INTERNATIONAL STANDARD

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Stationary source emissions — Determination of carbon monoxide, carbon dioxide and oxygen — Performance characteristics and calibration of automated measuring systems

Émissions de sources fixes — Détermination de la concentration de monoxyde de carbone, de dioxyde de carbone et d'oxygène — Caractéristiques de fonctionnement et étalonnage de systèmes automatiques de mesure

Reference number
ISO 12039:2001(E)

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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 3.

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 International Standard may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

International Standard ISO 12039 was prepared by Technical Committee ISO/TC 146, *Air quality*, Subcommittee SC 1, *Stationary source emissions*.

Annex A forms a normative part of this International Standard.

Introduction

Carbon dioxide, carbon monoxide and oxygen are gases found in the exhaust gases of combustion processes. Determination of the concentration of these gases may assist the operator in the optimization of the combustion process. The determination of O_2 and CO_2 is also necessary to normalize the measured concentration of other gases and dusts to defined conditions. There are a number of ways to measure concentrations of CO_2, CO and O_2 in ducts. This International Standard describes methods and equipment for the measurement of concentrations of these gases.

INTERNATIONAL STANDARD **ISO 12039:2001(E)**

Stationary source emissions — Determination of carbon monoxide, carbon dioxide and oxygen — Performance characteristics and calibration of automated measuring systems

1 Scope

This International Standard specifies the principles, the essential performance characteristics and the calibration of automated systems for measuring carbon dioxide, carbon monoxide and oxygen in the flues of stationary sources.

This International Standard specifies extractive and non-extractive systems in connection with several types of instrumental analyser. The following techniques have provided the basis for practical instrumentation:

- paramagnetism (O_2);
- magnetic wind (O_2);
- differential pressure (Quinke) (O_2);
- magnetodynamics;
- zirconium oxide (O_2);
- electrochemical cell (O_2 and CO);
- infrared absorption (CO and CO_2).

Other equivalent instrumental methods may be used provided they meet the minimum requirements proposed in this International Standard.

The measuring system may be calibrated with certified gases, in accordance with this International Standard, or comparable methods.

2 Normative references

The following normative documents contain provisions which, through reference in this text, constitute provisions of this International Standard. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

ISO 6145-2:—[1], *Gas analysis — Preparation of calibration gas mixtures using dynamic volumetric methods — Part 2: Volumetric pumps*

ISO 6879:1995, *Air quality — Performance characteristics and related concepts for air quality measuring methods*

ISO 10396:1993, *Stationary source emissions — Sampling for the automated determination of gas concentrations*

ISO 10849, *Stationary source emissions — Determination of the mass concentration of nitrogen oxides — Performance characteristics of automated measuring systems*

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[1] To be published.

3 Terms and definitions

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

3.1
air point
value obtained for O_2 when air is passed through the AMS

3.2
Automated Measuring System
AMS
system that can be attached to a duct to continuously measure and record the mass concentrations of CO, CO_2, O_2 passing through the duct

3.3
analyser
analytical part in an extractive or *in situ* AMS

3.4
calibration gas
gas of known and reliable composition that can be used to check the response of the AMS and should be used for the calibration of the AMS

3.4.1
span gas
gas used to adjust and check a specific point on a calibration curve

3.4.2
zero gas
gas or gas mixture used to establish the zero point on a calibration curve within a given concentration range

3.5
calibration
setting and checking of the AMS with a secondary or a working gas before determining the performance characteristics and before beginning any measurement of gases

NOTE This procedure should be carried out at every calibration interval.

3.6
calibration interval
period of time during which the AMS would normally be used between calibrations, respecting the indication given in periods of unattended operation

3.7
comparative measurements
measurements taken on the same duct in the same sampling plane for the same period of time with the AMS under test and with the comparative method at points a short distance from each other, providing pairs of measured values

3.8
comparative method
defined test method for obtaining comparative measurements of stationary source emissions containing CO, CO_2 and O_2

NOTE This can be a manual method or an AMS with a different measuring principle.

3.9
duct
stack chimney or final exit duct on a stationary process used for the dispersion of residual process gases

3.10
mass concentration

ρ

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

NOTE 1 Mass concentration is usually expressed as milligrams per cubic metre (mg/m^3).

NOTE 2 The conversion of data in ppm to mg/m^3 can be carried out as follows:

$$\rho\left(\text{mg/m}^3\right) = \rho\,(\text{ppm}) \cdot \frac{M_\text{r}}{22{,}4} \cdot \frac{273}{T} \cdot \frac{p}{101{,}3}$$

where

M_r	is the molecular mass;
T	is the actual temperature, in kelvins;
p	is the actual pressure, in pascals.

3.11
lag time

time taken from a sudden change in concentration at the sampling point until the instrument reads 10 % of the corresponding change in the instrument response

3.12
linearity

maximum deviation of the measured concentration from a linear calibration line

3.13
live zero

output signal of a device, which is capable of positive and negative adjustment around the zero value, that is equivalent to the minimum input signal

EXAMPLE 0 % to 10 % oxygen input to the analyser with an output of 4 mA to 20 mA capable of zero adjustment of 3,2 mA up to 5 mA when 0 % oxygen is applied to the instrument.

3.14
period of unattended operation

period for which given values of performance characteristics of an instrument can be guaranteed to remain within 95 % probability without servicing or adjustment

NOTE For long-term monitoring installations, a minimum of seven days of unattended operation is required.

3.15
response time

time taken to reach 90 % of the total change in instrument response

NOTE It is the combination of lag time and rise/fall time.

3.16
rise time (fall time)

time taken to pass from 10 % to 90 % (90 % to 10 %) of the total change in instrument response

NOTE For instruments where transient oscillations occur in the approach to the final reading, the latter should be replaced by the time taken for the oscillations to fall to less than 10 % of the total change in instrument reading.

3.17
verified AMS

AMS previously verified against International Standard ISO 12039

4 Symbols

s_A is the standard deviation. It is a measure of the working precision of the AMS and is calculated according to the usual formula for standard deviations;

s is the standard deviation derived from the difference in the pairs of measured values of CO, CO_2 and O_2, by the AMS under test condition and by a equivalent method;

s_c is the standard deviation of the comparative method;

s_D is the standard deviation of the paired values;

s_{x0} is the standard deviation of the blank readings.

5 Principle

With extractive systems, a representative sample gas is taken according to ISO 10396 with a sampling probe and conveyed to the analyser through the sample line and sample-gas conditioning system.

Non-extractive systems do not require any removal of sampling gases. For the installation it is essential that a representative place in the stack be chosen in accordance with ISO 10396.

The systems described in this International Standard measure CO_2, CO and O_2 concentrations using instrumental methods that shall meet the minimum performance specification given. Extractive systems usually give concentrations on a dry basis due to requirements for sample conditioning, and non-extractive systems usually give concentrations on a wet basis.

6 Sampling

Sampling and sample-gas conditioning systems for extractive and non-extractive methods shall conform to ISO 10396.

7 Description of the test methods

7.1 General

Examples of the typical methods available are described in 7.2 to 7.5.

Instruments that use these typical techniques shall meet the performance characteristics as described in 7.2.4.

7.2 Infrared absorption method (CO/CO_2)

7.2.1 Principle

The non-dispersive infrared absorption method is based on the principle that gases consisting of molecules with different atoms absorb infrared radiation at a unique wavelength. The measurement technique makes use of the principle as follows:

a) *Parallel beam method*

Radiation from an infrared source is divided into two parallel beams, with one beam passing through a reference cell and the other through a sample cell. The separate beam intensities are measured by a suitable detector to determine the concentration of the gas of interest.

b) *Single beam method*

There are three types of single beam method:

- Use of interference filters, with one filter at the absorption band for the gas being measured and the other filter at the reference wavelength. The gas concentration is then a function of the ratio of the measured and reference wavelengths.
- Gas filter correlation in which the measurement interference filter is replaced with a gas filter; otherwise the method is similar to above. This gives better sensitivity and rejection of cross-sensitivity effects. Additional gas filters to minimize interfering gases can be used.
- The single-beam single-wavelength method, in which only the measurement wavelength is used. These analysers have no compensation for obscuration of the cell, source/detector ageing, etc. and tend to drift badly. This is overcome by frequent autocalibrations.

c) *Fourier transform infrared spectroscopy*

A moving mirror is used to generate an absorption spectrum of the sample over a broad region of the infrared spectrum. This measured spectrum is evaluated against established library spectra to derive the concentration of the gaseous species of interest.

7.2.2 Instrument application

The infrared absorption method for CO_2 analysis is applicable for concentrations of CO_2 up to 20 %. For CO analysis, applicable concentrations are between 6 mg/m^3 (5×10^{-6} volume fraction) and 62 500 mg/m^3 (approximately 5 % volume fraction). It may be necessary to use multiple cells to achieve this range.

These concentrations are within the range of concentration of CO_2 and CO in typical combustion effluent streams and detectable by most instruments available on the market.

7.2.3 Selectivity (interference)

Selectivity shall be checked for each application of this method, as it will vary according to the nature of the sample. Potentially interfering components are present in many enclosed gas streams and can include particles, water vapour, sulfur dioxide, nitrogen oxides and hydrocarbons.

7.2.4 Performance characteristics

Performance characteristics shall be in accordance with clause 8.

7.3 Paramagnetic method (O_2)

7.3.1 Principle

Oxygen is strongly paramagnetic and is attracted into a magnetic field. All other gases, with few exceptions, are either weakly paramagnetic or diamagnetic. This property can be used to make an analysis which is specific to oxygen.

There are three basic detection techniques that can be used:

a) An element, usually a dumb-bell mounted on a torque suspension, is suspended in a strong, non-magnetic field. Oxygen molecules are attracted into the strongest part of the field, forcing the dumb-bell from its equilibrium (zero) position. The force required to return the dumb-bell to its zero position is proportional to the oxygen concentration.

b) A second technique uses the temperature coefficient of the paramagnetic effect. The paramagnetic coefficient is inversely proportional to the absolute temperature. If a strong magnetic field is combined with a temperature gradient, then a flow of oxygen gas will be created. The rate of flow (magnetic wind) is a function of oxygen concentration and can be measured, for example by thermal conductivity techniques.

c) The third technique utilizes a strong magnetic field across a tube. Oxygen molecules will be attracted into the field which then act as impedance to the flow of a reference gas (usually N_2) through the tube. The reduction in flow of the reference gas is a measure of the oxygen concentration.

7.3.2 Instrument application

The paramagnetic method for O_2 analysis is intended for use for oxygen concentrations in the range up to 25 % volume fraction, which covers the requirements of most conventional combustion systems.

Paramagnetic analysers are capable of measuring concentrations up to 100 % (pure oxygen).

7.3.3 Selectivity

Selectivity shall be checked for each application of the test method. This method is only susceptible to interference from gases having strong paramagnetic properties, such as NO and NO_2. These will not be present in quantities that are likely to affect the application of this method as applied to combustion effluent streams. Effective interferences shall be determined in accordance with A.4.2.3.

7.3.4 Performance characteristics

Performance characteristics shall be in accordance with clause 8.

7.4 Zirconium oxide method (O_2)

7.4.1 Principle

The zirconium oxide method measures the excess oxygen in a flue gas using an yttria-stabilized zirconium oxide cell with porous platinum electrodes coated on both its inner and outer surfaces. When this cell is heated to a high temperature, above 600 °C, it becomes permeable to oxygen ions. Vacancies in its crystal lattice permit the mobility of oxygen ions so that the cell becomes an oxygen-ion-conducting solid electrolyte.

The platinum electrodes on each side of the cell provide a catalytic surface for the change of oxygen molecules to oxygen ions and oxygen ions to oxygen molecules. Oxygen molecules on the high-concentration reference-gas side of the cell gain electrons to become ions that enter the electrolyte. Simultaneously, at the other electrode, oxygen ions lose electrons and are released from surface of the electrode as oxygen molecules.

When the concentration of oxygen is different on each side of the cell, oxygen ions migrate from the high oxygen-concentration side to the low oxygen-concentration side. This ion flow creates an electronic imbalance that results in a voltage potential between the electrodes which is a function of the temperature of the cell and the ratio of oxygen partial pressure on each side of the cell.

The output voltage as a function of temperature and oxygen concentrations in the sample and reference gases is given by the Nernst equation:

$$E = \left[\frac{RT}{4F} \ln \frac{p_1}{p_2} \right]$$

where

E is the output voltage;

R is the gas constant;

T is the absolute temperature;

F is the Faraday constant;

p_1 is the partial pressure of O_2 in the reference gas;

p_2 is the partial pressure of O_2 in the process gas.

NOTE In practice, certain zirconium cells may not exactly follow the Nernst equation.

7.4.2 Instrument application

The zirconium oxide method for O_2 analysis is intended for use for oxygen concentrations in the range of up to 25 % volume fraction, which covers the requirements of most conventional combustion systems.

7.4.3 Selectivity

Due to the high temperature and presence of platinum in the sensor, carbon monoxide and hydrocarbons can be oxidized, giving a strong negative interference if their concentrations are of the same order as oxygen.

7.4.4 Performance characteristics

Performance characteristics shall be in accordance with clause 8.

7.5 Electrochemical cell method (O_2 and CO)

7.5.1 Principle

Electrochemical cells can be used to measure O_2 and CO if the electro-oxidation or electro-reduction of the gas molecules at an electrode results in a current that is directly proportional to the partial pressure of the gas. In these cells, the gas diffuses through a selective semipermeable membrane to an electrode and electrolytic solution. The gas reacts at the electrode and a product of the reaction is transported to a counter-electrode where it, in turn, reacts. The current generated from the difference in electromotive force (emf) from the cathode/anode reactions is measured. A retarding potential can be maintained across the electrodes to prevent the oxidation of gas species that might otherwise interfere.

7.5.2 Instrument application

The electrochemical cell method is applicable for O_2 concentrations up to 25 % volume fraction.

The electrochemical cell method is applicable for CO concentrations between 20 mg/m^3 and 4 000 mg/m^3.

7.5.3 Selectivity

Selectivity shall be checked for each application of this method, as it will vary according to the nature of the sample. Potentially interfering components are present in many enclosed gas streams and may include particles, water vapour, sulfur dioxide, nitrogen oxides, CO_2, H_2 and hydrocarbons.

7.5.4 Performance characteristics

Performance characteristics shall be in accordance with clause 8.

8 Performance characteristics

In Table A.1 numerical values of performance characteristics and their applicability are given for automated measuring systems. These values represent the required specifications for the instrumental measurement of source emission levels of CO_2, CO and oxygen.

When measured in accordance with the respective methods given in annex A, the performance characteristics shall meet the requirements given in Table A.1.

The performance characteristics shall be determined with operative measuring equipment. The standard deviation s_A shall be determined during measurement under normal conditions, preferably at the type of plant or combustion source of interest; the other characteristics may be determined at a plant or in the laboratory.

NOTE The result of a measurement, corrected for the 95 % statistical certainty level calculated according to A.4.2.1, is presumed to be in an interval which contains the true value of the concentration. The difference between the upper and/ or lower limit of this interval and the corrected value, or the difference between the corrected value and the lower limit of this interval, is termed the uncertainty of measurement. Assuming that the measuring equipment meets the performance characteristics given in Table A.1, the uncertainty of measurement is $<$ 10 %, in relation to the full scale (at 95 % statistical certainty). The uncertainty of a measured value can be calculated by multiplication of the uncertainty mentioned above with the full-scale value, divided by the measured value.

9 Final reports

9.1 Instrument/supplier report

The report shall include the following information:

a) reference to this International Standard, i.e. ISO 12039;

b) full identification of the sample;

c) details concerning which tests were carried out in a laboratory and which on-site;

d) any operation not specified in this International Standard or regarded as optional;

e) all of the test results from clause A.4 and a statement as to whether the results comply with Table A.1;

f) details of the standard reference method or alternative AMS.

9.2 Commissioning/verification test report

The report shall include the following information:

a) objective of test;

b) method used, description of process;

c) operation protocol;

d) identification of equipment used;

e) name of the person who carried out the test;

f) results;

g) copies of raw data;

h) recent history of AMS test;

i) type of fuel;

j) duct gas temperature, pressure, velocity and moisture content;

k) location, time and duration of test;

l) plant operating conditions at the time of test;

m) date and time of sampling;

n) results from on-site calibration.

Annex A
(normative)

Determination of performance characteristics

A.1 General

This annex contains methods for determining the main performance characteristics of the automated measuring system (AMS) for CO, CO_2 and O_2 in stack gases. The calibration of the measuring system is always the first step, and the different methods of setting and checking the calibration are explained in A.4.1. These methods employ analytical gases and comparative techniques.

The method using analytical gases alone is applicable on plant where the flue gas composition is well known, or when the comparative method is considered too costly and time-consuming (e.g. in the event of intermittent use of the monitoring equipment).

Comparative methods are preferred when highly accurate results are required (e.g. when installing continuous monitoring equipment at large sources). These methods may be used at the time of installation and after some years of operation. The performance characteristics established after installation of the AMS require validation in the event of a change in operating conditions which could affect the AMS performance, such as a change in the type of fuel burned.

A.2 Principle

As a general principle, the numerical values of performance characteristics of automated measuring methods are evaluated using the complete measuring device, except as noted.

One simple method is to check only the zero and full-scale points of the analyser. Further information can be obtained by checking the entire scale of the analyser.

Three performance characteristics (lower detection limit, response time and effect of interfering substances) can be determined either on-site or in the laboratory using gases of known concentration (introduced, in the case of an extractive system, upstream of the sampling line of the AMS).

The standard deviation s_A of the AMS is then determined on-site by comparison with measurements taken with a standard manual method or a calibrated AMS using a different principle.

For determining the working precision of the AMS, the AMS shall be installed in the duct, and its response to various process conditions shall be compared with a number of manual samples (i.e. integrated sampling and analysis over at least 70 % of the range of the AMS, if the actual gas concentration is spread over this range), or be compared with the output of another AMS with a different measuring principle. The data obtained shall be used to determine certain performance characteristics listed in Table A.1. These shall be specified at standard conditions of temperature and pressure on a dry basis.

If no other measuring principle is available, two independent identical systems should be used.

A.3 Reagents

A.3.1 Zero gas

Zero gas shall not contain compounds which interfere with the measuring efficiency of the instruments. For all analysers, pure nitrogen (5,0 grade, with the impurity of components to be measured less than the analytical detection limit) is acceptable, however, for ZrO_2 the “air point” shall be used. With air as the sample gas, the ZrO_2 cell gives 0 mV output (but the analyser reads 21 % O_2).

Impurities shall register less than 0,4 % of full scale.

NOTE Methods other than the test case given may be used provided they are validated.

A.3.2 Calibration gases

The primary calibration gas used shall be of certified concentration and traceable to a national or International Standard. In the case of determination of oxygen levels, dry air shall be used.

Caution shall be exercised if oxygen is to be used by doing it outdoors, far from combustion sites.

A.4 Test procedures

A.4.1 Calibration checks

A.4.1.1 General

In the event of continuous use of the analyser, the zero and of the analyser scale shall be checked regularly, for example weekly. (When the analyser is in continuous use, the entire scale shall be checked at longer intervals, e.g. yearly or after repair of the analyser.)

A calibration check with analytical gases is in general sufficient for short-term measurement (intermittent use). In this case, calibration of the analyser shall be checked before and after the sample location for every use.

A.4.1.2 Calibration of the analyser

Set up the analyser according to the manufacturer's instructions. Feed zero gas (A.3.1) into the analyser and set the zero. Then feed a calibration gas (A.3.2) that has a known concentration of approximately 70 % to 80 % of the full-scale deflection of the analyser and set the scale reading accordingly.

NOTE For non-extractive point monitors (path-monitors), setting of the analyser is not applicable as it forms part of the AMS. Point monitors may be equipped to feed zero and span gas into the measuring cell.

A.4.1.3 Confirmation of correct setting of the AMS

Repeat the procedures given in A.4.1.2 but this time using the complete AMS. For extractive AMS, the zero gas and the calibration gas are introduced into the measuring equipment directly upstream of the sampling probe (if possible upstream of the filter) with the normal ambient pressure. In this way the influence of the sampling system is eliminated.

For non-extractive AMS, follow the manufacturer’s instructions. For example, install a tube matching the length of the measuring distance between the radiation source and the radiation receiver, or use manufacturer-provided absorption devices.

A.4.1.4 Verifying accuracy of the entire scale of the analyser

In order to check the entire scale, in measuring equipment with a linear analytical function use five uniformly distributed calibrated gas concentrations (approximately 20 %, 40 %, 60 %, 80 %, 90 % of full scale). The analytical gas used for setting purposes can be diluted gradually, in accordance with ISO 6145-2. In the case of a non-linear analytical function, 10 calibration points are recommended.

NOTE The input of analytical gas to check the entire scale can take place directly upstream of the analyser, because the analytical function is only dependent on the analyser.

A.4.2 Determination of performance characteristics by tests using analytical gases

A.4.2.1 General

Perform these tests on the complete AMS, in the laboratory and on-site with the sampling line installed in a duct.

For an extractive system, feed zero gas (A.3.1) and analytical gas (A.3.2) directly into the sample line as near as practicable to the sampling head and at such a pressure that the sample flow is obtained through the analyser as in A.4.1.3.

If the sampling head is installed in a duct, take steps to ensure that the analytical gases are not contaminated with the gas from the duct, by either:

a) removing the sampling head from the duct and inserted into analytical gas, or

b) installing a small airtight chamber in the duct around the sampling head, which is then filled with calibration gas.

For testing non-extractive path monitors and point monitors, special arrangements are necessary for the measurements with test gases. Test equipment shall include the appropriate mechanical components necessary to present test gases to the measurement path at the desired temperature and pressure.

A large optical cell with windows transparent to the wavelengths used by the analyser is required. This optical cell should be of sufficient diameter to accommodate the analyser beam width and of sufficient length to simulate the highest test gas concentrations required.

A point monitor is capable of accepting cylinder gases in the same manner as for extractive systems. It may be used as a sealed end-cap for the probe, with appropriate gas connections. This entire assembly is then placed within a furnace. The necessary devices are provided by the manufacturers.

A.4.2.2 Evaluation of the lower detection limit

Present zero gas if the instrument has no “live zero”, and offset the instrument by no less than 10 % of full scale. Carry out a minimum of 30 readings at time intervals no less than five times the instrument electronic time constant, by presenting zero gas (A.3.1) to the AMS as in A.4.2.1 and note the reading. Carry out these readings in the shortest time possible in order to minimize zero drift and any zero deviation due to temperature response.

Assuming the confidence level is 95 %, the lower detection limit, x, is given by the formula:

$$x = \overline{x}_0 + 2s_{\mathrm{x0}}$$

where

$\overline{x}_0$ is the mean of the blank readings;

s_{x0} is the standard deviation of the blank readings.

A.4.2.3 Evaluation of the effect of interfering substances

Using the method in A.4.2.1, pass test gas, free of the component to be measured, into the AMS. The test gas should contain uniformly mixed known concentrations of the interfering gas y_{i} corresponding to expected values. Note the measured value x_{si}, expressed as percent volume fraction as well as the mass concentration ρ_{si} of the interfering gas. Measurements of interfering gas shall be conducted at zero and 90 % of full scale.

Interfering gases such as H_2O, CO_2, CO, SO_2, NO_x and HCl shall not cause an influence greater than 4 % of the full-scale measured amount of CO, CO_2 and O_2 (Table A.1).

In cases where the change in measured value is linear with increases in mass concentration of a substance, the interfering effect of that substance can be given by one expression $x_{\mathrm{s}i}/\rho_{\mathrm{si}}$. If the change in measured value is not linear with the increases in mass concentration of a substance, the dependence of the interfering effect of that substance on mass concentration shall be determined for several different values of y_i.

To calculate the combined effect of the presence of several interfering substances, determine the interference for each individual interfering substance and for the mixture of all interfering substances to determine the maximum effect of the combination.

Calculate the interfering effect E_i of a typical mixture from the obtained individual values $x_{\mathrm{s}i}/\rho_\mathrm{si}$ of the interfering substances y_i by using the formula:

$$E_\mathrm{i} = \frac{1}{\rho_\mathrm{FS}} \cdot \sum_{i=1}^{n} \frac{x_\mathrm{si}}{\rho_\mathrm{si}} \cdot \rho_\mathrm{mi} \cdot 100$$

where

ρ_mi is the mass concentration of the interfering substance in the mixture;

ρ_FS is the range of measurement of mass concentration;

n is the number of interfering substances.

Compare this calculated value with the measured value of the mass concentration mixture of interferences. If these two values agree within 20 %, the effect of combination can be discounted and the interference effects for other mixtures of these compounds can be calculated.

NOTE The value given in Table A.1 is the sum of interfering effects caused by the maximum interfering substance concentrations in the measured sample.

Table A.1 — Main performance characteristics of AMS for measurement of carbon monoxide, carbon dioxide and oxygen

Performance characteristic	Numerical value	Test methods (see annex A)
Lag time	$<$ 180 s	
Lower detection limit (full scale)	$<$ 2 %[a]	A.4.2.1
Interference of the mixture	$<$ 4 % [a]	A.4.2.2
Response time	$<$ 200 s	A.4.2.3
Zero drift	$<$ 2% [a]	A.5.1
Span drift	$<$ 4 % to calibrate value	A.5.1
Fall time	$<$ 20 s [b]	
Rise time	$<$ 20 s [b]	
Linearity	$<$ 2 %	

[a] Full scale.

[b] For the analyser only.

A.4.2.4 Evaluation of response time of the overall measurement system

Using the method in A.4.2.1, pass into the AMS an analytical gas of mass concentration between 50 % to 90 % of full scale of the analyser.

Consider the response time as the average time interval between feeding in the analytical gas and reaching 90 % of recorded concentration (see ISO 6879:1995, 5.2.18).

A.4.2.5 Evaluation of standard deviation s_A and systematic errors

Determine the standard deviation of the AMS on-site only. Obtain the integral performance by carrying out a minimum of 10 measurements and a maximum of 16 measurements using the AMS under test.

Compare the results of the AMS with results obtained using a standard reference or another AMS verified according to ISO 10849 against a manual method, or another AMS based on a different measuring principle.

Because the uncertainty of the measuring results of the AMS (which depends on the quality of the complete AMS) is judged over the period of unattended operation, the comparative measurements, as described above, shall be carried out at intervals spread over this period.

Calculate the standard deviation s_A of the measured values of the AMS from the value of s_D (defined below) and the known standard deviation s_c for the measured values of the comparative reference method by the formula:

$$s_A = \sqrt{s_D^2 - s_c^2}$$

NOTE 1 It is not possible to determine the standard deviation s_A of an AMS under repeatable working conditions or in a laboratory because:

- commercially available calibration gas mixtures containing CO, CO_2 and O_2 do not have all the properties of actual waste gas and do not regard all possible influences, and
- it is not possible to maintain the properties of waste gas present in the waste gas flue in a waste gas sample transferred into a vessel.

Therefore the evaluation of the standard deviation of s_A is performed by comparison with an independent comparative method or an analyser with a different principle of detection. Standard deviation is calculated assuming normal distribution.

NOTE 2 The standard deviation s_A is a measure of the working precision under site conditions. Therefore it contains random errors, the effects of interfering substances, the effects of temperature changes and of any zero and span drifts, because they cannot be eliminated in practice. In addition, it includes the standard deviation of the comparative method (either an independent method or a verified AMS) and any variation due to varying response times.

The standard deviation s as defined above is an upper limiting value for the precision AMS.

NOTE 3 This procedure is suitable for finding the accuracy of the measuring result of the AMS as long as the standard deviation s_c of the measured values of the comparative method is significantly smaller than the standard deviation s_D of the difference in pairs of measured values.

If the AMS under investigation has a substantially smaller standard deviation (s_A) than the comparative method s_c, the method above can still be used, although the value of s_A will have a large uncertainty. If the uncertainty in s_c is unknown and hence the limits of s_A cannot be established, then the value of s_A can be used as a qualitative rather than a quantitative assessment of the AMS performance.

The standard deviation of an analytical system (s_c) which measures the unknown concentration of a compound is determined by comparative measurements of two identical systems, which are installed at the same duct and which are supplied by identical gas. The standard deviation s_c is calculated from the results of the comparative measurements (with two identical systems) according to the following formula:

$$s_c = \sqrt{\frac{\sum \left(\rho_{11} - \rho_{21}\right)^2}{2n}}$$

where

ρ_{11} and ρ_{21} are the mass concentrations, in milligrams per cubic metre, of the measured gas determined by the two identical systems of the comparative method;

n is the number of comparative measurements.

The value of s_D in milligrams per cubic metre is given by the formula:

$$s_\mathrm{D} = \left\{ \frac{1}{n-1} \left[\sum_{i=1}^{n} z_i^2 - \frac{1}{n} \left(\sum_{i=1}^{n} z_i \right)^2 \right] \right\}^{1/2}$$

where

s_A is the standard deviation integral performance;

s_c is the standard deviation of the comparative method;

s_D is the standard deviation calculated from the differences in pairs of measured values according to the equation for standard deviation;

$z_i = \rho_{i\mathrm{r}} - \overline{\rho}$ is the difference in the pairs of measured values;

$\rho_{i\mathrm{r}}$ is the mass concentration of the measured component determined by the independent reference method;

$\overline{\rho}$ is the mean recorded mass concentration of the measured gas;

n is the number of comparative measurements.

In order to check whether a significant systematic error is present or not, calculate the mean difference $\overline{z}$ by the formula:

$$\overline{z} = \frac{1}{n} \sum_{i=1}^{n} \left(\rho_{i\mathrm{r}} - \overline{\rho} \right)$$

If the mean difference lies outside its 95 % limits of confidence, there is statistical proof that a significant error is present.

A systematic error is present if, by using the following formula:

$$\left| \overline{z} \right| \geqslant 2 \frac{s_\mathrm{D}}{\sqrt{n}}$$

where $\left| \overline{z} \right|$ is the absolute value of the mean difference.

If a systematic error is present which exceeds 2 % of the measuring range, its cause shall be investigated and resolved.

The statistics referred to in this subclause are restricted to observed concentrations at lower concentration ranges. For integral performance measurement at higher concentrations where availability is concentration-dependent, ISO 13752 should be consulted.

A.5 Determination of additional performance characteristics

A.5.1 Evaluation of zero drift and span drift

Carry out the check operations given in A.4.2 at least once a day during a period (usually seven days) of unattended operation. Record the readings for each check.

Calculate the differences of the readings between the beginning and the end of the period of unattended operation relative to full-scale (zero drift) or to the measurement point (span drift).

NOTE The determination in the laboratory is easier to perform, but the on-site determination gives results which are characteristic of plant conditions.

A.5.2 Evaluation of temperature sensitive zero and span instabilities

Carry out the check operations given in A.4.2 at temperature intervals of 10 K (climate chamber) over the allowable temperature range. Record the readings for each check.

Calculate the differences of the readings from one temperature to the next higher or lower temperature point relative to full-scale (temperature-sensitive zero instability) or to the measurement point (temperature-sensitive span instability).

Carry out the operations as fast as possible to reduce the influence of drift effects.

Bibliography

[1] ISO 4225:1994, *Air quality — General aspects — Vocabulary*

[2] ISO 4226:1993, *Air quality — General aspects — Units of measurement*

[3] ISO 7504:—(1), *Gas analysis — Vocabulary*

[4] ISO 7935:1992, *Stationary source emissions — Determination of the mass concentration of sulfur dioxide — Performance characteristics of automated measuring methods*

[5] ISO 9169:1994, *Air quality — Determination of performance characteristics of measurement methods*

[6] ISO 10155:1995, *Stationary source emissions — Automated monitoring of mass concentrations of particles — Performance characteristics, test methods and specifications*

[7] ISO 10780:1994, *Stationary source emissions — Measurement of velocity and volume flowrate of gas streams in ducts*

[8] ISO 13752:1998, *Air quality — Assessment of uncertainty of a measurement method under field conditions using a second method as reference*

[9] IEC 61207 (all parts), *Expression of performance of gas analyzers*

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1) To be published. (Revision of ISO 7504:1984)

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