BS EN 61207-6:2015

BSI Standards Publication

Expression of performance of gas analyzers

Part 6: Photometric analyzers

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National foreword

This British Standard is the UK implementation of EN 61207-6:2015. It is identical to IEC 61207-6:2014. It supersedes BS EN 61207-6:1994, which will be withdrawn on 30 December 2017.

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Expression of performance of gas analyzers -
Part 6:Photometric analyzers
(IEC 61207-6:2014)

Expression des performances des analyseurs de gaz -
Partie 6: Analyseurs photométriques
(IEC 61207-6:2014)

Angabe zum Betriebsverhalten von Gasanalysatoren -
Teil 6: Fotometrische Analysatoren
(IEC 61207-6:2014)

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Foreword

The text of document 65B/947/FDIS, future edition 2 of IEC 61207-6, prepared by SC 65B "Measurement and control devices", of IEC/TC 65 "Industrial-process measurement, control and automation" was submitted to the IEC-CENELEC parallel vote and approved by CENELEC as EN 61207-6:2015.

The following dates are fixed:

• latest date by which the document has to be implemented at national level by publication of an identical national standard or by endorsement	(dop)	2015-09-30
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This document supersedes EN 61207-6:1994.

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The text of the International Standard IEC 61207-6:2014 was approved by CENELEC as a European Standard without any modification.

Annex ZA
(normative)

Normative references to international publications with their corresponding European publications

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

NOTE 1 When an International Publication has been modified by common modifications, indicated by (mod), the relevant EN/HD applies.

NOTE 2 Up-to-date information on the latest versions of the European Standards listed in this annex is available here: www.cenelec.eu.

Publication	Year	Title	EN/HD	Year
IEC 60079-29-1	-	Explosive atmospheres - Part 29-1: Gas detectors - Performance requirements of detectors for flammable gases	EN 60079-29-1	-
IEC 60079-29-4	-	Explosive atmospheres - Part 29-4: Gas detectors - Performance requirements of open path detectors for flammable gases	EN 60079-29-4	-
IEC 60654	series	Operating conditions for industrial-process measurement and control equipment	EN 60654	series
IEC 61207-1	-	Expression of performance of gas analyzers - Part 1: General	EN 61207-1	-
IEC 61207-7	-	Expression of performance of gas analyzers - Part 7: Tuneable semiconductor laser gas analyzers	EN 61207-7	-
ISO 9001	-	Quality management systems - Requirements	EN ISO 9001	-

CONTENTS

INTRODUCTION

Photometric analyzers utilize detectors which respond to wavelengths in the ultraviolet, visible and infrared part of the electromagnetic spectrum within the wavelength range 0,1 μm to 50 μm (see Figure A.1). Within this range of wavelengths, many gases have absorption and/or emission bands. Analyzers designed to utilize these bands employ several techniques, including sensing of specific absorbed radiation by the sample gas or emitted radiation from the gas sample after artificial excitation. The volume of gas measured may be contained within a sample cell and this sample may or may not be conditioned, or (for in-situ analyzers) the concentration may be directly measured within the sample gas itself (see Figure A.2).

EXPRESSION OF PERFORMANCE OF GAS ANALYZERS –

Part 6: Photometric analyzers

1 Scope and object

This part of IEC 61207 applies to all aspects of analyzers using photometric techniques for the measurement of concentration of one or more components in a mixture of gases or vapors. It should be used in conjunction with IEC 61207-1.

For photometric analyzers utilizing tuneable semiconductor laser absorption spectroscopy (TSLAS) for gas measurements, IEC 61207-7 should also be referred to.

This part of IEC 61207 applies to analyzers using non-dispersive and dispersive wavelength selection and using absorption, emission, wavelength derivative or scattering techniques.

It applies to analyzers which receive either a conditioned or unconditioned sample of gas either under vacuum, at ambient pressure or pressurized.

It applies to analyzers which measure gas concentrations directly within the sample gas.

The object of this part is:

- to specify the terminology and definitions related to the functional performance of gas analyzers, utilizing a photometric analyzer, for the continuous measurement of gas or vapor concentration in a source gas;
- to unify methods used in making and verifying statements on the functional performance of such analyzers;
- to specify what tests should be performed to determine the functional performance and how such tests should be carried out;
- to provide basic documents to support the application of standards of quality assurance ISO 9001.

2 Normative references

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

IEC 60079-29-1, *Explosive atmospheres – Part 29-1: Gas detectors – Performance requirements of detectors for flammable gases*

IEC 60079-29-4, *Explosive atmospheres – Part 29-4: Gas detectors – Performance requirements of open path detectors for flammable gases*

IEC 60654 (all parts), *Operating conditions for industrial-process measurement and control equipment*

IEC 61207-1, *Expression of performance of gas analyzers – Part 1: General*

IEC 61207-7, *Expression of performance of gas analyzers – Part 7: Tuneable semiconductor laser gas analyzers*

ISO 9001, *Quality management systems – Requirements*

3 Terms and definitions

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

NOTE The following definitions and examples of equipment and measuring techniques are for illustration and do not constitute a complete list of all possible measurement types. See Figure A.1 for the relationship between the different optical wavelength ranges.

3.1
light source

device that emits light within the wavelength range 0,1 μm to 50 μm

Note 1 to entry: A source may be, but is not limited to: a gas or solid state laser, semiconductor laser diode, light emitting diode, electric discharge source or incandescent filament.

3.2
light detector

device that is sensitive to light and that may be used to detect light within the wavelength range 0,1 μm to 50 μm

Note 1 to entry: A light detector may be, but is not limited to: a photomultiplier tube, semiconductor device (photovoltaic or photoconductive) such as a photodiode, avalanche photodiode or charge coupled device (CCD) and, additionally, in the infrared region: pyroelectric detector, bolometer or thermopile.

3.3
wavelength selection

wavelength or range of wavelengths selected for use in particular measurement

Note 1 to entry: A suitable wavelength transmission range may be selected by using an appropriate means including a band-pass optical filter or dispersive element such as a diffraction grating.

Note 2 to entry: The wavelength from the light source may be tuned or modulated such as by using the current or temperature for a semiconductor laser diode, varying the temperature of an incandescent source or varying the input angle to a band-pass filter.

3.4
optical sample cell

enclosed volume where the optical measurement of the sample gas takes place

Note 1 to entry: The optical measurement may take place by measuring the absorption or emission of the analyte after light of a suitable wavelength has been passed through an optical sample cell.

Note 2 to entry: The sample cell shall have some means of gas inlet and outlet, which may be via piping for flow or pressure driven systems or via diffusion through a mechanical filter.

Note 3 to entry: The cell may require a high integrity seal from the outside environment for extractive systems other than the gas inlet and outlet means.

Note 4 to entry: Cell windows of the appropriate optical transmission band are required for the light ingress and egress.

Note 5 to entry: Internal mechanical or optical features of the sample cell may be used to decrease stray light interference or to direct or concentrate the light where appropriate.

Note 6 to entry: The cell is designed to give an optical path length which is appropriate to the analyte and range required.

3.5
multi-pass sample cell

optical sample cell with increased effective absorption light path achieved by multiple reflections within the optical cavity of the sample cell

Note 1 to entry: The effect of the multi-pass cell is to increase the sensitivity of the measurement for the same total cell length.compared to a single pass cell.

Note 2 to entry: Typical design models used include Herriott or White cells.

3.6
environmental monitoring gas analyzer

photometric gas analyzer used for environmental monitoring purposes

3.6.1
open path monitoring

optical measurement where no containment for the sample gas is required

Note 1 to entry: This may be across a large space or an external measurement path.

Note 2 to entry: Typically, the light source and detector are separated by a distance and aligned to give a straight line absorption pathway.

Note 3 to entry: The net absorption will be the integrated effect across the whole of the absorption path length.

3.6.2
point monitoring

monitoring giving localized gas concentration information

Note 1 to entry: This gives monitoring information from a localized position rather than averaged data across an extended path length as per 3.6.1.

3.7
in-situ analyzer

analyzer where the volume of gas sensed, that is gas within the measuring path for a photometric analyzer, is situated within the process source fluid

Note 1 to entry: An in-situ analyzer may contain a fixed-length measuring cell within the duct and hence its calibration is not affected by the dimensions of the duct.

3.7.1
across duct or cross stack analyzer

analyzer where the measuring path is formed by the entire width of a process duct or stack

Note 1 to entry: The radiation source and detector can be mounted on opposite sides of the duct, or both can be mounted on the same side and a retroreflector employed. Where the retroreflector is within the duct, the analyzer is of the in-situ type.

3.7.2
across process line or pipe analyzer

analyzer where the measuring path is formed by the entire width of a process pipe

Note 1 to entry: The radiation source and detector can be mounted on opposite sides of the pipe, or both can be mounted on the same side and a retroreflector employed. Where the retroreflector is within the duct, the analyzer is of the in-situ type.

3.7.3
across firebox or other open process analyzer

analyzer where the measuring path is formed by the entire width of a firebox or other open process path

3.7.4
inside process line or duct analyzer

analyzer where the measuring path or point is inside the process duct itself

3.8
extractive analyzer
analyzer which receives a continuous stream of gas withdrawn from a process by a sample handling system

3.8.1
close coupled extractive analyzer
gas analyzer where the sensors are mounted at, or as close as possible to, the process take off point with a short extraction loop (typically <1 m) and with minimal sample handling, typically just particulate filtration

3.8.2
remote extractive analyzer
gas analyzer which is situated remote from the process to be measured (typically >1 m)

Note 1 to entry: This may require further sample handling, including maintaining the sample at an elevated temperature to avoid condensation.

3.9
sample-handling system
system which connects one or more process analyzers with the source fluid and the disposal points

Note 1 to entry: The performance of this system is not dealt with in this part except for dilution sampling systems.

3.10
dilution sampling system
system which samples process fluid and adds a diluent to the sample stream prior to measurement

Note 1 to entry: This type of system generally applies calibration gas prior to the dilution point and hence the dilution system is treated as part of an in-situ analyzer for the purposes of this part of IEC 61207.

3.11
conditioned sample
continuous stream of gas withdrawn from the source gas and filtered, cooled, and dried to within specified limits before application to a sampling analyzer

3.12
heated sample
continuous stream of gas withdrawn from the source gas, which may or may not be filtered but is maintained at a temperature above its dew-point, including within the analyzer

3.13
opacity
absorption of radiation, at the wavelengths used for measurement, by components of the sample gas, other than the component to be measured

Note 1 to entry: For example, this may be produced by dust or other contamination.

3.14
essential ancillary units
units without which the analyzer will not operate, e.g. ancillary electronic units processing sensor signals to produce the reading, dilution sampling system, air purge or other optical cleaning system, automatic calibration system, temperature or pressure compensation system

3.15

analyzers using light absorption

analyzers which detect the amount of light absorbed by a gas of interest from a light source through a sample gas to a light detector at a particular wavelength or wavelength range in order to determine its concentration

3.15.1

infrared absorption analyzer

electro-optical instrument consisting of a single source or multiple sources of infrared radiation and one or more infrared detectors separated from the source by a measuring path, wherein the specific spectral absorption of the component of interest is determined within the wavelength range 0,7 μm to 50 μm

Note 1 to entry: For the purpose of this part of IEC 61207, the analyzer is adjusted by the manufacturer to select only the spectral band(s) at which the component to be determined has its characteristic absorption, and the measuring path dimensions are appropriate for the rated range of concentration and application of the analyzer.

Note 2 to entry: Specific spectral sensitivity is obtained by a selective component such as a selective source, selective detector or selective filter, gas-filled cell or dispersive element, or any combination of these components.

3.15.2

ultraviolet (visible) absorption analyzer

analyzer as defined in 3.15.1 but where the spectral absorption of the component determined occurs at wavelengths between 0,1 μm and 0,7 μm, hence the source(s), detector(s) and other optical components operate in the visible light or ultraviolet part of the electromagnetic spectrum

Note 1 to entry: The visible part of the spectrum is included in this definition for ease of reference.

3.15.3

dual-beam analyzer

analyzer whereby the radiation passage through the measured gas and a reference gas follows separate physical paths

3.15.4

single-beam analyzer

analyzer whereby the radiation follows a single path through the sample gas, and measuring and reference signals are derived from wavelength selection (see 3.3 for example), or for a single-beam single-wavelength analyzer, no reference signal is generated

3.15.5

dual-wavelength filter-correlation analyzer

analyzer where measuring and reference signals are derived by optical filter wavelength selection within and outside an absorption band respectively

Note 1 to entry: These two signals are processed to derive a concentration value.

3.15.6

gas filter correlation analyzer

analyzer where measuring and reference signals are derived by utilizing a cell (gas filter) filled with the gas to be measured to absorb selectively radiation corresponding to the fine structure of the absorption line spectrum of that gas and another, otherwise identical cell, filled with a non-absorbing reference gas

Note 1 to entry: The two signals are processed to derive a concentration value.

Note 2 to entry: The gas-filled filter component may be part of the detector.

3.15.7
direct absorption analyzer

absorption measurements where the change in signal magnitude at the light detector due to optical absorption by the gas of interest is directly used as a means to determine the concentration of the gas of interest in a sample gas

3.15.8
wavelength derivative analyzer

analyzer which measures gas-component concentrations using wavelength modulation of the radiation, and thereby uses the first derivative or second derivative of intensity versus wavelength to measure the shape of the absorption band

3.15.9
tuneable semiconductor laser absorption spectroscopy
TSLAS

method of gas measurement using a tuneable semiconductor laser diode to determine the amount of light absorbed after transmission through a sample gas

Note 1 to entry: The light output wavelength from a laser diode may be tuned by using temperature and/or drive current of the laser diode. This allows the laser output wavelength to be scanned across an individual absorption band or bands of an absorbing gas species. The absorption information gained may be used to determine the gas concentration of the target species.

Note 2 to entry: In addition to note 1, a higher frequency modulation may be superimposed onto this lower frequency scan across the absorption band, in order to obtain enhanced speciation and/or measurement accuracy.

3.15.10
wavelength modulation spectroscopy
WMS

technique using TSLAS (see 3.15.9) where the laser optical frequency is typically modulated in the 10 kHz to 1 000 kHz region, usually in addition to a much lower frequency scan over the gas absorption line of interest

Note 1 to entry: The modulated laser beam is passed through the sample gas and the transmitted beam is detected using a fast photo-detector and the signal is then processed (demodulated) to obtain the gas absorption profile with high signal to noise ratio.

3.15.11
frequency modulation spectroscopy
FMS

technique similar to WMS (see 3.15.10) however, in FMS the optical frequency of the laser is modulated at a much higher frequency (tens of MHz to GHz region)

Note 1 to entry: The higher frequency modulation of FMS compared to WMS provides a performance improvement.

3.15.12
cavity ring down spectroscopy

method of gas measurement using the decay profile of optical energy with time within a multi-pass sample cell

Note 1 to entry: Laser light is coupled into an optical cavity usually using highly reflective mirrors for the intended wavelength.

Note 2 to entry: The decay of optical energy in the cell with time is monitored. The decay profile will be a function both of the reflectivity of the cell and any absorption taking place due to the presence of an absorbing sample gas.

Note 3 to entry: Due to the high reflectivity of the cavity, long effective absorption path lengths are obtained, leading to high sensitivity measurements.

3.15.13
fourier transform infrared (FTIR) analyzer

analyzer using an infrared spectrum as a means of calculating the absorption by the gas of interest

Note 1 to entry: The infrared spectrum is obtained by first collecting an interferogram of a sample signal using an interferometer, and then performing a Fourier Transform on the interferogram to obtain the absorption spectrum.

3.15.14
photoacoustic gas analyzer

analyzer for gas measurement using the acoustic signal generated by thermally induced pressure waves caused by the absorption of optical energy by gas molecules in a sample gas

Note 1 to entry: The sample gas is excited by a modulated light source, but instead of directly measuring the light absorbed, the signal due to thermally induced pressure waves caused by the absorption of optical energy by the gas molecules is detected as sound waves by a microphone. The characteristics of this acoustic signal are then used to determine the gas concentration.

Note 2 to entry: Strictly speaking, this is not a photometric measurement, since the detector is not an optical device, however, this technique has been included due to the fact that it is well known and uses optical excitation to generate the signal.

3.16
analyzers using light emission

analyzers which detect the amount of light emitted by a sample gas at a particular wavelength or wavelength range after being artificially excited, in order to determine the concentration of a component species

Note 1 to entry: The excitation of the gas of interest may occur by several different methods, examples of which are shown in 3.16.1, 3.16.2 and 3.16.3.

3.16.1
fluorescence analyzer

analyzer which measures gas-component concentrations by detecting the emission of radiation from excited state molecules on relaxation to a lower energy state

Note 1 to entry: This may be a steady state or time-resolved measurement. The components that cause excitation are part of the analyzer.

Note 2 to entry: Fluorescence can occur when molecules absorb short-wavelength radiation, an electron is excited to a higher energy level and subsequently relaxes with emission of radiation.

Note 3 to entry: Chemiluminescence analyzers utilize a chemical reaction to produce molecules in an excited state.

Note 4 to entry: The component concentration may be measured directly by excitation of the component of interest or may be deduced by the quenching (reduction in excited state lifetime) by the component of interest of another excited state molecule present.

3.16.2
plasma emission analyzer

analyzer for gas measurement using light emission from an artificially generated plasma

Note 1 to entry: A plasma is generated within the sample background gas.

Note 2 to entry: Impurities within a sample gas may be determined by measuring the light detected at particular wavelengths from emission due to those impurities after excitation from the plasma.

Note 3 to entry: An impurity within a sample gas may be deduced by the quenching (reduction in excited state lifetime) by the impurity of interest of another excited state molecule present.

3.16.3
infrared emission spectroscopy

method for gas measurement detecting the amount of light emitted by a gas of interest in the range 0,7 μm and 50 μm after being artificially excited in order to determine its concentration

Note 1 to entry: A gas sample is artificially excited to produce light emission in the infrared range from the gas of interest, which is then detected and measured by a variety of techniques, including FTIR and under continuous and time-resolved configurations.

3.17
analyzers using scattered light
analyzers which detect the scattered light from a light source after being passed though a sample gas in order to obtain both qualitative and quantitive information

3.17.1
Raman analyzer
analyzer for gas measurement using inelastic scattering of monochromatic light from a laser

Note 1 to entry: Raman spectroscopy is a spectroscopic technique used to study vibrational and rotational modes in a system. It relies on inelastic scattering (Raman scattering) of monochromatic light from a laser. The laser light interacts with molecular excitations in the system, resulting in the energy of the laser, photons being shifted up or down. The shift in energy gives information about the excitation modes in the system. This can also be used for quantitative measurements.

4 Procedure for specification

4.1 General

The procedures for specification are detailed in IEC 61207-1. This covers:

- specification of values and ranges;
- operation and storage requirements;
- limits of uncertainties;
- recommended standard values and ranges of influence quantities (see IEC 60654).

In this part of IEC 61207, specifications of ranges for ancillary equipment are given. Additional terms for specification of performance, and important aspects of performance relevant to photometric analyzers, are also detailed. The following documents may also be referred to where appropriate: IEC 60079-29-1 and IEC 60079-29-4.

4.2 Specification of essential ancillary units and services

The following should be specified where appropriate:

a) auxiliary supply requirements (e.g. compressed air, reference gases);
b) facilities for in-situ calibration or electronic and optical integrity checking;
c) facilities for automatic compensation for gas temperature or pressure variations;
d) methods and frequency of essential maintenance (e.g. cleaning of optical components or replacement of integral filter elements on across-duct or in situ analyzers).

4.3 Additional terms related to the specification of performance

To utilize a photometric analyzer, the gas to be measured shall be presented to the analysis system under defined conditions. The point in the system where these conditions are defined will vary, depending on the type of system. This standard refers to the analyzer as well as all parts subsequent to this point of application, which can be as follows:

- for an across-duct analyzer; the gas between the source and detector units, or source/detector unit and retro-reflector;
- for an in situ analyzer; the gas environment within which the measurement path is placed;
- for a dilution sampling system; the gas environment within which the dilution element is placed, that is normally the end of the probe;
- for an extractive system; the point at which the gas passes from the sampling system (not covered by this part) to the analyzer unit containing the optical cavity.

The following additional statements (a) to (f) are required to define the performance of the analyzer in terms of the conditions at this point of application:

a) rated range of gas temperature;

b) rated range of gas pressure;

c) rated range for duct width (appropriate for across-duct analyzers);

d) rated range of duct opacity (across-duct analyzers only);

e) rated range of interfering components;

NOTE These can normally include water vapor, carbon dioxide, nitric oxide, oxygen, hydrogen chloride and carbon monoxide.

f) rated range of flow rate or gas velocity.

5 Recommended standard values and range of influence quantities

The rated ranges and use of influence quantities for climatic conditions, mechanical conditions and mains supply conditions shall be in accord with those defined in IEC 60654.

6 Procedures for compliance testing

6.1 Verification of performance values

For the verification of values specifying the performance, see IEC 61207-1, together with Subclauses 6.2 to 6.4.

6.2 Test equipment

Test equipment for in-situ and across-duct analyzers shall include mechanical components required to present test gases to the measurement path at the appropriate temperature and pressure. For in-situ analyzers this may be a sealed end-cap for the probe, with appropriate gas connections. This entire assembly can then be placed within a furnace.

For across-duct monitors, a large optical cell is required with windows transparent to the wavelengths used by the analyzer. This optical cell should be of sufficient diameter to accommodate the analyzer beam width and of sufficient length to simulate the highest test gas concentrations required (e.g. for influence quantities). This optical cell should be placed in a furnace and arrangements made to measure the temperature of test gases within the optical cell.

$$\text{Minimum gas cell length} = \frac{P_2 L}{P_1}\,\text{m} \qquad (1)$$

where

P_1 is the pressure within the duct;

P_2 is the partial pressure in the duct of component to be tested (referring to the component of highest concentration);

L is the duct width to be simulated.

NOTE Apparatus which can be used to apply test gases to in-situ mounted and across-duct analyzers is illustrated in Figures A.3 and A.4.

6.3 Simulation of duct width

For across-duct analyzers, a duct of width L m can be simulated using a cell of length L_c m by selecting test concentrations to give appropriate concentration × length products as follows:

$$\frac{(P_2)}{P_1} L = \frac{(P_3)}{P_1} L_c \qquad (2)$$

where

P_3 is the partial pressure of test component;

L_c is the length of test cell;

hence

$\frac{(P_3)}{P_1}$ is the concentration of test gas within the optical cell.

NOTE This approximation is valid only at sufficiently low partial pressures such that the component to be simulated exhibits negligible resonance line broadening of the spectrum at the wavelengths used for measurements. It is valid for simulating parts per million concentrations of CO, NO, CO_2 or SO_2 when P_1 is the atmospheric pressure, but is not accurate when simulating percentage range concentrations of water vapor when P_1 is the atmospheric pressure.

6.4 Testing procedures

6.4.1 General

The following relevant testing procedures are detailed in IEC 61207-1:

- intrinsic uncertainty;
- linearity uncertainty;
- repeatability uncertainty;
- output fluctuation;
- drift;
- delay time, rise time and fall time;
- warm-up time;
- variations (influence uncertainties);
- interference uncertainties.

Additional test details required for photometric analyzers are given in Subclauses 6.4.2 to 6.4.4.

6.4.2 Linearity uncertainty

Spectroscopic properties of compounds are rarely a linear function of concentration, and most analyzers incorporate a linearizing function to provide an output signal that is linear with concentration. Where the output is provided as a non-linear function of concentration, linear regression analysis should not be performed.

6.4.3 Interference uncertainty

6.4.3.1 General

The specific interfering components and physical parameters shall be specified for each application. The values for testing and statement of interference uncertainties shall be agreed between the manufacturer and the user prior to testing. The manufacturer bears an obligation to indicate components and parameters that are expected, from experience, to provide interference equal to, or greater than, the minimum detectable concentration. In most cases, this will include water vapor and sample pressure.

6.4.3.2 Determining cross interference

Interference uncertainties are determined by first presenting the analyzer with calibration gas and then sequentially with gases which contain the two concentrations of interfering components, and which are otherwise identical to the calibration gas.

Zero calibration gas may be used where the interference uncertainty is not expected to vary significantly through the effective range.

Each test is repeated three times, and the average uncertainties are determined and recorded in terms of the equivalent concentration of the component to be determined.

6.4.3.3 Water vapor interference

Water vapor interference, after allowance for dilution, can be determined by the same procedures as stated in 6.4.3.2. However, as the method of preparation of gases with a known concentration of water vapor requires care, the following procedures may be applied where water vapor is not to be the primary measured component.

All pipework from the point of water vapor or other condensable vapor addition, up to and including the optical cell, shall be maintained above the dew-point.

The reference conditions will be with dry test gases.

For analyzers requiring conditioned samples, testing will normally only be required for a dew-point range within 0 °C to +20 °C. A water bubbler can be used to generate these dew-points approximately, see Figure A.3.

The use of dilute sulfuric acid of pH below 2 in the bubbler reduces the solubility of acid gases.

For analyzers requiring testing at high dew-points, the bubbler and sample pipework and cell may be operated at elevated temperatures. The partial pressure for water vapor may be calculated for the range 0 °C to 100 °C as in equation (B.1) in Annex B.

Alternatively, a permeation type humidifier may be used. In this case, water diffuses across a semi-permeable membrane. The rate of diffusion will be dependent on the gas permeability coefficient, the membrane surface area, the partial pressure difference across the membrane and the membrane thickness. Such designs will typically use a polymer membrane such as polytetrafluoroethylene (PTFE) tubing to add humidity to a sample or background gas. The amount of water vapor added will also be dependent on the temperature of the humidifier and flow rate of the gas to be humidified.

For in-situ analyzers or across-duct analyzers, when the optical cavity is operated at temperatures above 100 °C, liquid water and test gases can be applied directly to the gas feed pipe, providing the mixing-point is also within the furnace, see Figure A.4. Equations (B.2) and (B.3) in Annex B can be used to determine gas concentrations when there is a uniform pressure within the gas/liquid mixing system.

6.4.4 Delay time, rise and fall time

The size of test enclosure required for across-duct and in-situ analyzers may be such as to prevent rapid gas-change between presentation of samples of differing concentration. In such a case, the determination of these time intervals will represent an upper limit to the instrument characteristic determined, rather than an absolute value.

Annex A
(normative)

Techniques and systems of photometric analysis

The following Figures A.1 to A.4 are provided to assist in generic photometric gas measurements.

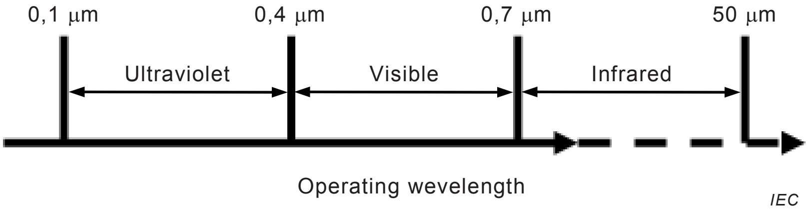


Figure A.1 – Wavelength range for photometric measurements

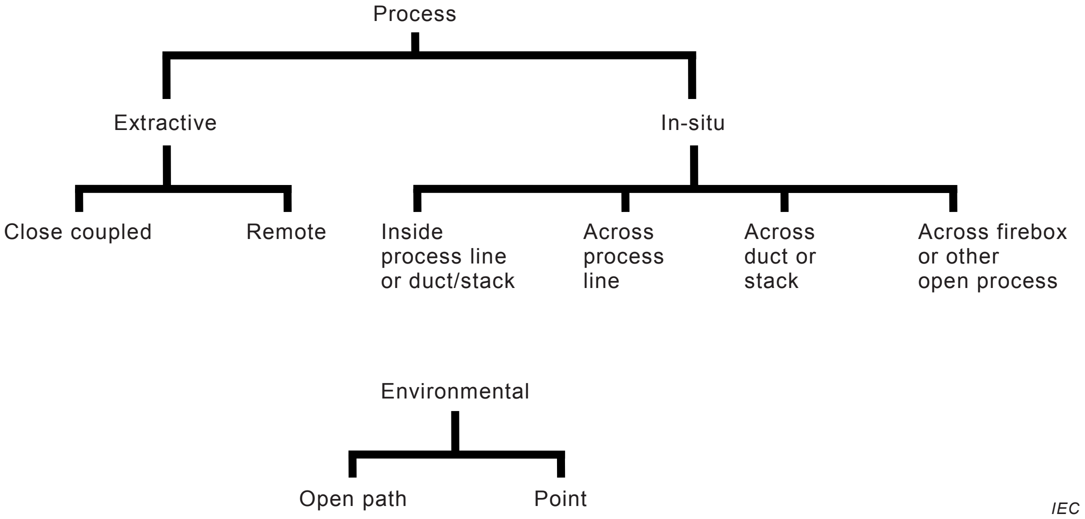
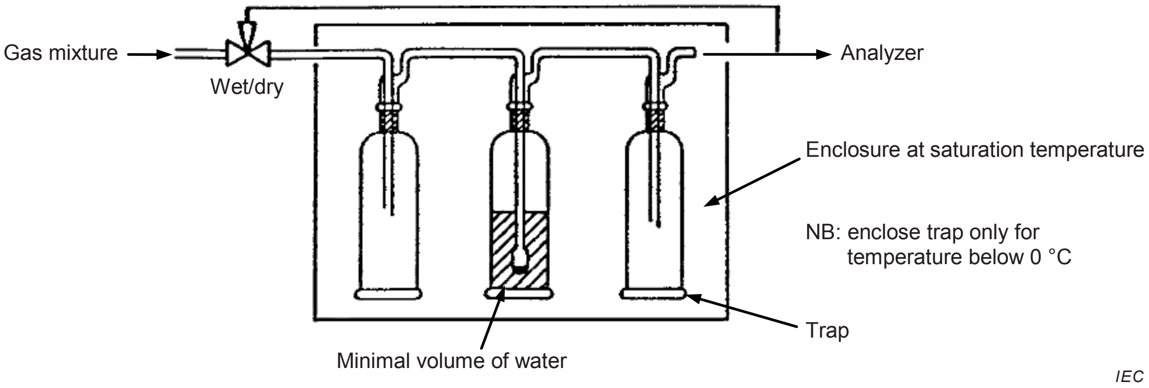
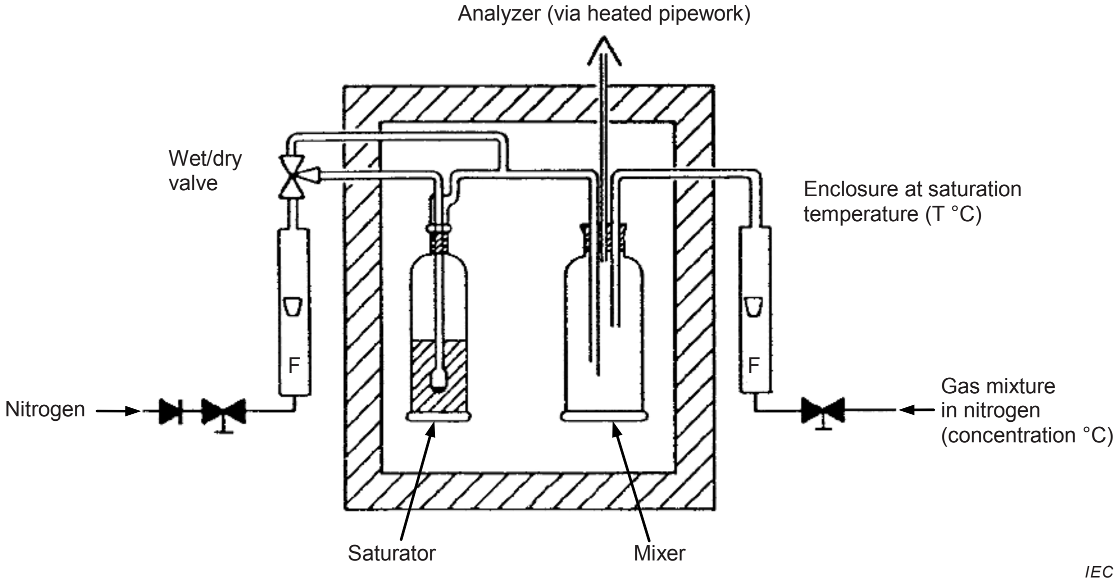


Figure A.2 – Analysis systems for gases



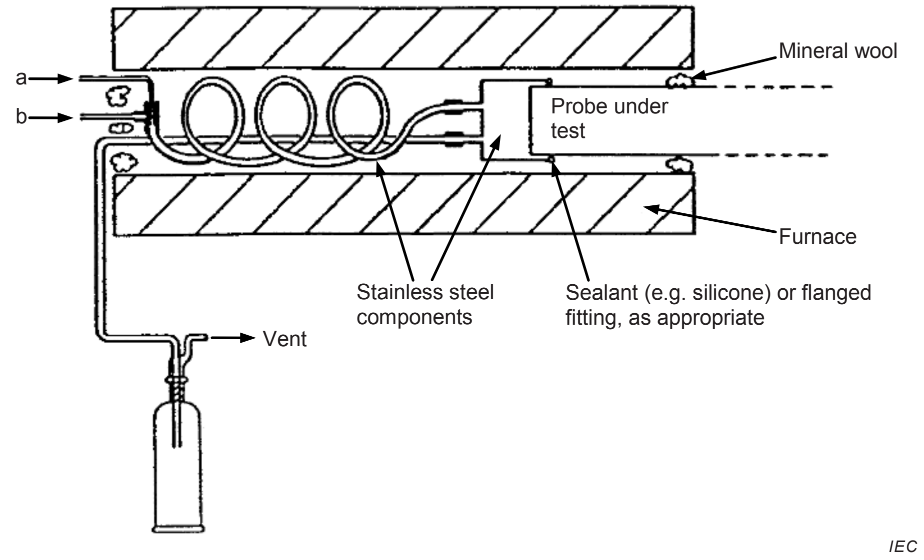
NOTE Long equilibration times will be required.

a) **Simple bubbler to apply water vapor to sampling systems**

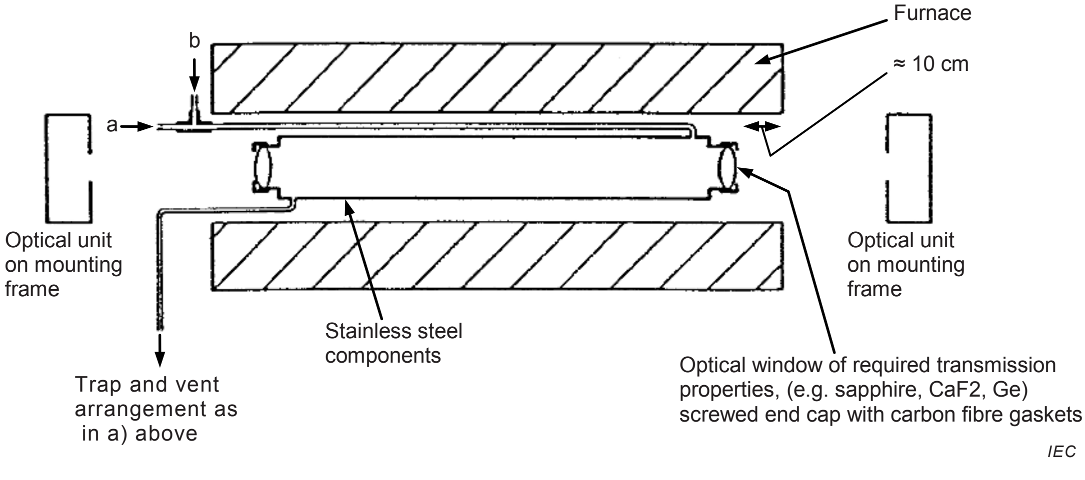


b) **Apparatus to apply water vapor at high concentrations or to avoid long equilibration times**

Figure A.3 – Test apparatus to apply gases and water vapor to analysis systems



a) **Apparatus to apply gas to a probe-end**



b) **Apparatus to simulate duct conditions for across-duct analyzers**

Figure A.4 – Test apparatus to simulate duct conditions for in-situ/across-duct analyzers

Annex B
(informative)

Methods of preparation of water-vapor in test gases

For water vapor:

$$\text{Partial pressure} = \text{Antilog}_{10} \frac{(t - 6{,}956\,6)}{33{,}449 + 0{,}139\,07(t - 6{,}956\,6)} \text{ kNm}^{-2} \tag{B.1}$$

where

t is the dew-point temperature, in degrees Celsius.

For mixing dry gases and water vapor in pipework above 100 °C, see Figure A.4.

$$C_{\text{water}} = \frac{0{,}455\, MT}{(f + 0{,}455\, MT)} \tag{B.2}$$

$$C_{\text{x}} = \frac{CI_{\text{x}}}{100}(100 - C_{\text{water}}) \tag{B.3}$$

where

C_{water} is the concentration of water vapor in the final gas mixture, in per cent;

CI_{x} is the concentration of component x in the dry gas prior to mixture with water, in any units;

C_{x} is the concentration x in the final gas mixture, in the same units as CI_{x};

M is the rate of addition of liquid water, in grams per unit time;

f is the flow rate of dry gas to the mixing point, in dm^3 per unit time;

T is the measurement temperature to which f refers, in kelvins.

Example for Figure A.3

The solubility of acidic gases is much reduced if the pH of the water is reduced below 2 by the addition of sulfuric acid. The effect on vapor pressure in the range 0,01 to 0,1 molar sulfuric acid is less than 1 %.

At saturation temperature = 15 °C

Partial pressure of water vapor =

$$\text{Antilog}_{10} \frac{(15 - 6{,}956\,6)}{33{,}449 + 0{,}139\,07(15 - 6{,}956\,6)} \text{ kNm}^{-2}$$

$$= 1{,}71 \text{ kNm}^{-2}$$

For gas passing through the bubbler at a pressure of 101,3 kNm^{-2}

$$\text{Concentration} = \frac{1{,}71}{101{,}3} \times 100 = 1{,}69\ \%$$

$$\text{Dilution ratio} = 1 - 0{,}016\,9 = 0{,}983$$

Example for Figure A.4

At saturation temperature = 60 °C

Partial pressure of water vapor = 19,9 kNm^{-2}

For a gas flow through the bubbler of 0,05 $\text{dm}^3\ \text{min}^{-1}$ and a dry gas flow of 0,45 $\text{dm}^3\ \text{min}^{-1}$:

final gas pressure flow $= 0{,}05\left(1+\dfrac{19{,}9}{101{,}3}\right)+0{,}45\ \text{dm}^3\ \text{min}^{-1}$

$= 0{,}510\ \text{dm}^3\ \text{min}^{-1}$

dilution ratio $= \dfrac{0{,}45}{0{,}510} = 0{,}883$

partial pressure of water vapor in gas mixture $= \dfrac{0{,}05\times 19{,}9}{0{,}510} = 1{,}95\ \text{kN m}^{-2}$

dew-point of gas mixture $= \dfrac{33{,}449\ \log 1{,}95}{1-0{,}139\,07\log 1{,}95}+6{,}956\,6\ ^\circ\text{C}$

$= 17{,}1\ ^\circ\text{C}$

Bibliography

BOLK, W.T. J., A *General Digital Linearising Method for Transducers*, Phys E Sci-Insts, Vol. 18, 1985

WASHBURN, E. W. *International Critical Tables,* Vol. 3, pp. 1/210-212, McGraw-Hill, 1933

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