
**Stationary source emissions —
Determination of total volatile organic
compounds (TVOCs) in waste gases
from non-combustion processes — Non-
dispersive infrared analyser equipped
with catalytic converter**

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Émissions de sources fixes — Détermination des composés organiques volatils totaux (COVTs) dans les effluents gazeux des processus sans combustion — Analyseur à infrarouge non dispersif équipé d'un convertisseur catalytique

ISO 13199:2012

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Contents	Page
Foreword	iv
Introduction	v
1 Scope	1
2 Normative references	1
3 Terms and definitions	1
4 Symbols and abbreviated terms	3
5 Principle	4
5.1 Method of measurement	4
5.2 Analyser equipment	6
5.3 Performance criteria fulfilment	6
6 Performance criteria and determination of the performance characteristics	6
6.1 Performance criteria	6
6.2 Determination of the performance characteristics and measurement uncertainty	6
7 Measurement procedure	8
7.1 General	8
7.2 Choice of the measuring system	8
7.3 Sampling	8
7.4 Data collection	8
7.5 Calculation	9
8 Quality assurance and quality control procedures	9
8.1 General	9
8.2 Frequency of checks	9
8.3 AMS for intermittent measurements	9
8.4 Permanently installed AMS	11
9 Test report	13
Annex A (informative) Schematic diagrams of NDIR analysers	14
Annex B (normative) Operational gases	17
Annex C (normative) Procedures for determination of the performance characteristics during the general performance test	19
Annex D (informative) Example of assessment of compliance of the NDIR method	23
Annex E (informative) Results of comparison tests	26
Bibliography	30

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

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

ISO 13199 was prepared by Technical Committee ISO/TC 146, *Air quality*, Subcommittee SC 1, *Stationary source emissions*.

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Introduction

Volatile organic compounds (VOCs) play significant roles in atmospheric chemistry, especially the formation of photochemical oxidants and/or ozone (O₃) and suspended particulate matter (SPM), which are known to have negative impacts on human health and biological systems. There are many areas of the world where their atmospheric concentrations are close to or above the level of the WHO guidelines for environmental standards in each nation. It is therefore strongly required in many nations to reduce the emission of VOC from various anthropogenic sources.

In order to manage VOC emission from stationary emission sources, it is essential for enterprises to evaluate the quantity of VOCs emitted from their facilities where organic solvents as well as other chemicals are used for industrial processes like painting, printing, cleaning, and degreasing.

A technique for continuously and precisely measuring the concentration of total VOCs (TVOCs) in waste gases emitted from ducts to atmosphere, which is easy to operate and to maintain, is very helpful for both governments and enterprises to control and reduce VOC emissions. This measurement method, based on the use of an NDIR analyser equipped with a catalytic converter for oxidation of TVOCs to CO₂, has some advantages compared to measurement methods using flame ionization detection (FID) and FID–GC (flame ionization detection–gas chromatography), namely:

- a) high-safety operation is possible, since no flame and no hydrogen are used;
- b) response factors of individual VOCs are not different from each other;
- c) no interference due to oxygen is observed.

Note, however, that this method is not applicable to waste gas from combustion processes.

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Stationary source emissions — Determination of total volatile organic compounds (TVOCs) in waste gases from non-combustion processes — Non-dispersive infrared analyser equipped with catalytic converter

1 Scope

This International Standard specifies the principle, the essential performance criteria and quality assurance/quality control (QA/QC) procedures of an automatic method for measuring total volatile organic compound (TVOC) content in waste gases of stationary sources, using a non-dispersive infrared absorption (NDIR) analyser equipped with a catalytic converter which oxidizes VOC to carbon dioxide.

This method is suitable for the measurement of TVOC emissions from non-combustion processes. This method allows continuous monitoring with permanently installed measuring systems, as well as intermittent measurements of TVOC emissions.

The method has been tested on field operation for painting and printing processes, where TVOC concentrations in the waste gases were from about 70 mg/m³ to 600 mg/m³.

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.

ISO 9169:2006, *Air quality — Definition and determination of performance characteristics of an automatic measuring system*

ISO 14956, *Air quality — Evaluation of the suitability of a measurement procedure by comparison with a required measurement uncertainty*

ISO 20988, *Air quality — Guidelines for estimating measurement uncertainty*

3 Terms and definitions

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

3.1 automatic measuring system AMS

measuring system interacting with the waste gas under investigation, returning an output signal proportional to the physical unit of the measurand in unattended operation

NOTE 1 Adapted from ISO 9169:2006, 2.1.2.

NOTE 2 In the sense of this document, an AMS is a system that can be attached to a duct to continuously or intermittently measure and record TVOC mass concentrations passing through the duct.

3.2 analyser analytical part in an extractive or *in situ* AMS

[ISO 12039:2001,^[3] 3.3]

3.3 calibration of an automatic measuring system
procedure for establishing the statistical relationship between values of the measurand indicated by the automatic measuring system and the corresponding values given by an independent method of measurement implemented simultaneously at the same measuring point

3.4 interference
negative or positive effect upon the response of the measuring system, due to a component of the sample that is not the measurand

3.5 interferent interfering substance
substance present in the air mass under investigation, other than the measurand, that affects the response

[ISO 9169:2006, 2.1.12]

3.6 lack of fit
systematic deviation, within the range of application, between the accepted value of a reference material applied to the measuring system and the corresponding result of measurement produced by the measuring system

[ISO 9169:2006, 2.2.9]

3.7 mass concentration
concentration of a substance in a waste gas expressed as mass per volume

NOTE 1 Adapted from ISO 12039:2001,^[3] 3.10.

NOTE 2 Mass concentration is often expressed in milligrams per cubic metre (mg/m³).

3.8 measurand
particular quantity subject to measurement

[ISO/IEC Guide 98-3:2008,^[4] B.2.9]

EXAMPLE The TVOC mass concentration (mg/m³) in waste gas.

3.9 performance characteristic
one of the quantities assigned to equipment in order to define its performance

NOTE Performance characteristics can be described by values, tolerances or ranges.

3.10 period of unattended operation
maximum interval of time for which the performance characteristics remain within a predefined range without external servicing, e.g. refill, adjustment

[ISO 9169:2006, 2.2.11]

NOTE The period of unattended operation is often called maintenance interval.

3.11 residence time
time period for the sampled gas to be transported from the inlet of the probe to the inlet of the measurement cell

3.12**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

[ISO 9169:2006, 2.2.4]

3.13**span gas**

gas or gas mixture used to adjust and check a specific point on a calibration curve

NOTE Adapted from ISO 12039:2001,^[3] 3.4.1.

EXAMPLE Normally a mixture of propane and air is used.

3.14**span point**

value of the output quantity (measured signal) of the automatic measuring system for the purpose of calibration, adjustment, etc. that represents a correct measured value generated by reference material

3.15**standard uncertainty**

uncertainty of the result of measurement expressed as a standard deviation

[ISO/IEC Guide 98-3:2008,^[4] 2.3.1]

NOTE The standard uncertainty of a result of measurement is an estimate of the standard deviation of the population of all possible results of measurement which can be obtained by means of the same method of measurement for the measurand exhibiting a unique value.

3.16**total volatile organic compounds
TVOCs**

by convention, total organic compounds present with a partial pressure below their saturated vapour pressure at ambient air pressure and temperature

NOTE Measured TVOC values (mass concentration or volume concentration) are usually referred to carbon.

3.17**uncertainty (of measurement)**

parameter, associated with the result of a measurement, that characterizes the dispersion of the values that could reasonably be attributed to the measurand

[ISO/IEC Guide 98-3:2008,^[4] 2.2.3]

3.18**zero gas**

gas or gas mixture used to establish the zero point on a calibration curve within a given concentration range

[ISO 12039:2001,^[3] 3.4.2]

3.19**zero point**

specified value of the output quantity (measured signal) of the AMS and which, in the absence of the measured component, represents the zero crossing of the calibration line

4 Symbols and abbreviated terms

γ TVOC mass concentration

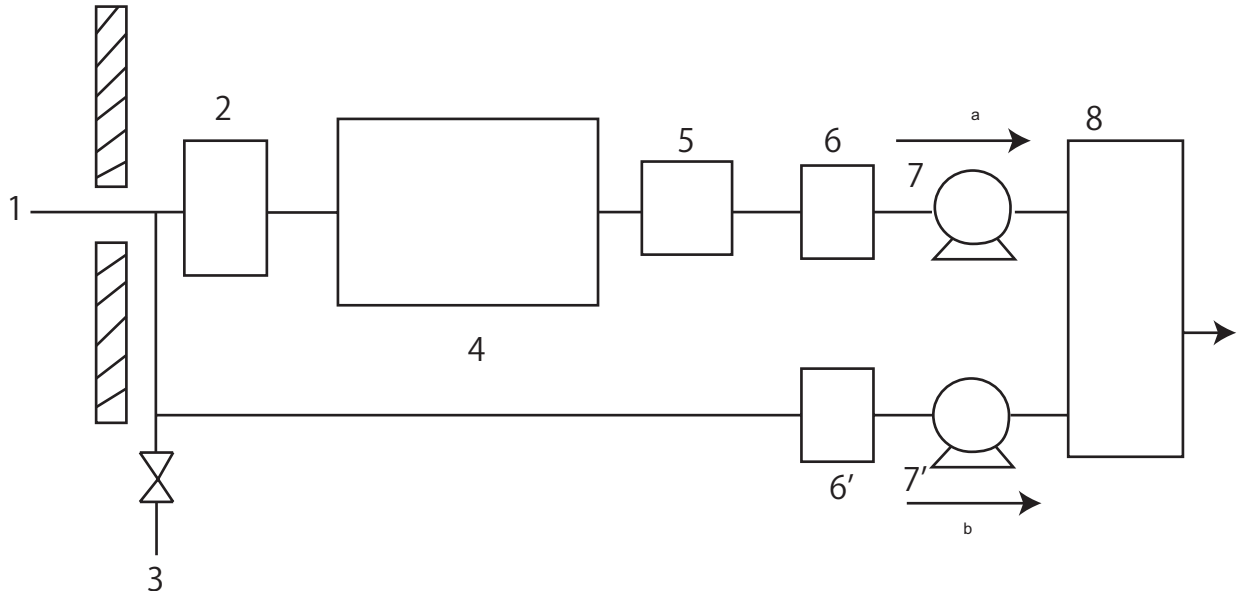
$\bar{\gamma}$	grand mean of measured TVOC mass concentration
φ	TVOC volume fraction (= 10^{-6})
e_i	residual (lack of fit) at level i
k	coverage factor
M_C	molar mass of carbon (= 12 g/mol)
n	number of measurements
s_j	standard deviation of level j
$s_{r,j}$	standard deviation of repeatability
$s_{R,j}$	standard deviation of reproducibility
u	standard uncertainty of TVOC mass concentration
$u(\gamma_{\text{TVOC}})$	combined uncertainty of TVOC mass concentration
$U(\gamma_{\text{TVOC}})$	expanded uncertainty of mass concentration
V_m	molar volume (22,4 l/mol)
$C_{V,r}$	coefficient of variation of repeatability
$C_{V,R}$	coefficient of variation of reproducibility
$C_{V,u}$	coefficient of variation of the standard uncertainty
\bar{x}	average of the measured values x_i
x_i	i th measured value
\bar{x}_i	average of the measured value at level i
\hat{x}_i	value estimated by the regression line at level i
AMS	automatic measuring system
NDIR	non-dispersive infrared absorption
QA	quality assurance
QC	quality control

5 Principle

5.1 Method of measurement

The measuring system consists of a sample conditioning system and the NDIR analyser for measuring CO₂ equipped with the converter for oxidation of TVOCs to CO₂ as shown in Figure 1. A portion of sample gas (gas A) passes through the converter (and the moisture removal system), and goes into the NDIR analyser, while another portion of sample gas (gas B) passes through (the moisture removal system), and goes into the NDIR analyser. The difference in the CO₂ concentration between gas A and gas B is equal to the concentration of CO₂ which comes from TVOCs.

The converter consists of oxidation catalyst such as platinum metal which is heated to around 450 °C for complete oxidation of TVOCs to CO₂. To avoid possible damage to the NDIR analyser due to halogens such as chlorine and/or chloride produced when halogenated organic compounds are oxidized, a halogen scrubber containing adsorbent is placed after the converter. Figure 1 shows an example of the measuring system including an NDIR analyser plus converter.



Key

- | | | | |
|---|--|-------|-------------------------|
| 1 | sampling probe, heated (if necessary) | 5 | halogen scrubber |
| 2 | particle filter (heated, if necessary) | 6, 6' | moisture removal system |
| 3 | zero and span gas inlet | 7, 7' | pump |
| 4 | converter | 8 | NDIR analyser |
| a | Gas A. | b | Gas B. |

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Figure 1 — Diagram of the measuring system (example)

Sampling is the process of extracting a small portion which is truly representative of the composition of the main gas stream from a large quantity of waste gas.

A partial flow of the waste gas is directly fed into the NDIR analyser containing the catalytic converter via the sampling probe, the particle filter and the sampling line. The sampling device, including the filter to remove fine particles that could affect the NDIR analyser, is heated to avoid sample condensation, if necessary.

The sampling device shall:

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

NOTE Stainless steel, polytetrafluoroethylene or polypropylenefluoride are well-proven construction materials.

- b) be designed to ensure a sample residence time less than 60 s — with long sampling lines or high flow resistance, the use of an external pump with bypass is recommended;
- c) have a filtering device upstream of the sampling line to trap all particles liable to impair the operation of the apparatus;
- d) have an inlet for applying zero and span gases at close to the entry nozzle of the sampling probe, upstream of the filter.

5.2 Analyser equipment

The gas analysers use, as the measurement principle, the absorption of infrared radiation (IR) by the component measured in characteristic wavelength ranges. The analysers operate according to the non-dispersive IR (NDIR) method, while the selectivity of measurement is achieved by the radiation detector which is filled with the component to be measured. Schematic diagrams of a typical NDIR analyser for measuring TVOC mass concentration are given in Figures A.1, A.2, and A.3.

5.3 Performance criteria fulfilment

5.3.1 General. The automatic measuring system (AMS) based on the NDIR method shall comply with the performance criteria specified in Table 1. The associated performance characteristics are determined as specified in 5.3.2 to 5.3.4.

5.3.2 General performance test. The manufacturer of the measuring system shall demonstrate in a general performance test that the relevant performance criteria listed in Table 1 are fulfilled by the instrument type. The procedure of this general performance test shall comply with the relevant standards.

5.3.3 Ongoing quality assurance (QA) and quality control (QC) in the laboratory. The user of AMS shall demonstrate during regular laboratory tests conducted within the ongoing QC programme that the relevant performance criteria listed in Table 1 are fulfilled for the specific AMS.

5.3.4 Quality assurance during operation in the field. The user of AMS shall check during field operation that the relevant performance criteria listed in Table 1 are fulfilled.

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6 Performance criteria and determination of the performance characteristics

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6.1 Performance criteria <https://standards.iteh.ai/catalog/standards/sist/7c9009a-30e9-43d0-9972-64f30e5dbf11/iso-13199-2012>

Table 1 gives an overview of the relevant performance characteristics and performance criteria of the analyser and measurement system to be evaluated at three levels, during a general performance test, by means of ongoing QA/QC in the laboratory and during field operation. In the rightmost column, values included in the calculation of the expanded uncertainty are indicated.

6.2 Determination of the performance characteristics and measurement uncertainty

6.2.1 Performance test

The performance characteristics of the AMS shall be determined during the general performance test in accordance with applicable international or national standards. The values of the performance characteristics determined shall meet the performance criteria specified in Table 1. The procedures for the determination of these performance characteristics are described in Annex C.

The ambient conditions applied during the general performance test shall be documented.

The expanded uncertainty of the AMS measured values shall be calculated in accordance with ISO 14956 on the basis of the performance characteristics determined during the general performance test and shall meet the uncertainty specified for the measurement objective.

6.2.2 Ongoing quality control

The user shall check specific performance characteristics during ongoing operation of the measuring system with a periodicity specified in Table 2.

The measurement uncertainty during field application shall be determined by the user of the measuring system in accordance with applicable international or national standards. It can be determined by a direct or an indirect