IEC

IEC 61207-2

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INTERNATIONAL STANDARD

NORME INTERNATIONALE

**Expression of performance of gas analyzers –
Part 2: Measuring oxygen in gas utilizing high-temperature electrochemical sensors**

**Expression des qualités de fonctionnement des analyseurs de gaz –
Partie 2: Mesure de l'oxygène contenu dans le gaz en utilisant des capteurs électrochimiques à haute température**

IEC 61207-2:2019-06(en-fr)

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INTERNATIONAL ELECTROTECHNICAL COMMISSION

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EXPRESSION OF PERFORMANCE OF GAS ANALYZERS –

Part 2: Measuring oxygen in gas utilizing high-temperature electrochemical sensors

FOREWORD

1) The International Electrotechnical Commission (IEC) is a worldwide organization for standardization comprising all national electrotechnical committees (IEC National Committees). The object of IEC is to promote international co-operation on all questions concerning standardization in the electrical and electronic fields. To this end and in addition to other activities, IEC publishes International Standards, Technical Specifications, Technical Reports, Publicly Available Specifications (PAS) and Guides (hereafter referred to as "IEC Publication(s)"). Their preparation is entrusted to technical committees; any IEC National Committee interested in the subject dealt with may participate in this preparatory work. International, governmental and non-governmental organizations liaising with the IEC also participate in this preparation. IEC collaborates closely with the International Organization for Standardization (ISO) in accordance with conditions determined by agreement between the two organizations.

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International Standard IEC 61207-2 has been prepared by sub-committee 65B: Measurement and control devices of IEC technical committee 65: Industrial-process measurement, control and automation.

This second edition cancels and replaces the first edition published in 1994. This edition constitutes a technical revision.

This edition includes the following significant technical changes with respect to the previous edition.

a) all the terms and definitions relating to the document have been updated where appropriate;

b) the description of the principle of the galvanic cell has been expanded and clarified;

c) new definitions and illustrations have been added for different measurement methods for oxygen using solid electrolytes for galvanic cells;

d) new illustrations have been added for existing descriptions for ion pump cells;

e) a more detailed description of the effect of the presence of oxidizable gases has been added;

f) all references to “errors” have been replaced by “uncertainties” and appropriate updated definitions applied.

The text of this International Standard is based on the following documents:

FDIS	Report on voting
65B/1156/FDIS	65B/1158/RVD

Full information on the voting for the approval of this standard can be found in the report on voting indicated in the above table.

This publication has been drafted in accordance with the ISO/IEC Directives, Part 2.

This International Standard is to be used in conjunction with IEC 61207-1:2010.

A list of all parts in the IEC 61207 series under the general title *Expression of performance of gas analyzers,* can be found on the IEC website.

The committee has decided that the contents of this publication will remain unchanged until the stability date indicated on the IEC website under "http://webstore.iec.ch" in the data related to the specific publication. At this date, the publication will be

- reconfirmed,
- withdrawn,
- replaced by a revised edition, or
- amended.

INTRODUCTION

This part of IEC 61207 includes the terminology, definitions, statements and tests that are specific to oxygen analyzers, which utilise high-temperature electrochemical sensors.

Oxygen analyzers employing high-temperature electrochemical sensors operating at temperatures usually in excess of 500 °C, have a wide range of applications for the measurement of oxygen in gas samples. Such samples are typically the result of a combustion process or oxygen impurity measurements.

Two main types of analyzer exist, the in situ analyzer, where the sensor is positioned within the process duct work, and the "extractive" analyzer, where the sample is drawn from the duct via a simple sample system and presented to the sensor.

An analyzer will typically comprise a sensor head, mounted on the process duct, and a control unit remotely mounted, with interconnecting cable.

EXPRESSION OF PERFORMANCE OF GAS ANALYZERS –

Part 2: Measuring oxygen in gas utilizing high-temperature electrochemical sensors

1 Scope

This part of IEC 61207 applies to all aspects of analyzers using high-temperature electrochemical sensors for the measurement of oxygen in gas.

It applies to in-situ and extractive analyzers and to analyzers installed indoors and outdoors.

The object of this part is:

– to specify the terminology and definitions related to the functional performance of gas analyzers, utilizing a high-temperature electrochemical sensor, for the continuous measurement of oxygen concentration in a sample of gas;
– to unify methods used in making and verifying statements on the functional performance of such analyzers;
– to specify what tests are performed to determine the functional performance and how such tests are carried out;
– to provide basic documents to support the application of internationally recognized quality management standards.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

IEC 61207-1:2010, *Expression of performance of gas analyzers – Part 1: General*

3 Terms, definitions, and concepts

3.1 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- IEC Electropedia: available at http://www.electropedia.org/
- ISO Online browsing platform: available at http://www.iso.org/obp

3.2 Concepts

3.2.1 High-temperature electrochemical sensor

3.2.1.1 General

The sensor is usually controlled at a stable, high temperature, typically in excess of 500 °C. This high temperature is normally maintained by an electric heater, however, in some high-temperature in-situ applications, the sensor may require cooling to be applied. The sensor may also be run in passive mode with temperature sensing, where the heating is provided by the sample environment and the measured temperature is used in the calculation of the oxygen concentration. The high-temperature electrochemical sensor can be constructed in two basic forms:

a) galvanic concentration cell;

b) ion pump cell.

3.2.1.2 Galvanic concentration cell (gauge cell)

3.2.1.2.1 General

Most commercially available analyzers employ the galvanic concentration cell consisting of two gas volumes or chambers, separated by an oxygen ion conducting solid electrolyte, and provided with a porous electrode on each side. The two sides are filled with sample gas on the one side and a fixed oxygen partial pressure reference gas on the other side. The reference gas shall contain some oxygen. The reference gas is usually air, but could be another constant oxygen partial pressure mixture or even a sealed reference where the oxygen partial pressure is maintained by a metal/metal oxide mixture.

The electrodes are catalytic and the electrode/solid electrolyte interface at elevated temperature allows the formation of oxygen ions (O^{2-}) which can then diffuse across the solid electrolyte interface. This interface remains an impenetrable barrier for the other gases present and thus provides a selective means of determining the partial pressure of oxygen present in the sample gas. The solid electrolyte is typically yttrium oxide (yttria)-stabilized zirconium oxide (zirconia), and the porous electrode is platinum based, although other materials may be used. The signal magnitude is temperature dependent and thus requires a low uncertainty of temperature measurement of the solid electrolyte interface by employing temperature sensors as given in IEC 60584 and IEC 60751, and stability of heating provided to achieve the high temperatures required for efficient and sensitive operation.

When the sensor is brought to a temperature at which the solid electrolyte conducts oxygen ions, and the e.m.f. between the two electrodes is measured, the output will be related to the logarithm of the ratio of the partial pressures of oxygen at each of the electrodes in accordance with the Nernst formula:

$$E = \frac{RT}{4F} \ln \frac{P_1}{P_2} \quad (1)$$

$$E = k \log_{10} \frac{P_1}{P_2} \quad (2)$$

$$E(\text{mV}) = 0{,}0496\, T \log_{10} \frac{P_1}{P_2} \quad (3)$$

where

P_1 is the partial pressure of oxygen in the reference gas;

P_2 is the partial pressure of oxygen in the sample gas;

E is the electromotive force output from the cell in mV;

R is the gas constant (8,314 4 J K^{-1} mol^{-1});

T is the absolute temperature (K);

F is the Faraday constant (9,648 53 x 10^4 C mol^{-1});

k is the Nernstian coefficient (slope factor).

Thus, provided the oxygen partial pressure is known at one electrode (P_1), then the potential difference between the two electrodes will enable the unknown oxygen pressure to be determined at the other electrode (P_2).

Note that in the above formulae, it is the partial pressure of oxygen on the two sides which is important, not the fractional component of the oxygen. Therefore, if equal component mixtures containing oxygen (e.g. air), but at different absolute pressures, are applied to either side of the solid electrolyte barrier, the signal will not be 0 mV, but proportional to the logarithm of the ratio of the absolute pressures of the gases on each side.

The Nernstian response of the high-temperature electrochemical ceramic sensor holds over a very wide range of oxygen partial pressures differences, and the sensor output increases logarithmically with linear reduction of the oxygen's partial pressure at a given temperature. The sensor output is directly proportional to temperature, and hence for quantitative analysis, the temperature of the cell should be closely controlled and/or measured, and the necessary corrections applied in Formula (1).

Theoretically, the output e.m.f. of the sensor, when the partial pressures of the sample gas and reference gas are equal, is 0 V. However, in some sensors, a zero offset is measured and is considered as being largely due to thermo-electric effects and thermal gradients across the electrodes. This offset can be considered theoretically as an extra constant (asymmetry potential).

$$E(\text{mV}) = k \log_{10} \frac{P_1}{P_2} + U_a \quad (4)$$

$$E(\text{mV}) = 0{,}0496 \log_{10} \frac{P_1}{P_2} + U_a \quad (5)$$

where

U_a is the asymmetry potential (mV).

Non-ideal oxygen ion conduction can also be compensated for by introducing modifications to the slope factor k.

In practice, manufacturers whose sensors exhibit zero offset may supply practical average values of U_a to help in calibration. Modern equipment can automatically compensate the asymmetry potential during air point calibration (i.e. air in both chambers).

Typical applications are in combustion control, which measures the oxygen level which can be in the order of a few percentage points under normal working conditions or in oxygen contamination, for example in nitrogen production and purification using ASUs (air separation units), where the oxygen level is in the region of a few parts per million. Therefore, it can be seen that this technique provides a very wide potential measuring range of the oxygen level from 100 % down to sub parts per million. In practice, the ultimate lower quantitative

measurement limit depends on the leak integrity of the device and the limitations of the electronics. The solid electrolyte sensors may have the gases actively flow fed or diffusionally fed to the sample and reference sides of the solid electrolyte interface.

Some examples in 3.2.1.2.2 to 3.2.1.2.6 are given of generic sensor designs. For simplification, the temperature sensors in these illustrations have been shown as being positioned at the solid electrolyte interface, however, the practical implementation of a generic design may limit the actual physical location of the temperature sensor. Any non-ideal location may give rise to a voltage offset (U_a) as illustrated in Formulae (4) and (5).

NOTE Platinum is frequently used for the electrodes, and the ceramic electrolyte is usually zirconium oxide, fully or partially stabilized with yttrium oxide, calcium oxide or thorium oxide, which, when heated above 500 °C, allows the charge transfer mechanism to be predominantly oxygen ion conduction.

3.2.1.2.2 Flow through tube sensor

The solid electrolyte tube is given porous electrodes on the inner and outer surfaces. The tube is hermetically sealed to inlet and outlet pipes and sample gas flows through the inner tube, whilst the reference gas (air) surrounds the outer surface. This is shown schematically in Figure 1.

3.2.1.2.3 Test tube sensor

A solid electrolyte tube is sealed at one end and porous electrodes placed on the inner and outer surfaces. The sample either flows past or diffuses around the outside of the tube. A reference gas (air) is in the middle of the tube. External heating provides the high temperature required. This is shown schematically in Figure 2.

3.2.1.2.4 Disc sensor

A solid electrolyte disc with porous electrodes on each face is sealed into a tube with matched coefficient of thermal expansion. The outside surface is exposed to sample gas and the inside surface to a reference gas (air). The high temperature is provided by an internal heater on the reference side. This configuration is suitable for use as part of an in situ probe for oxygen measurements. This is shown schematically in Figure 3.

3.2.1.2.5 Twin chamber design

In this design, the sample and reference gases are either flowed or diffusionally fed into two chambers separated by a solid electrolyte interface. The high working temperature required is provided by a band heater or equivalent around the outer surface of the solid electrolyte tube, which gives a relatively wide area of flat thermal gradient leading to a highly stable reading. This arrangement is best suited for an extractive or close coupled extractive arrangement. This is shown schematically in Figure 4.

3.2.1.2.6 Sealed reference design

This has similarities to the above generic configurations, however, instead of using a continuously replenished reference gas (air), a sealed reference volume is used. It is important to retain a constant partial pressure of oxygen within this volume, and this is normally achieved by using a mixture of metal and metal oxide powders which maintains an equilibrium within the reference cavity and acts both as a source and sink for oxygen. This has the advantage of not requiring a reference gas; however it is more susceptible to the influence of any breach of the hermetic seal on the reference side. This equilibrium is shown in Formula (6) where a and b are constants and M and O represent a metal and oxygen. This arrangement is illustrated schematically in Figure 5. This type of sensor may have a limited lifetime, depending on working conditions.

$$aM + \frac{b}{2}O_2 \leftrightarrow M_aO_b \tag{6}$$

3.2.1.3 Ion pump cell

If a direct current is made to flow between the electrodes of a cell, with reference gas (air) in one chamber and an inert gas in the other chamber, the current flow will cause a pumping of oxygen molecules from one side to the other. The action obeys Faraday's laws and the quantity of oxygen pumped by diffusion into the inert gas is given by:

$$Q = \frac{I}{4F} \tag{7}$$

where

Q is the quantity of oxygen pumped, in mol s^{-1};

I is the current (A);

F is the Faraday constant (9,648 53 x 10^4 C mol^{-1}).

This is used generally in two basic configurations.

3.2.1.4 Limiting current

A diffusion restriction such as a pinhole limits the rate of arrival of oxygen molecules at the measuring electrode, and a constant voltage across the electrodes ensures that all the oxygen arriving at the measuring electrode is pumped to the other side. This reduces the partial pressure of oxygen at the cathode close to zero. In this limiting condition, the current flowing is determined by the rate of diffusion of oxygen through the restriction, which in turn is proportional to the oxygen concentration in the sample gas. The current generated is quantitatively related to the number of oxygen molecules transferred. An example is shown in Figure 6.

3.2.1.5 Fixed volume (pump-gauge devices)

This configuration consists of two sets of electrodes arranged across a small fixed volume. The first set comprises a concentration (gauge) cell, the second set the ion pump. The volume is initially swept free of oxygen molecules by the ion pump to a predetermined low level as determined by the concentration cell. Pump action is then initiated in the opposite direction until the concentration cell reading shows that the oxygen concentration in the volume and that outside at the sample side, are the same. The current and time required to achieve this are related to the oxygen concentration of the sample gas. An example is shown in Figure 7.

3.2.2 Reference gas

All analyzers using the high-temperature electrochemical concentration cell require some form of reference. This could be an applied reference gas of known and constant partial pressure – for convenience usually air is employed – although in principle it could be any known, stable oxygen partial pressure. In some instances, a sealed reference is used, where the oxygen partial pressure is maintained at a constant level (see 3.2.1.2.6).

NOTE The sensor output is a function of the partial pressure of oxygen in the sample, provided the reference has a constant partial pressure of oxygen.

3.2.3 In situ analyzer

The in situ analyzer has the high-temperature electrochemical sensor situated in the sample; however the sensor may require a filter to remove particulates.

One version of the in situ analyzer controls the temperature of the sensor in the range of 500 °C to 900 °C. In this case the sample temperature cannot exceed the control temperature. The second version relies on the temperature of the sample to attain the operating temperature. It is then necessary to measure the sensor temperature to enable the oxygen value to be calculated.

3.2.4 Extractive analyzer

This can be subdivided into two groups: close coupled and extractive. In the "extractive" analyzer the sensor head is installed outside the gas stream to be measured, and the sample is drawn through a sample probe and presented to the sensor which is maintained at a controlled temperature to ensure ionic conduction (typically in the range of 500 °C to 900 °C).

Additionally, the extractive analyzer may require sample conditioning. The extractive analyzer may require a filter to remove particulates, and a driving force (often an aspirator) to move the sample. The pipework involved should be minimized and maintained above the dew-point of any condensable species to prevent formation of any condensation.

3.2.5 Hazardous area

Area in which an explosive gas atmosphere is present, or may be expected to be present, in quantities such as to require special precautions for the construction, installation and use of devices

3.2.6 Flame trap

A device used to prevent a flame, resulting from the ignition of a flammable gas mixture, from propagating.

3.2.7 Essential ancillary units

Essential ancillary units are those without which the analyzer will not operate (e.g., pumps for aspirators, calibration systems, etc.).

4 Procedures for specification

4.1 General

The procedures for specification are detailed in IEC 61207-1. They cover:

– operation and storage requirements;
– specification of ranges of measurement and output signals;
– limits of uncertainties;
– recommended reference values and rated ranges of influence quantities.

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 high-temperature electrochemical sensors are also detailed.

4.2 Specification of essential units and ancillary services

4.2.1 General

All oxygen analyzers utilizing high-temperature electrochemical concentration cells require a reference gas supply. This is usually air, filtered to remove moisture and oil. Analyzers require facilities for calibration after installation. Bottled calibration gases and pressure regulation facilities are generally required.

4.2.2 Rated range of reference gas pressure

Reference gas pressure in practice may have small effects on uncertainty.

The reference gas pressure will also affect the reference gas flow. High flows can cause cooling of electrodes and subsequent uncertainties.