

H₂S 48

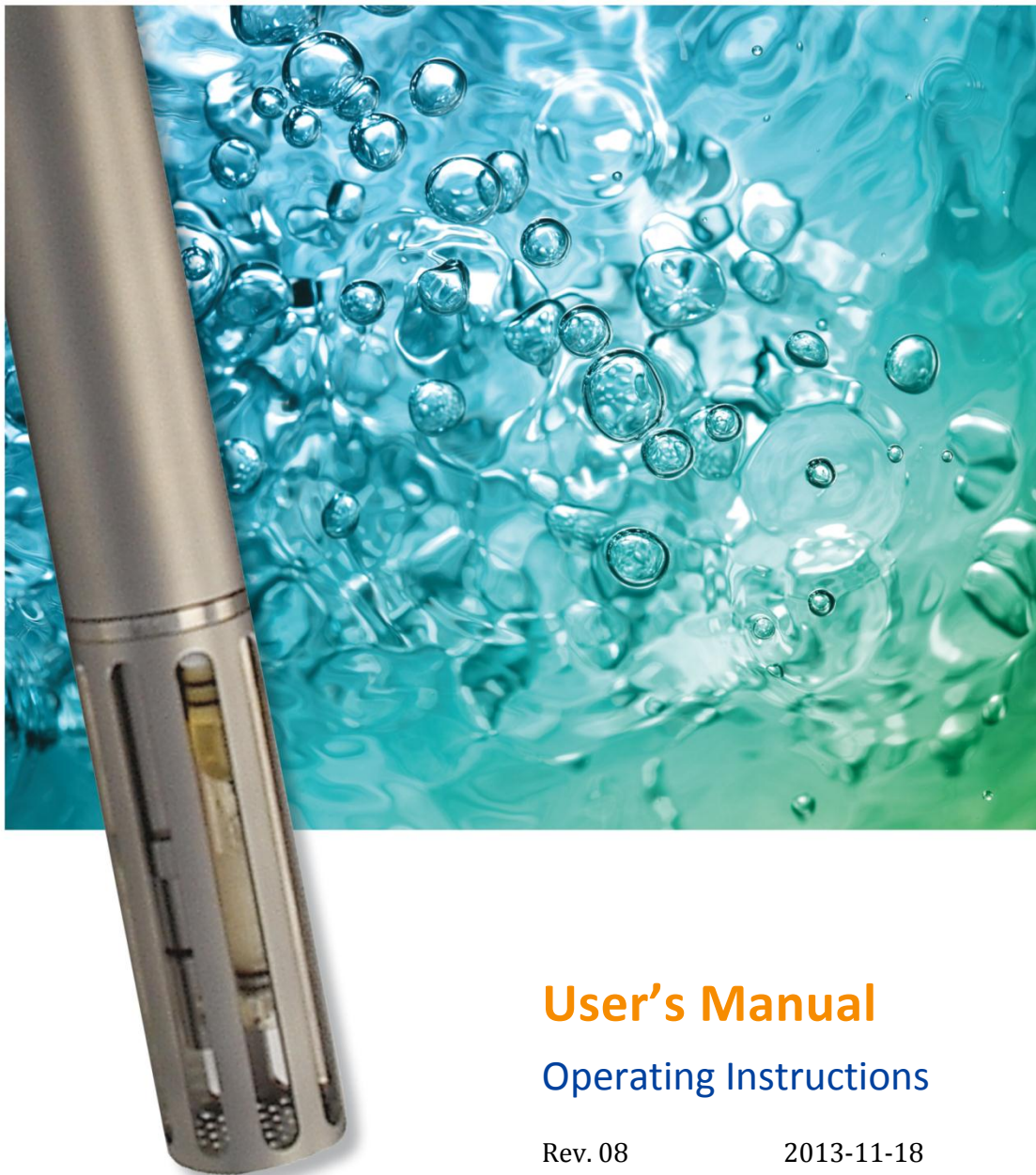
Submersible H₂S/Sulphide
Probe System for Shallow Water



Sea & Sun
Technology



AMT Analysen-
messtechnik GmbH



User's Manual

Operating Instructions

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Manufactured by



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05	2009-10-03		
06	2013-07-22	New cover pages with new company logo. Table of contents updated.	Lyssewski
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1 Important hints to the user

Read carefully the following short remarks in order to avoid problems and to cover the guarantee. Ignoring the following remarks leads to a loss of warranty. For detailed information please read the special chapters of this operating instructions.

1.1 Power supply

Supply voltages may range from 9 to 30 V DC. Supply above 30 Volt cause destruction of components. Damage due to excess voltage is not covered by the guarantee. Connection to unregulated power supplies, in particular to unbuffered motor-driven emergency power supplies is not recommended and should be avoided.

1.2 H₂S sensor

Never leave the probe unpowered, if the H₂S sensor is in contact with H₂S. Exposure to H₂S without power leads to destruction of the H₂S sensor. Avoid H₂S overstress by considering the measuring range. Make sure, that the H₂S sensor is used and stored only within 0 and 30°C. Especially temperatures below zero should strictly be avoided. Protect the H₂S sensor and avoid any touch of the sensitive parts.

1.3 pH sensor

Do never touch the sensitive tip. Protect the pH-sensor with the delivered wetting cap containing the storage solution and avoid any dry out of the sensitive tip. Avoid any air inside the wetting cap, fill completely with 3 M KCl for long-time storage. For short-time storage pH4 or pH7 buffer with 3 M KCl is a good choice. Do never use any other protective cap to avoid a damage of the sensor. Do never try to bend the pH-sensor. This can destroy the sensor.

1.4 Probe

Damaging by mechanical stress (think about the threads!) is not covered by the warranty. Clean the threads carefully before screwing anything. Rinse the probe carefully with fresh water after finishing the measurements. Sensor replacement is only allowed if the probe is in a dry condition. Water drops that get in contact with the internal plugs and connectors will affect the accuracy of pH and H₂S measurement. Avoid any contact of the sensitive sensor tips to detergents, mineral oils and organic solvents.

1.5 Protection cages and sensor caps

The probe's titanium protection cage is delivered separately and has to be mounted always before starting the measurements to protect the sensors. For this purpose please remove first the protective cap of the H₂S sensor and screw off the storage bottle from the pH-sensor.

If the measurements are finished, push the H₂S-cap on the H₂S-sensor and screw the plastic bottle on the pH-sensor with enough solution inside. This will protect the sensors.

2 General description of the H₂S measuring system

The submersible H₂S/Sulphide probe for shallow water use is a small, budget-priced and handy microprocessor controlled, multiparameter probe for the *in-situ* determination of dissolved total sulphide/H₂S in waste water, natural lakes, sea water and groundwater for depths of up to 100 m. The accurate determination of dissolved total sulphide/H₂S requires additional parameters like temperature and pH which are necessary for the calculation of total sulphide concentration. Additionally a pressure sensor allows the measurement of vertical distribution of the total sulphide/H₂S concentration in the water column.

The H₂S probe is a very robust and solid construction probe nearly completely made of titanium (except some sensor parts made of glass, stainless steel and plastics), corrosion proofed and with a high chemical resistance. In order to prevent corrosion, the housing and the measuring circuitry are not electrically connected to each other. This applies both for the supply and for the data lines.

Due to its very low weight, small size and low power consumption the submersible H₂S/sulphide probe is particularly suited for portable employment with battery supply. The very small diameter of the instrument admits profiling operation even in 2" boreholes. The probe is either equipped with a RS232 driver output, which can be directly connected to a PC, or optionally a RS485 output. A kevlar reinforced polyurethane multi-conductor cable (four wires) is available and guarantees a safe supply and data transfer over distances up to several hundred meters.

A data acquisition software running under Windows 95, 98, 2000 and XP is included in the delivery of each system. The SDA program can be used for storage of raw data, online display of all measured and calculated parameters and conversion into ASCII. For more details, refer to the manual of the SDA software.

3 Introduction to H₂S measuring

This probe is equipped with an amperometric H₂S micro-sensor, which has to be polarized all the time if the sensor is exposed to H₂S. In combination with a pH-sensor it is possible to determine the analytically most interesting total dissolved sulphide amount.

3.1 The general working principle of the sensor

Because of the partial pressure of gaseous H₂S dissolved in the sample, the analyte is separated by permeation through the membrane. The membrane is only pervious for gases, so that liquids, ions and solids are not able to reach the inner electrolyte of the sensor. Inside the sensor contains a buffer solution with a redox catalyst (= redox mediator) and 3 electrodes. At the electrodes a special polarization voltage is adjusted to realize a well-defined concentration ratio of the oxidized and of the reduced form of the redox catalyst. If the H₂S passes now the membrane, the hydrogen sulphide reacts first chemically with the redox catalyst to form a reaction product followed by the electrochemically oxidation of the reaction product at the working electrode. Caused by the polarization voltage the system is now endeavoured to adjust the former concentration ratio. This causes a current similar to the dissolved molecular H₂S amount in the sample. In opposite to ionsensitive electrodes (ISE) measuring the *sulphide ion activity*, the amperometric sensor determines the *H₂S-concentration*. Besides, the current flow in the amperometric sensor leads to a rapid decrease of the analyte inside the sensor resulting in *very fast response times* also, if a rapid change from high to very low concentration levels is necessary. It opposite to that ISE's are not suitable for measurements with a rapid change of concentration levels, because only with long-time diluting of the analyte a steady state potential at the solid-state electrode is achieved. Because of the pH dependent dissociation of H₂S in two steps the amperometric H₂S micro-sensor operates at a pH range of 0...8.5. If the pH of the analyte is above 8.5, there exists no more H₂S (< 2% of the total sulphide amount), so that the application of the sensor is limited by this fact. The calculation of the total sulphide amount (total sulphide amount = sum of the dissolved H₂S in the sample + hydrogen sulphide + sulphide) is possible very easy by means of the pH dependence of the acid-alkaline fractions (see fig. 1 below). Therefore *only one measurement is necessary for the determination of the H₂S- and of the total sulphide amount*.

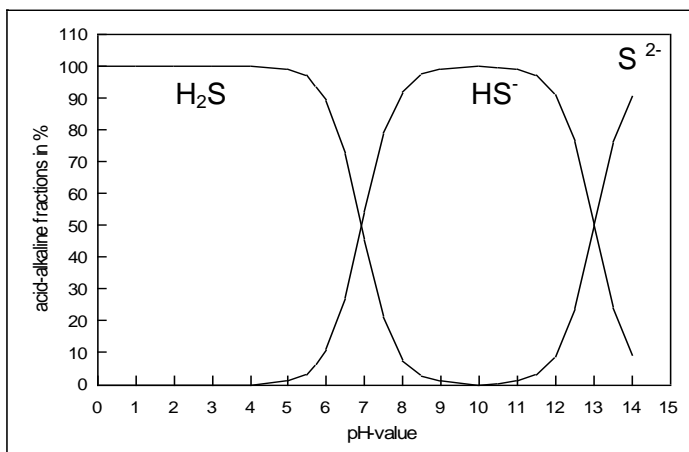


Figure 1: Acid-alkaline fractions depending on the pH.

3.2 The advantages of the micro-sensor technology

For manufacturing the amperometric H₂S sensor a special geometric design has been chosen to build a real **micro-sensor**. Electrode diameters below 25 µm, a very thin special membrane with small diameters, extremely short diffusion distances for the H₂S to the working electrode and a negligible analyte consumption on the electrodes are leading finally to *response times ($t_{90\%}$) of down to 200 milliseconds*. The *analyte consumption effects are negligible* too, so that *streaming of the sensor membrane and stirring is not necessary*. Besides, the dimensions of the sensitive tips within a range of some micrometers allow *in-situ* measurements without destroying equilibriums, concentration gradients and geometrical structures. This is very important, if measurements in muddy sediments or biofilms are required.

Measuring ranges:

- Type III (0.01...3 mg/l H₂S)
- Type II (0.5...50 mg/l H₂S)
- Type I (0.05...10 mg/l H₂S)
- others on request

Signal interferences:

No signal interferences in the presence of:

- carbon dioxide (up to 25.38 vol.%)
- methane (up to 5.78 vol.%)
- hydrogen (up to 0.544 vol.%)
- ammonia (up to 1000 ppm(v))
- carbon monoxide (up to 92 ppm(v))
- CS₂ (up to 5 vol.%)
- organic solvents (max. 20 Vol.%)
- acetic acid (up to 1 mol/l)
- dimethyl sulfide
- HCN
- salt concentrations of up to 40 g/l

Only small signal interferences:

- SO₂ (pH < 4): 100 ppm SO₂ = 1 ppm H₂S

3.3 Comparison of the amperometric H₂S measuring with other determination methods

Apart from the *ionsensitive electrodes* the *amperometric micro-sensor* is the one and only H₂S *in-situ* measuring system without any sampling. Besides the *methylene blue method* as a spectral photometric measuring procedure is well known but unsuitable for in-situ analysis.

In the case of the *methylene blue method* with a concentration range of approximately 0.06 to 1 mg/l without dilution steps there is only a very small working range. Furthermore this method is not applicable for turbid samples and the observed standard deviations of 5...10% are not acceptable. Sometimes comparative measurements of numerous laboratories using the methylene blue method revealed disastrous results. Mostly unavoidable mistakes during the sampling lead to very bad and scattering results when using this method. Problematically is the fact, that the procedure of the determination requires the addition of a strong acidic reagent resulting in a decrease of the samples pH and in the decomposition of precipitated heavy metal sulfides. In this case false results with higher total sulphide concentrations are observed. If the purpose of the determination is to check the danger potential caused by *dissolved* sulphide/hydrogen sulfide and H₂S, the consideration of precipitated heavy metals is not required. Therefore, the methylene blue method is a very doubtful method for the determination of the total sulphide amount. Shortly new developed spectrophotometric methods as well are not able to solve this problem, because sampling, addition of strong acids and numerous dilution steps are required now as ever. When measuring in sewage there is an additional disadvantage,

because detergents and reaction products of oxidized sulphides (e.g. $\text{Na}_2\text{S}_2\text{O}_3$) may occur and leading to an essential distort of the analysis results.

Ionensensitive electrodes (ISE) have also a lot of disadvantages. The measuring signal depends only on the *ion activities* and not directly on the ion concentration to be determined. Using a ISE, measurements are possible within a pH range of 14 to 11. At pH ranges below 11 the share of sulphide related to the total sulfide amount is below 1% and decreases rapidly with decreasing pH values. In addition to that diffusion potentials at the diaphragm of the reference electrode may occur. When using the Nernstian equation it is found, that already 1 mV (one concentration decade is equivalent to about 29 mV) results in a mistake of about 8%. Considering the fact, that in alkaline and acid solutions caused by the high mobility of OH^- and H^+ ions diffusion potentials of up to 10 mV are observed, the possibility of false results is evident. Furthermore, the change from high concentrations to lower concentrations is very time consuming, because - in opposite to amperometric sensors - the potentiometric electrode is not suitable to consume the analyte realizing fast response times. Therefore only long and carefully rinsing with the new lower concentrated sample leads to a steady-state of the potential. In addition to that, it's sometimes troublesome to activate the electrodes for a longer time in sulphide containing solutions.

When using an *amperometric micro-sensor* these disadvantages may be avoided. The amperometric H_2S sensor is suitable within a pH-range of 0 to 8.5. Therefore a direct measurement in natural waters is possible not only in lakes, rivers and oceans with $\text{pH} = 6 \dots 8.5$ but also in strong acidic brown coal lakes. Caused by the miniaturization of the sensor and it's very low analyte consumption, streaming of the membrane or stirring of the analyte solution, as it is well-known from other Clark-type oxygen sensors, is not necessary. Besides there is no necessity of conditioning the sensor in sulphide containing solutions as in the case of ISE's. Considering the response times, the amperometric micro-sensor is head and shoulders above to the commercially available ion sensitive electrodes. The detection limit is about $3 \mu\text{g/l}$ and the signal resolution is approximately $2 \mu\text{g/l}$. In opposition to that, ISE's have only a signal resolution within a range of $50 \dots 100 \mu\text{g/l}$. Besides, there is only a logarithmic dependence of the measured voltage on the sulphide ion concentration (1 decade = 29 mV).

4 Mechanical characteristics of the H₂S probe

All parts of the probe exposed to water, are made of corrosion-proof materials mainly titanium. Only some parts of the pH- and H₂S-sensor are made of glass, plastics or stainless steel because of technological reasons. Essentially the probe consists of the following mechanical structural components (refer to the following drawing):

Tube

Probe base (bottom end cap)

Top end cap)

Sensor protection cage

Sensors (P, T, pH, H₂S)

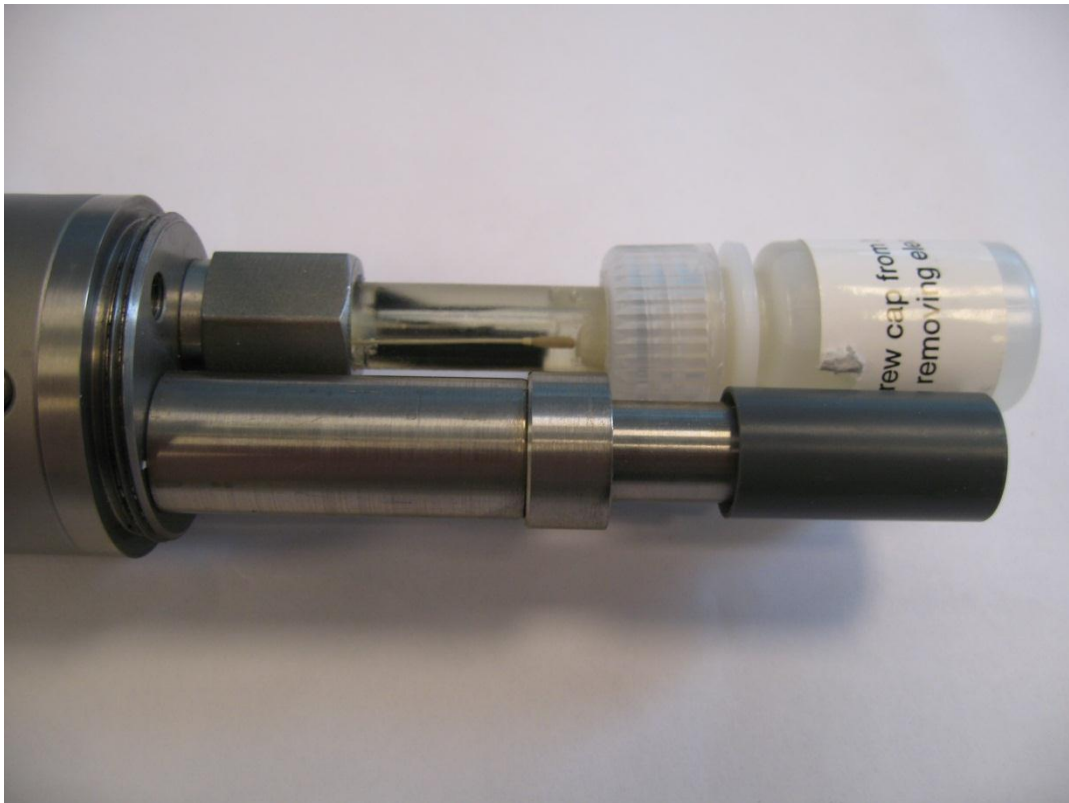
4.1 Tube

The pressure pipe is made of a solid-drawn seamless titanium tube with a diameter of 48.3 mm and a wall thickness of 2.8 mm and is generally able to withstand 2000 m water depth (please take note, that the deployment depth is limited to 100 m because of the H₂S sensor). There are four holes in 90° graduation situated 6 mm away from each tube end which are used for the fixing of top and bottom caps with 4 screws M 3*4 on each side.

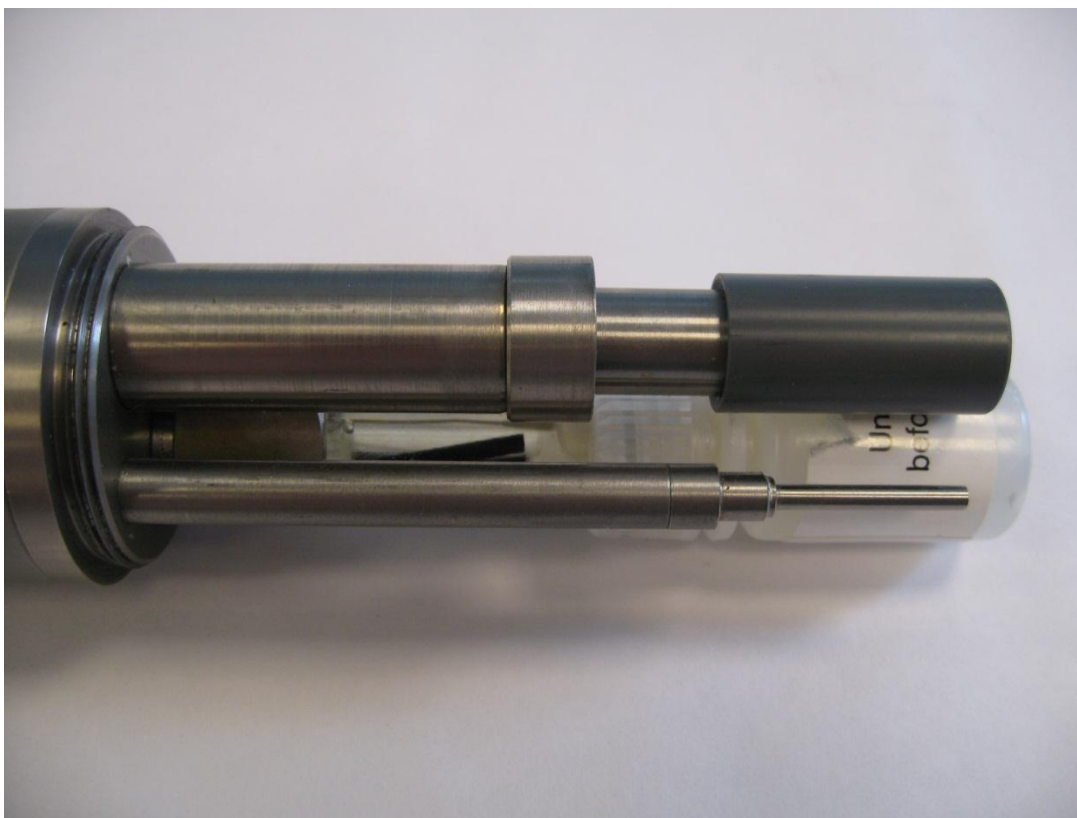
4.2 Probe base

The probe base (made of solid titanium ø 48.3 mm) serves as mounting support for sensors and printed circuit board. Both the H₂S- and the pH-sensor have the same G1/4 thread while the temperature sensor is screwed into a M6 fit. The pressure transducer is inserted into the bottom cap from inside and held by a round aluminium plate against the outside pressure. A 1/4" UNF28THD tapped hole is used as calibration connection for a hydraulic tube to a pressure gauge. For Details please refer to the following pictures.

Base and tube are sealed by an O-ring 39*2.5 mm and fixed with 4 M3*4 screws, while the sensor protection cage has a thread M46*1.5 too and can be unscrewed by 3 turns counter clockwise.



pH and H₂S-sensors mounted on the bottom cap, in the foreground the calibration connection for the pressure gauge



temperature sensor and H₂S mounted on the bottom cap

4.3 Top end cap

The top cap has the same dimensions as the base and is also made of solid titanium. Fastening and sealing are identical to that of the base. An underwater bulkhead connector is screwed into the lid and a suspension bolt with a loop for hanging it onto a shackle.

The connection to the sensor electronics is established by a separable cable-connection.

4.4 Sensor protection tube

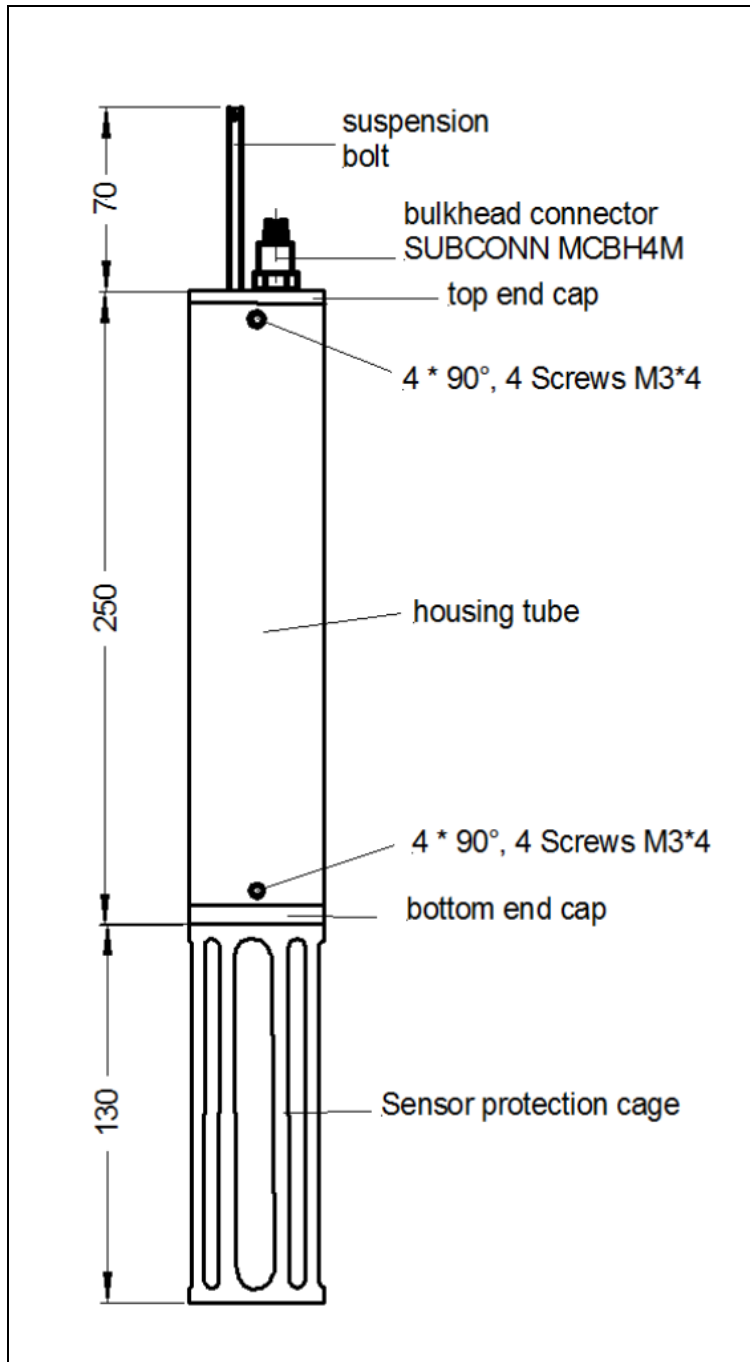
The sensor protection tube is made of titanium from a tube 48.3*2.8 mm with a length of 130 mm. The tube has 8 slots of size 120*10 mm in order to ensure a fine water flow through the sensors but yet enough stability to protect the sensors against shock and ground contact on the water-floor. An additional perforated plate is pressed into the bottom of the protection tube in order to guarantee better safety for the highly sensitive tip of the H₂S sensor.



Sensor protection tube

4.5 Dimensions and weights

-	pressure tube length	240 mm
-	probe diameter	48 mm
-	protection tube length	130 mm
-	length of suspension bolt	70 mm
-	total length	450 mm
-	gross weight in air	1 kg
-	material	titanium grade 2



5 Sensors

The submersible H₂S/Sulphide probe system for shallow water is equipped with 4 sensors:

- Pressure transducer
- Temperature sensor
- pH-sensor
- H₂S-sensor

5.1 Pressure transducer

A piezoresistive full bridge in OEM version with a diameter of 15 mm and a total height of 6 mm is used as pressure transducer (produced by the Swiss manufacturer KELLER). The casing and diaphragm are made of alloy C276. The transducer is delivered with a small SMD-PCB which includes the temperature compensation of the pressure transducers zero point and sensitivity. The sensor is plugged into the base of the probe, the SMD-board is mounted on the analogue main board of the probe.



Technical characteristics

- Manufacturer	KELLER, Switzerland
- Model	PA7LHE/10bar
- Dimensions	15 mm diameter, 5 mm height
- Full scale range	5, 10 bar
- Bursting pressure	150 % of FS range
- Repeatability	0.1 % of FS range
- Zero drift	0.01 %/°C
- Precision	0.1 % in the range of -2°C...36°C.

5.2 Temperature sensor

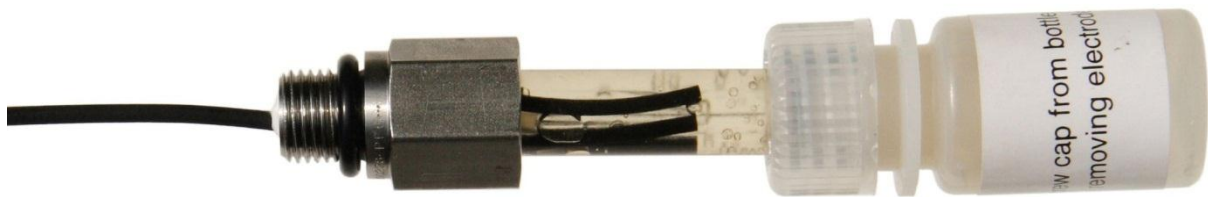
The temperature sensor is a platinum resistor Pt100 in a tiny ceramic carrier of 6 mm length and 2 mm diameter. It is fitted in a slender titanium tube 3*0.25 mm, about 30 mm long. This tip is resistant to a pressure of 200 bar. The platinum resistor is connected in 4-wire technique. The Pt100 resistor is part of a highly linearized Wheatstone bridge, the signal output of the temperature channel is quite linear to the medium temperature.

Technical data

Manufacturer	SST GmbH
Type	ISOTECH P100/0620
Measuring range	-2°C – 36°C
Response time	approx. 1sec.
Repeatability	< 0.001°C
Accuracy	0.01°C

5.3 AMT pH sensor

The pH combined electrode is a robust sensor for a maximum pressure of 1200 dbar. The sensor is equipped with a reference system using a solid gel (stiff polymer mass containing Ag^+ -free KCl) and a ceramic pore diaphragm and with a pressure stable pH-sensitive glassy electrode. The pH sensor is a replacement part and has to be exchanged periodically. If the sensor has reached the lifetime, it has to be replaced by a new one. The sensor has a stainless steel thread G1/4A (titanium on request) which is screwed into a flange. The electrical contact is made by a socket in the flange. Sealing between sensor and flange is achieved by an O-ring which is part of the sensor.



Technical data:

Manufacturer	AMT GmbH
Model	SW24023-S
Measuring range	pH 0-14
Maximum depth	1200 m
Shaft diameter	12 mm
Shaft length	84 mm
Shaft material	transparent plastics
Thread material	stainless steel
Length with flange	117 mm
Response time	approx. 1 sec $t_{63\%}$
Accuracy	0.05 pH

5.4 H₂S sensor

The amperometric H₂S micro-sensor measures the dissolved H₂S partial pressure in the water. Its micro-sized glass tip is membrane covered and only permeable for H₂S gas. If it is combined with a pH and temperature sensor, the following units can be determined: H₂S gas dissolved in the sample and total dissolved sulphide amount in the sample.



Technical data:

Manufacturer	AMT GmbH
Model	SW-UF-SA
Measuring ranges	Type III (0.01...3 mg/l H ₂ S) Type II (0.5...50 mg/l H ₂ S) Type I (0.05...10 mg/l H ₂ S)
Maximum depth	100 m
Shaft material	titanium
Sensitive tip	glass
Response time	< 1 sec
Accuracy	2% of measuring value
Measuring principle:	amperometry, membrane covered sensor with redox mediator
Polarization:	necessary, realized by means of integrated electronic board
Polarization time:	10-15 minutes after switching on the probe (increases with sensor life)
Temperature range:	0°C ... 30°C for storage and measurement
pH-range:	0 ... 8.5
Average life time:	9 months (depends on the H ₂ S amount and on the sample)

6 Replacement of sensors

The chemical sensors pH and H₂S have to be replaced periodically, if the lifetime is over or if the user needs a different measuring range for H₂S/sulphide. Exchange of these sensors is very easy, the probe generally doesn't have to be opened. First remove the sensor protection tube by turning it counter-clockwise. Please proceed for exchanging the sensors as follows:

pH sensor

The pH sensor has to be unscrewed counterclockwise very carefully without damaging the other sensors by using a spanner type SW19 or 3/4". Be carefully especially when starting and prohibit a slip off with the spanner. After unscrewing pull lightly until the cable connector is visible. Disconnect the small 2 pin round connector and ensure that the loose end of the plug will not withdraw into the housing. Connect the new sensor and screw it carefully into the G1/4 fit. Screw on the protection cage clockwise. Be careful not to bend the sensor to prevent mechanical damage.

After a pH sensor replacement the user should carry out a calibration in order to achieve the highest accuracy of sulphide determination. Don't forget to enter the new coefficients into the software.

H₂S sensor head

The user has only to unscrew the coupling ring by hand and slightly pull out (Do not twist!) the sensor head out of the flange. Disconnect the small round connector and secure the cable end of the plug. Connect now the spare sensor and push it carefully into the flange. Consider that the red points on the connector and on the socket have to face each other before pushing on. Do not twist! Turn on the coupling ring and screw on the protection tube. A sensor exchange is a matter of few minutes. After a H₂S sensor replacement please don't forget to input of the new coefficients into the software.

Pressure sensor

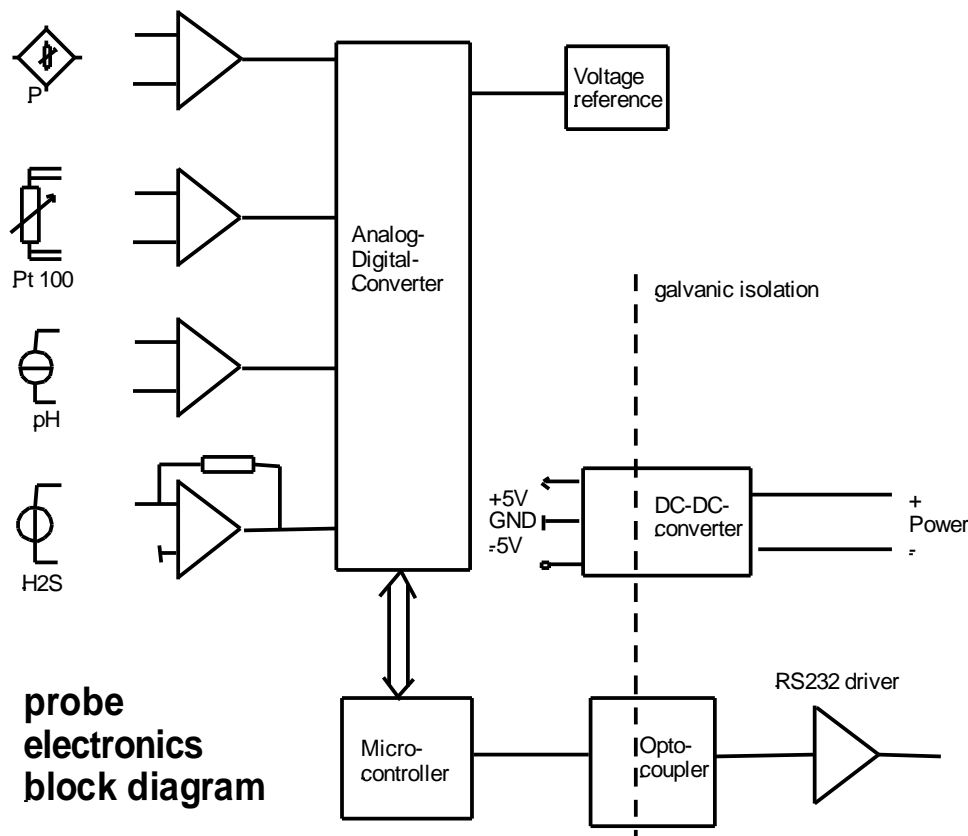
Typical average lifetime of the pressure transducer is about 5 years. Lifetime has finished when the membrane is corroded, which can easily be detected by oil leakage at the calibration thread and unstable values. The exchange of a pressure transducer is a matter of the manufacturer.

7 Probe electronics

All electronics parts of the probe are mounted on a single board of size 35 mm * 150 mm. This PCB contains the following circuitry (refer to the block diagram):

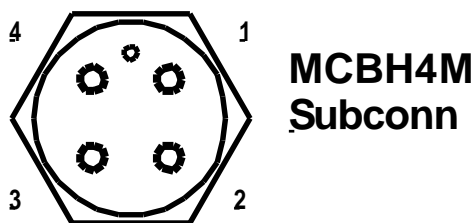
- DC-DC-converter
- RS232 driver
- Microcontroller
- 4 channel 20 bit ADC
- Temperature bridge
- Pressure amplifier (with separate Progress-print)
- H₂S amplifier
- pH amplifier
- FSK module (option), separate PCB

The input power and RS232 output driver are galvanic isolated from the measuring circuitry. The supply voltage may range from 9 to 30 VDC, the DC-DC converter generates regulated split supply voltage of 5 Volt. Neither the input power lines nor the data lines have any galvanic connection to the measuring circuitry and probe housing, all parts which are exposed to water are completely floating.



8 Connector pin assignment and power supply

The Submersible H₂S/Sulphide probe has a 4-pin underwater connector which allows the probe to be operated in different modes. The standard connector is SUBCONN MCBH4M made of titanium.



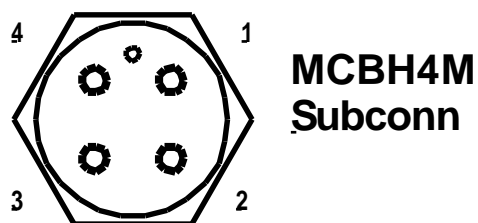
- Pin1 +I_C, FSK signal, positive constant current supply
- Pin2 TxD (RS232) serial output "Transmit Data"
- Pin3 -U_b / -I_C negative constant current supply, Power GND
- Pin4 + U_b + power input

Constant current supply with FSK data transmission is available as option and requires a separate power supply interface.

8.1 Operation with multicore cables

The use of multicore cables is advisable for shorter distances between probe and PC and particularly in a laboratory. The probe is then supplied either by a battery or a regulated power supply. The voltage is applied to pin3 (negative) and pin4 (positive). Data transfer to the PC is via pin2 (Transmit data TxD) and pin3 (GND).

The wiring of such a cable is described below.



- Pin 1 not connected
- Pin 2 TxD transmit data
- Pin 3 power GND and RS232 GND
- Pin 4 + 12 V power

Inline connector MCIL4F
H₂S-probe

9-pole SUB-D plug DB9S
Computer and power supply (battery)

Pin 2	TxD-----	RS232 RxD	Pin 2
Pin 3	RS232 GND-----	RS232 GND	Pin 5
Pin 3	Power GND-----	Power GND	banana plug black
Pin 4	+Power-----	+ Power	banana plug red

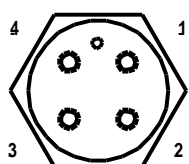
The probe is designed for connection to 12 volt batteries or to regulated power supply. The supply voltage may range from 9 to 30 volt DC. The current consumption is about 35 mA (12 volt) or 20 mA (24 volt). The maximum supply voltage is 30 volt.

Supply voltages above 30 volt cause destruction of components. Damage due to excess voltage is not covered by the guarantee. Connection to unregulated power supplies, in particular to unbuffered motor-driven emergency power supplies, is not recommended.

The maximum length of the multicore cables depends mainly on the cable resistance and capacity and can at best be several hundred meters. A specific interface between probe and PC is not necessary.

8.2 Operation with single conductor cable (FSK option)

Profiling performed via winches with slip rings require single conductor cables. The H₂S probe is then supplied by constant current, the FSK signal is superimposed on the constant current as voltage modulation. An interface between PC and winch (probe) generates the constant current and converts the FSK-signal from the probe into PC-compatible RS232 data. The maximum voltage of the current source depends on the cable resistance (cable length). The wiring is as follows:



MCBH4M	Signal
pin 1	+ 100 mA, FSK frequencies out
pin 2	n.c.
pin 3	- 100mA
pin 4	n.c.

Inline cable	Signal	Sea cable
Pin 1	+I/FSK-signal	inner wire
Pin 3	-I, signal GND	shield

The basic version has a constant current of about 100 mA. The voltage drop between Pin 1 and Pin 3 is approximately 17-18 volt. The FSK signal is a sinusoidal signal of approx. 5Vpp and modulated on the constant level of the current supply. A logical LOW-level is the equivalent to a low frequency 2400 Hz, a logical HIGH-level is equivalent to the higher frequency 4800 Hz.

9 Probe service and maintenance

The best maintenance for the probe is to handle it with care. Despite the fact that the probe is sturdily and robust designed, unnecessary strains like knocking and shocks should be avoided. Apart from that, there are only few instructions and maintenance rules which should be heeded or met to, so as to ensure a longer life-span and correct measuring results.

9.1 Underwater connector

The underwater connector is actually maintenance-free. However, it is advisable to lubricate the sealing surfaces of the pins with sea water-proof grease.

This reduces wear whilst plugging and unplugging. Further tips:

- Clean the plugs with warm soapy water. They do not have to be dried. Chemicals should be avoided.
- To avoid corrosion never plug or unplug whilst under water.
- To conserve the cable plug never unplug by pulling on the cable. Avoid bending radiuses and above all narrow sharp kinks.
- Unused plugs should never be left blank. They should always be protected against corrosion and therefor closed by a dummy cap.

9.2 Pressure sensor

The pressure sensor doesn't require special attendance or maintenance. Personnel experience has shown however, that the pressure sensors should never be tested by pressing a pin onto the membrane. This often causes damage to the membrane or dents it, which can lead to pressure reading mistakes or to a total damage. Pressure sensors damaged in such a way are not covered by the guarantee. For calibrating to zero please press the menus: calibrate → pressure comp. → air calibration → now → save + exit.

9.3 Temperature sensor

The temperature sensor is maintenance free. Dirt and plant cover only prolong the time constant but have no effect on the precision.

9.4 H₂S sensor

The H₂S sensor has an average life of approximately 9 months. It depends on the H₂S stress/amount and on the matrix, which life time is reached. There is no difference in the life time, whether the sensor is used or if the sensor is stored only. But to ensure a long sensor life, please consider the following:

- Do never contact the sensor with H₂S solution, if the probe is switched off.
- After measurements have finished, rinse the sensor carefully with distilled water to avoid any contamination with H₂S after switching off. (Dive in the sensor/probe into a beaker with distilled water).
- Switch on the probe 10-15 minutes before starting the measurements. This is recommended to ensure, that the sensor polarization time is sufficient to bring the residual current into the steady state.
- Protect the sensor during long breaks with the plastics cap.
- Do never touch the sensor's glass body. This may lead to the damage of the sensor. There is no warranty for mechanical damage!

Due to the very small dimensions of the sensor tip, shock and impacts should be avoided during handling procedure on board the ship. The sensor has to be polarized/switched on all the time, if the sensor is stressed with H₂S. Otherwise the sensor may be damaged, changes the sensor slope and/or the life time decreases. Streaming or stirring of the sensor is not necessary.

9.5 pH sensor

The pH sensor has to be rinsed carefully with distilled water after finishing the measurements. Protect the sensor with the delivered wetting cap (other caps may destroy the sensor). Make sure, that 3 M KCl is used for long-time storage. Short-time storage is possible with pH 4 or pH 7 buffer with some chloride.

After the sensor's life span has ended, the corresponding sensor has to be replaced. When unscrewing the sensor, avoid that moisture (e.g. water drops) may reach the contacts (dry beforehand). A single drop of saltwater is enough to cause long-lasting incorrect measurements – this is due to the high output impedance of 100 – 400 MΩ. So only replace sensors under clean and dry conditions please.

The sensor has to be protected against drying out during long-time storage by using the enclosed wetting cap filled with 3 M KCl or Cl⁻-containing pH 4 or pH 7 buffer. It is not allowed to use other wetting caps in order to avoid any air pressing into the diaphragm leading to sensor malfunctions or damage. Damage because of using other wetting caps or storage without any wetting cap is not covered by the guarantee.

10 Serial output data format

The probe data can be fed into any serial port of the PC (USB-to-serial adapters can be used, too). The standard settings of the probe are:

Baud rate: 1200
Character length: 8
Number of stop bits: 1
Parity: odd
Protocol: none, asynchronous
Signals: GND, TxD, RxD

Serial data is transmitted as binary data. Each sensor requires 3 successive bytes (16 bit measuring values, 5 bit sensor address and 3 bit status). The data transmission format is presented in the following chart:

Sensor	LSB							MSB
1.Byte	H	D0	D1	D2	D3	D4	D5	D6
2.Byte	H	D7	D8	D9	D10	D11	D12	D13
3.Byte	L	D14	D15	A0	A1	A2	A3	A4

DO – D15 16 bit binary data (decimal value 0 – 65535)

AO – A4 5 bit binary address (decimal sensor address 0-31)

H, H, L 3 status bits.(H = logic HIGH level, L = logic LOW level)

Sensor transmission starts with the first byte (LSB first) and ends with the third byte (MSB last). Each sensor in the probe has a specifically assigned binary address. Address and corresponding measuring value are transmitted in a 3 byte block. The status bits are useful for the PC data acquisition program to compose the 3 bytes in the correct sequence. A complete data set begins with the lowest address sensor and ends with the highest address sensor. All addresses between 0 and 31 may occur. The transmitted physical addresses are identified by the data acquisition program and compared to those registered in the EEPROM configuration. The addresses of the H₂S48M are listed below:

Address 2 pressure

Address 3 temperature

Address 6 pH

Address 7 H₂S

Complete dataset for H₂S48:

	LSB								MSB
1.Byte	1	0	P1	P2	P3	P4	P5	P6	
2.Byte	1	P7	P8	P9	P10	P11	P12	P13	
3.Byte	0	P14	P15	0	1	0	0	0	
4.Byte	1	T0	T1	T2	T3	T4	T5	T6	
5.Byte	1	T7	T8	T9	T10	T11	T12	T13	
6.Byte	0	T14	T15	1	1	0	0	0	
7.Byte	1	pH0	pH1	pH2	pH3	pH4	pH5	pH6	
8.Byte	1	pH7	pH8	pH9	pH10	pH11	pH12	pH13	
9.Byte	0	pH14	pH15	0	1	1	0	0	
10.Byte	1	H0	H1	H4	H3	H4	H5	H6	
11.Byte	1	H7	H8	H9	H10	H11	H12	H13	
12.Byte	0	H14	H15	1	1	1	0	0	

P0..P15 16 bit **P**ressure binary raw data
 T0..T15 16 bit **T**emperature binary raw data
 pH0..pH15 16 bit **pH** value binary raw data
 H0..H15 16 bit **H₂S** binary raw data

11 Calculation of physical units

Data transmission and data storage are performed solely in binary words. The calculation of the physical values from the raw data and their display is carried out by the PC-data acquisition program. Generally the calculation of physical values is made by a polynomial of n^{th} order:

$$\text{Measurement value: } V = \sum A_i * n^i \quad i = 1 \dots 5$$

n : = raw data count (0...65535)

A_i : = calibration coefficients

The calibration constants are determined by the manufacturer by calibration measurements against a normal or subnormal and subsequent regression calculations.

Pressure

To achieve 0.1 % accuracy the pressure has to be calculated by a cubic polynomial

$$P[\text{dbar}] = A_0 + A_1 * n + A_2 * n^2 + A_5$$

The calibration coefficients A_0 , A_1 , A_2 are referred to an air pressure of 1000mbar. Since the pressure transducer measures absolute (against vacuum) the variation of air pressure or the height above sea level affects the accuracy of the depth determination. Therefore the user has the possibility to set the calculated pressure to zero before he starts measuring (H_2S probe in air). This is executed by the data acquisition program by modification of the constant A_5 . After a calibration A_5 is automatically set to zero.

Temperature

Temperature linearity is better than 1mK in the range of -2 to 36°C . Therefore the physical value is approximated by a linear function

$$T[^\circ\text{C}] = A_0 + A_1 * n$$

Any deviations of the proclaimed linearity indicates faults either in the electronic circuitry, temperature sensor or in the calibration procedure.

pH

The pH value is calculated by a linear function too.

$$\text{pH} = A_0 + A_1 * n$$

If a regression calculation after a calibration results in a polynomial of higher order then either any buffer solution may be wrong or the sensor is near the end of its lifetime.

H₂S concentration

In order to maintain the usual AMT calibration procedure and calculation formulas the H₂S analog channel of the probe is calibrated in millivolts [mV].

$$\text{analog value H}_2\text{S [mV]} = A_0 + A_1 * n$$

Based on this “analog raw data output” the user can carry out the same calibration and test procedures as he is accustomed with AMT’s analog H₂S sensors (refer to next chapter).

12 Calibration procedure

12.1 Calibration of H₂S sensor

If a calibrated sensor has been ordered, all the necessary coefficients ($a_{20^{\circ}\text{C}}$, $a_0 \dots a_3$) are delivered with the sensor, except the residual current, which has to be determined as follows: Dive in the probe into H₂S-free water until the end of the protection cage of the probe's body as minimum. Wait for the adjustment of the residual current. Now enter the sensor's residual current in the software. It is recommended to check up and to enter the residual current periodically before starting a new measurement.

If the sensor's membrane is not contaminated with any precipitations because of the samples matrix and if the sensor is not overstressed, the sensor's slope $a_{20^{\circ}\text{C}}$ is valid for approximately 120 measuring hours. After this a check up, or if necessary a recalibration is recommended. For this purpose we recommend to use AMT's coulometric generator for the online generation of standard solutions. It is possible to purchase this device from AMT or to send the sensor head to AMT for recalibration. This is done within 1-2 working days.

The following inputs into the probe's software are necessary:

1. Click "SST Standard Data Acquisition"
2. Select "Calibrate" followed by "Show coefficients"
3. Go to the window "Select a sensor" and use the pull down menu for selection of:

- a) "H₂S" → enter → "H₂S a₂₀", make the input of $a_{20^{\circ}\text{C}}$
"Zero Voltage", input of residual current (H₂S-free solution)
- b) "Sulfid" → enter → "H₂S a₂₀", make the input of $a_{20^{\circ}\text{C}}$
"Zero Voltage", input of residual current (H₂S-free solution)
- c) "T_H₂S" → enter → make the inputs in "Coeff A [0]" "Coeff A [1]"
"Coeff A [2]" "Coeff A [3]"

Select now any other window (e.g. "Coeff A [2]" to activate the window "Save + Exit" and press "Save + Exit" to take over all the necessary coefficients a)-c)

12.2 Calibration of pH-sensor

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.

For the sensor calibration please use 3 buffer solutions (e.g. pH = 4; 7; 10) as minimum. **Take care, that the buffer solutions have all the same temperature and that the temperature sensor is immersed too in the buffer solutions.**

Select now "Table" in the "SST-SDA Quick" window. Dive in the probe into the buffer solution and follow the adjustment in line pH_Tc, raw data. Write down the pH of the buffer solution (consider the temperature by using the bottles table!), the raw data and the temperature. Repeat this with the other buffer solutions.

Make a regression of first order with:

$\text{pH} = A_1 \cdot n + A_0$ in order to determine A_1 and A_0

The following inputs into the probe's software are necessary:

1. Click "SST Standard Data Acquisition"
2. Select "Calibrate" followed by "Show coefficients"
3. Go to the window "Select a sensor" and use the pull down menu for selection of:

"pH" → enter → "pH A[0]", make the input of determined A_0
"pH A[1]", make the input of determined A_1

"pH_Tc" → enter → "Calib. Temperat", make the input of the calibration temperature

Select now any other window (e.g. "pH A[1]" to activate the window "Save + Exit" and press "Save + Exit" to take over all the necessary coefficients.

Grab Sample calibration is a technique where the process electrode has been calibrated and placed online 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.

13 Spare parts and accessories

- | | |
|---------------------------|-------------------------------------|
| - pH sensor | SW24023-S (AMT) |
| - Pressure sensor | KELLER PA7-10 Progress 0.1 - 2 Volt |
| - H ₂ S sensor | SW-UF-SA (AMT) |

O rings

- | | |
|-------------------------------|-----------------|
| - Base and lid | 39 * 2.5 mm |
| - pH Sensor | 10 * 2.5 mm |
| - pressure sensor | 13 * 1 mm |
| - Temperature tip | 4 * 1 mm |
| - Temperature flange | 5 * 1.5 mm |
| - H ₂ S sensor tip | 9.75 * 1.78 mm |
| - H ₂ S flange | 10 * 2.5 |
| - Subconn MCBH4M | 12.42 * 1.78 mm |

Plugs and cables

- | | |
|--------------------|----------------|
| - Dummy cap | SUBCONN MCDC4F |
| - Locking sleeve | SUBCONN MCDLSF |
| - Inline connector | SUBCONN MCIL4F |