

# Amperometric H<sub>2</sub>S micro-sensor - L

- Operating Instruction -



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# 1 Preface

This laboratory OEM version of the amperometric H<sub>2</sub>S micro-sensor has been developed for the *in situ* determination of dissolved H<sub>2</sub>S/sulphide in liquid samples.

Because of the partial pressure of the gaseous H<sub>2</sub>S, the analyte is separated by permeation through the membrane. Inside the sensor the hydrogen sulphide reacts with a redox mediator. The electrochemical oxidation of this formed compound at the working electrode causes a current corresponding to the concentration of the dissolved molecular H<sub>2</sub>S amount.

The sensor has very short response times and streaming as it is well known from nearly all kind of Clark-type oxygen sensors is not necessary. So profiling becomes possible with very high signal and local resolution. The sensor works highly selective and there are no signal interferences e.g. to CO, CO<sub>2</sub>, H<sub>2</sub>O-vapour, CH<sub>4</sub>, CS<sub>2</sub>, dimethyl sulfide (DMS), acetic acid or NH<sub>3</sub>. Both salt concentrations of up to 40 g/l and turbid or coloured solutions do not interfere with the signal.

For measuring the total sulphide concentration within a range of pH = 5 to 8,5, the sensor has to be combined with a pH-electrode and always with a temperature measurement.

All sensors are delivered with calibration and temperature compensation data and also with mathematical formulas to calculate the total sulphide concentration.

**The perfect functioning and operational safety of the measuring device can only be ensured if the user observes the safety precautions as well as the specific safety guidelines stated in the present operating instruction.**

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## 2 Technical Data<sup>\*)</sup>

measuring principle:	amperometric sensor with redox mediator, 3 electrodes
polarization time:	10-15 minutes (increases due to natural aging)
power supply:	9 ... 30 VDC
output:	0 ... + 3 VDC
connector:	Fischer-type
materials:	titanium (housing), silicone (membrane), glass (sensor), epoxy resin
dimensions:	total length (without connector): 205.0 mm diameter housing (main body): 12.7 mm diameter housing (largest part): 16.7 mm
housing:	titanium
concentration ranges:	type I: 50 µg/l ... 10 mg/l H <sub>2</sub> S type II: 500 µg/l ... 50 mg/l H <sub>2</sub> S type III: 10 µg/l ... 3 mg/l H <sub>2</sub> S others on request
accuracy:	2% (measuring value)
pressure range:	up to 10 bar
pH-range:	0 ... 8,5 pH
temperature range:	0...30°C (for measuring and storage !)
response time:	t <sub>90%</sub> : down to approx. 1 second
duration of life:	approximately 5...9 months (depends on H <sub>2</sub> S stress and on matrix of the analyte)
special features:	exchangeable sensor tip, integrated electronic device for the transformation of the current into 0...+3 V DC and for provision of polarisation voltage

<sup>\*)</sup>Changes for technical improvement are reserved.

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### 3 Structure of the H<sub>2</sub>S micro-sensor



Connector

Titanium Housing

Sensitive part for measuring

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## 4 Putting into operation

Please use only the delivered adapter kit, power supply and cable connections. For putting into operation please act as follows:

- 1 Link the sensor with the sensor cable. Do not twist. Make sure by means of the red points at the sensor plug and cable socket which have to face each other, that the connection is safe and correct.
- 2 Link the plastic box with the delivered cables to the voltage measuring instrument.
- 3 Select a suitable voltage range.
- 4 Link the power supply unit with the plastic box and switch on the power supply. The sensor is now ready for measurements. The observed following adjustment time is only due to temperature and concentration equilibrium adjustments.
- 5 Remove the protection cap from the sensor tip (without pull off of the sensor electronic housing !). Make sure that the glassy tip will not be destroyed mechanically by any solids or by handling or by cross forces near the sensor tip. This is not covered by the warranty.

## 5 Measurement and calibration

**Caution ! Do not forget to remove the protective cap during measurement. Otherwise the sensor tip may be destroyed !**

Please take note, that for the determination of the total sulphide concentration the measurement of pH and temperature is necessary. If the pH is below 5, a pH measurement is not necessary because of

$$C_{\text{total sulphide}} \approx C_{\text{H}_2\text{S}}$$

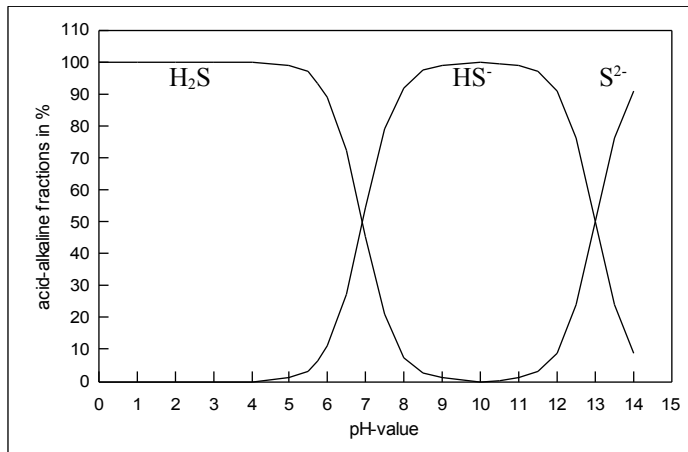
### *Temperature*

The amperometric H<sub>2</sub>S sensor works within a temperature range of 0 ... 30°C. For any temperature a temperature correction factor (E<sub>T</sub>) has been calculated, delivered with the sensor (at the end of this operating instructions). The chemical reaction of the redox mediator with H<sub>2</sub>S causes depositions inside the membrane. This influences the diffusion. Changes in the sensor slope at 20°C (=a<sub>20°C</sub>) of more than 50% require a new temperature compensation too.

Please note, that rapid temperature changes of some degrees may lead to some short troubles caused by equilibrium interferences inside the sensor. In this case please wait some seconds and go on after the adjustment.

### *pH dependence*

The amperometric H<sub>2</sub>S sensor operates within a pH range of 0 up to 8,5 pH and measures the partial pressure of gaseous H<sub>2</sub>S dissolved in liquids, which is direct proportional to the H<sub>2</sub>S concentration. If the pH of the analyte is above 8,5, there exists no more H<sub>2</sub>S, so that the application of the sensor is limited by this fact. Figure 1 shows, that below pH=5 the H<sub>2</sub>S concentration is quite similar to the total sulphide concentration.



**fig.1:** acid-alkaline fractions depending on the pH.

The necessary mathematical formulas for the the total sulphide concentration calculation and for the calibration are summarized as follows. A practical example you will also find in the appendix.

***Measurement and calibration of H<sub>2</sub>S micro-sensors with consideration of temperature and pH-value - mathematical formulas***

*1. Regression for temperature compensation table, delivered with the sensor*

$$E_T = f(T) = a_3 T^3 + a_2 T^2 + a_1 T + a_0$$

(E<sub>T</sub>-calculation for temperatures above 30°C is not possible by means of this equation !)

a<sub>20°C</sub>, a<sub>3..0</sub> are sensor specific data delivered with the sensor data sheet (see last page).

*2. Determination of the sensor slope (a<sub>20°C</sub>) - recommended after approx. 120 measuring hours*

Take several concentration – sensor signal pairs at a pH below 5 and measure the temperature. Calculate the slope at the measuring temperature a<sub>Tm</sub> by means of regression of first order, use the correct E<sub>T</sub> according to the enclosed table and calculate a<sub>20°C</sub> as follows:

$$a_{20^\circ C} = a_{Tm} / E_T$$

*3. Measurement of the H<sub>2</sub>S-concentration:*

$$c_{H_2S} = a_{20^\circ C} \times (U - U_G) \times E_T$$

c <sub>H<sub>2</sub>S</sub>	H <sub>2</sub> S-concentration
a <sub>20°C</sub>	sensor slope at 20°C
U	measured voltage
U <sub>G</sub>	voltage at 0 mg/l H <sub>2</sub> S
E <sub>T</sub>	temperature compensation E <sub>T</sub> = f(T)

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#### 4. Total sulphide calculation

$$c_G = c_{H_2S} \times \left( c_{H^+}^2 + c_{H^+} K_1 + K_1 K_2 \right) / c_{H^+}^2 \qquad c_G \approx c_{H_2S} \times \left( 1 + 10^{pH-6,919} \right)$$

The factor  $\left( c_{H^+}^2 + c_{H^+} K_1 + K_1 K_2 \right) / c_{H^+}^2$  is also called "G" and has been listed in a table at the end of this operating instructions in the appendix for a quick orientation.

$$c_{H^+} = 10^{-pH}$$

$$K_1 = 10^{-6,919}$$

$$K_2 = 10^{-13}$$

$c_G$  total sulphide concentration

$c_{H_2S}$  measured H<sub>2</sub>S-concentration

$c_{H^+}$  concentration of H<sup>+</sup>-ions

$K_1, K_2$  equilibrium constants

#### Calibration

For accurate measurements an accurate calibration is required. That 's why we recommend for the calibration the coulometric generator for the stepless *on line* production of H<sub>2</sub>S-/sulphide standard solutions. This generator is also available from AMT Analysenmesstechnik GmbH. Calibration is also possible as service if requested. The frequency of calibration depends on the H<sub>2</sub>S stress of the sensor. A check up of the sensor or a recalibration is recommended after approximately 120 measuring hours. Calibrations should be done always with acidic standard solutions of pH below 5 ! For the calibration please act as follows:

- push the sensor (without wetting cap !) into the AMT flow through cell (please order extra)
- connect the tube with the standard solution with the tube on the bottom of the flow through cell
- put the other tube into a waste bottle (e.g. bottle with KMnO<sub>4</sub> for fast oxidizing of the H<sub>2</sub>S-waste)
- pump the standard solution through the cell
- read about 4-8 different current-concentration pairs
- measure the temperature of the solution
- calculate the slope of the sensor at 20°C (a<sub>20°C</sub>) by linear regression; use the correction factors of the enclosed table (E<sub>T</sub>)

**Caution ! If H<sub>2</sub>S permeates through the membrane without polarizing the sensor, a decrease of signal resolution and increasing of residual currents follows. The sensor may be also destroyed !**

## 6 Troubles and errors during measurement

Most of the disturbances are not caused by the sensor itself or by the electronic device. Please take note, that H<sub>2</sub>S/sulphide solutions are chemically highly reactive, especially diluted solutions in trace amounts. The oxidation of the analyte on air or by dissolved oxygen happens in a few seconds. Adsorption/desorption and gas/liquid equilibriums lead also to a loss of the analyte.



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## 7 Switching off

If measurements have been finished, rinse the sensor carefully with distilled water or dive in the sensor approximately 5 minutes into a H<sub>2</sub>S free solution (water). After this, please check up the expected residual current. If the residual current has been reached, the interruption of the link between the sensor and the probe is possible. For storage do not forget to put on the protective cap.

**If H<sub>2</sub>S permeates through the membran without polarizing the sensor, a decrease of signal resolution and increasing of residual currents follows. A destruction of the sensor is also possible ! Do never store the sensor at temperatures below 0°C and above 30°C !**

## 8 Maintenance

Mechanical stress of the sensor tip, especially cross forces, unintentional touch downs or strong vibrations have to be avoided. The sensor tip is very weak. Do not touch it. Mechanical damage of the sensor tip excludes that the repair is covered by the guarantee.

For cleaning the sensor tip rinse it in water only. Do not use organic solutions. If there should be any biofouling at the sensor tip, it is recommended to clean the sensor tip by immersing it into very diluted acetic acid (2-5%) or diluted 0.02 mol/l NaOH (up to maximum of 24 hours). Higher concentrations may damage the sensor tip.

Protect the sensor tip with the wetting cap during long breaks. You can fill the wetting cap with less than ¼ with distilled water. Also a dry storage is possible.