ZIROX
Sensoren und Elektronik GmbH

ZIROX - Oxygen Measuring Technology

Measuring System

Oxygen Probe SS31H/SS31HP
Electronic Unit E2000HP

Manual

Sensoren und Elektronik GmbH
ZIROX GmbH · Am Koppelberg 21 · 17489 Greifswald

www.zirox.de

ZIROX
Sensoren und Elektronik GmbH

MEASURING SYSTEM SS31H/SS31HP – E2000HP FOR MEASUREMENTS OF THE OXYGEN CONCENTRATION IN FLUE AND PROCESS GASES

MANUAL

Measuring range: 0.01 … 20.64 vol%

Power supply: 230 V AC   50 … 60 Hz (110 V AC as option)

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Table of contents

1 General information

1.1 Introduction

This operation manual describes composition, mode of operation and use of the oxygen measuring system for measurements in flue gases (FGM) of the ZIROX Sensoren & Elektronik GmbH.

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The manufacturer guarantees that this manual was written in accordance with the functional and technical features of the FGM.

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

Proper operation of the device 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 device.

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

Pages, charts and figures are numbered consecutively.

1.2 Copyright

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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.

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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.

⚠
danger

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 device, its single components or other material assets as well as minor injuries may result.

⚠
attention

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 device or its single components may result.

NOTE

2 Application fields

Designated use

The measuring system serves the continuous measuring of the oxygen concentration in exhaust gases of combustion systems (power plants, heat plants, scrap removal systems).

Main application areas of the measuring system are:

- Emission measurements and burning optimization in heavy firing plants; emission measurements in waste combustion plants
- Emission measurements in hazardous waste combustion plants
- Measurement and control of furnace gases (oxidizing and reducing phases) in the ceramic industry
- Measurements in flue gases of production processes (e.g. in burning or sinter furnaces)

⚠ ATTENTION

Using the FGM in explosive gas mixtures, in gas atmospheres with halogens in high concentration and sulphuric gas mixtures (e.g. SO_2) is not permitted.

Functions

With the measuring system

- the oxygen concentration is measured and displayed continuously
- deviations of the oxygen concentration from set values are signalized
- the generation of gas atmospheres with defined oxygen concentration can be provided, possible under reducing conditions.

The requirements and limit values shown 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 measuring system. 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.

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 a heated oxygen probe (SS31H) and a control and evaluation electronics (E2000HP). The SS31HP has a measuring channel for in-situ measurement and, if applicable, calibrations.

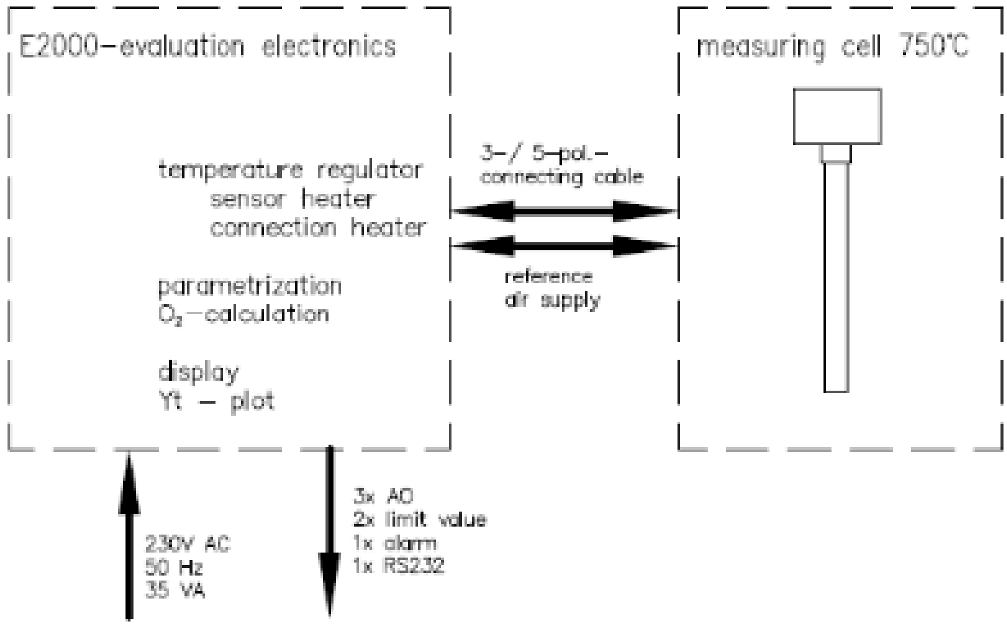

Fig. 1: *The ZIROX flue gas measuring system (the SS31HP has an additional channel for the measuring gas supply)*

4.2 Measuring principle

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

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

NERNST-equation

$$\boxed{U = \frac{RT}{4F}\ln\frac{p_{O2,\,air}}{p_{O2,\,measuring\ gas}}} \qquad \textbf{(I)}$$

U – cell voltage in V, *R* – molar gas constant, R = 8.314 J/ (mol · K), *T* – measuring temperature in K,

F – faraday constant, F = (9.648 · 10^4 C/mol

$p_{O2,air}$ – partial pressure of the oxygen at the reference electrode in dry air in Pa

$p_{O2,measuring\ gas}$ – partial pressure of the oxygen at the measuring electrode in Pa.

Equation for oxygen concentration

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 (guaranteed by furnace atmosphere).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.

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:

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

φ_{O_2}– oxygen concentration in 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 can be in free or bound form in the measuring gas (see appendix 1).

The following dependencies apply:

$U \sim T$ – 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 H_2/H_2O- or CO/CO_2-mixtures).

Reducing gas compounds

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.

Air factor λ

When intentionally producing and monitoring reducing exhaust gases from the reaction of fuel with air, the air factor λ can be calculated and displayed if the chemical compounds and their concentration in the fuel are known.

For $\lambda < 1$ the calculation and indication of the CO-, CO_2-, H_2- and H_2O-concentrations is possible. For this, special counseling from the manufacturer is required.

4.3 Use of an immersion sleeve

In heavily dust-laden gases or gases with a high flow rate it can be useful to install the probe in a protective tube. The following drawing shows an example (the protective tube can be metallic in colder gases).

Such an immersion sleeve can also be useful when the flue gas has an extremely high temperature. The probe inside the immersion sleeve can be drawn back into the brickwork in order to reduce the thermal load.

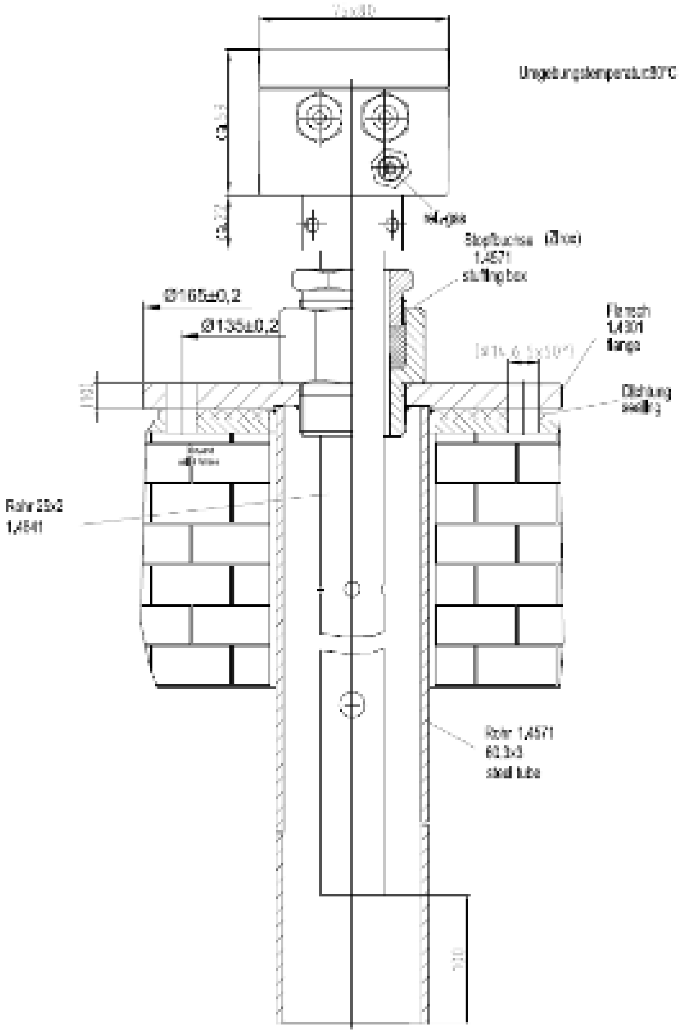

__Fig. 2:__ SS31 with immersion sleeve (schematic)

5 Technical data

5.1 Probe

Use temperature range	0…800 °C
Probe diameter	25 mm
Probe length	0.3…1.5 m
Reference gas connection	4 mm hose nipple
Measuring gas connection (option)	4 mm hose nipple

5.2 Electronic E2000HP

5.2.1 Measuring data

Measuring range	0.01…20.6 Vol% (measuring range up to 100 Vol% or special starting values on request)
Measuring accuracy at normal pressure	Rel. error < 5%
Max. pressure of the measuring gas	10 kPa overpressure (over 1 kPa an error correction is necessary)

5.2.2 Mechanical data

Dimensions (D x W x H in mm)	120x300x300
Weight	8 kg

5.2.3 Electrical data/electronics

5.2.3.1 General data

Degree of protection	IP 65
Using conditions	5…40 °C
Storage conditions	-20…60 °C

Power supply

Voltage	100-240 V/47…63 Hz SK I
Power consumption	35 VA

Keypad and display

keypad	Membrane keypad with 6 keys
plain text display	LCD dot-matrix

5.2.3.2 Interfaces

Analog output	2 x 0/4…20 mA, electrically insulated

Serial interface RS 232

Transfer rate	Max. 19200 Baud, adjustable

Stop bits	1
Data bits	8
Parity	None
Handshake	Without

***Chart 1**: Protocol of the serial interface (CR = carriage return)*

Input	Response	Parameter
M2CR	M2x.xxExxCR	Output channel 1
M1CR	M1x.xxExxCR	Output channel 2
A1CR	A1xxxCR	Cell voltage, mV
A2CR	A2xxxCR	Measuring temperature, °C

***Chart 2**: Error messages*

Error code	Meaning
Error0	Transfer error
Error11	Measuring temperature too low
Error16	Thermocouple defective
Error 20	System error

Alarms	Two limit values: 2 relays Device error: 1 relay Relay limit values: max. 1 A, 125 V AC, 60 V DC, 62 VA, 30 W

6 Installation and initiation

6.1 Installation of the electronics E2000HP

6.1.1 General description

The electronics performs the following tasks:

- Reference air supply of the probe (normally adjusted to 5 l/h)
- Measuring and processing of cell voltage and thermocouple signal of the probe
- Digital display of measuring values, status and error signals and, if requested, display of the measuring value as yt-chart (value vs. time)
- Display of the programming menus and operation via keypad
- Cyclic testing of the measuring cell
- Permanent monitoring of the thermocouple
- Supply of output signals

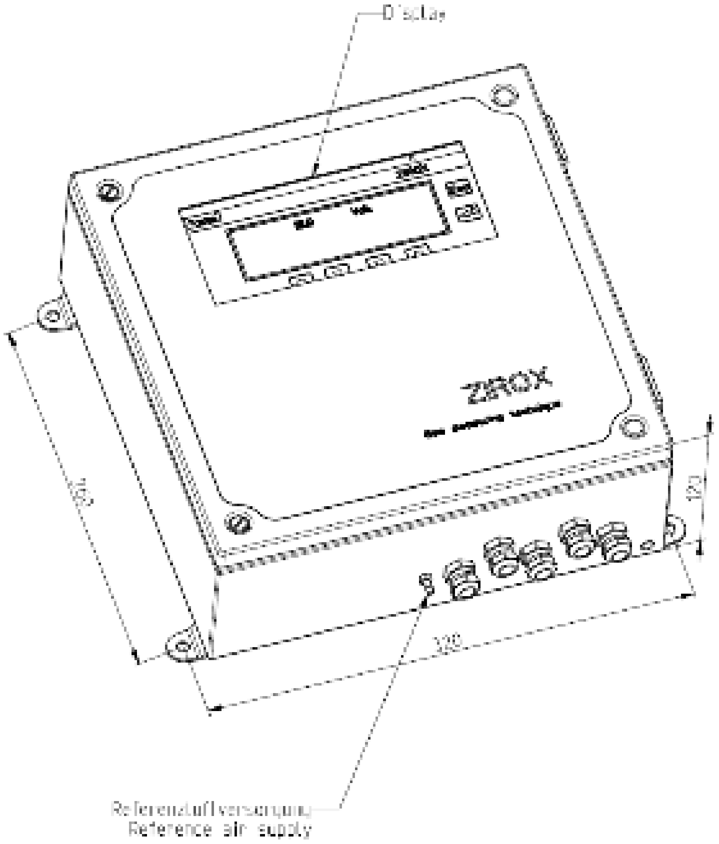

Fig. 3: *Scale drawing of the electronic housing.*

6.1.2 Clamp assignment

6.1.2.1 Clamp assignment at the electronics

Four separated clamp blocks exist in the housing:

1. X1 connection to the probe
2. X2 analog/digital outputs
3. X3 heater transformer (factory-wired, heater voltage depends on model or purchase order (after consultation with manufacturer)
4. X4 power supply

Block X1 (measuring cell)

Clamp-No.	Description	Remark
1	AGND	Analog mass
2	Vz	Cell voltage
3	Vt	Thermal voltage
4	Heater	
5	Heater	

Block X2 (Analog/digital)

Clamp-No.	Description	Remark
1	OUT1 +	Analog output 1
2	OUT1 -	Analog output 1
3	OUT2 +	Analog output 2
4	OUT2 -	Analog output 2
5	RXD	RS232
6	TXD	RS232
7	GNDS	RS232
8	Vp +	External pump
9	Vp -	External pump
10	N.C.	Alarm relay
11	COM	
12	N.O.	
13	N.C.	Limit value relay 1
14	COM	
15	N.O.	
16	N.C.	Limit value relay 2
17	COM	
18	N.O.	

Block X3 (heater transformer)

Clamp-No.	Description	Remark
1	24 V AC (36 V AC option)	Model depends on system installation conditions (manufacturer consultation!)
2	24 V AC (36 V AC option)	
3	1L	
4	N	

Block X4 (power supply)

Clamp-No.	Description	Remark
PE	PE	230 V AC, 50 ··· 60 Hz[1]
L1	L1	
N	N	

6.1.2.2 Clamp assignment at probe

In the probe housing there is only one block connected with the electronic unit.

3 x 0.5 shielded cable for clamp 1-3 and 2 x 1.5 for clamp 4-5 are recommended.

Clamp-No.	Description	Remark
1	Signal mass	To electronics
2	Cell voltage	To electronics
3	Thermal voltage	To electronics
4	Heater	To electronics
5	Heater	To electronics

6.2 Probe mounting

Dependent on the application case several probes can be used. A typical probe is shown in figure 4. For the mounting of the probes several kinds of stuffing boxes or an immersion sleeve can be applied. After marking the insert depth the probe can be inserted. High-temperature probes should be inserted very slowly in the hot gas (approx. 5 cm/minute). The reference air has to flow from the beginning of insertion. After inserting, the probe must be fixed by tightening of the stuffing box. After that, the heating must be started up as soon as possible for sensor protection.

Please 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.

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[1] 110 V optional

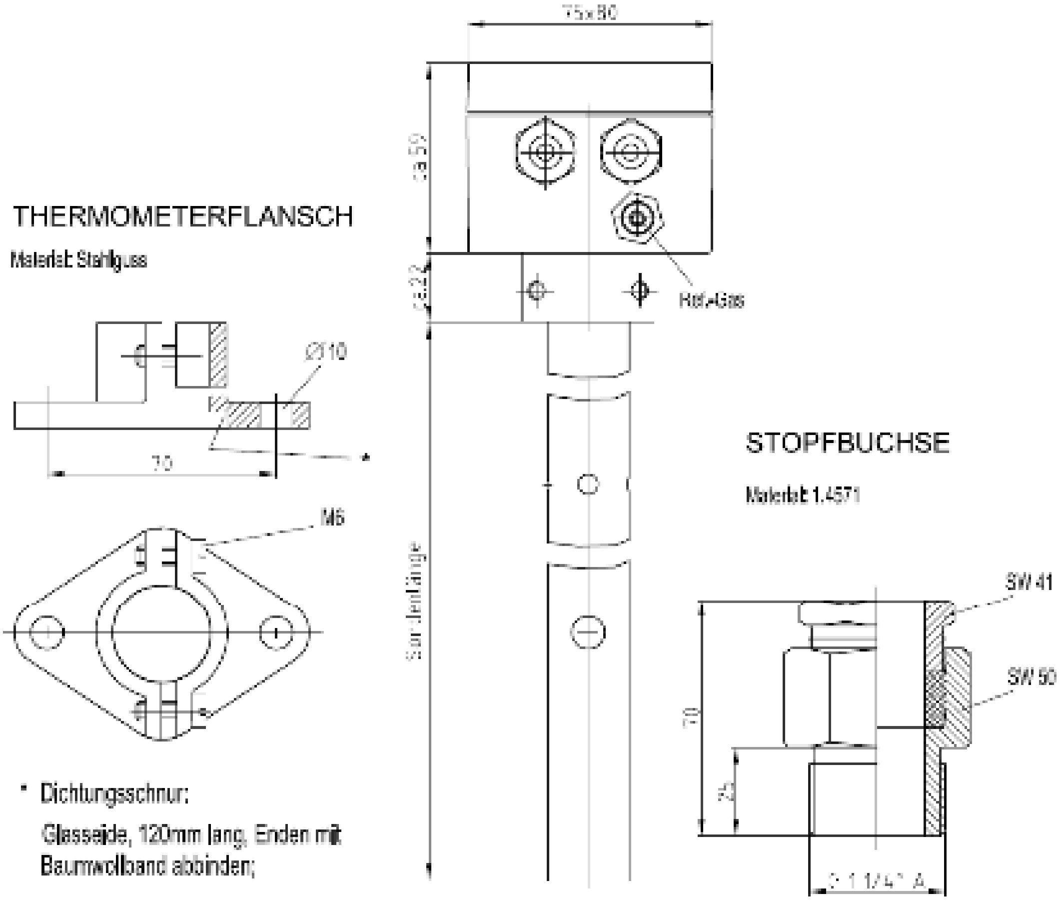

***Fig. 4**: Scale drawing of probe, stuffing box, immersion sleeve*

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

DANGER

6.3 Reference air supply

The probe has to be supplied with reference air. For it, a pump and a flow meter exist in the electronics. The flow is adjusted to 5 l/h. A PVC-hose connects electronics and probe.

6.4 Initiation and programming

After wiring, the device can be connected with the power supply. The display shows measuring values, special messages or error messages.

Furthermore, the current assignment of the soft keys is displayed in the bottom line. The keys lead to different menus specified in the following chapters.

Normally, with both left keys the requested line in the displayed menu is selectable. For changing a value, it can be activated with ↵ and changed with the lower keys. After that, the value is to be confirmed with ↵ . Exit the menu by pressing ESC!

6.4.1 Password protection

The programmable values can be protected with a password (standard is 0000).

Effective protection is provided when:

1) a new password is entered before
2) a wrong password is entered and
3) the electronics is switched OFF and ON.

6.4.2 Display and settings

Figure 5 shows the display and the soft keys. The 4 keys below the display have several functions. The current measuring value is displayed as a digital value and as an analog bar. Below the bar both the limited value and the measuring range are displayed. On the left, the reference gas pump is monitored, displaying the gas flow.

Below the bar on the right, a second measuring value can be displayed. The display of cell voltage or cell temperature can also be programmed. On the left below the bar, the status or error message is shown. The more important message has priority.

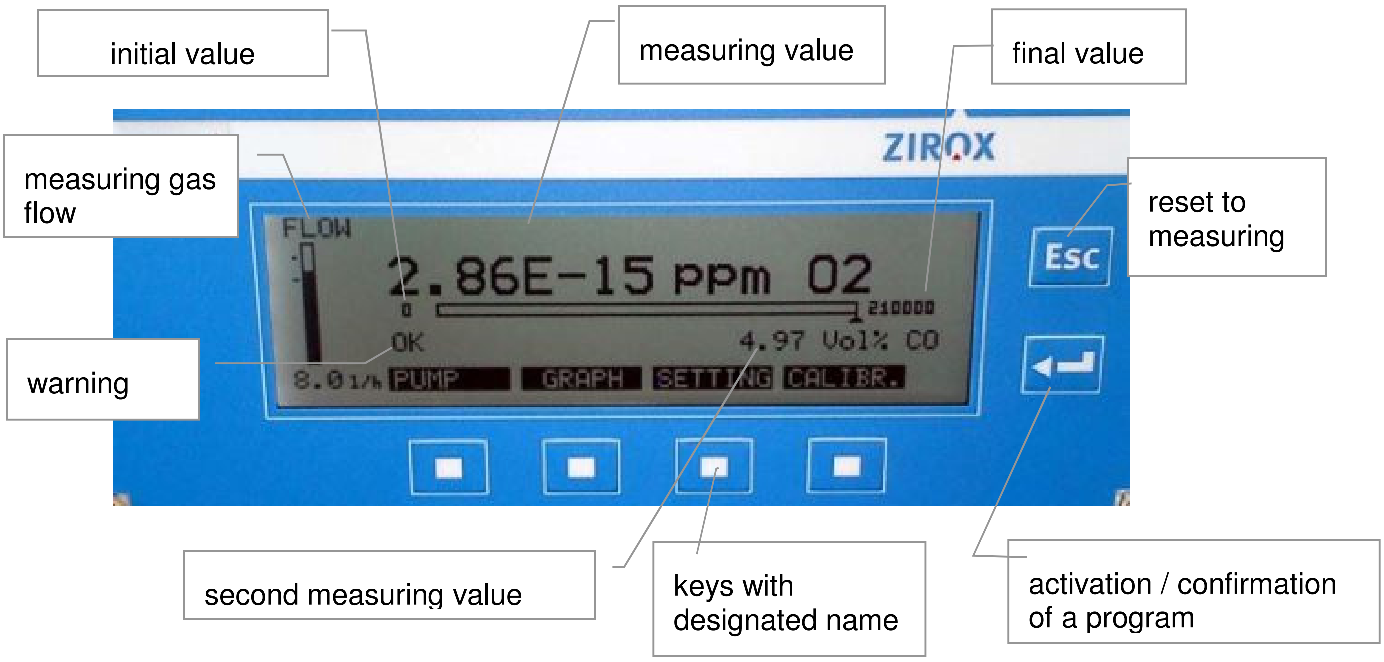

Fig. 5: Display of E2000HP

The keys below the display lead to the following menus (the actual meaning of the keys is shown on the display): A parameter is activated by the ↵ -key, changed by the four keys below the display and confirmed by the ↵ -key. The examples in the second line are the delivery state.

6.4.2.1 Settings

SETTINGS		This menu is accessible via 3rd key in the display menu.
1 GENERAL		
2 LIMITS		
3 OUTPUT 1		
4 OUTPUT 2		
1 2	3 4	

6.4.2.2 General settings

GENERAL SETTINGS		
USER CODE:	0000	
NEW USER CODE:	0000	Max. 4 numeric characters
LANGUAGE:	ENGLISH	Alternatively German
BAUD RATE:	19200	Alternatively 4800, 9600
▼ ▲	SAVE RETURN	

6.4.2.3 Limit values

LIMIT VALUES		
LIMIT VALUE 1:	> 209000 ppm	
LIMIT VALUE 2:	> 209000 ppm	
DELAY TIME	1 – 99 sec	
▼ ▲	**SAVE RETURN**	

6.4.2.4 Output 1

OUTPUT 1		:
VALUE:	Vz	**Options: O2lin, O2log, O2auto**
RANGE:	4 – 20 mA	0-5 V
RANGE ZERO POINT:	0 Vol%	
RANGE END MARK:	10 Vol%	
AVARAGE FACTOR:	1 sec	
▼ ▲	SAVE RETURN	

The same applies to output 2.

6.4.2.5 Calibration (for SS31HP only, see chapter 6.5)

CALIBRATION	20.6 vol% O2	Access via 4th key in display menu
ZERO GAS:	20.6 vol% O2	Calibration of zero-point (calibration of offset voltage)
CALIBR. ZERO POINT:	Ok (0.0)	Status and calibration value see calibration status
SPAN GAS:	1 vol%	Set bottle value
CALIBR. SPAN GAS:	Ok (1.0)	Status and calibration value
▼ ▲	START RETURN	

6.4.2.6 Yt-graph

Yt-graph		Access via 2nd key in display menu
CURVE:	Vol% O2	Alternat. measuring value of second analog output
Yaxis-min:	0 ppm	
Yaxis-max:	21 vol%	
Xaxis-max:	3 min	Admissible: 3…60 min
▼ ▲	SAVE RETURN	

The measurements are moved to the left after reaching the end time or around ¼ of the results. The display results are not available in a memory.

6.4.2.7 Pump control

PUMP	XY-PLOT	SETTING	CALIBR.	PUMP
PUMP :	ON	OFF	RETURN	PUMP :

6.5 System calibration

For measurements with high accuracy requirements, a calibration is highly recommended.

There are two steps: Zero calibration and span gas calibration (SS31 H**P** only). Before calibration, the system must be warmed up for 2 hours (minimum).

Furthermore, make sure to secure regulators connected to the measuring system (e.g. combustion process) in order to avoid accidents. **During calibration, the measuring system provides the frozen last measuring value as an initial value.**

6.5.1 Zero calibration

The zero calibration serves the balance of the offset voltage of the ZrO2-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.% O2.

For the zero calibration, air (surrounding air by pump, 5…10 l/h) is supplied at the test gas inlet. After 3 to 5 minutes the zero correction can be started (the displays shows the current measuring value on the top right during the whole calibration process, which enables to judge the compensation process of the test gas inlet. After that, the program can be exited (a safety question appears) or the span gas calibration can be started. **Attention:** After the calibration the test gas channel has to be closed (fault gas could influence the measuring value).

6.5.2 Span gas calibration

For this procedure a certified test gas must flow into the probe SS31H**P** (span gas inlet, 5…10 l/h). The oxygen concentration should be about the same as in the subsequent measuring gas. A span gas < 2 vol% O_2 is recommended (differences between span gas and measuring gas of more than 15 % should be avoided – measuring errors could occur). After a compensation time of 3 to 5 minutes (stable current measuring value) the calibration can be started.

The stability of the measuring value is checked during the calibration. The real calibration process starts as soon as the signal produced by the test gas is stable. Therefore, the duration of the calibration process can vary (variation under 1 % in 4 seconds). If stability is not provided, the calibration will be terminated after 60 sec.

For leaving the calibration press return (safety question!). Attention: Please close the span gas inlet of the probe.

6.5.3 Limits of the calibration

Any deviations of measuring value from set value are evaluated. During zero point calibration +/- 20 mV (cell voltage), during span gas calibration +/- 20 % of the measuring value (cell voltage) are allowed. If those limit values are exceeded, the calibration process will be terminated.

For the adjustment the following equation applies: Vcellkorr=(Vz+A)*B

With Vz=measured cell voltage, A=cell voltage at zero point, B=factor for final value adjustment.

Zero gas is always clean ambient air. Depending on the order, 20.6 or 20.9 vol% are displayed[2].

Report of the calibration status:

OK (1.5)	Last calibration OK (calibration value)
WAIT! 5	Calibration running
CANCELLATION	Cancel by pressing key
ERROR STABIL.	Stability not reached within 60 sec
ERROR RANGE	Range exceeded
ERROR SENSOR	Device error

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[2] Dry air has an oxygen concentration of 20.96 vol%. Air with 50 % rH has 20.64 vol% - several manufacturers have inserted one of these values - ZIROX can meet the customer's demand.

7 Status messages

On the display specific states are shown:

No.	Display	Remarks
1	OK	
2	LIMIT 1	
3	LIMIT 2	
4	LIMIT 1/2	
5	RANGE <<<	
6	RANGE >>>	
7	FLOW <<	< 5 l/h
8	FLOW >>	>10 l/h
9		
10		
11		
12		
13		
14	WARM-UP	Cell or head temperature too low and <30 min
15	LOW CELL TEMP.	< 740° and >30 min
16	ERROR THERMOCOP.	
17		
18		
19		
20	SELF-TEST FAILED	

- Status >15 - serious error, alarm relay active and current signal zero
- Status 13 ··· 15 - slight error, alarm relay active, current signal zero if prepared for O_2, Lambda, CO_2 or CO. (calculated sizes)
- Status 5 ··· 12 - warnings, only alarm relay active

8 Faults and fault clearance

Fault	Cause	Clearance
Display off	System off	Switch on FGM
	Power supply cancelled	Check power supply and correct position of the supply cable
	Equipment fuse tripped	Change equipment fuse
Error message „Flow too low“	Gas supply blocked, too long for the chosen cross-cut or leaky	Check tube, remove blockages, produce tightness
	Pump defective	Replace pump
Measuring value near 20 % although much lower value is expected	Probe is not supplied with reference air	Check reference air supply
Measuring value is much lower than expected	Components reacting with oxygen exist in measuring gas (e.g. hydrocarbons)	Using of probe impossible Call manufacturer!
Warning: Warm-up	Probe has not reached operating temperature	Wait 5 minutes
Message: cell temperature too low	Heater fuse activated	Change heater fuse F 2 (4 A T)
	Heater or regulator defective	Consult service
Warning: Thermocouple break	Connection to the probe or thermocouple defective	Check cables or consult service
Warning: SELF TEST FAILED	General device failure	Consult service
Warning: range <<< or range >>>	Adjusted range exceeded or underrun	Error effects the analog outputs

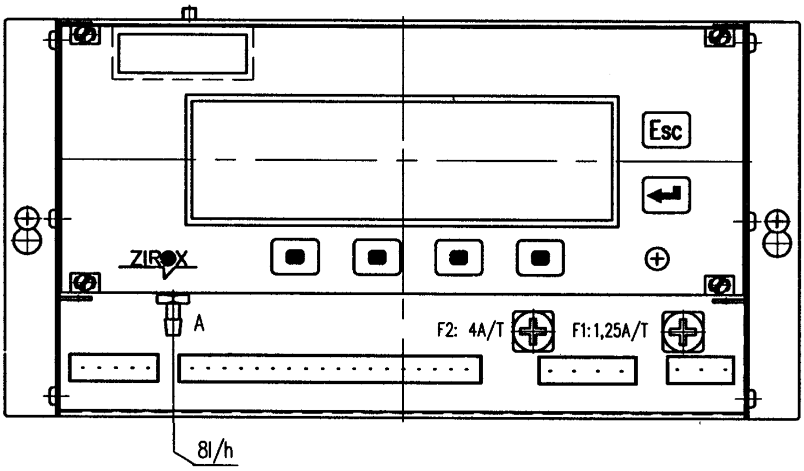


Fig. 6: View of the fuses

9 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. SO_2) is not permitted.

The contact of the products with siliconic 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: During installation of 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.

10 Appendix

10.1 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 ZrO_2 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 m^3, kg or mol shorten themselves when forming the ratio). If volume is the quantity that is used, lambda is given by the following equation:

λ = v(air volume fed) / v (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:

$$C_nH_m + \lambda \cdot (n + m/4)\ O_2 \rightarrow n\ CO_2 + m/2\ H_2 + (\lambda - 1) \cdot (n + m/4)\ O_2$$

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:

$C_nH_m + [(1\text{-}a/2) \cdot n + (1\text{-}b) \cdot m/4]\, O_2 \rightarrow (1\text{-}a) \cdot n\, CO_2 + a \cdot n\, CO + (1\text{-}b) \cdot m/2\, H_2O + b \cdot m/2\, H_2$,

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 lambda, the following equations can be derived:

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

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

$CO_2 = CO + 1/2\, O_2$ $\qquad \lg K_C = 4.505 - 14700\ K/T$,

$H_2O = H_2 + 1/2\, O_2$ $\qquad \lg K_H = 2.947 - 13008\ K/T$.

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:

$1/2\ O_2(\text{gas}) + 2\ e^-(\text{platinum}) + V_O(\text{solid electrolyte}) = O^{2-}(\text{solid electrolyte})$,

$H_2O(\text{gas}) + 2\ e^-(\text{platinum}) + V_O(\text{solid electrolyte}) = O^{2-}(\text{solid electrolyte}) + H_2(\text{gas})$

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, either the platinum has 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

$\mu(O_2) = \mu(O_2)^{\cdot} + R \cdot T \cdot \ln p(O_2)$.

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 $\mu(O_2)^{\cdot}$ 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):

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

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:

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

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:

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

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

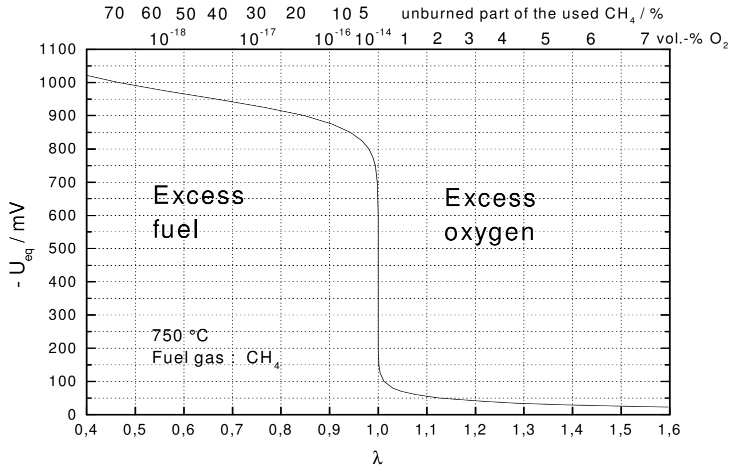
If a gas is present at the measuring electrode that mainly consists of reducing components, the chemical standard potentials do not drop out when the cell voltage equation is derived. In this case, a NERNST equation is obtained for reaction cells with concentration-independent terms, e.g. cells with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

$U_{eq}(H_2, H2O\text{-}air)/mV = -1280.6 + \{ 0.3165 + 0.0992 \cdot \lg [\varphi(H_2O)/\varphi(H_2)] \} \cdot T/K$ +/-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.

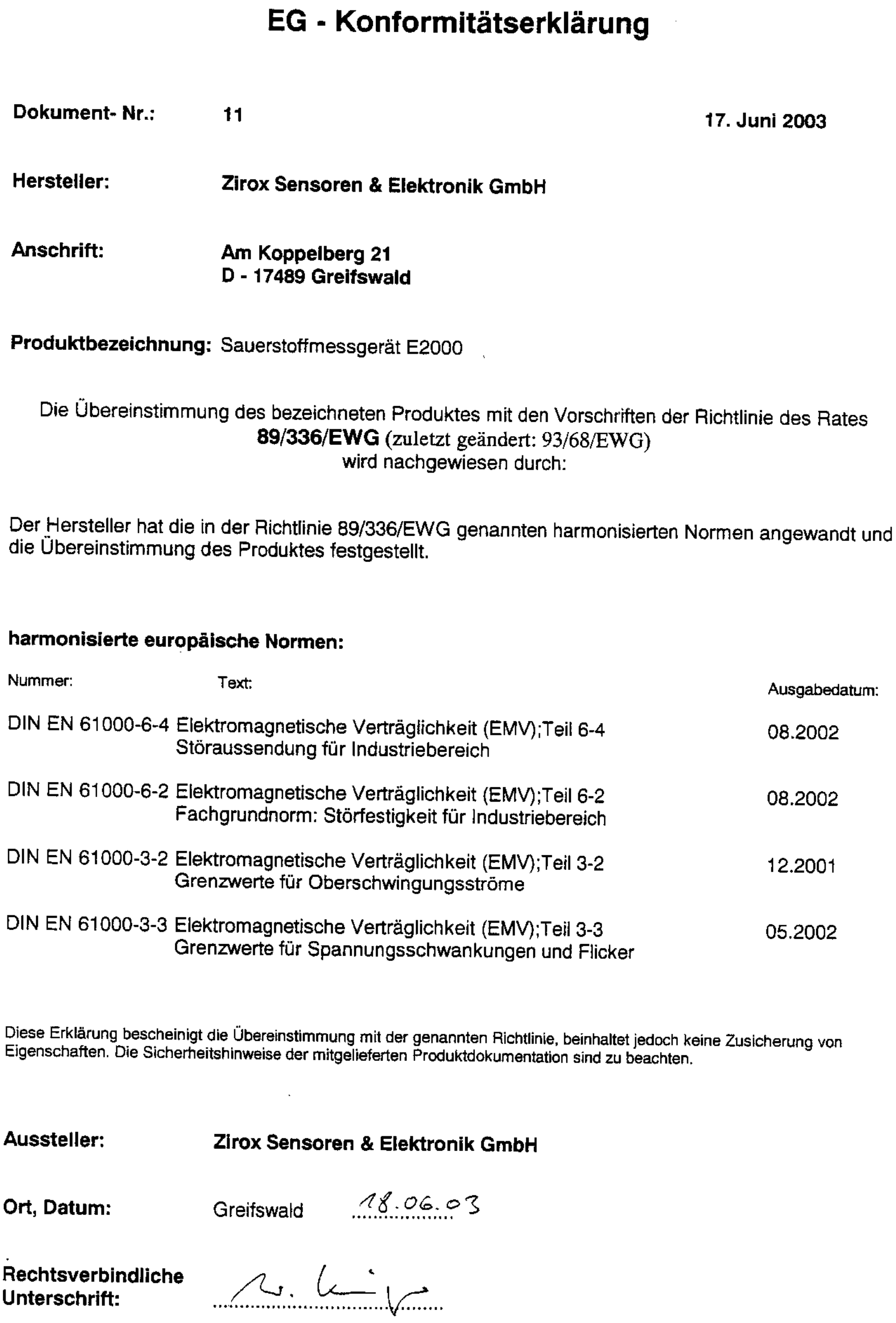
In the diagram plotted below the dependence of the equilibrium cell voltage on λ, the oxygen concentration, and an excess CH_4 in methane combustion is shown.



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 λ > or < 1, and they are less suitable for precise gas potentiometric analysis.

10.2 Declaration of conformity



EG - Konformitätserklärung

Dokument- Nr.: **11** **17. Juni 2003**

Hersteller: **Zirox Sensoren & Elektronik GmbH**

Anschrift:
Am Koppelberg 21
D - 17489 Greifswald

Produktbezeichnung: Sauerstoffmessgerät E2000

Die Übereinstimmung des bezeichneten Produktes mit den Vorschriften der Richtlinie des Rates **89/336/EWG** (zuletzt geändert: 93/68/EWG) wird nachgewiesen durch:

Der Hersteller hat die in der Richtlinie 89/336/EWG genannten harmonisierten Normen angewandt und die Übereinstimmung des Produktes festgestellt.

harmonisierte europäische Normen:

Nummer:	Text:	Ausgabedatum:
DIN EN 61000-6-4	Elektromagnetische Verträglichkeit (EMV);Teil 6-4 Störaussendung für Industriebereich	08.2002
DIN EN 61000-6-2	Elektromagnetische Verträglichkeit (EMV);Teil 6-2 Fachgrundnorm: Störfestigkeit für Industriebereich	08.2002
DIN EN 61000-3-2	Elektromagnetische Verträglichkeit (EMV);Teil 3-2 Grenzwerte für Oberschwingungsströme	12.2001
DIN EN 61000-3-3	Elektromagnetische Verträglichkeit (EMV);Teil 3-3 Grenzwerte für Spannungsschwankungen und Flicker	05.2002

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 18.06.03

Rechtsverbindliche Unterschrift: ....