

pH Shallow water sensor

- Operating Instruction 1,200 meter version -



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1 Preface

The pH-combined shallow water sensor with integrated electronic device has been developed for the *insitu* determination of pH in natural waters like oceans, lakes, rivers and estuaries for depths of up to 1,200 m with CTD probe systems.

The sensor consists of a pressure balanced glass-electrode and a reference electrode (Ag/AgCl) in a plastic rod. It is equipped with a ceramic diaphragm containing a high number of pores. The electrolyte is a KCl containing gel without silver ions to allow also measurements in H₂S and sulphide containing samples. The pH shallow water sensor is equipped with a titanium housing including the electronic device, with a plastics protection cage and a BH 4 M SUBCONN titanium connector. All electrodes are delivered with a wetting cap containing pH 4 buffer/KCl and covering the measuring end. Do never use small wetting caps of laboratory pH-sensors. This could lead to pressing air bubbles into the sensor followed by a damage of the sensor.

The pH-sensor shows an analogue output of 0...5 V DC. The whole pH-range of 0-14 is spread into this voltage output changes by means of an amplifier with a reserve for temperature. Please do never forget, that this signal output is not equal to the output of a normal laboratory pH-sensor with voltage outputs within a range of ± 300 mV.

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.

2 Technical Data of the pH shallow water sensor^{*)}

measuring principle:	potentiometry, combined electrode consisting of a glass electrode and a reference electrode
reference electrode:	Ag/AgCl system, gel electrolyte/liquid electrolyte combination, ceramic diaphragm with pores
power supply:	9-30 V DC
current uptake:	approx. 13 mA
signal output:	0...5 V DC, others on request galvanically isolated output
dimensions:	diameter: 37 mm with protection cage max. 30 mm (without protection cage) length: 240 mm over all
connector:	Subconn BH-4M, titanium
accuracy:	0,05 pH
resolution:	0,003 pH
pressure range:	up to 1,200 dbar
response time:	t _{63%} approx. 1 second
temperature range:	-2...60°C

^{*)} Changes for technical improvement are reserved.

Pin assignments of the sensors plug BH-4M:

- 1 power GND
- 2 analog GND
- 3 pH: 0...5 V DC (analog output)
- 4 power supply: 9-30 V DC

3 Structure of the pH-combined sensor



4 Putting into operation

All electrodes are shipped with a wetting cap covering the measuring end. This cap contains a solution of pH 4 buffer with potassium chloride for single junction combination electrodes.

Gently remove the wetting cap from the electrode by unscrewing the bottle from the cap and then sliding the cap and O-ring off of the electrode body. Save the cap for future long term storage. Do never use a small laboratory pH-sensor wetting cap in order to avoid the pressing of air through the sensor pores. This may lead to a sensor damage.

During shipping the air space inside the pH glass internal may have moved into the bulb. Grasp the electrode near the cable end and gently swing it through an arc to force the internal electrolyte into the pH bulb.

Rinse the electrode with distilled water and it is ready for use.

For putting into operation please act as follows:

- 1 Look at your pin connections at your probe system and compare with the pin-outs of the sensor as described in chapter 2.
- 2 Grease the plug and link it with your probe system or interfacing cable.
- 3 Switch on the power supply.
- 4 Remove the wetting cap.
- 5 Soak in neutral buffer solution for approx. 10 minutes.
- 6 If necessary, calibrate the sensor according to instructions in chapter 5.

If the sensor has dried out, soak the pH electrode in a in potassium chloride solution (3 mol/l) for a period of 24 hours.

Some of the potassium chloride solution may leak out of the wetting cap during transport, leaving a crust of KCl solution after drying. This layer of salt is harmless and can be rinsed off with water.

5 Calibration and temperature dependence

Formulas for pH temperature compensation:

$$U = a_1 (\text{pH}-7) + a_0 \quad (1)$$

$$a_1(20^\circ\text{C}) = a_1(T) \times f(T) \quad (2)$$

$$pH = \frac{f(T)(U - a_0)}{a_{1(20^\circ C)}} + 7 \quad (3)$$

$$f(T) = A_0 + A_1 T + A_2 T^2 \quad (4)$$

with: $A_0 = 1,0732$
 $A_1 = -3,9093 \times 10^{-3}$
 $A_2 = 1,2333 \times 10^{-5}$

T	measuring temperature in °C
U	measured voltage (output signal of pH-sensor)
a ₁	coefficient of linear regression (slope), equation 1
a ₀	coefficient of linear regression, equation 1
f(T)	temperature correction factor (Nernst factor)
A ₀ ...A ₂	coefficients for f(T) equation

For the sensor calibration please use 3 buffer solutions (e.g. pH = 4; 7; 10). Take care, that the temperature is equal for the three buffers. Take 3 U/pH values. Please wait for the adjustment as long as necessary. **Use as many buffer solution as necessary to reach the metal part of the sensor with the buffer. Otherwise all measuring values are wrong !**

Please use equation (1) for linear regression after this to find out the coefficients a₁ and a₀. The calibration has to lead back to 20°C. So if the calibration temperature should be e.g. 23°C, use equation (2) for correction to find out a₁(20°C).

Attention ! Please take note, that the pH-value of a buffer changes, if the temperature decreases or increases.

An electrode measuring many samples a day should be calibrated once a day. The frequency of calibration will depend on the level of accuracy required and the coating/fouling nature of the samples being measured.

Electrodes that are continuously monitoring a sample should be checked at least once a week or whatever period experience dictates.

Grab Sample calibration is a technique where the process electrode has been calibrated and placed on line for some period of time. Its output is then verified by measuring the pH of a sample with another electrode. The grab sample should be measured as soon as possible to avoid errors caused by changes in the samples temperature or changes in the samples pH due to exposure to the atmosphere.

6 Measurement

Determine the output value of the pH-sensor and the temperature of the sample. **Use as many**

sample solution as necessary to reach the metal part of the sensor with the liquid. Otherwise all measuring values are wrong !

Calculate $f(T)$, take your $a_1(20^\circ\text{C})$ and a_0 and use equation (3) for the calculation of pH.

Some tips and techniques:

Stirring the buffers and samples improves the stability and speed of response of the measurement.

Rinse the electrode with distilled water between samples and lightly blot the water on a paper towel before immersing it in the next sample.

Rinsing the electrode with a small amount of the sample before immersing it will eliminate any contamination of the sample.

The temperature of the electrode, the sample and the calibration buffers should be the same. Allow the electrode to come to temperature equilibrium with the sample before recording the measurement value. Measurements made more than 20°C from the calibration temperature should include a one point calibration at that temperature for maximum accuracy.

Low ionic strength samples, highly viscous samples and salt brines all slow the speed of response of the electrode. While the electrode will be stable to a change in pH buffers after 10-15 seconds it may take up to 5 minutes for the electrode to stabilize in a difficult sample.

Rinse the solution carefully with distilled water immediate after finishing the measurements and use the wetting cap with the storage solution in order the reach a long sensor life.

7 Maintenance

Slow response and large offsets may indicate the electrode has become coated. The nature of the coating will dictate the type of cleaning technique that should be used.

Soft coatings, like foodstuffs or bacterial films are best removed using a squirt bottle or the water jet from a faucet. If this is not successful then wiping with a soft wet cloth is the best choice.

Hard coatings, like calcium or lime scale are best removed with a solvent appropriate for the particular coating. A 5% solution of HCl would be a good choice for the calcium scale. If unsure of the proper solvent to remove a hard mineral coating alternate between a 5% HCl and a 4% NaOH for 10 minutes each. After treating the electrode with these strong acids or bases rinse the electrode with water and soak it in pH 4 buffer for at least $\frac{1}{2}$ hour.

Greasy and oily coatings are best removed with a solvent that will not attack the electrodes body. Methanol and isopropyl alcohol are good choices for solvents. Acetone, MEK (Methyl-Ethyl-Keton), THF or trichloroethane will irreparably harm the electrode. A soft toothbrush can be used with the detergent to remove stubborn coatings.

The pores of the reference junction may become clogged and surface cleaning may not restore proper function. The electrode should then be heated to 60°C in 3 molar KCl and allowed to cool in the same solution. Rinse it with distilled water and soak in pH 4 buffer for ½ hour before testing.

Electrodes age with time and eventually become desensitised. Extended periods of service at temperatures greater than 80°C or exposure to deionised water accelerate this phenomena. As a last resort dip the electrode in a 10% ammonium bifluoride solution for 10-20 seconds, then rinse it with tap water and soak it in 5-6 molar HCl for 30 seconds. Rinse it with tap water and soak it in pH 4 buffer for ½ hour before testing.