

ZIROX – Oxygen Measuring Technology



Measuring System Oxygen Probe SS27/MS27 Electronics E2010

For the measurement of oxygen concentrations
in flue gases and furnace atmospheres

Manual

Power supply: 24 V DC

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1 General information

1.1 Introduction

This manual describes composition, mode of operation and use of the oxygen measuring system SS27/MS27-E2010 of the ZIROX GmbH.

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The manufacturer guarantees that this manual was written in accordance with the functional and technical features of the delivered SS27/MS27-E2010.

This manual is not subject to the amendment service. If the manufacturer modifies the SS27/MS27-E2010 with the aim of making technical improvements, the user is responsible for inserting the additional or updated pages supplied.

Proper operation of the SS27/MS27-E2010 can only be ensured if the contents of this manual are known. Therefore, all chapters of this manual must be read carefully prior to operating the SS27/MS27-E2010.

The values on the device display in this manual are examples or preset parameters of the manufacturer. Process-specific parameters must be set by the user.

Pages, charts and figures are numbered consecutively.

1.2 Copyright

This operation manual is copyright protected.

It must not be partially or completely reproduced, copied, or distributed, without prior written permission of the manufacturer. The use for competitive advantages or the distribution to third parties are not authorized either.

All rights reserved.

1.3 Commonly used symbols

Symbol for imminent danger:

This symbol refers to imminent danger to persons' life and health.

In case of disregard fatal injuries may result.



Symbol for indirect danger:

This symbol indicates indirect danger.

The degree of the damage depends on the circumstances and the actions of the persons involved.

In case of disregard, destruction or damage of the SS27/MS27-E2010, its single components or other material assets as well as minor injuries may result.



Symbol for proper handling:

This symbol appears where the manual refers to the adherence to rules, instructions and proper operation.

In case of disregard, damage or destruction of the SS27/MS27-E2010 or its single components may result.

NOTE

2 Application fields

The measuring system serves the continuous measurements of the oxygen concentration in furnace atmospheres and in flue and process gases.



Due to the robust construction, the MS27 is mainly used for the application in flue gases. Due to the construction, the measuring range is limited to 0.1 – 20.64 vol% O₂ (in contrast to conventional zirconia sensors).

Using the measuring system in explosive gas mixtures is strictly forbidden. The probe is an ignition source!

Using the measuring system in explosive gas mixtures, in gas atmospheres with halogens in high concentration and sulphuric gas mixtures (e.g. SO₂) is not permitted.



Properties of the measuring system:

- Continuous measurement of the oxygen concentration
- Deviations of the oxygen concentration from set values are signaled
- Signal processing
- Output of measuring value via standard interface
- Process monitoring via standard interfaces

Functions

The requirements and limit values provided in “Technical data” must be strictly observed.

Any other use is treated as non-authorized use.

3 Safety regulations

The following regulations for industrial safety provide basic information about potential danger during the operation of the SS27/MS27-E2010. Therefore, they must be observed and strictly followed by the responsible staff.

- A failure-free and functional operating of the device can only be guaranteed with knowledge of this manual. Therefore, all chapters of this manual must be read carefully before the installation and initiation of the device.
- The device is to be used for the functional operation only (see chapter 2).
- The device is to be installed, operated, and serviced by trained staff only.

Explosive gas mixtures, halogens in high concentration, and sulphuric gases (e.g. SO₂) are not permitted to be measured by this measuring system. It must not be used in potentially explosive atmosphere.



The probe is heated electrically and the peak is very hot. Please use the probe carefully to avoid burns by hot peak.

Special safety instructions for potential danger during certain working processes are given in relevant text passages.

4 Functional description

4.1 Composition

The following picture provides an overview of the complete system. It consists of probe (MS27 or SS27) and electronics (E2010).

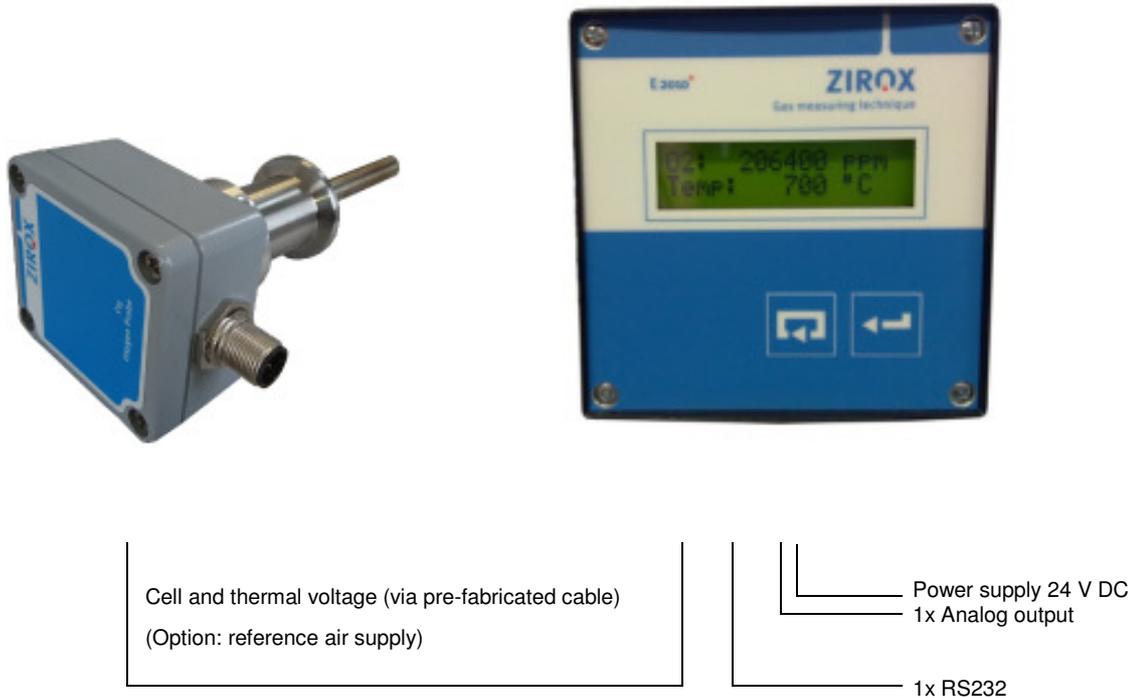


Fig. 1: Schematic diagram of the measuring system

4.2 Measuring principle

The determination of the oxygen concentration in gas atmospheres is a frequent demand. Mostly, it is measured in gases with oxygen concentrations independent of temperature.

The determination of the oxygen concentration by the ZIROX flue gas measuring system is based on the NERNST law:

NERNST-equation

$$U = \frac{RT}{4F} \ln \frac{p_{O_2, air}}{p_{O_2, measuring gas}} \quad (I)$$

U – cell voltage in V, R – molar gas constant, $R = 8.314 \text{ J}/(\text{mol} \cdot \text{K})$, T – measuring temperature in K, F – faraday constant, $F = (9.648 \cdot 10^4 \text{ C/mol})$

$p_{O_2, air}$ – partial pressure of the oxygen at the reference electrode in dry air in Pa

$p_{O_2, measuring gas}$ – partial pressure of the oxygen at the measuring electrode in Pa.

The sensor of the device is based on the conductivity of oxide ions in a special ceramic substance (zirconium dioxide) with stabilizing additions. The conductivity of these oxide ions increases exponentially with the temperature and reaches a sufficiently high temperature above 600°C (standard adjustment of probe heater: 700°C). The oxide ion conductor is a ceramic, gas-tight tube and has a platinum electrode inside and outside. Air flows around the inside electrode. It serves as the reference electrode with constant, known electrode potential. The gas to be measured works on the outer electrode.

The ceramic tube is located axially symmetrically in an electrical furnace. (In the case of high temperature probe the hot gas is used for heating).

Based on the assumption that the total pressures of the gases are almost the same at both electrodes (in this case the volume concentrations may be used in the calculation instead of the partial pressures) and replacing the parameters by numbers in equation (I), the following equation applies:

Equation for oxygen concentration

$$\varphi_{O_2} = 20.64 \cdot e^{(-46.42 \cdot \frac{U}{T})} \quad (II)$$

φ_{O_2} – oxygen concentration of the measuring gas in Vol.-%

U – potential difference in mV

T – measuring temperature in K (mostly 973.15K)

20.64 – oxygen concentration in air with rH of 50% in vol%.

The oxygen in the measuring gas can be in free or bound state¹ (see appendix 1).

The following dependencies apply for the cell voltage U :

$U \sim T$ – for free oxygen

$U \sim \frac{1}{T}$ – for bound oxygen

The equation (II) for calculating the oxygen concentration is valid for measuring gases with free oxygen as well as for reducing gas mixtures in which oxygen only exists in bound form (e.g. in H₂/H₂O- or CO/CO₂-mixtures).

In reducing gas compounds, the oxygen partial pressure is inversely proportional to the temperature. For converting the measured value at the measuring temperature into other temperatures special thermodynamic equations are required.

Reducing gas compounds

¹ If there is not enough **free oxygen** besides combustible components, a chemical equilibrium establishes at the hot platinum electrodes. The cell measures the concentration of the **equilibrium oxygen**.

5 Technical data

5.1 Probe SS27/MS27

Working range	20.6 vol% ... 15 ppm O ₂ (SS27) 20.6 ... 0.1 vol% O ₂ (MS27)
Installation length.....	65 mm (M18x1.5), 75 mm (DN40KF) (others on request)
Diameter	10 mm
Weight	Approx. 0.5 kg
Dimensions clamp head.....	64 x 58 x 36 mm
Protection degree	IP52, others on request
Heater voltage	24 V, controlled (PWM)
Warm-up.....	Approx. 5 min (operating state reached after 60 min due to thermal balance processes)
Accuracy.....	< 5 % rel. error
Working temperature	700 °C
Gas temperature.....	Max. 300 °C (up to 600 °C special construction only)
Surrounding conditions	0...50 °C, rH < 85 %
Gas flow	Max. 10 m/s (>10 m/s: immersion sleeve recommended)
Reference gas	Ambient air (supply by diffusion)
Storing conditions	-10...50 °C, rH < 85 %
Cross sensitivity.....	None (but combustible components consume oxygen – the equilibrium oxygen is measured)
Pressure dependence.....	In case of deviations from normal pressure, the measuring value must be corrected: corr. value = measuring value x gas pressure/101325 Pa

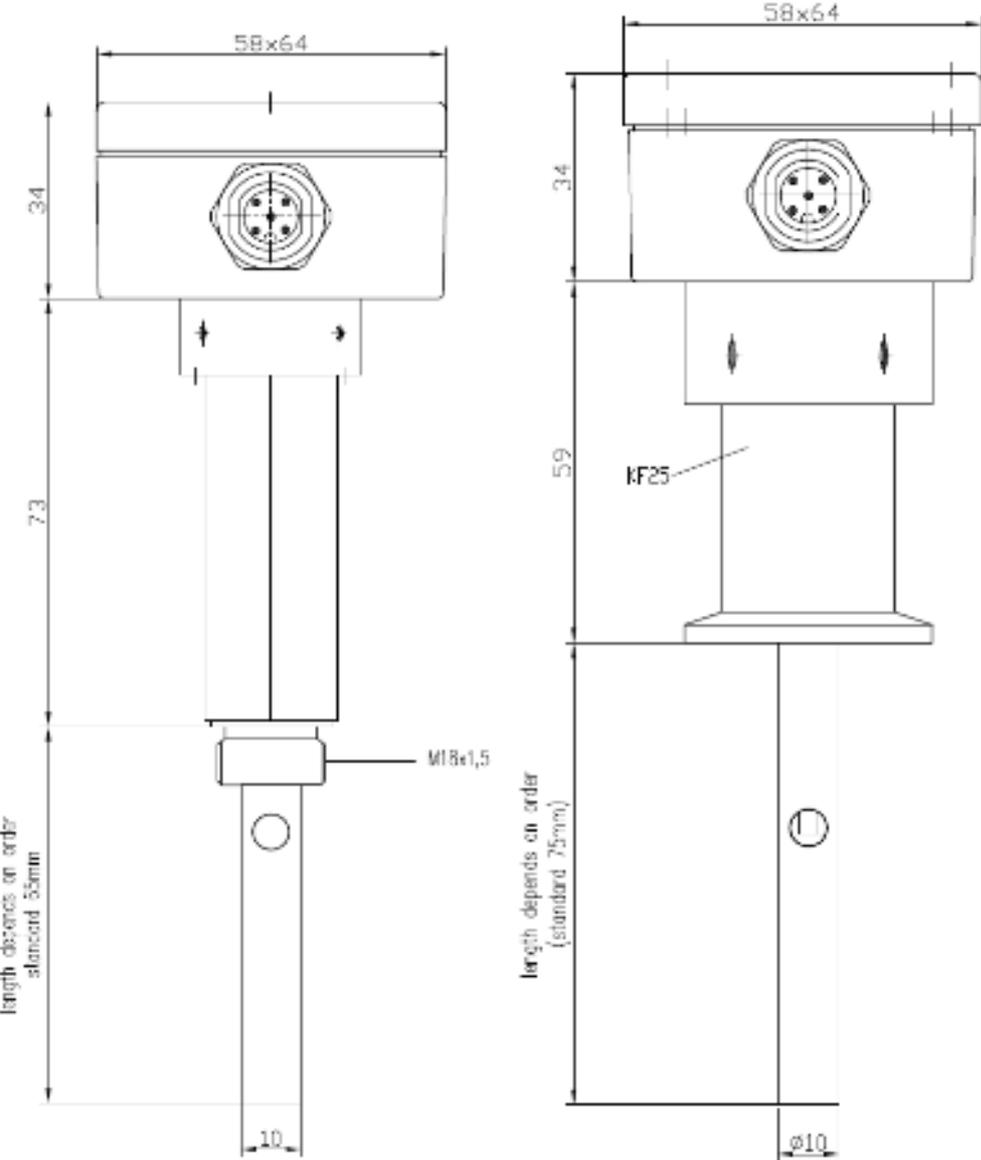


Fig. 2: Scale drawings of probe with screw-in thread (left) and flange (right)

5.2 Electronic unit E2010

Dimension (D x W x H in mm).....	96 x 96 x 125
Weight.....	650 g
Power supply.....	24 V DC +/- 10 %
Power consumption.....	30 W
Protection degree.....	IP 30 (Front IP52)
Fuse.....	2.5 A, resettable
Working temperature.....	0...40 °C
Storage temperature.....	0...50 °C
Set temperature.....	700 °C
Display.....	Double-spaced LCD-display 2 x 16 digits
Input signal.....	Sensor and thermoelectric voltage
Output signal.....	4...20 mA (0...10 V option)
Keypad.....	2 keys (membrane keypad)
Alarm indication.....	Current output goes to 0 mA
Interface (option).....	RS232

6 Composition

6.1 Front, keys

The display and the keys for parametrization are located on the front.



Menu key: scroll or select the requested parameter



ENTER key: activate or enter adjusted parameter (save change)



Fig. 3: Front view E2010 with keys and display

6.2 Rear, connections

All connections and outputs are located on the rear.

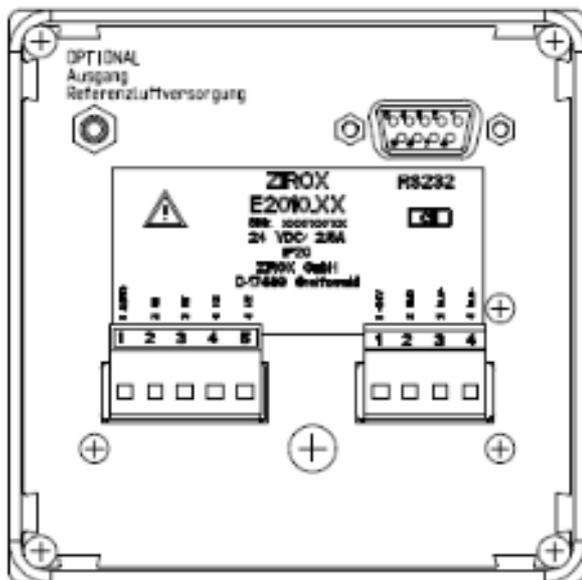


Fig. 4: Rear view E2010 with connections

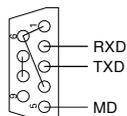
Terminal strip X1 (Sensor connection)

Plug-Pin	Designation	Color (for cable < 5m, pre-fabricated)	Color (for cable > 5m, special construction)
1	AGND (common ground for cell and thermal voltage)	brown	brown
2	Cell voltage U_z	white	white
3	Thermal voltage U_T	blue	green
4	Heater U_H	black	yellow
5	Heater U_H	grey	grey

Terminal strip X2 (Power supply/output signal)

Pin	Description
1	+24V DC
2	GND
3	OUT +
4	OUT -

RS 232-Interface (9600 Baud)



Pin assignment RS 232

The RS232 interface must be connected with a computer by SUB-D-cable (9pol., 1:1, uncrossed)!

Transfer rate: max. 9600 Baud, adjustable

Stop bits	1	Parity	None
Data bits	8	Handshake	Without

Protocol of the serial interface (CR = carriage return)

Set	Feedback signal (example)	Transferred measuring value	Parameter
M2CR	M2x.xxExxCR M22.06E+05	$2.06 \cdot 10^5$ ppm O ₂	Oxygen concentration in ppm
A1CR	A1xxx.xCR A120.9	20.9 mV	Cell voltage in mV
A2CR	A2xxx.xCR A2749.9	749.9 °C	Measuring temperature in °C

The parameters are set with the keys on the front panel (see chapter 6.1).

PC-software for display and storage of the measuring values is available on request (surcharge).

Error messages via RS232

ERROR0	Transfer error RS232 (or wrong/invalid command)
ERROR1	Warm-up (Cell temperature too low, < 30 min)
ERROR2	Cell temperature too low (< Set temp. – 10 °C, > 30 min)
ERROR3	Thermocouple broken
ERROR6	System error

7 Installation and initiation

7.1 Installation

The clamps on the rear must be connected with the sensor clamps (s. chapter 6.2).

The power supply is 24 V DC.

7.2 Reference air supply for ZIROX probes

This paragraph only applies to special probe constructions, which require reference air supply because of their length.

Reference air input of the sensor and the reference air output of the E2010 must be connected by a flexible hose (inner diameter 3 mm). The reference air flow is preset by the manufacturer.

After starting the system (E2010 with connected sensor) the reference air flow must be checked by an inserted flow meter (5 - 10 l/h resp. approx. 100 - 200ml/min) and, if applicable, adjusted via display.



7.3 Waiting for operating state

Depending on the connected sensor the E2010 needs a certain period of time until the operating state is reached (for further information see technical data of sensor). Due to thermal balancing effects, the sensor needs approx. 60 minutes until the ultimate operating state after reaching the operating temperature.

The keys are locked before reaching the operating state!

The electronic unit E2010, developed for panel mounting, provides the power supply for ZIROX sensors, evaluates signals and displays measuring results in the form of a standard signal (4-20 mA) for process control.

The electronics realizes the following functions:

- Power supply and control of sensor heating
- Processing of the thermoelectric and cell voltage of the probe to the oxygen concentration
- Output of the oxygen concentration as a standard signal
- Calibration
- Reference air supply by internal pump (option)

NOTE

7.4 Probe mounting

The probes are mounted with a screw-in thread M18x1.5 or flange DN40 KF (according to order, others on request).

Note: If the installation depth is too low, the measuring cell of the probe can be in layers of false air existing in the margin of the device and causing measuring errors. Make sure to seal the slot tightly to protect the probe from false air intrusion and avoid measuring errors. Too high inflow can cause failure of the heater regulator. The probe must be protected from dust and condensate. In all cases, the use of an immersion sleeve is recommended (see next chapter).

When pulled out after a running process the probe is very hot. Burn and fire hazards!



7.5 Use of immersion sleeve

At high flow velocities or dust strain, the installation of the probe in a protective tube (immersion sleeve) can be practical.

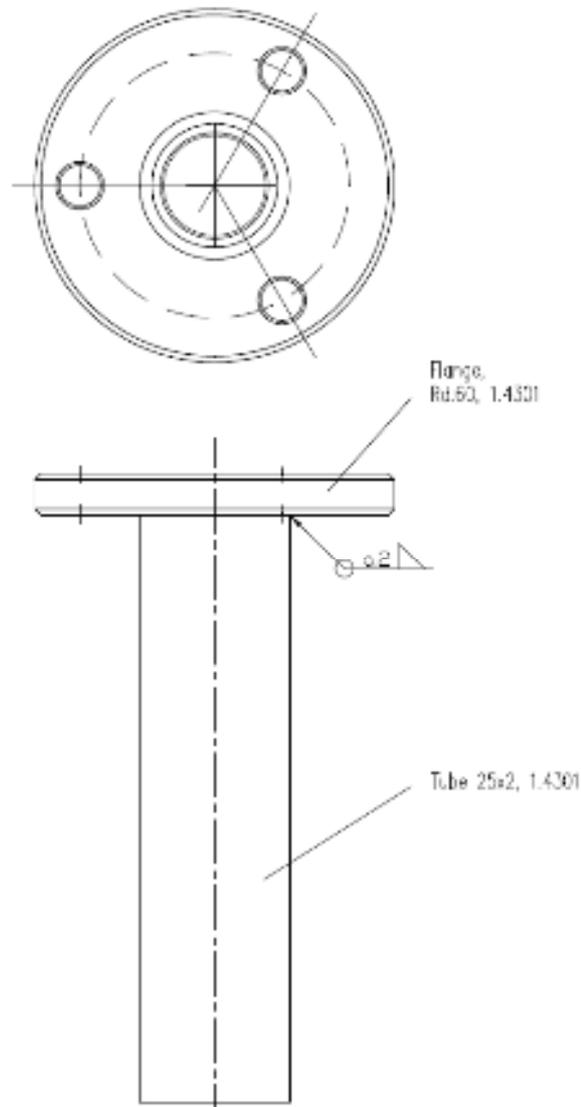


Fig. 5: Immersion sleeve with screw-in thread for SS27 and MS27

8 Parametrization

8.1 Menu operation – an example

WARM UP
Temp: 555 °C

After switch-on, the warm-up starts. From 400 °C on, the current temperature is displayed in the second line. After reaching the working temperature, the oxygen concentration is displayed in the first line.

O2: 20.6 Vol.-%
Uz: xx.x mV

By pressing  several values can be displayed in the second line. (see chapter 6.1).

Calibration

With help of both keys an offset-calibration („zero point calibration“) in **clean air** and a span gas calibration is possible. The complete menu is shown schematically in figure 6, p.22.



The sensor can be very hot for a while after switch-off and during operation.

CAUTION – VERY HOT – DO NOT TOUCH!

8.2 Display

E2010
Version 2.4.6

Start display, approx.3sec
Software version

E2010
THERMOCO. TYP B

Start display, approx.3sec
Thermocouple type

WARM-UP
Temp: 450 °C

Warm-up of the ZIROX-sensor

O₂: 20.64 Vol%
Temp: 700 °C

O₂: 20.64 Vol%
Vz: -2 mV

O₂: 20.64 Vol%
SETTINGS

O₂: 20.64 Vol%
CALIB.ZERO POINT

O₂: 20.64 Vol%
CALIB. SPAN GAS

8.3 Adjustable parameters

The following parameters are adjustable in the menu SETTINGS.

OUTPUT VALUE Vol % O ₂	<i>Valid for display and analog output!</i> <i>Vol ppm O₂, mbar O₂, atm O₂, Vz [mV]</i>
---	--

OUTPUT VALUE log[10]	<i>linear (for Vz linear only)</i>
--------------------------------	------------------------------------

OUTPUT 4 - 20 mA ZERO: 400 ppm	<i>Current output</i> <i>Zero point 400 ppm corresponds to 4 mA</i>
---	--

OUTPUT 4 - 20 mA SPAN: 206400 ppm	<i>Terminal value 206400 ppm corresponds to 20 mA</i>
--	---

RETURN ? NO YES

SAVE VALUES ? NO YES

8.4 Zero calibration

The E2010 has a calibration function. Based on that function the zero point calibration and, if requested, the span gas calibration can be conducted (see figure 6). The zero calibration must be conducted in clean air.

It serves the balance of the offset voltage of the ZrO_2 -sensor. The offset is caused by the construction (when the electrode has a disadvantageous position in the heating field) and can occur due to aging of the sensor.

Before calibration, the sensor is flushed with ambient air. The gas flow is set by internal or external pump at the value which is used for measuring the measuring gas.

With the zero calibration, the working point in ambient air is calibrated with 20.64 vol.% O_2 .

NOTE

8.5 Span gas calibration

After calling the SPAN GAS concentration in the calibration menu (see figure 6) the setting options are activated by pressing the enter key. The flashing digit can be set by pressing the menu key. After changing all the digits this menu is deactivated by ENTER and left by the menu key.

Now the calibration can be started.

8.6 Reset calibration

If in the main menu **CALIB.ZERO POINT** or **CALIB.SPAN GAS** is displayed and both keys are pressed for 3 seconds, **RESET CAL.ZERO?** or **RESET CAL.SPAN** will be displayed.

By pressing ENTER, the calibration values will be reset to 0 or 1.

8.7 Error messages during calibration

CALIBR. FAILED
OUT OF RANGE

//limits: $\pm 50mV$ resp... $\pm 50\%$ of V_z

CALIBR. FAILED
*** TIMEOUT ***

//no steady measuring value in 20sec.

8.8 Menu navigation of calibration (diagram)

In the first line the current measuring value is shown!

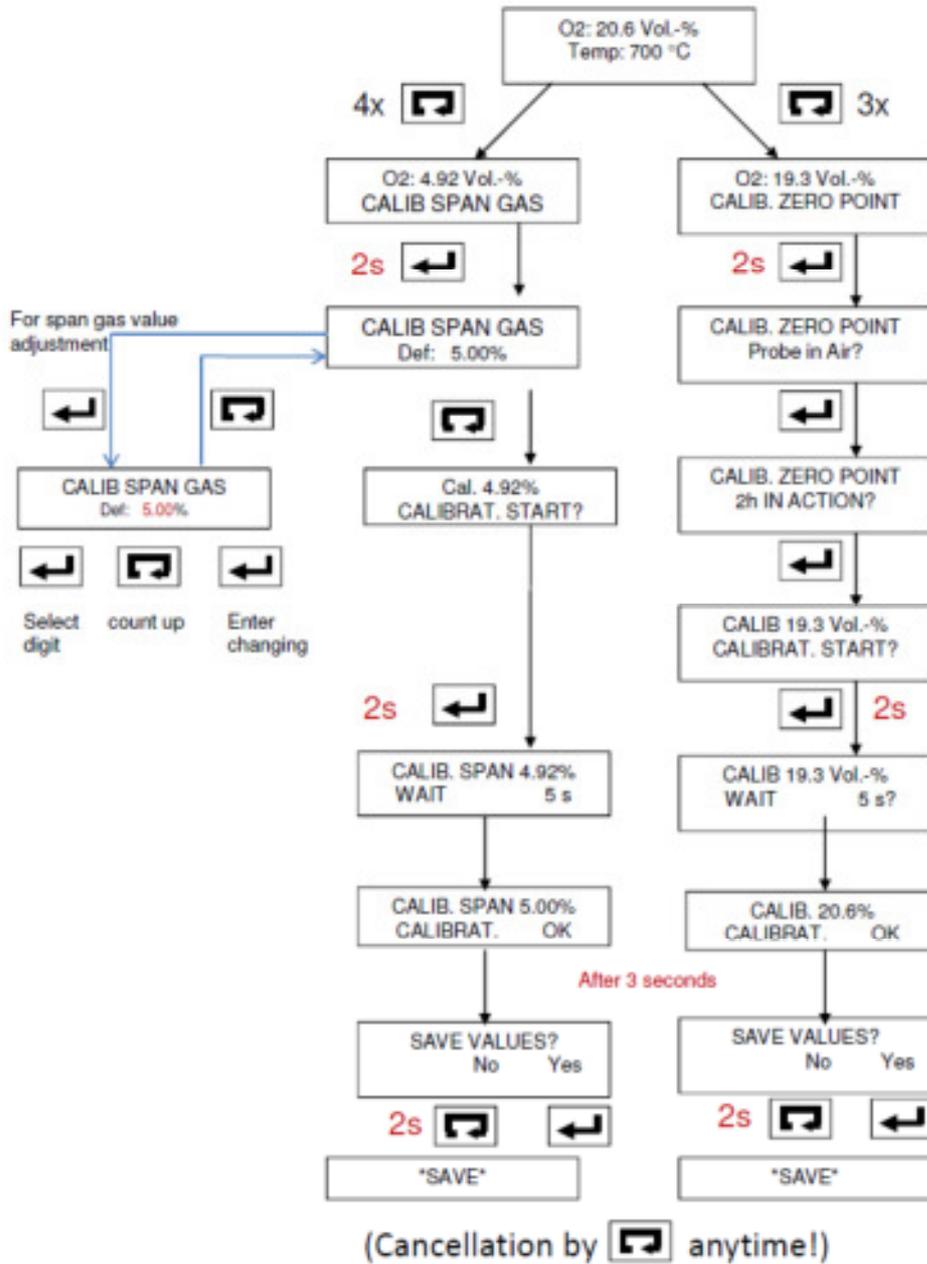


Fig. 6: Diagram offset and span gas calibration

9 Status display /Error messages

No.	Display	LED red	LED green
1	OK	off	on
2	Limit value	on	on
3	Probe temperature < 700 °C	flashing	off
4	Thermocouple broken		
5	System error		

In status 3 to 5 the current output is 0 mA!

10 Faults and fault clearance

During operation the probe is permanently controlled. Typical errors are identified.

The following error messages and faults can appear:

Fault	Cause	Clearance
No output signal LED off	No power supply	Check power supply
Display: WARM UP TEMP: 543°C	System just connected and still heating	
Display: LOW PROBE TEMP:	Probe temperature too low (< 690 °C)	Probe cooling caused by excess gas velocity
Display: +++ ERROR +++ THERMOCOUPLE	Broken thermocouple, wires or clamps defective	Check cables, check thermocouple resistance ($R < 20 \Omega$) or contact service
Display: +++ ERROR +++ COLD JUNCTION	Cold junction in E2010 defective (only TC type K)	Consult service, send probe back to manufacturer
Relatively high measuring value near 20 vol% when a lower value is expected	Probe defective, leak	Consult service, send probe back to manufacturer
Measuring value is much lower than expected	Components reacting with oxygen in the measuring gas (e.g. hydrocarbons) at high temperature and under oxidizing conditions	Use of probe is not applicable Contact service

11 Maintenance

11.1 General information

Zirox sensors and probes with thermocouple type B are calibration- and maintenance-free. Only special products with thermocouple type K (e.g. oxygen probe SS51 for measurements in flue gases) must be calibrated periodically.

11.2 Calibration

Depending on the sensor type, a regular zero point calibration and (if sensor with thermocouple type K) a span gas calibration is necessary (see chapter 8). The corresponding frequency is outlined in the technical data of the sensor.

11.3 Storage

The device must be stored in a dry and dust-free room at 0...50 °C. Please use the original packing!

12 Appendix

12.1 Fundamentals of the use of potentiometric ZrO₂ solid electrolyte sensors for the optimal running of combustion processes

In various technological processes (e.g. production of glass or ceramics fibres, firing of porcelain, and generation of energy or crude gas from solid or liquid fuels etc.), the optimization and repeatable running of combustion processes ensure a consistently good product quality and exploitation of resources. Quality standards like ISO 9000 stipulate the collection and documentation of process-relevant data in order to guarantee the product quality. For the monitoring and controlling of such installations measuring values are required as controlled quantity. These values are recorded in a wide range of gas compounds, preferably in real-time, and can be clearly assigned to completely established gas equilibrium.

Nowadays, those signals are generally obtained by using potentiometric ZrO₂ solid electrolyte sensors. The ZIROX company in Greifswald has developed both short and very long probes, which are equipped with sensors (either unheated or electrically heated), for operating in situ in various kinds of combustion installations, technical furnaces, and flames, producing the required signals. Apart from that, ZIROX produces devices with electrically heated sensors for the analysis of externally pre-mixed fuel-air compounds or of siphoned flue gases.

The chemical, thermodynamic, and electrochemical fundamentals, which the application of potentiometric solid electrolyte sensors (i.e. galvanic solid electrolyte cells) in the running of combustion processes is based on, are described in the following.

Oxygen concentration and air factor lambda

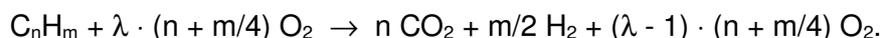
The best way to describe the conversion of gaseous, liquid or solid fuels with air is by using the air factor lambda. This quantity represents the ratio of the amount of air which is fed to the combustion process and the amount of air that is needed for a stoichiometric conversion of the supplied fuel. The amount of air can be indicated in volume, mass, or amount of substance (which are proportional to each other according to the ideal gas law; units like m³, kg or mol shorten themselves when forming the ratio). If volume is the quantity that is used, lambda is given by the following equation:

$$\lambda = v(\text{air volume fed}) / v(\text{air volume needed for stoichiometric combustion}).$$

If too much air is fed to the process (excess air), then $\lambda > 1$. If too little air is fed to the process (air deficiency), then $\lambda < 1$. In case of exact stoichiometric combustion $\lambda = 1$.

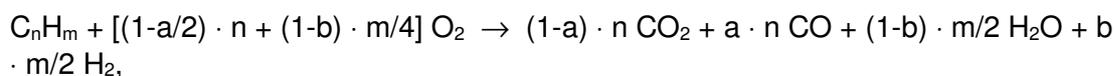
(Only in automotive engineering a different definition applies. In engine test benches the amount of consumed fuel is weighed, and the supplied air volume is converted into mass. When the air mass is divided by the fuel mass, e.g. for pure octane a value of 15.3 is obtained in an exact stoichiometric conversion.)

For the combustion of hydrocarbon (in motor fuel, natural gas, liquid gas) with the gross formula C_nH_m, the following reaction equation is obtained for λ in case of complete combustion in excess air:



In combustion processes with air deficiency, sufficiently high temperature and, if necessary, with catalysts for the establishment of complete gas equilibrium, a mixture of nitrogen, hydrogen, water vapor, carbon monoxide and carbon dioxide (the so-

called "water gas" which can be produced from coal and water) develops from all organic substances. The reaction formula for air-deficient combustion cannot be described merely by the parameters λ , n and m . Rather, the following equation applies:



when a and b are quantities determined by λ and the position of the temperature-dependent water gas equilibrium $CO + H_2O = CO_2 + H_2$.

Gas potentiometry with solid electrolyte cells only produces the oxygen concentration $\varphi(O_2)$ in the respective measuring gas. However, in many cases the determination of λ is desired. For the calculation of λ , the following equations can be derived:

$$\lambda_l = \frac{1 + \frac{\varphi(O_2)}{1 + 2V}}{1 - \frac{\varphi(O_2)}{\varphi(O_2)_{Luft}}} \quad \lambda_r = 1 - \frac{1}{1 + 2V} \left[\frac{V}{1 + \frac{\sqrt{\varphi(O_2)}}{K_C}} + \frac{1}{1 + \frac{\sqrt{\varphi(O_2)}}{K_H}} \right]$$

These equations, valid for single hydrocarbons for $\lambda > 1$ (lean burn) and $\lambda < 1$ (rich burn), contain the carbon/hydrogen-ratio in the hydrocarbon $V = 2 n/m$ and the thermodynamic equilibrium constants of the reactions



In practice, however, usually compounds of different hydrocarbons are present. Fuel gases can also contain hydrogen, carbon monoxide, and nitrogen. Apart from that, the supplied air with its humidity and carbon-dioxide content also contributes to the gas equilibrium. In correspondingly modified equations, average values of V must be used. Thinning with nitrogen has some influence on λ in the lean burn range but not in the rich burn range because the equilibrium between the water gas components does not depend on pressure, and thus does not depend on the water gas concentration.

The change in the kind of equation that is needed for the calculation of λ , if the conditions change from excess of oxygen to lack of oxygen, constitutes a special problem. In that case for each measurement the concentrations of the water gas components have to be calculated. Depending on whether $\varphi(CO) + \varphi(H_2)$ is higher or lower than $2 \varphi(O_2)$, one has to use either the one or the other equation (DE 43 23 879). The software developed for this purpose by the company *GO MESSTECHNIK Greifswald* produces the results virtually without time-delay.

Gas potentiometry using solid electrolyte sensors

Crystals of mixed oxides from ZrO_2 and CaO or Y_2O_3 have vacancies in the oxygen ion sublattices. Oxygen ions can migrate across them at high temperatures. Thus, they are solid electrolytes (i.e. solid ion conductors). At platinum layers on ceramic bodies of stabilized ZrO_2 (stabilized against breaking), electrode reactions with the oxygen ion vacancies V_O are possible:



Oxygen atoms separated off molecular oxygen or water vapor take up electrons on the surface of the platinum and move to oxygen vacancies of the solid electrolyte where they form oxide ions. This process, however, quickly comes to a stand-still if the electrode is in an open circuit, and neither electrons nor oxygen ions can flow. In this state, the output of chemical work from the particle transfer equals the effort that has to be made in terms of electric work. An electrochemical equilibrium exists in this case which is a dynamic equilibrium. The electrode reactions still occur but equally fast in both directions. The larger the so-called exchange current density, the less sensitive is the electrode to disturbances.

In electrochemical equilibrium, the platinum has either given off electrons and is positively charged, or it has taken up electrons and is negatively charged. The first is to be expected in oxygen, the second in hydrogen.

If two oxygen electrodes are exposed to different oxygen concentrations on opposite sides of a gastight sintered ZrO_2 solid electrolyte, the electrode exposed to the higher oxygen concentration will be charged more positively than the electrode exposed to the lower oxygen concentration in electrochemical equilibrium. A cell potential can be measured between the electrodes. The more the oxygen concentrations at the two electrodes differ, the higher is the cell potential.

In 1889, NERNST was the first to describe the quantitative connection between the cell potential and the particle concentrations at the electrodes with the so-called NERNST equation. In electrochemical thermodynamics this equation can be derived from the chemical potentials (consisting of energy and entropy components) of the particles participating in the cell reaction (i.e. sum of the electrode reactions). The chemical potential of the oxygen is given by

$$\mu(O_2) = \mu(O_2)' + R \cdot T \cdot \ln p(O_2) .$$

For a solid electrolyte cell with two oxygen electrodes, the cell reaction is merely the transfer of oxygen from higher to lower partial pressure. The chemical work in cell reactions is described with the molar free reaction enthalpy (Gibbs free energy) $\Delta_R G$, which equals the difference in chemical potentials:

$$\Delta_R G = \mu(O_2)' - \mu(O_2)'' = R \cdot T \cdot \ln [p(O_2)'/p(O_2)''] .$$

In isothermal cells, the standard potentials $\mu(O_2)'$ on both sides are equally high, and thus drop out. $\Delta_R G$ equals the maximum work that can be won for an infinitely slow reaction, i.e. at extremely slow current flowing through the external circuit. It can be calculated using the equilibrium cell voltage U_{eq} , the molar charge F (Faraday's constant), and the amount of electrons that are exchanged in the cell reaction (4 electrons in case of O_2):

$$W_{\text{electric}} = 4 \cdot F \cdot U_{eq} .$$

From this the NERNST equation for the equilibrium cell voltage follows:

$$U_{eq} = (R \cdot T / 4 \cdot F) \cdot \ln [p(O_2)'/p(O_2)''] .$$

In gas potentiometry, one of the electrodes is fed with a gas of known composition (reference electrode), and by measuring U_{eq} and T the gas at the measuring electrode is analyzed. Inserting the values for R and F into the equation above and converting it into the \lg -form, the following equation is obtained for dry air under normal pressure at the reference electrode:

$$U_{eq}/mV = 0.049606 \cdot T/K \cdot \lg [p(O_2) / (0.2093 \cdot 1013.25 \text{ mbar})].$$

In practice, the oxygen concentration $\varphi(O_2)$ in vol% is often used for calculations, which relates to the partial pressure as $p(O_2) = \varphi(O_2) \cdot p / 100$. If the total pressure does not vary much from the normal pressure (1013.25 mbar), the following equations are used for calculations :

$$U_{eq}/mV = 0.049606 \cdot T/K \cdot \lg [\varphi(O_2) / 20.93 \text{ vol}\%],$$

$$\varphi(O_2) / \text{vol}\% = 20.93 \cdot 10^{(U_{eq}/mV)/(0.049606 \cdot T/K)}.$$

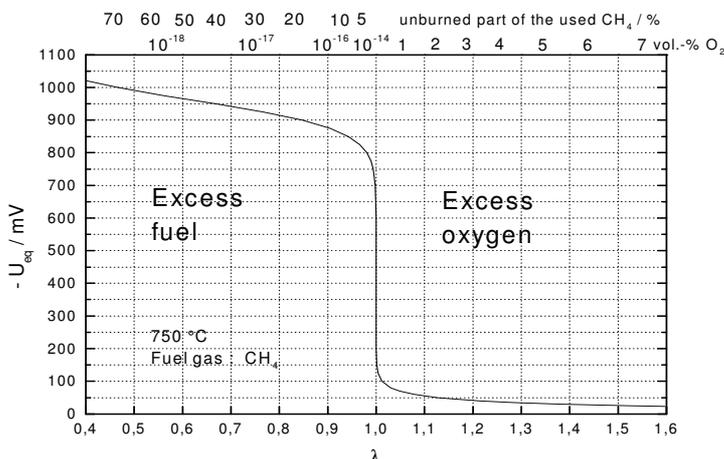
If a gas is present at the measuring electrode that mainly consists of reducing components, the chemical standard potentials do not drop out when the cell voltage equation is derived. In this case, a NERNST equation is obtained for reaction cells with concentration-independent terms, e.g. cells with hydrogen and water vapor at one of the electrodes and air at the other electrode the equation, valid in the range 400...1000 °C,

$$U_{eq}(H_2,H_2O\text{-air})/mV = -1280.6 + \{ 0.3165 + 0.0992 \cdot \lg [\varphi(H_2O)/\varphi(H_2)] \} \cdot T/K \ +/-1.$$

In several technical processes the quotient $Q = \varphi(H_2O)/\varphi(H_2)$ has to be known. It can be calculated from this equation.

If the measuring electrode is the negative pole of the cell, the cell voltage is signed negatively.

In the diagram plotted below the dependence of the equilibrium cell voltage on λ , the oxygen concentration, and an excess CH_4 in methane combustion is shown.



The cell voltages calculated with the above-mentioned equations and presented in the diagram are only valid for isothermal cells with equal temperature at both electrodes. Such isothermal cells have been realized very carefully in the ZIROX products. Unlike these, the well-known lambda probes used in automobiles with catalysts in the exhaust tube are not isothermal. Their main purpose is indicating $\lambda >$ or $<$ 1, and they are less suitable for precise gas potentiometric analysis.

12.2 Warranty conditions

ZIROX Sensoren & Elektronik GmbH warrants that the products manufactured and sold are free from manufacturing and material defects at the time of dispatch. In case of defects and faults within 12 months (probe) and 24 months (electronics assembly) respectively after dispatch, ZIROX will clear faults at its own option by repair or replacement. The purchaser must give prompt written notice to ZIROX. The purchaser is not entitled to claim other legal remedies based on this warranty.

ZIROX does not warrant supplied products which are subject to normal wear and tear (e.g. reference gas pump).

Corrosive gases and solid particles may cause damage and require repair or replacement due to normal wear and tear.

The contact of the products with explosive gas compounds, halogens in high concentrations and sulphuric gases (e.g. SO₂) is not permitted.

The contact of the products with silicic or phosphoric compounds is not permitted either.

A connection of ZIROX and non-ZIROX products voids any warranty claims.

Warranty and warranty claims are only accepted if they are in accordance with the "General Sales and Delivery Conditions" of the manufacturer.

Warranty and liability claims for damage to persons and/or property are void if they are subject to the following:

- Normal wear and tear
- Improper use of the product
- Disregard of the manual's instructions
- Improper installation, initiation, operation and maintenance of the product
- Operation of the product without protective measures
- Unauthorized functional and technical modification of the product
- Dismantling of parts as well as installation of spare parts or additional units which are not delivered or permitted by the manufacturer
 - Improper repairs or faulty operation
- External impact
- Acts of God

Attention: When installing the equipment, the customer must ensure that all necessary supply lines are connected and the operating temperature of the probe is reached. Experience has shown that products installed but not in use may be damaged by the process or by external influence. ZIROX will not accept any responsibility for such damage.

12.3 Declaration of conformity

EG - Konformitätserklärung	
Dokument- Nr.:	27 Dezember 2010
Hersteller:	Zirox Sensoren & Elektronik GmbH
Anschrift:	Am Koppelberg 21 D - 17489 Greifswald
Produktbezeichnung:	E2010
Die Übereinstimmung des bezeichneten Produktes mit den Vorschriften der Richtlinien des Rates	
2006/108/EG	Elektromagnetische Verträglichkeit
wird nachgewiesen durch:	
Der Hersteller hat die in den oben aufgeführten Richtlinien genannten harmonisierten Normen angewandt und die Übereinstimmung des Produktes festgestellt.	
harmonisierte europäische Normen:	
Nummer:	Text:
DIN EN 61000-6-2	Elektromagnetische Verträglichkeit (EMV) Teil 6-2: Fachgrundnorm: Störfestigkeit für Industriebereich
DIN EN 61328	leitunggeführte Störaussendung Gestrahlte Störaussendung
Diese Erklärung bescheinigt die Übereinstimmung mit der genannten Richtlinie, beinhaltet jedoch keine Zusicherung von Eigenschaften. Die Sicherheitshinweise der mitgelieferten Produktdokumentation sind zu beachten.	
Aussteller:	Zirox Sensoren & Elektronik GmbH
Ort, Datum:	Greifswald <u>3.12.2010</u>
Rechtsverbindliche Unterschrift:	 ZIROX Sensoren & Elektronik GmbH Am Koppelberg 21 17489 Greifswald