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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

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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.

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*

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