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Stationary source emissions — Determination of the mass concentration of individual volatile organic compounds (VOCs) in waste gases from non-combustion processes

Émissions de sources fixes — Détermination de la concentration en masse de composés organiques volatils (COV) individuels dans les gaz résiduaires issus de processus sans combustion

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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This document was prepared by Technical Committee ISO/TC 146, *Air quality*, Subcommittee SC 1, *Stationary source emissions*.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

There are various volatile organic compounds (VOCs) emitted from stationary sources where organic solvents are used for painting, printing, cleaning, degreasing and chemicals production. In order to understand how to reduce the environmental risk due to VOCs, it is necessary to measure not only the concentration of total VOCs but also the concentration of individual VOCs in waste gases. This is because individual VOCs have different potentials to form O_3 and suspended particulate matter (SPM). Also, there are VOCs of high toxicity (e.g. benzene, toluene, propyl acetate, propanol, formaldehyde, some chlorinated organic compounds) of concern.

Fourier Transform Infrared (FTIR) spectrometry is proposed to provide these measurements as it provides a measurement in the infrared (IR) region over a wide spectral band. Analysis of the recorded spectra enables the concentration of a wide number of compounds to be quantified simultaneously. Overlap of IR absorption features with each VOC can affect the quantification of each compound. However, by using appropriate chemometric procedures for the overlapping IR spectra of VOCs, the concentrations are quantified for the individual compounds of interest.

This document specifies the measurement method for determining concentrations of individual VOCs in waste gases from non-combustion processes by using FTIR spectroscopy.

Stationary source emissions — Determination of the mass concentration of individual volatile organic compounds (VOCs) in waste gases from non-combustion processes

1 Scope

This document specifies the use of FTIR spectrometry for determining the concentrations of individual volatile organic compounds (VOCs) in waste gases from non-combustion processes. The method can be employed to continuously analyse sample gas which is extracted from ducts and other sources. A bag sampling method can also be applied, if the compounds do not adsorb on the bag material, and is appropriate in cases where it is difficult or impossible to obtain a direct extractive sample.

The principle, sampling procedure, IR spectral measurement and analysis, calibration, handling interference, QA/QC procedures and some essential performance criteria for measurement of individual VOCs are described in this document.

NOTE 1 The practical minimum detectable concentration of this method depends on the FTIR instrument (i.e. gas cell path length, resolution, instrumental noise and analytical algorithm) used, compounds, and interference specific (e.g. water and CO_2).

2 Normative references

There are no normative references in this document.

3 Terms and definitions

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

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

3.1 Terms related to FTIR

3.1.1
absorbance
negative logarithm of the transmission, $A = -\log(I/I_0)$, where I is the transmitted intensity of the light and I_0 is the incident intensity

3.1.2
resolution
minimum separation that two spectral features can have and still, in some manner, be distinguished from one another

3.2 Terms related to performance characteristics

3.2.1
reference spectrum
plot of absorbance versus wavenumber for a known gas or known mixture of gases, which are obtained under controlled conditions of pressure and temperature, path length, and known concentration

Note 1 to entry: The reference spectra are used to prepare the chemometric model used to obtain the unknown concentrations of analytes in sample spectra.

Note 2 to entry: See 10.3.1.

3.2.2
validation spectrum
plot of absorbance versus wavenumber for *calibration verification gas* (3.2.6)

Note 1 to entry: See 10.3.4.

3.2.3
background spectrum
plot of absorbance versus wavenumber for *zero gas* (3.2.5)

3.2.4
response time
time interval between the instant when a stimulus is subjected to a specified abrupt change and the instant when the response reaches and remains within specified limits around its final stable value, determined as the sum of the lag time and the rise time in the rising mode, and the sum of the lag time and the fall time in the falling mode

[SOURCE: ISO 9169:2006, 2.2.4]

3.2.5
zero gas
high purity nitrogen (99,999 %) or synthetic air (99,999 %) is used to measure a *background spectrum* (3.2.3) and to determine the limit of detection, as well as to purge sample lines and sampling system components, to dilute sample and *calibration verification gas* (3.2.6), and to conduct blank measurements

3.2.6
calibration verification gas
gas or gas mixture where the concentration(s) and uncertainty(ies) are known, used to check the high level concentration point of the measuring system

Note 1 to entry: The gas or gases used is included in the analytical algorithm used to quantify the concentration of target analyte, and have absorption lines distinguishable from baseline noise at wavenumbers that are within the upper and lower wavenumber limits where the target analyte displays absorption lines distinguishable from baseline noise. An absorption feature is considered distinguishable from baseline noise if it is greater than three times the standard deviation of the baseline noise.

Note 2 to entry: This concentration is often chosen around 70 % to 80 % of full scale.

3.2.7
lack of fit
systematic deviation within the range of application between the measurement results obtained by applying the calibration function to the observed response of the measuring system, measuring reference materials and the corresponding accepted value of such reference materials

Note 1 to entry: Lack of fit can be a function of the measurement result.

[SOURCE: ISO 9169:2006, 2.2.9]

3.2.8
analytical interference
situation that arises when two or more compounds have overlapping absorbance bands in their infrared spectra

3.2.9
limit of detection
LOD
minimum concentration of a compound that can be detected by an instrument with a given statistical probability

Note 1 to entry: Usually the detection limit is given as three times the standard deviation of noise in the system.

3.2.10
analytical algorithm
method used to quantify the concentration of the target analytes and interferences in each FTIR spectrum

Note 1 to entry: The analytical algorithm should be used to account for the *analytical interferences* (3.2.8) by conducting the analysis in a portion of the infrared spectrum that is the most unique for that particular compound.

3.2.11
chemometrics
chemical discipline that uses mathematical and statistical methods, (a) to design or select optimal measurement procedures and experiments, and (b) to provide maximum chemical information by analysing chemical data

3.2.12
independent reading
reading that is not influenced by a previous individual reading as the two individual readings are separated by at least four response times

4 Symbols and abbreviated terms

I_0	intensity of incident radiation
I	intensity of transmitted radiation
A	absorbance
T	transmittance
α	absorptivity
l	optical path length
c	sample concentration
C_{CLS}	the known concentration from the reference spectra
C_{VAL}	the predicted concentrations from the validation spectra
FTIR	Fourier transform infrared
CLS	classical least squares

PLS partial least squares

ILS inverse least squares

SEV standard error of validation

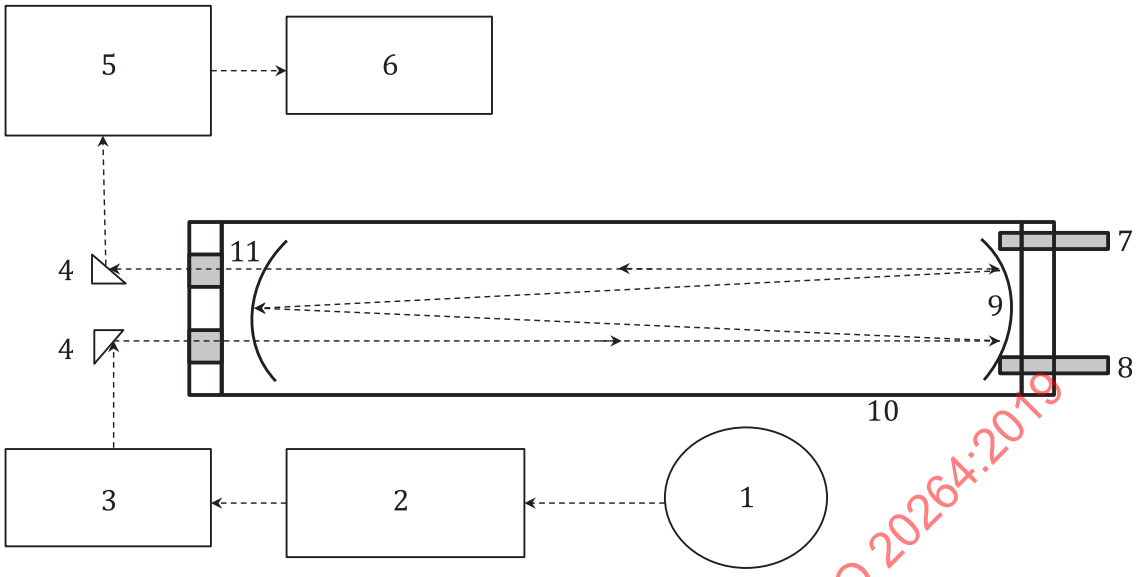
5 Measurement principle

5.1 General

A sample gas is extracted from ducts and other sources via a sampling system and continually introduced into a gas cell of an FTIR system. The IR spectra of the sample gas is measured using an FTIR spectrometer. When a sampling bag is used, the gas sampled in the bag is transferred to the gas cell. IR spectra obtained are analysed by using analytical algorithm. Some VOCs might adsorb onto the sampling bag surface, reducing meaured VOC concentration. Losses by absorption shall be tested and documented before sampling.

5.2 FTIR Spectrometer components

Figure 1 illustrates the basic FTIR spectrometer configuration required for gas phase analyses. The IR radiation emitted by the IR source contains energy at all wavelengths between 2,5 and 14 µm, which is 700 to 4 000 cm^{-1} for most IR systems conducting these analyses. The IR radiation passes through an interferometer, where the motion of an optical element — usually a mirror — optically modulates the IR beam. The modulated IR beam then enters an absorption cell through a window and interacts with the gases of interest. In “multi-pass” (for example “White”) absorption cells, mirrors within the cell direct the IR beam through the sample gas multiple times; in such cells, the absorption pathlength can be from 4 to 50 (or more) times the cell’s physical length. (A larger absorption path length generally leads to greater sensitivity.) The IR beam then exits the sample cell via a second window and is re-focused onto an IR detector.



Key

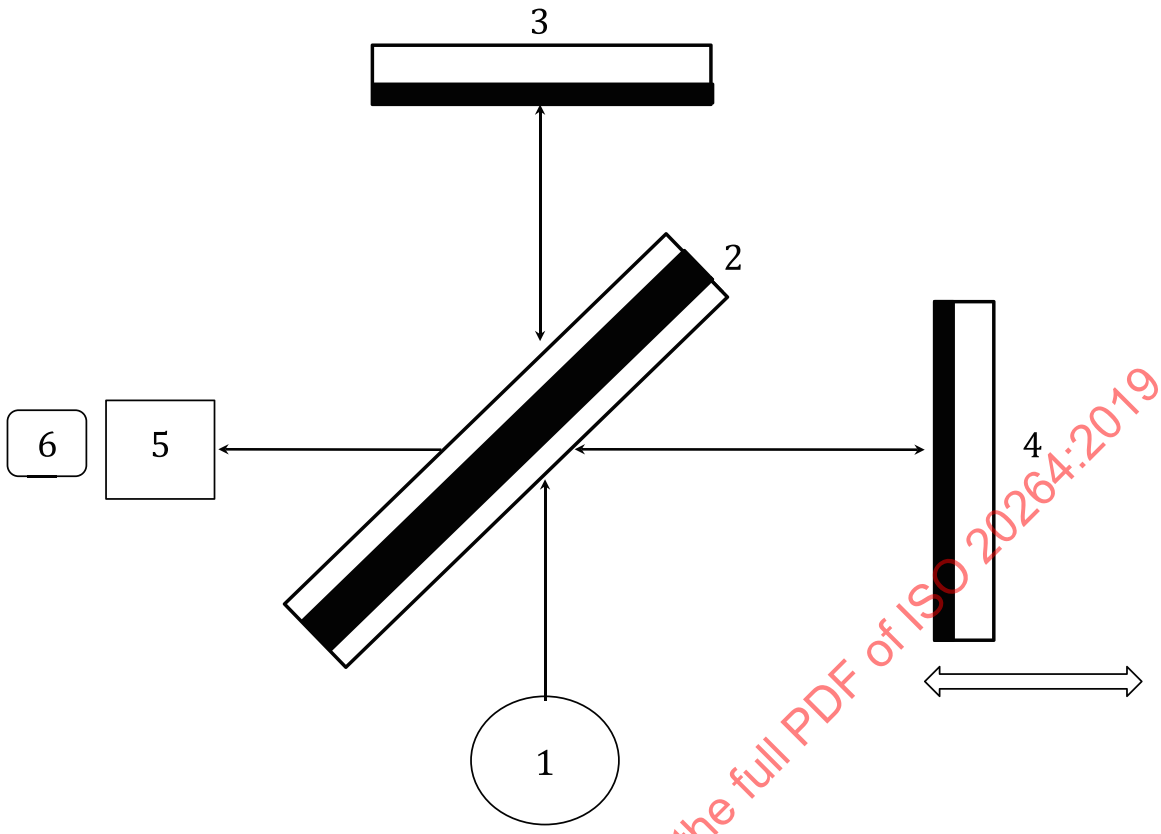
1	IR source	7	absorption cell exhaust
2	aperture or filter 1 (optional)	8	absorption cell inlet
3	interferometer	9	mirror
4	focusing optics	10	absorption cell
5	aperture or filter 2 (optional)	11	infrared window
6	IR detector		

Figure 1 — FTIR spectrometer components and beam path

5.3 Interferogram

A beam of the broadband IR radiation is divided into two or more paths with different optical path lengths and is recombined to give a detector signal with repetitive interference maxima and minima with the aid of an interferometer. Figure 2 shows the Michelson interferometer as an example.

The interferogram is obtained by plotting the detector signal against the difference in optical path length. Given a difference in optical path lengths corresponding to an even multiple of the wavelength, the interference is constructive, and given an odd multiple, the interference is destructive. An additional laser with its own detector is contained in an FTIR system. The radiation emitted by the laser and the broad band IR source passes through the interferometer simultaneously, although the interferograms are recorded by separate detectors. From the positions of the peaks of the interferogram of the laser irradiation, it is possible to determine the difference in the optical path length, as the laser's input frequency is known and is constant (e.g. 632,8 nm for a HeNe laser).



Key

1 IR source
2 beam splitter
3 fixed mirror
4 movable mirror
5 absorption cell
6 detector

Figure 2 — Principle of the Michelson interferometer

5.4 Fast Fourier transform

Every data point in the interferogram contains intensity information about every infrared wavelength transmitted from the source to the detector. It is possible to recover the intensity information as a function of wavelength through application of a fast Fourier transform, from which the FTIR technique's name is derived. This digital transformation of the interferogram can be thought of as the mathematical inverse of the optical modulation applied to the infrared beam as it passes through the interferometer.

5.5 Beer's law

The direct proportionality of the absorbance of a compound in a homogeneous sample to its concentration. See Formula (1) which also describes the more general case of gas mixtures.

$$\log\left(\frac{I_0}{I}\right) = -\log\left(\frac{1}{T}\right) = A = \alpha l c \tag{1}$$

where

I_0 is the intensity of incident radiation;

I is the intensity of transmitted radiation;

A is the absorbance;

T is the transmittance;

α is the absorpitivity;

l is the optical path length;

c is the sample concentration.

6 Equipment

6.1 Sampling system

The sampling is the process of extracting a small portion which is representative of the composition of the main gas stream from a large quantity of waste gas. A partial flow of the waste gas is directed into the gas cell of the FTIR spectrometer via a sampling probe, a particle filter and sampling line.

An example of the sampling system using a gas cell of the FTIR system is shown in Figure 3. The system consists of an extractive probe and heated filter to remove fine particles, a bypass valve for N_2 purging gas cell with thermometer and pressure gauge, an FTIR spectrometer, a mass flow meter for controlling the flow rate of sample gas into the gas cell, a shut-off valve and a sampling pump. When the sampling line is long, the bypass pump is set to remove a residual gas in the sampling line. The sampling pump should be installed downstream of a gas cell to prevent adsorptive losses of analytes or other contamination by the pump. If the pump is made with inert materials and is heated, it can be installed upstream of a gas cell. The sampling line and the gas cell of the FTIR spectrometer need to be heated if there is any risk of condensation. The temperature of the upstream sampling components should be the same as or slightly lower than that of the gas cell. The gas cell temperature and pressure shall be measured and compensated and should be at the same or a similar temperature and pressure to that of the reference spectra. Gas flow rate and temperature shall be recorded.

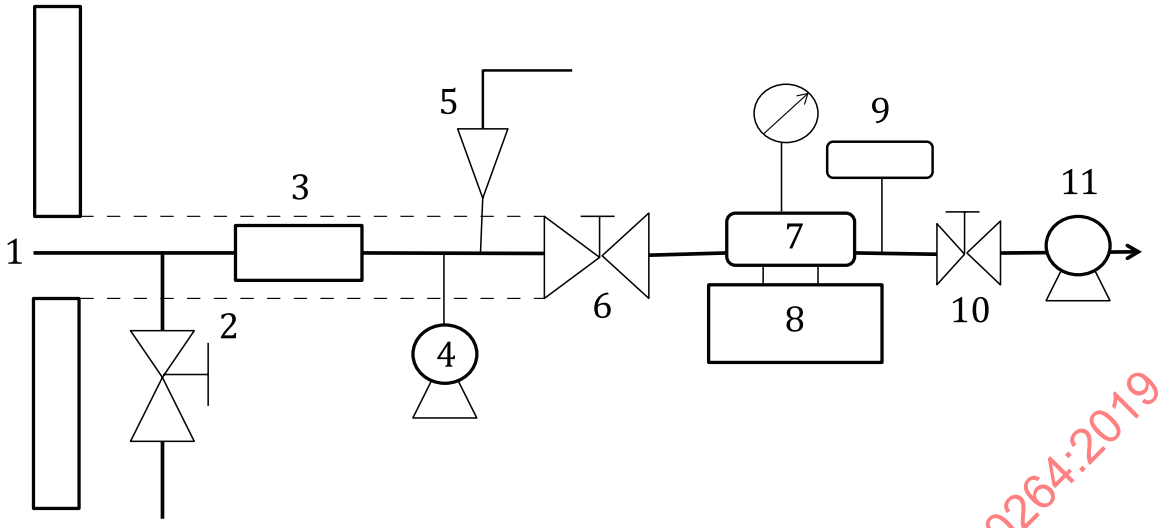
The sampling system including sample lines and particle filter device shall:

a) be made of a material that is chemically and physically inert to the constituents of the waste gas under analysis;

b) be designed to ensure a short residence time (with long lines or high flow resistance, the use of an external pump with bypass is recommended);

c) have an inlet for applying a test gas close to the sampling probe, upstream of the particle filter.

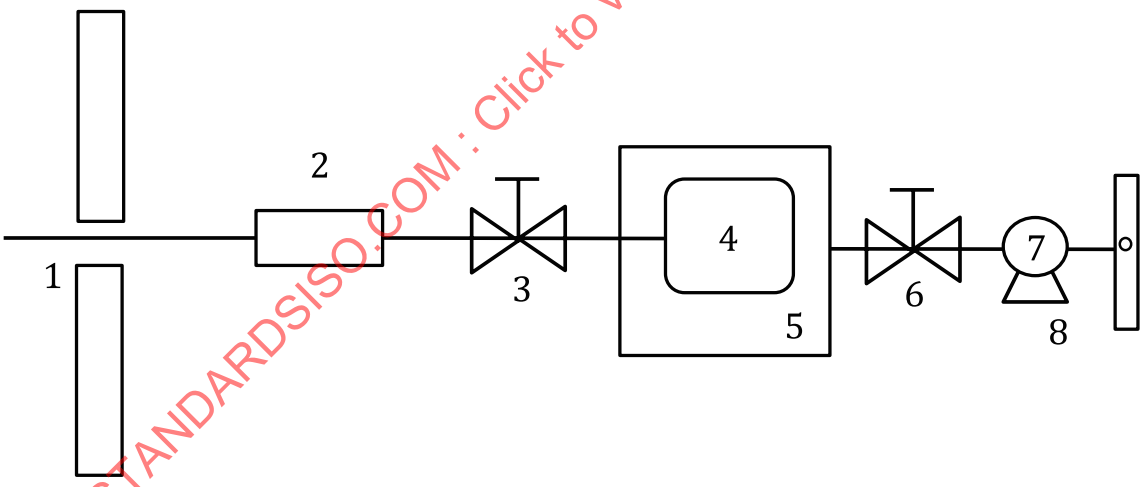
When a sampling bag is used, the gas sampled in the bag is to be transferred to the gas cell of the FTIR spectrometer. The system using the sampling bag is shown in Figure 4. This system constitutes a sampling probe, a filter, a sampling valve, a sampling bag, a sampling vacuum box, a valve, a sampling pump and a flow meter to introduce the waste gas into a sample bag. The sampling bag shall be made of a material which prevents the adsorption of VOCs. This is not a recommended procedure unless it is not possible to get the sample extractively.



Key

1 sampling probe
2 valve for introducing test gases
3 particle filter
4 bypass pump (if necessary)
5 bypass valve for N_2 purging
6 sampling valve
7 gas cell with thermometer and pressure gauge
8 FTIR spectrometer
9 mass flow meter
10 shut-off valve
11 sampling pump

Figure 3 — An example of a sampling system using a gas cell of an FTIR spectrometer



Key

1 sampling probe
2 particle filter (if necessary)
3 sampling valve
4 sampling bag
5 sampling vacuum box
6 valve
7 sampling pump
8 flow meter

Figure 4 — An example of a sampling system using a sampling bag

6.2 Analytical apparatus (FTIR)

The FTIR spectrometer consists of an IR source, an aperture or filter, an interferometer, an IR detector, a gas cell, a mirror and an optical window.

The devices of an FTIR spectrometer recommended for the measurement of VOCs are as follows:

a) gas cell:

— the cell should be made of materials which prevent the adsorption of VOCs;

— materials of the cell shall be Ni, Al, glass or stainless steel (stainless steel is not suitable for measurement at a high temperature);

— the temperature of the cell should be set at an appropriate temperature to prevent the condensation of VOCs;

— the volume of the cell is related to a response time (cell volume shall be small enough to obtain a short response time);

— the cell may be either a multi pass cell or a single pass cell;

— the consists of inert materials such as a gold coated mirror and a focus mirror;

— the optical path length can be adjusted by changing an angle of the mirror or it can be permanently fixed;

— the proper concentration range for measurement depends on both the absorptivity of compound and the path length.

NOTE For ethylene in nitrogen, the proper concentration against path length is 100 to 400 ppm-m (for example, a standard of 10 ppm to 40 ppm ethylene in nitrogen is recommended for a 10-meter absorption cell).

b) optical window:

— the window can be selected from the following materials; KBr (40 000 cm^{-1} ~ 340 cm^{-1}), ZnSe (10 000 cm^{-1} ~ 550 cm^{-1}) and BaF_2 (50 000 cm^{-1} ~ 770 cm^{-1});

NOTE 1 KBr cannot be used for waste gas with high water content.

NOTE 2 If IR spectra in a low wavenumber region are measured, ZnSe is recommended.

c) detector:

— semiconductor (e.g. MCT) or pyroelectric (e.g. DTGS) detectors can be used.

NOTE For semiconductor detectors, cooling with liquid nitrogen improves sensitivity. See Reference [2].

d) interferometer:

— device that devides a beam of radiant energy into two or more paths, generates an optical path difference between the beams, and recombines them in order to produce repetitive interference maxima and minima as the optical retardation is varied.

7 Measurement procedure

7.1 General

Comprehensive measurement planning shall be performed before the measurement, taking into consideration the specific measurement task.

7.2 Choice of the measuring system

To choose an appropriate analyser, sampling line, and conditioning unit, the following characteristics of waste gases should be known before the field test.

The target VOCs are based on the known composition of the paints, VOCs used in processing, etc. and their expected concentration range. Examples for IR spectra absorption features of VOCs using the printing and painting processes are described in Annex B. The effect of the waste gas composition should be considered in the design of the sampling system. To do so, the following condition of the waste gas should be estimated:

a) the temperature of the waste gas;

b) the water vapour content of the waste gas (dew point temperature);

c) the expected dust load and composition of the waste gas;

d) the pressure of the waste gas;

e) the expected concentration of potentially interfering substances.

To avoid long response time and memory effects, the sampling line shall be as short as possible; if necessary, a bypass pump should be used.

Before conducting field measurements, the user shall verify that the necessary QA/QC procedure has been performed.

7.3 Sampling

7.3.1 Sampling location

The sampling location chosen for the measurement devices and sampling shall be of sufficient size and construction to enable a representative emission measurement suitable for the measurement task to be obtained. In addition, the sampling location shall be chosen with regard to the safety of the personnel, accessibility and availability of electrical power.

7.3.2 Sampling point(s)

It is necessary to ensure that the gas concentrations measured are representative of the average conditions inside the waste gas duct. Therefore, the sampling point(s) shall be selected to allow for a representative sampling.

7.3.3 Extractive sampling

The sampling probe is inserted into the waste gas duct, and the sampling system from the probe to the inlet of the gas cell is purged with the sample gas by using the sampling pump through the bypass (see Figure 3). A sampling rate of 1–10 l/min is generally acceptable. Higher sampling rates decrease the effect of adsorption of target analytes in the sampling system, but higher flows increase the rate of calibration verification gas use. Therefore 1–10 l/min has been successfully used in the past.

A continuous sample gas flow rate through the FTIR at known temperature and pressure is kept while the analyser continuously scans the sample gas. Periodically a concentration update is processed by the software depending on the number of scans. This update is between 5 seconds and 5 minutes.

7.3.4 Sampling with a gas bag

If a sampling bag approach is unavoidable, the sampling bag shall be purged with nitrogen gas or dry air to remove contaminants. The inlet of sampling bag is then connected to the sampling system after a number of purges to determine if the bag is acceptable for use. The sampling probe is inserted into the duct and the sampling system purged with sample gas through the probe by using the pump (see Figure 4). Afterwards, the sample gas is introduced into the bag by opening the inlet of the bag.

7.4 Pre-test and sample quantification procedures

The sampling procedures are described in 7.3.3 or 7.3.4.

1) Before conducting any sample measurements, prepare the instrument according to the manufacturer's instructions. Acquire an optical background by introducing the zero gas directly into the FTIR measurement path. The purpose of the background (I_0) is to remove any infrared adsorption interferences from the instrument optical components.

2) Analyse the zero gas and acquire 10 sequential samples. The purpose of these zero gas analyses is to calculate an instrument level of detection (LOD) for each of the components in their analyses range. Calculate the equivalent concentration for each of these 10 samples for the target analytes of interest, and calculate their standard deviations. Apply a factor of 3 to each target analyte standard deviation result to produce an equivalent estimated LOD.

3) Analyse the calibration verification gas through the entire sampling system, including the filter. It should be in the approximate range as the expected concentrations of the source gas. If the source gas concentration is unknown, the calibration verification gas should approximate a regulatory limit, an occupational exposure limit, etc.

4) Ensure that all results for the calibration verification gas meet the quality assurance criteria of this method or take corrective action before proceeding to step 5).

5) Collect source samples for a period of 1 hour or another agreed time period reflective of representative source conditions.

6) Quantify the source samples and determine the effective residual for each target analyte. It is considered that negligible interference is present if the maximum absolute peak to peak absorbance in the residual is not greater than 5 % of the maximum absolute peak to peak absorbance in the sample spectrum. If this test is failed, it may be considered that there is negligible interference present if it can be demonstrated that the maximum absolute peak to peak absorbance in the residual is not greater than twice the maximum absolute peak to peak absorbance of a measurement of zero gas across the same wavenumbers. If this test is also failed then an interfering compound might be present in the analysis region. In such cases the analytical program used would need to be refined if the test program QA needs cannot be met.

7) Present the results as ppm (v) or mg/m^3 actual and also corrected to normal conditions for temperature, 273,15 K, and pressure 101,325 kPa.

8 Performance characteristics and criteria

8.1 General

The performance characteristics and criteria for the measurement system of VOCs by using an FTIR are described in this clause. The methods for determination of the FTIR performance parameters such as noise equivalent absorption, line position, etc. shall be done according to Annex A prior to performance tests.

8.2 Performance criteria

Table 1 gives the performance characteristics and performance criteria of the measurmement system of VOCs by using an FTIR. The tests of the performance characteristics with using the zero gas, and calibration verification gas during field operation shall be conducted and the results of tests shall meet the performance criteria in Table 1.

Table 1 — Performance characteristics and criteria of the measurement system of VOCs by FTIR

Performance characteristics	Performance criteria	Reference
Zero check	<±2,0 % of range	8.2.1
Repeatability of calibration verification gas	<±2,0 % of range	8.2.2
Response time	<200 s	8.2.3
Losses and leakages in the sampling line	<±2,0 % of range	8.2.4

8.2.1 Zero check

Base line shall be determined by directing zero gas through the entire sampling system including the primary particulate matter filter. One blank spectra is recorded with the same settings as subsequent samples from the process. The sample is quantified with the same model as the subsequent samples from the process. The reading shall be within the limit of detection determined in 7.4 2). If the data quantification methodology in 10.3 is changed after analysis, it is necessary to quantify the zero check samples from 7.4 2) and 8.2.1 again as the detection limit can change.

8.2.2 Repeatability of calibration verification gas

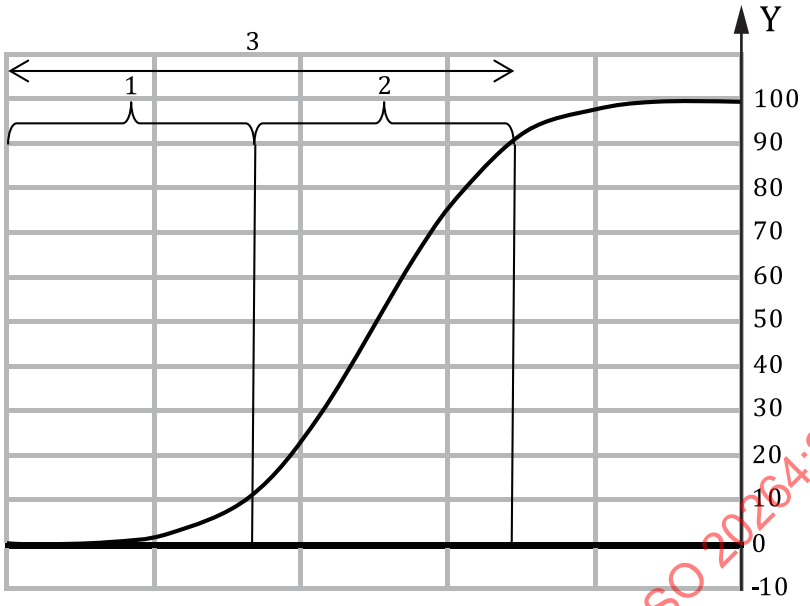
After performing 8.2.1 and 8.2.3, apply calibration verification gas upstream of any particle filters in the probe. The measured signals of the FTIR shall be determined after application of calibration verification gas by waiting for the time equivalent to one independent reading and then recording 10 consecutive individual readings. The repeatability standard deviation shall be calculated by using the measured signals obtained to determine the repeatability of calibration verification gas.

8.2.3 Response time

After performing the zero check as described in 8.2.1, apply calibration verification gas upstream of any particle filters in the probe. The step change shall be made by swiching the valve from zero gas to calibration verification gas. Wait for the reading to stabilize at 90 % of final stabilized reading and then apply zero gas in the same manner. Wait for the reading to stabilize within 10 % of the final stabilized reading.

The response time is the time interval between application of calibration verification gas to the probe and the instant when the reading reaches and remains within 90 % of the final stabilized reading. This time includes lag time and rise time (or fall time). Lag time is the interval between application of gas and the first instance where the concentration changes by 10 %. Rise time is the time it takes for the concentration to increase from 10 % of the final stabilized reading to 90 % of the final stabilized reading, and the fall time is the time it takes for the concentration to decrease from 90 % of the final stabilized reading to 10 % of the final stabilized reading. Determine both rise time and fall time for the instrument.

When reporting the average concentration value of the samples from the process, the shortest allowed averaging period is ten times the rise time or ten times the fall time if fall time exceeds rise time. See Figure 5 for illustration of lag time and rise time.



Key

1 lag time
2 rise time
3 response time
Y instrument reading (percentage of target value)

Figure 5 — Illustration of lag time and rise time

8.2.4 Losses and leakage in the sampling line

Losses and leakage are tested in conjunction with response time. When applying calibration verification gas upstream of any particle filters as described in 8.2.2, the stabilized reading shall be within 2,0 % of calibration verification gas concentration. When applying zero gas after the calibration verification gas, the stabilized reading shall not deviate from zero by more than 2,0 % of the calibration verification gas concentration.

9 Quality assurance and quality control procedure

At least the following checks are needed for QA and QC for each analyte;

1) acquire 10 sample spectra of the zero gas and determine the limit of detection as 3 × STDEV of the zero level readings;

2) measure a calibration verification gas injected upstream of the particle filter in the probe. If multiple analytes are being measured simultaneously or if the analytes are so reactive that a compressed gas cylinder is not commercially available, a surrogate gas with absorption peaks in the same analytical window as the analyte can be used instead;

3) perform sample measurements;

4) repeat calibration verification gas through the probe to ensure 95 % or better sample recovery;

5) repeat zero gas measurement through system to ensure that LOD has not changed during the sample measurement.

10 Data quantification

10.1 General

IR spectra obtained from Clause 7 (measurement procedure) are analysed by using an analytical algorithm that is usually provided within the FTIR manufacturer's software. It should be determined that the manufacturer's software is appropriate to complete the required analysis and data quality checks.

10.2 Data quantification techniques

The gas concentrations in FTIR sample spectra can be quantified via univariate or multivariate analysis (MVA) techniques. It is assumed that the complexity of any sample to be analysed will need to make use of MVA techniques, although univariate analysis can be used if the sample analysis is simple enough i.e. one gas species over a low range.

The most common technique to apply MVA to FTIR data is the Classical Least Squares (CLS) or approach. For a CLS method, all of the species absorbing in the same wavelength region used for the analysis of the analyte need to be known. The concentration of all gases in the calibration set shall also be known.

Alternative analytical algorithms, such as partial least squares (PLS), inverse least squares (ILS) and others can also be applied. These alternative methods can offer benefits over CLS, such as PLS whereby the concentration of interfering gases in the calibration set does not need to be known.

10.3 Data quantification methodology

10.3.1 Calibration set

For each gas species to be measured, a set of reference spectra at a number of concentrations spanning the range of the required measurement should be collected. The analytical range is the maximum concentration spectrum in the calibration set. The reference spectra should be collected with, or have the same collection parameters as the sample spectra i.e. resolution, temperature, path length, pressure and interferogram processing settings. External library (e.g. NIST) or synthetic (e.g. derived from HITRAN database) reference spectra can only be used if suitable checks have been done to ensure compatibility with the sample spectrum for the instrument used.

For FTIR instruments with low resolution in measuring gases with narrow spectral features, i.e. CH_4, non-linear responses (deviation from Beer's law) are observed. Any non-linearity should be accounted for by including more calibration points in the method and ensuring non-linearity correction techniques are present in the analysis software. Analysis techniques such as PLS can account for non-linearity in the analysis algorithm.

Reference spectra of all interfering species which will be present in the gas sample at appropriate concentrations shall also be included in the calibration set.

Reference spectra can be pre-processed in a suitable manner before being used to for analysis. This includes, but is not limited to, mean-centring, variance scaling, peak-fitting and baseline correction. Some manufacturer's software can apply propriety pre-processing to data. It should be ensured that the same processing is consistently applied to all data; calibration, validation and sample.

10.3.2 Analysis band selection

An analysis band will need to be chosen for each gas species to be measured. The selection of analytical band should be made based on the following selection criteria:

— it should be the primary region in which specific gas has its major spectral absorption;

— avoid areas of interfering gas overlap, if possible;

— avoid areas of water and CO_2 absorption, if possible;

— ensure that the absorption peaks are minimized (under 0.6 absorbance unit), if possible, to reduce the effects of non-linearity. A detailed pictorial example of analysis band choice is shown in Annex C and D.

10.3.3 Lack of fit (linearity) of the analytical software

The analytical software (either directly, or indirectly via exporting) should be able to report predicted versus actual values for the calibration data to show a linear response over the required measurement range in the analytical band of choice.

The linearity deviation shall not be outside the limits of ±2 % of range.

10.3.4 Validation of analytical model

Validation data (data previously unseen by the model) should be used to challenge the method built with reference spectra. The predicted concentrations from the validation spectra should be compared to the known concentration values. The Standard Error of Validation (SEV) should be used to determine the accuracy of the analytical algorithm. SEV is calculated by Formula (2).

$$SEV = \left[\sqrt{\frac{\sum_{i=1}^{n} (C_{\mathrm{CLS},i} - C_{\mathrm{VAL},i})^2}{n-1}} \right] \tag{2}$$

where

C_{CIS} is the known concentration from the reference spectra;

C_{VAL} is the predicted concentration from the validation spectra;

n is number of spectral points.

The value for SEV shall be <2 % of the range of the calibration.

The quality analysis of the chemometrics shall be conducted before each measurement. The general procedure is as follows:

1) use 2 data sets: reference spectra and validation spectra;

2) build analysis with reference spectra;

3) check analysis with validation spectra.

The error derived from the analysis of the chemometrics should be within ±2 % of a maximum of the measurement range.

For example, when the concentration of CH_4 is in the range from 0 to 100 mg/m^3, the reference spectra at 10, 20, 40, 50, 60, 90, 100 mg/m^3 and the validation spectra at 30 mg/m^3 and 70 mg/m^3 are set. Then the model is built with reference spectra and the results of the validation are checked. The validation results should be 30 mg/m^3 ± 2 mg/m^3 and 70 mg/m^3 ± 2 mg/m^3.

10.3.5 Sample analysis

The data analysis method can be predefined and applied to the FTIR instrument before the sample collection, to give real-time measurements if needed. This is most appropriate for well-defined, repeatable processes.

For changing or new processes, as is more common with VOC measurements, it is not always possible to predefine a complete analysis method before sampling. In this case, an algorithm analysis method based on the best-available information on the process should be applied. The analytical algorithm can then be revised offline before final results issued.

It is to be confirmed that the analytical software can recalculate the analysis offline on the saved sample spectra, for this purpose.

10.3.6 Sample result validation

Along with the concentration predications from analysis, the analytical report should:

— state if concentration values are outside the range of the analysis, for each spectrum;

— state if the sample spectra residual is high, for each spectrum analysed;

— produce residual and predicated spectra for comparison with the sample, for each spectrum.

If the analytic report shows that any samples are out of range or have a high residual, a revision to the analysis method is needed. The method should be altered, either with further reference spectra added to the calibration set or with a revision to the analysis bands, and the sample data re-processed to account for all variations.

10.3.7 Residual check

A minimum of three residual checks shall be carried out on the sample data for each gas measured: one at or close to the maximum concentration value recorded during the sampling; one at or close to the minimum concentration value recorded during the sampling; and one at or close to the average concentration value recorded during the sampling.

Alternative analytical algorithms have different methods of residual derivation. However, as a minimum, a residual spectrum shall be constructed for each of the three residual checks (either automatically or via manually generation of synthetic residual) where the residual spectrum is the predicted spectrum subtracted from the spectrum of sample.

A large residual spectrum indicates:

— a possible interfering gas species not accounted for in the calibration method; or

— a higher range sample spectrum than accounted for in the calibration method; or

— a high level of noise in the sample spectrum, possibly due to instrument performance degradation.

A scalar residual can be derived from the residual spectrum and pass/fail placed on this value, as indicated by the manufacturer's software. The residual should be below 5 %.

11 Validation and uncertainty

This ensures that the measurement uncertainty is representative of the application at the specific plant. The results of validation and uncertainties for the determination of concentrations of VOCs in the waste gases from painting and printing processes are described in Annex E.

Annex A
(normative)

Determination of the FTIR performance parameters

A.1 Check the instrument resolution and minimum instrumental linewidth

Verify and record the system resolution by flowing ambient air through the gas sample cell, and allowing the pressure of the cell to stabilize at sub-atmospheric pressure (approximately 13,3 kPa). Collect an absorbance spectrum and measure the resolution at the ½ width and ½ maximum height of the water vapour lines in the region 1 918 cm^{-1}, or from 3 045 to 3 050 cm^{-1} or other suitable region that remains constant. It shall be checked that FWHM (full wide half maximum) is within 1 cm^{-1} ± 0,15 cm^{-1}. This test is not applicable for medium to low resolution instruments and instruments with sample cells at atmospheric pressure. This test can be replaced by the residual check in 10.3.7. If there is an issue with line position and shape, the residual will show this.

A.2 Wavenumber reproducibility

Determine the system line position by flowing ambient air through the gas sample cell and acquiring a spectrum. Determine and record the wavelength that corresponds to the maximum peak absorbance (line position) of water vapour in the region 1 918 cm^{-1}, or from 3 045 cm^{-1} to 3 050 cm^{-1} (or another suitable spectral region that remains consistent). It shall be checked that the peak of water at 1 918 cm^{-1} is within ±0,15 cm^{-1}.

As in A.1, this can be replaced by a residual check.

A.3 Detector linearity

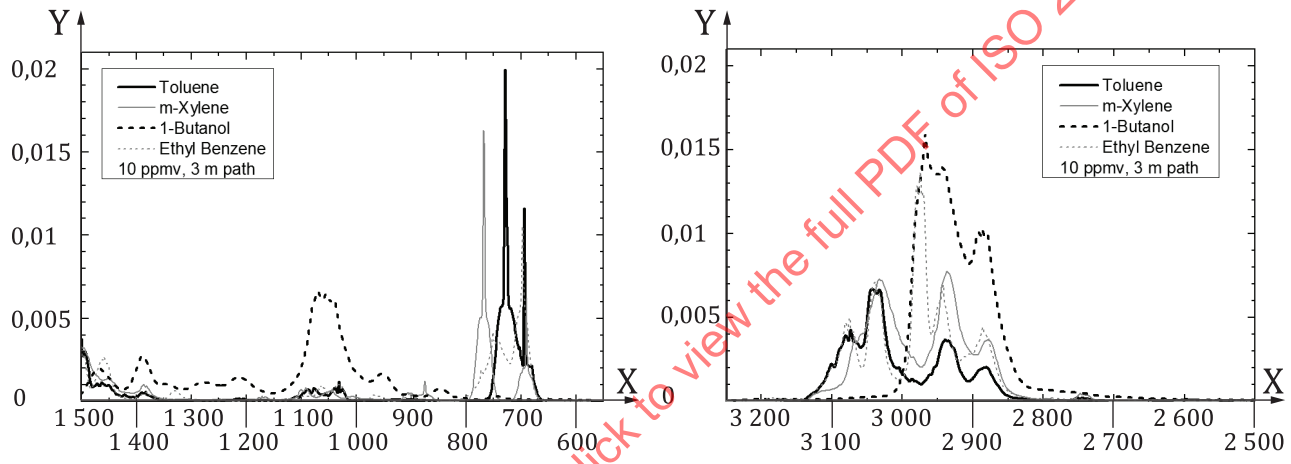
Mix the calibration verification gas with zero gas at three different concentrations and note the lack of fit of the concentration readings. If all three readings are within 2,0 % of the target value, the instrument response is sufficiently linear and the test is passed. The digital signal processing electronics of the FTIR spectrometer or the data quantification software may include linearization correction algorithms. Therefore the test is performed with test gas so that these are taken into account. If the test is not passed, refer to instrument manufacturer for corrective action.

Annex B
(informative)

Example for IR spectral absorption features of VOCs

This annex gives information about the overlapped spectrum of typical VOC mixture sample in waste gases from painting and printing processes.

The IR spectra of VOCs (toluene, *m*-xylene, ethylbenzene, 1-butanol) for painting process at 10 ppm and 3 m in path length, 2 cm^{-1} of resolution are synthesized on the basis of the IR database of National Institute of Standards and Technology (NIST) as shown in Figure B.1. For printing process IR spectra of VOCs (toluene, 1-butanol, 2-propanol, methylethyl ketone, ethyl acetate) synthesized as well as same procedure of Figure B.1 are shown in Figure B.2.



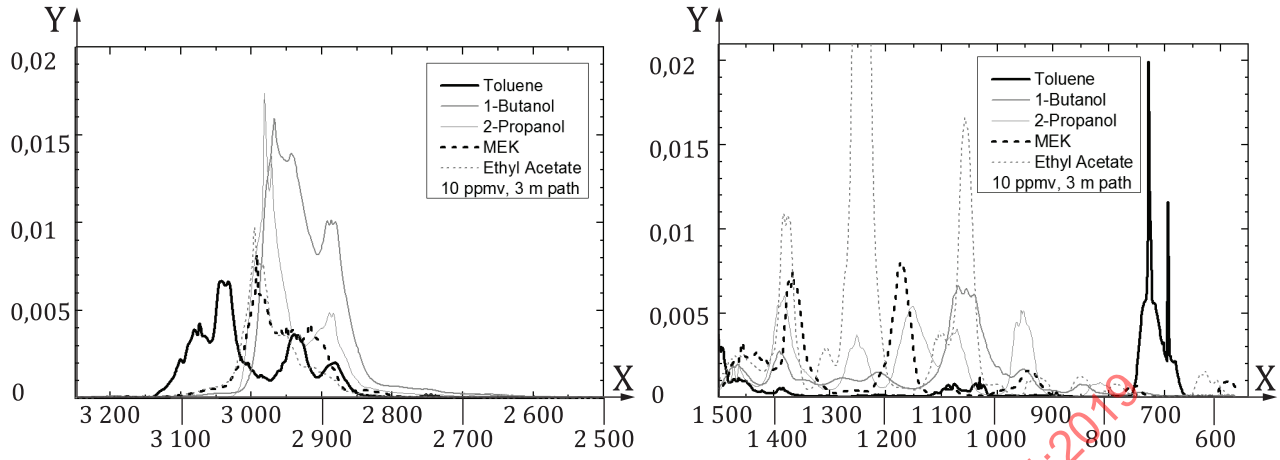
Key

X wavenumber (cm^{-1})

Y absorbance

Figure B.1 — The IR spectra of toluene, *m*-xylene, 1-butanol, and ethylbenzene

For Figure B.1, IR spectra of three aromatic compounds and one alcohol are overlapped in the region from 2 800 cm^{-1} to 3 100 cm^{-1}. The fingerprint peaks of toluene, *m*-xylene and ethylbenzene are present in the region from 800 cm^{-1} to 650 cm^{-1}. The 1-butanol has an intense peak in the range from 1 000 cm^{-1} to 1 100 cm^{-1}.



Key

X wavenumber (cm^{-1})

Y absorbance

Figure B.2 — The IR spectra of toluene, 1-butanol, 2-propanol, methylethyl ketone and ethyl acetate

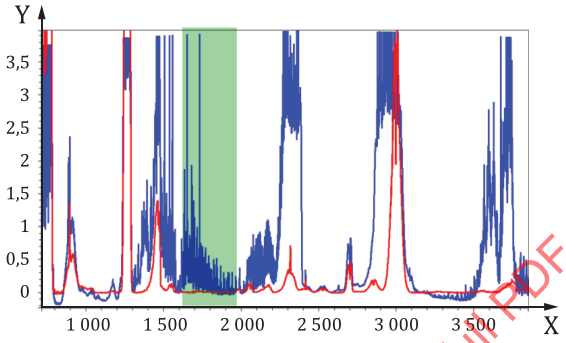
For Figure B.2, these compounds are selected as representatives of aromatic, alcohol, ketone and ester compounds which have a fingerprint region (650 cm^{-1} to 1 400 cm^{-1}) assigned to C-O or C-O-C stretching. The IR spectra assigned to C-H stretching vibration of all kinds of VOCs in the range from 3 100 cm^{-1} to 2 800 cm^{-1}. Toluene has the intense IR absorption in the region from 3 050 cm^{-1} to 3 150 cm^{-1} and at 710 cm^{-1}.

Annex C
(informative)

Examples for analytical band choice

Figures C.1 to C.6 show several examples of analytical bands to be chosen or not for quantification of dichloromethane (red spectrum). The blue spectrum is the typical sample spectrum from the waste gas.

1. Regions where no specific features for dichloromethane exist should not be chosen.



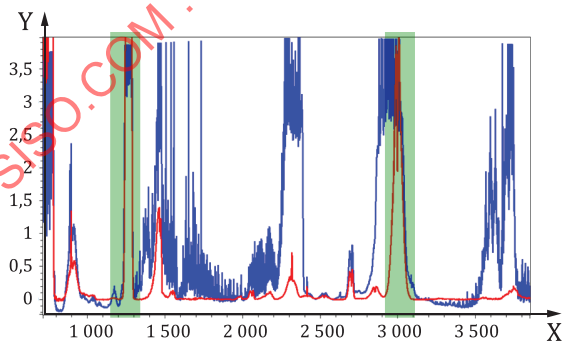
Key

X wavenumber (cm^{-1})

Y absorbance

Figure C.1 — The typical sample spectrum from the waste gas

2. Regions where sample peaks are off scale should not be chosen.



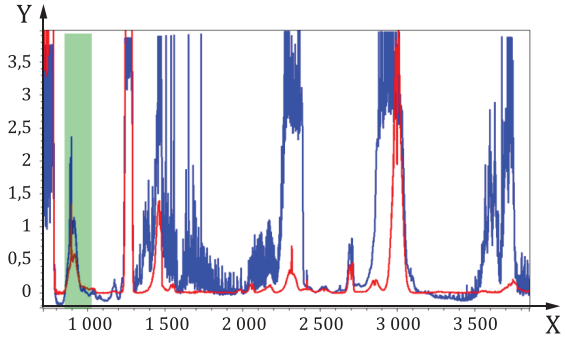
Key

X wavenumber (cm^{-1})

Y absorbance

Figure C.2 — The typical sample spectrum from the waste gas

3. Regions over 0,6 absorbance unit should not be chosen.



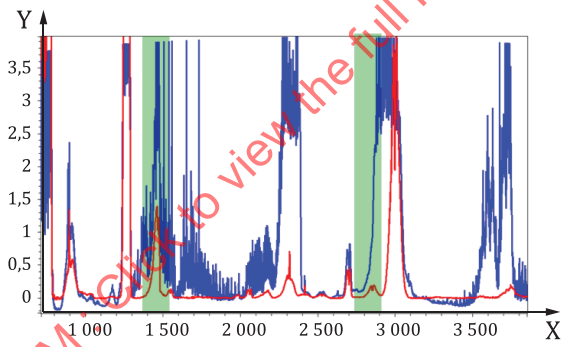
Key

X wavenumber (cm^{-1})

Y absorbance

Figure C.3 — The typical sample spectrum from the waste

4. Regions with large amounts of interference should be avoided.



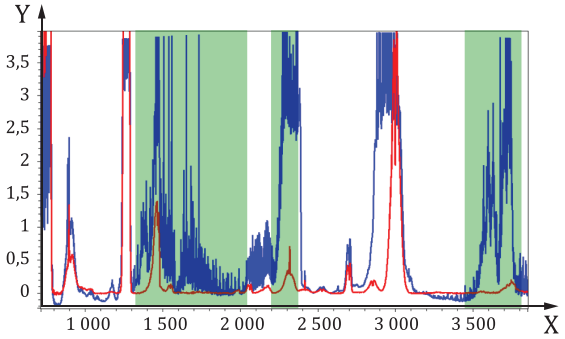
Key

X wavenumber (cm^{-1})

Y absorbance

Figure C.4 — The typical sample spectrum from the waste

5. Avoid regions of water and carbon dioxide absorption if possible.



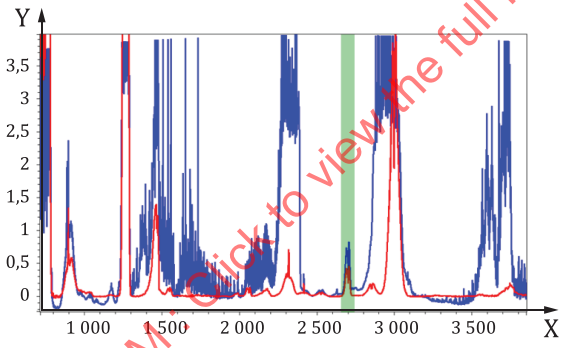
Key

X wavenumber (cm^{-1})

Y absorbance

Figure C.5 — The typical sample spectrum from the waste

6. In this example the band highlighted below is the most suitable analysis band.



Key

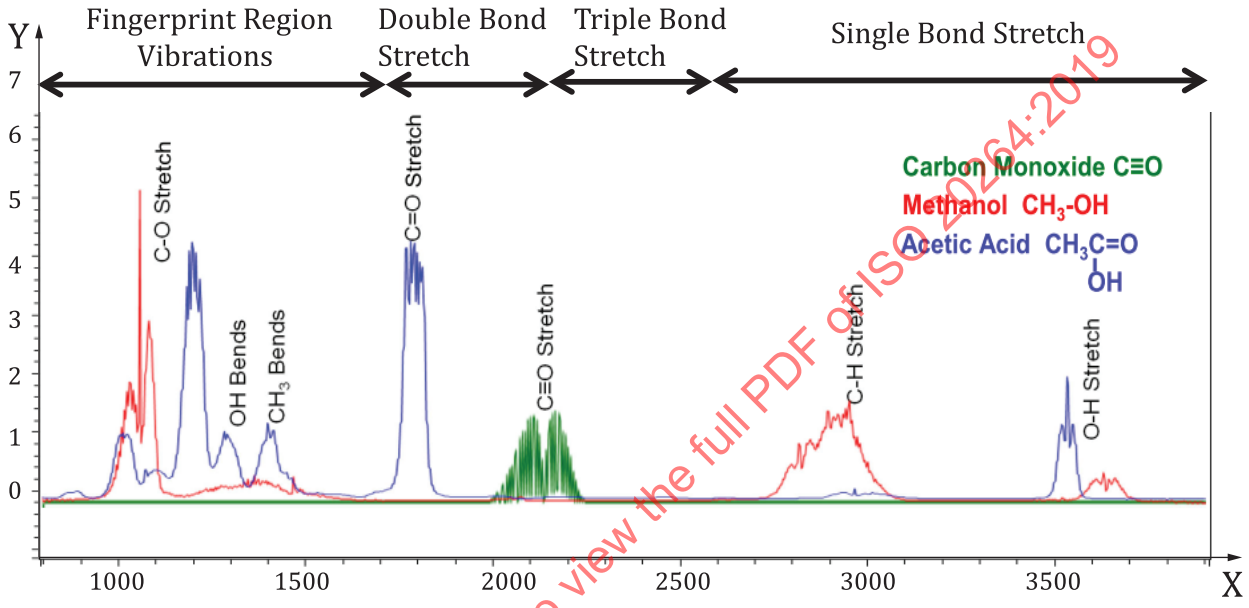
X wavenumber (cm^{-1})

Y absorbance

Figure C.6 — The typical sample spectrum from the waste

Annex D
(informative)

The typical spectral regions for the different bond types of VOCs



OH stretch- free OH	3 610-3 645 (sharp)	C=-C stretch : C-C=-C-C=-CH	2 040-2 200
OH stretch-intramolecular bond	3 450-3 600 (sharp)	C=O stretch: non conjugated	1 700-1 900
OH stretch-intramolecular bond	3 200-3 550 (broad)	C=O stretch: conjugated	1 590-1 750
chelates	2 500-3 200 (v broad)	C=O stretch: amides	~1 650
NH stretch- free NH	3 300-3 500	C=C stretch: non conjugated	1 620-1 680
NH stretch-H bonded NH	3 070-3 350	C=C stretch: conjugated	1 585-1 625
CH stretch : =-C-H	3 280-3 340	CH bend: CH_2	1 405-1 465
CH stretch : =C-H	3 000-3 100	CH bend: CH_3	1 355-1 395, 1 430-1 470
CH stretch : C-CH_3	2 862-2 882, 2 652-2 972	C-O-C vibration: formates	~1 175
CH stretch : O-CH_3	2 815-2 832	C-O-C vibration: acetates	~1 240, 1 010-1 040
CH stretch : N-CH_3 (aromatic)	2 810-2 820	C-O-C vibration: benzoates	~1 275
CH stretch : N-CH_3 (aliphatic)	2 780-2 805	C-OH stretch : cyclic alcohols	990-1 060
CH stretch : -CH_2	2 843-2 863, 2 916-2 936	CH bend: -CH=CH_2	905-915, 985-995
CH stretch : -CH	2 880-2 900	CH bend: -CH=CH-cis	650-750

SH stretch : free SH	2 550-2 600	CH bend: -CH=CH-trans	960-970
C=-N stretch non conjugated	2 240-2 260	CH bend: -CH=CH_2	885-895
C=-N stretch conjugated	2 215-2 240		
C=-C stretch : C=-CH terminal	2 100-2 140		
C=-C stretch : C-C=-C-C	2 190-2 260		

Annex E
(informative)

The validation of measurement of individual VOC in waste gas

E.1 General

Field tests for determination of individual VOCs in waste gas from a painting process and a printing process by using two kinds of FTIR and GC-PID were conducted for validation of measurement uncertainty. Individual VOCs in the waste gas from the painting process consisted of toluene, *m*-xylene, 1-butanol and ethyl benzene, and those from the printing process were toluene, methyl ethyl ketone (MEK), 2-propanol, ethyl acetate and propyl acetate. The set of measurement conditions of two FTIRs is shown in Table E.1.

Table E.1 — Set of conditions for two FTIRs

	Optics	**Detector**	**Resolution** (cm^{-1})	**Scan time** (scan/min)	**Measurable** wavelength (cm^{-1})
FTIR A	ZnSe	DTGS	1	3	550-8 500
FTIR B	ZnSe	MCT	8	10	600-4 200
	Cell temp. (°C)	Cell volume (l)	Cell path length (m)	Algorithm	Sampling rate (l/min)
FTIR A	180	0,3	4,2	PLS	2,5
FTIR B	180	0,4	2,5	CLS	3,0

E.2 Validation of measurement of VOCs by comparision with two measuring FTIR systems

E.2.1 The results of measurement of individual VOCs from painting and printing processes

The results of measurement of individual VOCs from painting processes are shown in Tables E.2, E.3, E.4 and E.5.

Table E.2 — The results of concentration of toluene measured from the painting process

Toluene		
Index j	**FTIR A system** $y_{1,j}$ mg/m³	**FTIR B system** $y_{2,j}$ mg/m³
1	70,6	95,6
2	82,1	100,0
3	85,5	100,2
4	69,3	101,5
5	212,0	233,6
6	220,3	237,5
7	215,3	234,7

Table E.2 *(continued)*

Toluene		
Index j	**FTIR A system** $y_{1,j}$ mg/m^3	**FTIR B system** $y_{2,j}$ mg/m^3
8	243,2	233,2
9	318,1	369,2
10	324,2	375,0
11	326,2	371,4
12	312,6	371,9

Table E.3 — The results of concentration of *m*-xylene measured from the painting process

***m*-xylene**		
Index j	**FTIR A system** $y_{1,j}$ mg/m^3	**FTIR B system** $y_{2,j}$ mg/m^3
1	13,1	14,1
2	19,4	19,6
3	13,8	17,7
4	29,5	21,9
5	29,8	19,1
6	21,6	22,0
7	19,4	23,1
8	32,3	37,3
9	36,9	34,6
10	31,2	35,9
11	32,0	35,9

Table E.4 — The results of concentration of ethyl benzene measured from the painting process

Ethyl benzene		
Index j	**FTIR A system** $y_{1,j}$ mg/m^3	**FTIR B system** $y_{2,j}$ mg/m^3
1	23,0	27,0
2	24,3	27,3
3	22,7	26,7
4	58,4	44,6
5	53,3	43,2
6	51,7	43,8
7	64,4	45,3
8	87,6	69,8
9	86,9	68,1
10	88,4	69,8
11	86,3	70,1