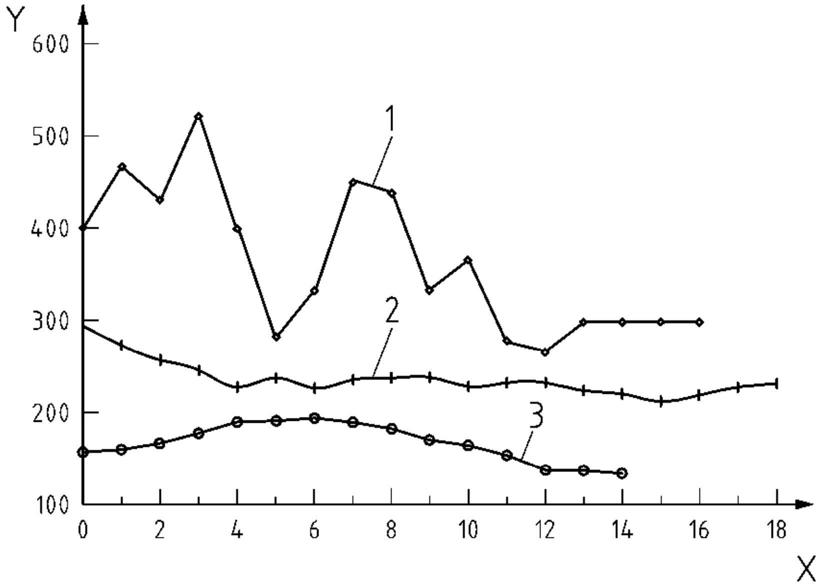
At a measuring station having rural surroundings (Melpitz station near Leipzig) the diurnal variation of climatically relevant gases was studied [54]. The results are shown in Figures J.10 and J.11.

Figure 4 in 8.2 shows the results of a number of measurements of climatically relevant gases over relatively long time periods in urban surroundings. The monostatic analytical configuration here is installed on the flat roof of a relatively large building complex. The monitoring path is 128 m. A pause in measurements of ten minutes is then introduced. A small excerpt of the results for CH_4, CO, N_2O and NH_3 is shown in Figure 4. In addition to the FTIR measurements, the meteorological parameters such as wind direction and wind speed, air pressure, atmospheric humidity and temperature and precipitation, global radiation and visibility were determined continuously. From the measurements there is obtained important information on the concentrations of the climatically relevant gases and the behaviour of the FTIR system under the most varied meteorological situations [16]. The N_2O mixing ratio, at 340 ppb, is somewhat above the global average of approximately 300 ppb [17]. Not until there was a sudden breakthrough of relatively high clean air masses in the night of January 25, 1995 to January 26, 1995 did the N_2O mixing ratio decrease to 300 ppb. This air exchange can also be recognized in the CH_4 mixing ratios. Another approach for measuring climatically relevant gases is determining the anthropogenic contribution by measuring sources. Most emissions of climatic relevant gases are diffuse and extensive and can be quantified poorly or not at all by point measurements and then only by enclosing the source. Measurement downwind of the source using the length-averaging FTIR spectroscopy and an inverse propagation modeling offers new possibilities here [41].



Key
1 H_2O-mixing ratio by volume in %
2 CH_4-mixing ratio by volume in ppm
3 CO_2 mixing ratio by volume in ppm
4 N_2O mixing ratio by volume in ppb
X time (relative unit)
Y mixing ratio

Figure J.10 — Diurnal variations in air pollution measurements for H_2O, CH_4, CO and N_2O in Melpitz on August 29, 1992 (10:00 h to 17:00 h), time unit 30 min



Key
1 on August 29, intervals: 30 min
2 on October 27, intervals: 15 min
3 on December 10, intervals: 30 min
X time (relative unit)
Y mixing ratio in ppb

Figure J.11 — Diurnal variations in air pollution measurements for CO (Melpitz)

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