Amperometric H_2S micro-sensor for probe systems

- Operating Instruction shallow water version -

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1 Preface

This version of an amperometric H_2S micro-sensor has been developed for the *in situ* determination of dissolved H_2S/sulphide in natural waters, waste waters, oceans and lakes for depths up to 100 m with CTD probe systems.

Because of the partial pressure of the gaseous H_2S, the analyte is separated by permeation through the membrane. Inside the sensor the hydrogen sulphide reacts with a redox mediator. The electroche-mical oxidation of this formed compound at the working electrode causes a current corresponding to the concentration of the dissolved molecular H_2S 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_2, H_2O-vapour, CH_4 , CS_2 , dimethyl sulfide (DMS), acetic acid or NH_3. 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 temperature measurement.

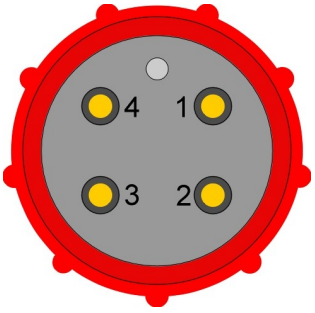
All sensors are delivered with calibration and temperature compensation data and also with mathe-matical formulas to calculate the total sulphide concentration.

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.

2 Technical Data of the H_2S sensor for shallow water

measuring principle:	amperometric sensor
power supply:	9 ... 30 VDC
output:	0 ... + 5 VDC
dimensions:	maximum diameter: 24 mm total length: 235 mm
connector:	wet con BH-4-MP, titanium (others on request)
housing:	titanium
concentration ranges:	type I: 50 µg/l ... 10 mg/l H_2S type II: 500 µg/l ... 50 mg/l H_2S type III: 10 µg/l ... 3 mg/l H_2S others on request
accuracy:	2% (measuring value) 1 digit
pressure range:	up to 10 bar
pH-range:	0 ... 8,5 pH
temperature range:	0...30°C (for measuring and storage !)
response time:	$t_{90\%}$: approx. 1 second
duration of life:	5..9 months (depends on H_2S stress and on matrix of the analyte)
special features:	exchangeable sensor head, integrated electronic device for transformation of current into 0...+5 V DC and for provision of polarisation voltage
warranty:	3 months for the sensor tip; 12 months for the electronic body. Warranty does not cover damaged caused by poor handling or mishandling of the sensor.

Pin definitions of the sensors plug:



Pin 1: ground

Pin 2: not connected

Pin 3: H_2S-signal output: 0 ... +5 V DC
(main working range: 0...500 mV)

Pin 4: power supply 9 ... +30 V DC

Wiring:

Grey .... Power Ground

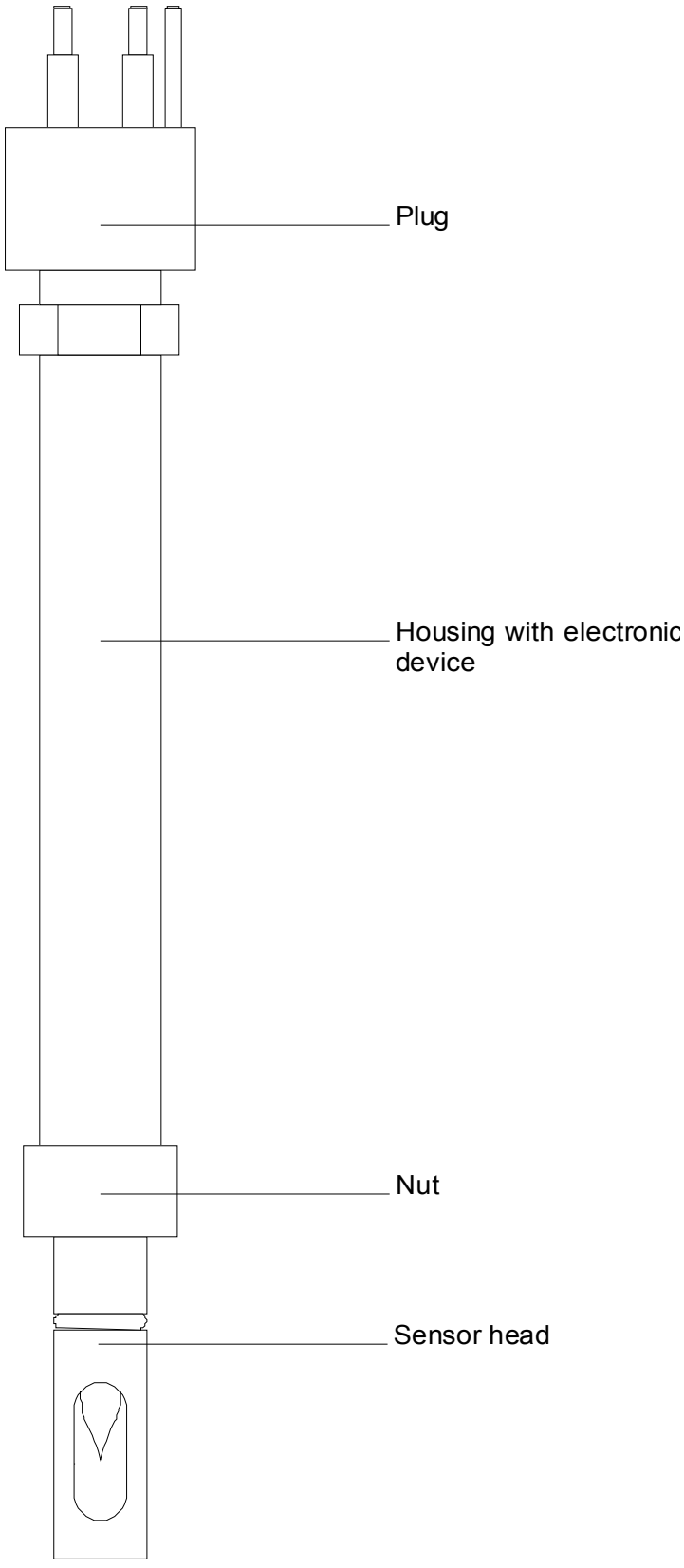
White ... Signal Ground

Brown ... 0 to 5 V DC Signal

Green ... 12 to 30 V DC

Shield ... Power Ground

3 Structure of the H_2S micro-sensor



4 Putting into operation

Each sensor is delivered with a protective cap. The protective cap serves to avoid mechanical damages and to avoid the evaporation of the inner electrolyte of the sensor during long-time storage. Therefore some destilled water (fill only 1/4 as maximum) should be always inside the protective cap, when you put the cap on after measurements have been finished. For putting into operation please act as follows:

1 Look at your plug connections at your probe system and compare with the plug connections of the sensor as described in chapter 2.
2 Remove the protective cap from the sensor by pull out carefully.
3 Moisten the bulk head connector of the sensor and link it with your probe system or interfacing cable.
4 Put the sensor tip in a H_2S free solution (e.g. distilled water).
5 Switch on the power supply. The polarisation of the sensor starts automatically and has been finished after some minutes. The end of the polarisation is reached, if the signal is adjusted. This value is called "residual current" (=U_G).

Now the sensor is ready for H_2S measurements.

5 Measurement and calibration

Caution ! Do not forget to remove the protective cap during measurement. Otherwise the sensor head 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 $c_{\text{total sulphide}} \approx c_{H_2S}$

Temperature

The amperometric H_2S sensor works within a temperature range of 0 ... 30°C. For every temperature a temperature correction factor (E_T) has been calculated, delivered with the sensor at the end of this operating instructions. The chemical reaction of the redox mediator with H_2S causes depositions inside the membrane. This influences the diffusion. Changes in the sensor slope at 20°C (=$a_{20°C}$) 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 adjustment.

pH dependence

The amperometric H_2S sensor operates within a pH range of 0 up to 8,5 pH and measures the partial pressure of gaseous H_2S dissolved in liquids, which is direct proportional to the H_2S concentration. If the pH of the analyte is above 8,5, there exists no more H_2S, so that the application of the sensor is limited by this fact. Figure 1 shows, that below pH=5 the H_2S concentration is quite similar to the total sulphide concentration.

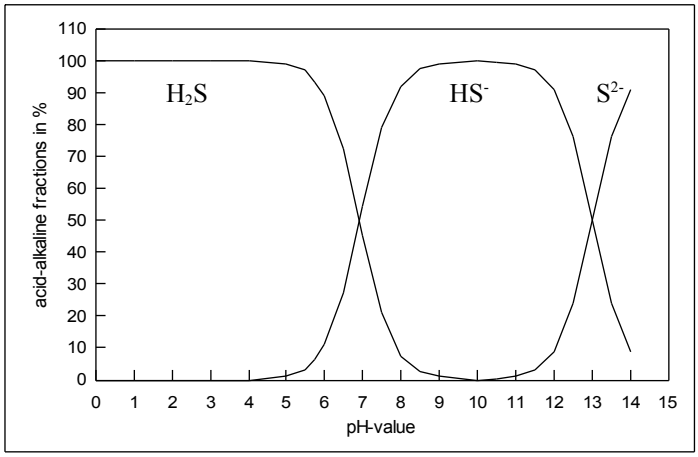


fig.1: acid-alkaline fractions depending on the pH.

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_2S micro-sensors with consideration of temperature and pH-value - mathematical formulas

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

$E_T = f(T)=a_3T^3 + a_2T^2 + a_1T + a_0$

(E_T-calculation for temperatures above 30°C is not possible by means of this equation !)

$a_{20°C}$, $a_{3..0}$ are sensor specific data delivered with the sensor data sheet (see last page).

2. *Determination of the sensor slope ($a_{20°C}$) - 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_{Tm} by means of regression of first order, use the correct E_T according to the enclosed table and calculate $a_{20°C}$ as follows:

$a_{20°C} = a_{Tm}/E_T$

3. Measurement of the H_2S-concentration:

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

c_{H_2S}	H_2S-concentration
$a_{20°C}$	sensor slope at 20°C
U	measured voltage
U_G	voltage at 0 mg/l H_2S
E_T	temperature compensation $E_T = f(T)$

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_2S-concentration
c_{H^+}	concentration of H^+-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_2S-/sulphide standard solutions. Calibration is also possible as service if requested. The frequency of calibration depends on the H_2S stress of the sensor. Check up of the sensor or calibration is recommended after approximately 120 measuring hours. Calibrations should be done always with acidic standard solutions of pH below 5 ! For 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 $KMnO_4$ for fast oxidizing of the H_2S-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 ($a_{20°C}$) by linear regression; use the correction factors of the enclosed table (E_T)

Caution ! If H_2S 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 or by the electronic device. Please take note, that H_2S/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.

Caution ! Handle the sensor carefully and avoid strong vibrations or unintentional touch downs. Protect the glass tip against solids to avoid a breaking of the sensitive glass body.

7 Switching off

If measurements have been finished, rinse the sensor carefully with destilled water and dip in the sensor 5 minutes into a H_2S free solution (water). After this check up the expected residual current. If the residual current has been reached, interruption of the link between the sensor and the probe is possible. For storage do not forget to put on the protective cap filled with some destilled water (not more than 1/4 !).

If H_2S permeates through the membrane without polarizing the sensor, a decrease of signal resolution and increasing of residual currents follows. A destruction of the sensor is also possible! Never store the sensor at temperatures below 0°C and above 30°C !

8 Maintenance and exchange of sensor heads

Mechanical stress of the sensor tip, especially cross forces and strong vibrations have to be avoided. The sensor tip is very weak. Do not touch it. For cleaning the sensor head rinse it in water only. Do not use organic solutions.

Do not twist the sensor head in the sensor body. This could destroy the electrical connection inside. For changing the sensor head unscrew first the screw and pull off the sensor head. Be very carefully when pushing the new sensor head into the housing. Use the small red points on the sensor head and inside the electronic housing as orientation. The sensor head has to click in to ensure, that the O-ring is situated correct.

Do not store the sensor at temperatures below 0°C and above +30°C.
Each sensor is delivered with a wetting cap. The wetting cap serves to avoid the evaporation of the inner electrolyte of the sensor during long-time storage. Therefore some distilled water (less than 1/4) should be always inside the wetting cap, when you put the cap on after measurements have been finished.

Please take note, that it takes some more time than normally for the first polarization of the sensor after long break periods.

A P P E N D I X

Measurement and calibration of AMT micro-sensors with consideration of temperature and pH-value (example):

typical sensor data, delivered with the sensor: $a_{20°C}$= 0,014428 mg/l mV

$E_T = f(T)=a_3T^3 + a_2T^2 + a_1T + a_0$ (T=°C)
$E_T = f(T)= -4{,}4x10^{-5}\ T^3$
$+0{,}003512\ T^2$
$-0{,}11897\ T$
$+ 2{,}328831$
e.g.: T=22,0°C ---> E_T=0,9400

Measurement of the H_2S-concentration:

U_M= 359 mV (sensor signal output with H_2S)
U_G= 7 mV (sensor signal output without H_2S = residual current)

$c_{H_2S} = a_{20°C} \times (U - U_G) \times E_T$ = 0,014428 mg/l mV x (359 mV - 7 mV) x 0,9400
= 4,7739 mg/l

c_{H_2S} H_2S-concentration
$a_{20°C}$ sensor slope at 20°C
U measured voltage
U_G voltage at 0 mg/l H_2S
E_T temperature compensation E_T = f(T)

Depth correction factor (not absolutely required for depths up to 100 m !)

K_T = exp -(32,06 g/mol x 0,001 x 9,81 m/s x d /(8,314 J/molK x (273,15+T)))
e.g.: 65 meter
K_T = 0,9917034
resulting in:
c_{H2Sd} = c_{H_2S} x K_T = 4,7739 mg/l x 0,9917034 = 4,73429 mg/l
(= H_2S-concentration with depth correction)

Total sulphide calculation (inclusive depth correction):

e.g.: pH=7,14

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

c_{H+} = 10^{-pH}
K_1 = $10^{-6{,}919}$
K_2 = 10^{-13}
c_G total sulphide concentration
c_{H2Sd} measured H_2S-concentration
c_{H^+} concentration of H^+-ions
K_1, K_2 equilibrium constants

c_G = 12,60938 mg/l

pH	Correction factor G for the determination of total sulphide									
value	0,00	0,01	0,02	0,03	0,04	0,05	0,06	0,07	0,08	0,09
4,0	1,001	1,001	1,001	1,001	1,001	1,001	1,001	1,001	1,001	1,001
4,1	1,002	1,002	1,002	1,002	1,002	1,002	1,002	1,002	1,002	1,002
4,2	1,002	1,002	1,002	1,002	1,002	1,002	1,002	1,002	1,002	1,002
4,3	1,002	1,002	1,003	1,003	1,003	1,003	1,003	1,003	1,003	1,003
4,4	1,003	1,003	1,003	1,003	1,003	1,003	1,003	1,004	1,004	1,004
4,5	1,004	1,004	1,004	1,004	1,004	1,004	1,004	1,004	1,005	1,005
4,6	1,005	1,005	1,005	1,005	1,005	1,005	1,006	1,006	1,006	1,006
4,7	1,006	1,006	1,006	1,006	1,007	1,007	1,007	1,007	1,007	1,007
4,8	1,008	1,008	1,008	1,008	1,008	1,009	1,009	1,009	1,009	1,009
4,9	1,010	1,010	1,010	1,010	1,010	1,011	1,011	1,011	1,012	1,012
5,0	1,012	1,012	1,013	1,013	1,013	1,014	1,014	1,014	1,014	1,015
5,1	1,015	1,016	1,016	1,016	1,017	1,017	1,017	1,018	1,018	1,019
5,2	1,019	1,020	1,020	1,020	1,021	1,021	1,022	1,022	1,023	1,023
5,3	1,024	1,025	1,025	1,026	1,026	1,027	1,028	1,028	1,029	1,030
5,4	1,030	1,031	1,032	1,032	1,033	1,034	1,035	1,036	1,036	1,037
5,5	1,038	1,039	1,040	1,041	1,042	1,043	1,044	1,045	1,046	1,047
5,6	1,048	1,049	1,050	1,051	1,053	1,054	1,055	1,056	1,058	1,059
5,7	1,060	1,062	1,063	1,065	1,066	1,068	1,069	1,071	1,073	1,074
5,8	1,076	1,078	1,080	1,081	1,083	1,085	1,087	1,089	1,091	1,094
5,9	1,096	1,098	1,100	1,103	1,105	1,107	1,110	1,112	1,115	1,118
6,0	1,121	1,123	1,126	1,129	1,132	1,135	1,138	1,142	1,145	1,148
6,1	1,152	1,155	1,159	1,163	1,166	1,170	1,174	1,178	1,182	1,187
6,2	1,191	1,191	1,195	1,200	1,205	1,209	1,214	1,219	1,224	1,230
6,3	1,240	1,246	1,252	1,258	1,264	1,270	1,276	1,282	1,289	1,296
6,4	1,303	1,310	1,317	1,324	1,332	1,340	1,348	1,356	1,364	1,372
6,5	1,381	1,390	1,399	1,408	1,418	1,428	1,438	1,448	1,458	1,469
6,6	1,480	1,491	1,502	1,514	1,526	1,538	1,551	1,564	1,577	1,590
6,7	1,604	1,618	1,632	1,647	1,662	1,678	1,693	1,710	1,726	1,743
6,8	1,760	1,778	1,796	1,815	1,834	1,853	1,873	1,893	1,914	1,935
6,9	1,957	1,979	2,002	2,026	2,050	2,074	2,099	2,125	2,151	2,178
7,0	2,205	2,233	2,262	2,291	2,321	2,352	2,384	2,416	2,449	2,482
7,1	2,517	2,552	2,589	2,626	2,663	2,702	2,742	2,782	2,824	2,866
7,2	2,910	2,954	3,000	3,046	3,094	3,143	3,193	3,244	3,296	3,350
7,3	3,404	3,460	3,518	3,576	3,636	3,698	3,760	3,825	3,891	3,958
7,4	4,027	4,097	4,169	4,243	4,319	4,396	4,475	4,556	4,639	4,724
7,5	4,811	4,899	4,990	5,083	5,178	5,276	5,375	5,477	5,581	5,688
7,6	5,797	5,909	6,023	6,140	6,260	6,383	6,508	6,636	6,768	6,902
7,7	7,039	7,180	7,324	7,471	7,622	7,776	7,934	8,096	8,261	8,430
7,8	8,603	8,780	8,961	9,147	9,337	9,531	9,729	9,933	10,141	10,354
7,9	10,572	10,795	11,023	11,256	11,495	11,740	11,990	12,246	12,508	12,776
8,0	13,050	13,331	13,618	13,912	14,213	14,520	14,835	15,158	15,487	15,825
8,1	16,170	16,523	16,885	17,255	17,634	18,021	18,418	18,823	19,239	19,663
8,2	20,098	20,543	20,998	21,464	21,941	22,428	22,928	23,438	23,961	24,496
8,3	25,043	25,603	26,176	26,763	27,363	27,980	28,605	29,248	29,906	30,580
8,4	31,269	31,974	32,695	33,433	34,189	34,962	35,753	36,562	37,391	38,239