# Amperometric $H_2S$ Micro-sensor

## Determination of $H_2S$ and total sulphide in aqueous solutions

The amperometric $H_2S$ micro-sensor has been developed for the *insitu* determination of $H_2S$/ Sulphide containing aqueous solutions. Therefore the sensor is suitable for direct measurements in lakes, estuarines, rivers, oceans and of course in sewage pipes, waste waters and sediments.

### The general working principle of the sensor

Because of the partial pressure of gaseous $H_2S$ 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 $H_2S$ 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 $H_2S$ amount in the sample. In opposite to ionsensitive electrodes (ISE) measuring the *sulphide ion activity,* the amperometric sensor determines the *$H_2S$-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 $H_2S$ in two steps the amperometric $H_2S$ 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 $H_2S$ (< 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 $H_2S$ 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 $H_2S$- and of the total sulphide amount.*

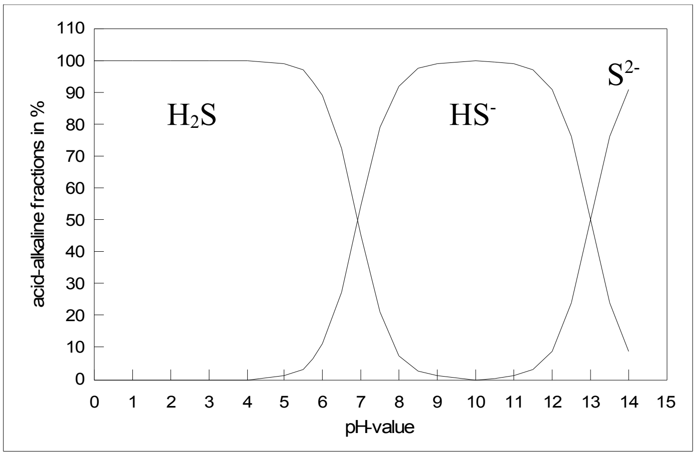

Figure 1: Acid-alkaline fractions depending on the pH.

## The advantages of the micro-sensor technology

For manufacturing the amperometric $H_2S$ sensor a special geometric design has been choosen to built a real **micro-sensor**. Electrode diameters below 25 µm, a very thin special membrane with small diameters, extremly short diffusion distances for the $H_2S$ 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 s*treaming of the sensor membrane and stirring is not necessary*. Besides, the dimensions of the sensitive tips within a range of some micrometers allow *insitu* measurements without destroying equilibriums, concentration gradients and geometrical structures. This is very important, if measurements in muddy sediments or biofilms are required.

## Technical data of all $H_2S$ micro-sensor heads independent from the sensor design *)

- measuring principle: amperometry, membrane covered (=Clark-type) sensor
- 3 sensor electrodes
- polarization voltage necessary (realized by means of integrated electronic devices or by means of the measuring device)
- ready for measurements after switching on: 5...15 minutes
- streaming of the membrane or stirring of the analyte is not necessary
- very small analyte consumption
- concentration range: - type I: 0,05 ... 10 mg/l $H_2S$
  - type II: 0,5 ... 50 mg/l $H_2S$
  - type III: 0,01 ... 3 mg/l $H_2S$

  and others on request
- accuracy: better than 2% of the measuring value
- temperature range: 0°C ... 30°C
- pH-range: 0 ... 8,5
- response times: $t_{90\%}$: down to 200 milliseconds
  (The response times perceptible at the display of a measuring device may increase because of the type of electronics used for interfacing the sensor. But nevertheless the real response times of the micro-sensor head are not influenced.)
- average life time: 5...9 months (depends on the $H^2S$ stress and on the matrix)
- pressure stability: up to 10 bar
- no signal equivalents in 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)), $CS_2$ (up to 5 vol.%), organic solvents (max. 20 Vol.%), acetic acid (up to 1 mol/l), dimethyl sulfide, HCN
- small signal equivalents: $SO_2$ ($pH < 4$): 100 ppm $SO_2$ = 1 ppm $H_2S$
- measurements are also possible without interferences in solutions with salt concentrations of up to 40 g/l

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*) Changes for technical improvement are reserved.

## Comparison of the amperometric $H_2S$ micro-sensor with other determination methods

Apart from the *ionsensitive electrodes* the *amperometric micro-sensor* is the one and only $H_2S$ *insitu* measuring system without any sampling. Besides the m*ethylene blue method* as a spectral photometric measuring procedure is well know but unsuitable for insitu 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 methode 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 obeserved. If the sence of the determination is to check the danger potential caused by *dissolved* sulphide/hydrogen sulfide and $H_2S$, 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 methodes 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. $Na_2S_2O_3$) 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 diaphragma 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 potentiales 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 stady-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 pH = 6...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 µg/l and the signal resolution is approximately 2 µg/l. In opposition to that, ISE's have only a signal resolution within a range of 50...100 µg/l. Besides, there is only a logarithmic dependence of the measured voltage on the sulphide ion concentration (1 decade = 29 mV).

## Comparison of the methylene blue method with the amperometric $H_2S$ micro-sensor

| Feature | Methylene blue method | Amperometric micro-sensor |
|---|---|---|
| The measuring value contains.... | dissolved $H_2S$, sulphide and hydrogen sulphide; precipitated heavy metal sulphides dissolved by adding acidic reagents | dissolved $H_2S$; when considering the pH the determination of the dissolved total sulphide amount ($H_2S$ +$HS^-$ + $S^{2-}$) in one step is possible |
| What samples could be used for the determination ? | clear and not coloured solutions without any solids swimming in the sample | clear, turbid, coloured, muddy samples, samples with high salt content |
| Accuracy | ± 5...10% | ± 1% |
| Concentration range | 0,1 ... 1 mg/l, other concentration ranges are only accessible with dilution and therefore with unavoidable mistakes | type I: 0,05...10 mg/l $H_2S$<br>type II: 0,5 ... 50 mg/l $H_2S$<br>type III: 0,01 ... 3 mg/l $H_2S$<br>(others on request) |
| Detection limit | approx. 0,04...0,06 mg/l | Approx. 0,002 mg/l |
| Resolution | variable, approx. 50 µg/l steps within a range of 0,1 ... 1 mg/l | Depending on the sensor type, down to 1 µg/l steps |
| local resolution of the measuring signal | average of a minimum volume of 20...50 ml | high signal resolution in µl steps |
| Signal equivalents and troubles | coloured solutions, solids, turbid solutions, high salt amounts, detergents, thiosulfates | $SO_2$ within a pH range of 0...4 (100 mg/l $SO_2$ is equivalent to 1 mg/l $H_2S$), organic solvents with contents of more than 20-Vol.% |
| consumption of chemicals | reagents: N,N-Dimethyl-p-phenylenediammin (DMPD, toxic !), $FeCl_3$ for oxidation and sometimes Cd- or Zn-salts for conservation of samples | no consumption of chemicals |
| time for the determination of 1 sample | Depending on the procedure, 20...120 minutes (reaction time and full formation of the colours) without consideration of preparing solutions and calibration curve | some seconds if a calibrated sensor is ordered |
| preparation time for the determination | approx. 15 minutes (without calibration) for 3 determinations | Only once 5 minutes (polarization time for the sensor) |
| necessity of sampling | Yes | no,<br>insitu determination possible |
| online-determination | No | yes |

## Sensor designs of amperometric $H_2S$ micro-sensors

### *1.) Laboratory micro-sensor with integrated electronic device*

This sensor has been developed for laboratory and simple field use and has to be combined with one of the offered measuring devices. The sensor consists of a titanium housing, a waterproof connection with the cable (IP 68), an exchangeable sensor head and a removable protection cage (on your own risk - no guarantee in the case of mechanical destruction). This sensor could be equipped both with the $H_2S$ sensor heads type I (0,05...10 mg/l $H_2S$), type II (0,5...50 mg/l $H_2S$) and type III (0,01...3 mg/l $H_2S$) and with the oxygen sensor head (0...200%). Other concentration ranges can be delivered on request.The exchange of the sensor head is very easy by pull off and push on. Please take note, that no liquid can get in to the plug connection when changing the sensor head.

### *2.) Shallow water micro-sensor for probe systems*

The shallow water sensor has been developed for use in combination with so called CTD-probe systems up to depths of 100 meters. Therefore every shallow water sensor is equipped with a special underwater connector, type wet con BH-4-MP. Further characteristics are the integrated electronic device, the titanium housing and the exchangeable sensor head. This sensor could be equipped both with the $H_2S$ sensor heads type I (0,05...10 mg/l $H_2S$), type II (0,5...50 mg/l $H_2S$) and type III (0,01...3 mg/l $H_2S$) and with the oxygen sensor head (0...200%). Other concentration ranges can be delivered on request. The exchange of the sensor head is very easy by pull off and push on. Please take note, that no liquid gets in to the plug connection when changing the sensor head.

## Use of amperometric $H_2S$ micro-sensors

1. Laboratory use:
   - laboratory sensor with integrated electronic device
   - \+ measuring device with cable
   - \+ pH-measuring device with temperature sensor

2. Field measurements (up to 1 m water depth):
   - a) laboratory sensor with integrated electronic device
     - \+ measuring device with cable
     - \+ pH-measuring device with temperature sensor
   - b) $H_2S$-probe with sensors for $H_2S$ (shallow water version), pH, pressure (depth), temperature
     - \+ multi-core sea-cable
     - \+ notebook/personal computer
     - \+ software

3. Online insitu measurements (up to 100 meter water depth)
   - a) $H_2S$-probe with sensors for $H_2S$ (shallow water version), pH, pressure (depth), temperature
     - \+ multi-core sea-cable
     - \+ notebook/personal computer
     - \+ software or
   - b) Interfacing of a $H_2S$ shallow water sensor to already existing probe systems, provided that the probe system contains one more free channel and is equipped already with sensors for pH, temperature and pressure
     - \+ integration of the mathematical formula for the calculation of the total sulphide amount into the probe's software

# Help for choosing the sensor type

The parameters pH-value, resolution and expected $H_2S$-concentration (resp. the total dissolved sulphide amount) have to be well known for choosing the correct sensor type.

| Sensor type | Range for $H_2S$ [mg/l] | **Resolution [µg/l Total Dissolved Sulphide Amount per mV] at** | | | | |
|---|---|---|---|---|---|---|
| | | pH = 1 ... 5 (≅ 100% $H_2S$) | pH = 6 (89,2%) | pH = 7 (45,3%) | pH = 8 (7,7%) | pH = 8,5 (2,5%) |
| I | 0,05 ... 10 | 25 | 28,0 | 55,2 | 324,7 | 1000,0 |
| II | 0,5 ... 50 | 125 | 140,0 | 275,9 | 1623,4 | 5000,0 |
| III | 0,01 ... 3 | 7,5 | 8,4 | 16,6 | 97,4 | 300,0 |

With the help of the table the maximum of the detectable total dissolved sulphide amount can be calculated for a special pH-value. For Example: If the maximum of the expected $H_2S$ concentration at a pH of 7,0 is about 3,0 mg/l and the minimum of the resolution should be better than 20 µg/l TDSA per mV, the sensor type III should be choosen. The final value of the sensor type III is 3,0 mg/l $H_2S$. At a pH-value of 7 only 45,3% of the total sulphide exists as $H_2S$. Therefore the maxi-mum of the detectable total sulphide with sensor type III at pH=7 is about 6,62 mg/l.

maximum of detectable total sulphide = $c_{H2S}$ [mg/l] x 100 : $x_{H2S}$ [%] = 3,0 x 100 : 45,3 = 6,62 mg/l

# Help for choosing the sensor type

The parameters pH-value, resolution and expected $H_2S$-concentration (resp. the total dissolved sulphide amount) have to be well known for choosing the correct sensor type.

| Sensor type | Range for $H_2S$ [µM] | **Resolution [µM Total Dissolved Sulphide Amount per mV] at** | | | | |
|---|---|---|---|---|---|---|
| | | pH = 1 ... 5 (≅ 100% $H_2S$) | pH = 6 (89,2%) | pH = 7 (45,3%) | pH = 8 (7,7%) | pH = 8,5 (2,5%) |
| I | 1,56...312 | 0,78 | 0,87 | 1,72 | 10,13 | 31,2 |
| II | 15,6...1556 | 3,89 | 4,36 | 8,59 | 50,52 | 155,6 |
| III | 0,31...93,6 | 0,23 | 0,26 | 0,52 | 3,04 | 9,63 |

With the help of the table the maximum of the detectable total dissolved sulphide amount can be calculated for a special pH-value. For Example: If the maximum of the expected $H_2S$ concentration at a pH of 7,0 is about 90 µmol/l and the minimum of the resolution should be below 0,5 µmol/l TDSA per mV, the sensor type III should be choosen. The final value of the sensor type III is 93,6 µmol/l $H_2S$. At a pH-value of 7 only 45,3% of the total sulphide exists as $H_2S$. Therefore the maximum of the detectable total sulphide with sensor type III at pH=7 is 206,62 µg/l.

Maximum of detectable TDSA=$c_{H2S}$ [µM] x 100 : $x_{H2S}$ [%] = 93,6 x 100 : 45,3 = 206,62 µM