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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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Contents

Page

Foreword

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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

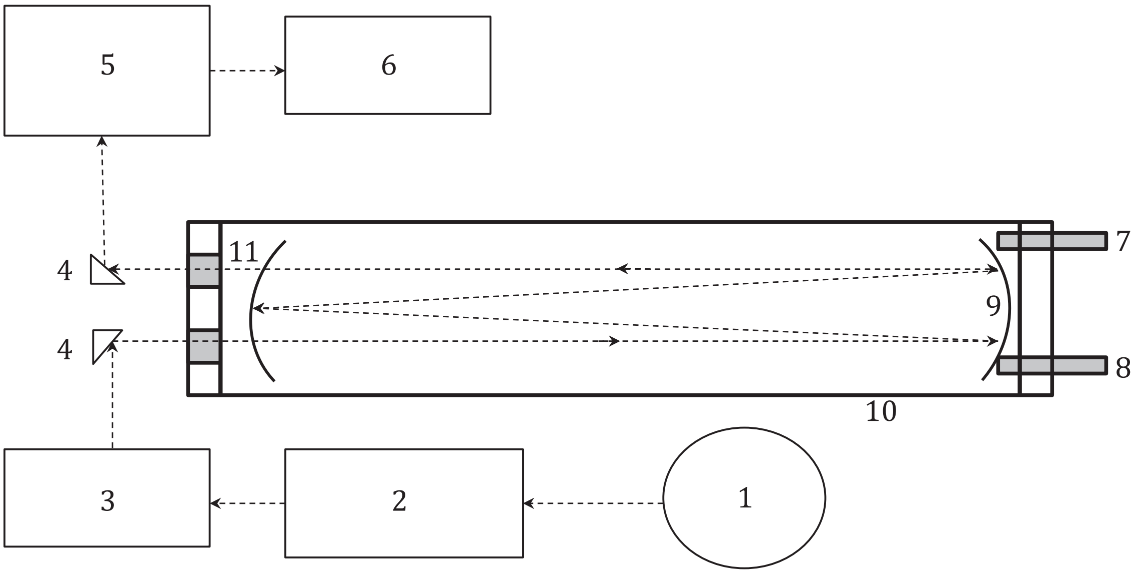
5 Measurement principle

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

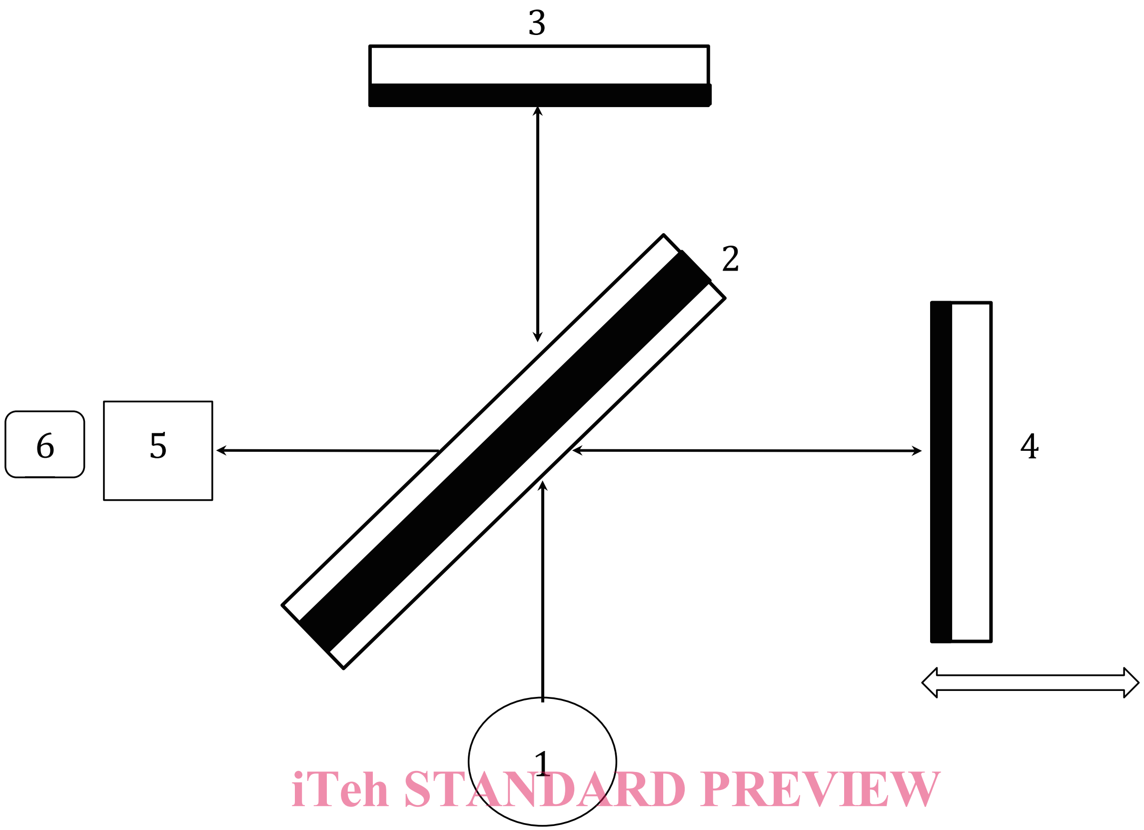
1	IR source
2	aperture or filter 1 (optional)
3	interferometer
4	focusing optics
5	aperture or filter 2 (optional)
6	IR detector
7	absorption cell exhaust
8	absorption cell inlet
9	mirror
10	absorption cell
11	infrared window

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.

$$\log\left(\frac{I_0}{I}\right) = -\log\left(\frac{1}{T}\right) = A = \alpha lc \qquad (1)$$

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 absorptivity;

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.