Hydrogen Sensor

User Manual

UNISENSE
SCIENTIFIC

Hydrogen Sensor User Manual

UNISENSE A/S

Version: August 2026

TABLE OF CONTENS

1. WARRANTY AND LIABILITY

1.1 Notice to Purchaser

This product is for research use only. Not for use in human diagnostic or therapeutic procedures.

1.2 Warning

Microsensors have very pointed tips and must be handled with care to avoid personal injury and only by trained personnel. Unisense A/S recommends users to attend instruction courses to ensure proper use of the products.

1.3 Warranty and Liability

The Hydrogen sensor is covered by a 90 days limited warranty. Microsensors are a consumables. Unisense will only replace dysfunctional sensors if they have been tested according with the instructions in the manual within 14 days of receipt of the sensor(s). The warranty does not include repair or replacement necessitated by accident, neglect, misuse, unauthorized repair, or modification of the product. In no event will Unisense A/S be liable for any direct, indirect, consequential or incidental damages, including lost profits, or for any claim by any third party, arising out of the use, the results of use, or the inability to use this product.

Unisense mechanical and electronic laboratory instruments must only be used under normal laboratory conditions in a dry and clean environment. Unisense assumes no liability for damages on laboratory instruments due to unintended field use or exposure to dust, humidity or corrosive environments.

1.4 Repair and Adjustment

Sensors and electrodes cannot be repaired. Equipment that is not covered by the warranty will, if possible, be repaired by Unisense A/S with appropriate charges paid by the customer. In case of return of equipment please contact us for return authorization.

For further information please see the document General Terms of Sale and Delivery of Unisense A/S as well as the manuals for the respective products.

2. CONGRATULATIONS WITH YOUR NEW PRODUCT!

2.1 Support, ordering, and contact information

The Hydrogen microsensor is a miniturized sensor for measuring partial pressure of H_2 in the micromolar range.

If you wish to order additional products or if you encounter any problems and need scientific/technical assistance, please do not hesitate to contact our sales and support team. We will respond to your inquiry within one working day.

E-mail: sales@unisense.com
Unisense A/S
Langdyssen 5
DK-8200 Aarhus N, Denmark
Tel: +45 8944 9500

Further documentation and support is available at our website www.unisense.com.

3. REPLACEMENT OF SENSORS UNDER WARRENTY

Unisense will replace sensors that have been damaged during shipment provided that:

- The sensors were tested immediately upon receipt in accordance with the delivery note and this manual
- The seal is still intact.
- The sensors are returned to Unisense for inspection within two weeks.
- The sensors are correctly packed for return to Unisense, in accordance with the packing guide included in the sensor box.

4. OVERVIEW

This manual covers all the Unisense H_2 and H_2-X sensors.
For a complete list of sensors sizes and types please go to www.unisense.com.

IMPORTANT: Unisense sensors are neither intended nor approved for use in humans

The standard hydrogen sensor type, the H_2-type, is for use in environments where H_2S is not expected to occur. The H_2S insensitive type, the H_2-X-type, has an H_2S trap in front of the H_2 sensing part, allowing the sensor to be used in H_2S containing environments (see "**6.4 Interference**").

Figure 1: H_2 sensor

The Unisense hydrogen microsensor is designed for research applications within physiology, biotechnology, environmental sciences, and related areas. With the minute tip size, excellent response time, and good sensitivity the Unisense hydrogen sensor facilitates reliable and fast measurements with a high spatial resolution.
The H_2-X sensor has a slightly longer response time than the corresponding H_2 sensor.

The Unisense hydrogen microsensor is a miniaturized Clark-type hydrogen sensor with an internal reference electrode and a sensing anode. The sensor must be connected to a high-sensitivity picoammeter where the anode is polarized against the internal reference. Driven by the external partial pressure, hydrogen from the environment will pass through the sensor tip membrane and will be oxidized at the platinum anode surface. The picoammeter converts the resulting oxidation current to a signal.

5. GETTING STARTED

The H_2-type and H_2-X-type sensors are used in the same way. Only the sensitivity to H_2S and the response time differ between the two types of hydrogen sensors.

IMPORTANT: The H_2 sensor cannot be used with the tip pointing upwards. The sensor can be horizontal or the tip can point downwards. The sensor has a gas bubble inside and if the sensor points upwards, it will float into the narrow part of the sensor and block electrical connectivity in the electrolyte. This will result in no or very little response to H_2.
See section 9. Troubleshooting for how to resolve this problem.

WARNING: Do not remove the seal and protective plastic tube before these steps and calibration are succesfully completed.

5.1 Unpacking a new sensor

When receiving a new microsensor remove the shock-absorbing grey plastic net.

5.2 Polarization

The signal from the hydrogen sensor is generated in picoampere. Therefore the hydrogen sensor must be connected to a polarizing picoammeter (e.g. a UniAmp series amplifier).

WARNING: Incorrectpolarization may destroy the sensor.

The anode of the hydrogen sensors should be polarized at +100 mV relative to the cathode. This happens automatically on the Unisense UniAmp series instruments. On the Unisense Multimeter, Monometer and PA-2000 instruments this must be set manually. Please consult the relevant the instrument manual for how to adjust polarization. If you are using a PA2000, please check the polarization voltage before connecting the sensor, since incorrect polarization may destroy the sensor.

5.3 Connecting the microsensor

Insert the connector into a pA input terminal on the amplifier. The connector contains connections for both internal reference electrode and sensing anode.

NOTE: The software converts the raw pA sensor signal into mV.
Standard setting is 1 mV = 1 pA.
This may be modified by changing the Pre-Amp setting (mV/pA) in the software (UniAmp) or on the instrument (Multimeter, Monometer, and Field Multimeter).

5.4 Pre-polarization

Just after connecting the sensor, the signal will be very high and unstable then drop rapidly over the first few minutes and then stabilize. Therefore, a short period of polarization is necessary before you can use the sensor. This is called the pre-polarization period.

IMPORTANT: Hydrogen sensors are sensitive to temperature and salinity.

The signal should stabilize at 0-10 mV (on the PA2000, the sign will be negative since sensor is positively polarized) for zero hydrogen concentration, depending on the specific sensor. If the sensor is new or has not been operated for several days, it will take a little longer to stabilize after being polarized.
The signal depends on the specific sensor type (see the value in the specifications that came with the sensor). If the signal does not stabilize or is too high or too low, refer to the 'Trouble-shooting' section of this manual.

5.5 Calibration

The calibration procedure is the same for the H_2 and H_2-X sensors.

IMPORTANT: Calibration must be performed after pre-polarization when the sensor signal has stabilized. Always use a calibration solution with the same temperature and salinity as the sample solution.

Hydrogen sensors respond linearly in the range of 0 to 100 % hydrogen (Low Range sensor from 0 - 10% H2) and signals can be linearly converted to H_2 content in the unit you choose when starting an experiment file.

Calibration must be performed after the sensor signal has stabilized during pre-polarization.

NOTE: Hydrogen sensors are affected if H_2 gets into the rear end, where the reference electrode is located. If this happens, the sensor signal will become negative. Hydrogen may enter the rear end of the sensor through the black plastic shaft. When bubbling water with H_2 during calibration, the sensor will be exposed to H_2 on the shaft so, do not leave H_2 sensors for a long time in the calibration chamber or in any other H_2-rich environments.

5.5.1 Calibration in Liquid

Because of the sensor's linear response to H_2, only a two-point calibration is needed.
This is typically one known H_2 concentration and zero H_2.

Zero reading: Place the sensor in air or water without H_2. Let it stabilize and save the first calibration point. Make sure the temperature is the same as for the known H_2 concentration.

Known H_2 concentration: It is considered good practice that the H_2 standard has a higher concentration than the samples. Preparing such a standard is easily done using the Unisense Calibration Chamber by bubbling with H_2 gas.

The Standard Range H_2 sensor can be calibrated with a 100% H_2 gas which gives a concentration of approximately 800 µmol/L in water at room temperature. The Low Range H_2 sensor measures up to 10% H_2, corresponding to approximately 80 µmol/L in water at room temperature, and a gas with a lower H_2 content should be used, or the H_2 saturated water can be diluted. The H_2 concentration in water as a function of temperature and salinity can be found in the table at the end of this manual, using the H_2 Calculator in the Tools menu in the Unisense software, and using the Unit Converter on the Unisense website: https://unisense.com/unit-converter/#/.

Equilibrating liquid with a H_2 gas: When bubbling with gas through water in the chamber, the aim is that the water will come into equilibrium with the gas. That means that the partial pressure of the gas is the same in water and gas. To obtain this, the bubbling must go on for a period of time, and the bubbling rate must be sufficiently high.

Procedure:
1. Place the sensor in the chamber (Fig. 1)
2. Make sure the bottom of the sensor protection tube is not resting on the bottom of the calibration chamber. Place the O-ring on the sensor protection tube so that is clearly above the bottom, so that water inside the protection tube can be exchanged. Make sure that the sensor tip is in the liquid.

3. Close the holes in the lid that are not in use. If they are left open, then air will get into the headspace in the chamber and get mixed into the water. This will remove some of the gas being bubbled with and equilibrium will not be reached.
4. Start bubbling.

Figure 1: Calibration chamber with sensor. All extra holes in the lid are closed, and the sensor protection tube is lifted from the bottom of the chamber securing circulation of calibration liquid inside the tube. It is held in place with an O-ring.

5. Follow the sensor signal to see that it increases with time. The signal will reach a plateau. This could mean that equilibrium between gas and water is reached. However, if the flow rate is not sufficiently high, air may be mixed into the water, diluting the bubbling gas. If that is the case, there will not be equilibrium between gas and water.
6. To check if the gas flow rate is high enough, increase the flow rate of the gas.
7. Follow the sensor signal to see if it increases after bubbling has been increased.
   - If the sensor signal stays the same, then the first flow rate was high enough to obtain equilibrium.
   - If the sensor signal increases, then the first flow rate was not high enough to obtain equilibrium. If this is the case, repeat the increase in flow rate and check of sensor signal until an increase in flow rate does not result in a higher sensor signal (Fig. 2).

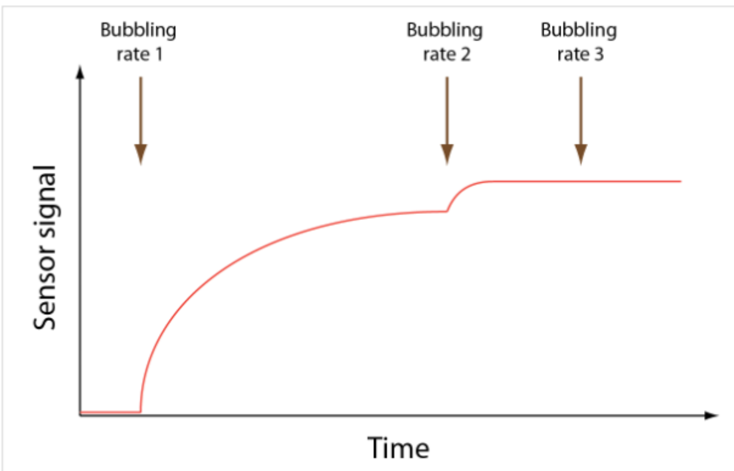


Figure 2: Sensor signal as a function of time at three different gas bubbling rates. At bubbling rate 1, a plateau was reached. The bubbling rate was then increased, rate 2, which resulted in a higher sensor signal. Bubbling rate 1 was thus not high enough to ensure equilibrium between gas and water. A new plateau was reached with bubbling rate 2. The bubbling rate was then increased again, rate 3. This time the increased bubbling rate did not result in a higher signal. Bubbling rate 2 was thus sufficient for obtaining equilibrium.

5.5.2 Calibration in Gas

Figure 3

The H_2 sensor responds linearly to H_2, so a two-point calibration is sufficient. The two points are typically zero H_2 and one known H_2 content. This can be done by exposing the sensor to air for the zero point and a gas with a known H_2 content for the second calibration point.

When recording the sensor response for a gas with a known H_2 content, the calibration gas, it is important to create a system where the tip is exposed to 100% of the calibration gas. This setup will depend on the sensor configuration you have available. Some examples of how this can be done are given below.

1. Sensors with flow cells: Simply connect the tubing from the source of H_2 containing gas directly to the flow cell.
2. Sensors with protection tubes: Mount the black calibration cap on the protection tube (Figure 3). Adjust the flow rate so that all atmospheric air is expelled and the gas at the sensor tip is pure calibration gas. Make sure that overpressure doesn't build up.
3. All sensors: Use a closed container which is flushed with the calibration gas until the container contains pure calibration gas.

5.5.3 General calibration advice

1. For all calibrations that involve continuous flow of calibration gas it is important to test if the gas flow rate is sufficiently high to prevent dilution by atmospheric air. For calibration in gas, the gas flow must ensure that the sensor tip is exposed to pure calibration gas. For calibration in liquid, the gas flow must ensure that there is equilibrium of H_2 in gas and liquid. To test this, let the sensor signal stabilize at a given flow rate. Then increase the flow rate. If the sensor signal doesn't change, then the flow rate is high enough. If the sensor signal increases, then the previous flow rate was too low. Repeat this until the sensor signal remains constant at higher flow rates.

2. Rubber tubing is not 100% gas tight, and the composition of the calibration gas will change when passing through rubber tubing. This problem increases with gas permeability of the rubber tubing and length of the tubing. Therefore, keep the tubing short and use rubber tubing that is relatively impermeable to gases. Silicone rubber is very permeable to gases, whereas Iso-Versinic, butyl rubber, or Viton tubing are much less permeable to gases.

3. Sensors respond to partial pressure of the gas, and the partial pressure of H_2 in the gas is linearly dependent on the total pressure in the gas. Therefore, it is important to avoid increase in total pressure in any of the gas calibration methods suggested above.

4. Check and repeat calibration at appropriate intervals to ensure that all measurements can be converted to correct concentrations. When the sensor is new, the appropriate interval may be every 2 hours; later it may be 24 hours or even less frequent. To minimize the need for calibrations, keep the sensor polarized between measurements, unless the time between measurements exceeds several days. The membrane permeability of hydrogen microsensors changes with time, so a change in signal of up to 10% per month may occur.

Hydrogen sensors respond linearly in the range of 0 to 100 % hydrogen (Low Range sensor from 0 - 10% H_2) and signals can be linearly converted to partial pressure.

Check and repeat calibration at appropriate intervals to ensure that all measurements can be converted to correct concentrations. When the sensor is new, the appropriate interval may be once or twice per day; later it may be weekly or even less frequent. To minimize the need for calibrations, keep the sensor polarized between measurements, unless the time between measurements exceeds several days or weeks. The membrane permeability of hydrogen microsensors changes with time, so a change in signal of up to 10% per month may occur.

If the sensor functions according to the criteria given in the delivery note, the seal and protective plastic tube can be carefully removed before making measurements.

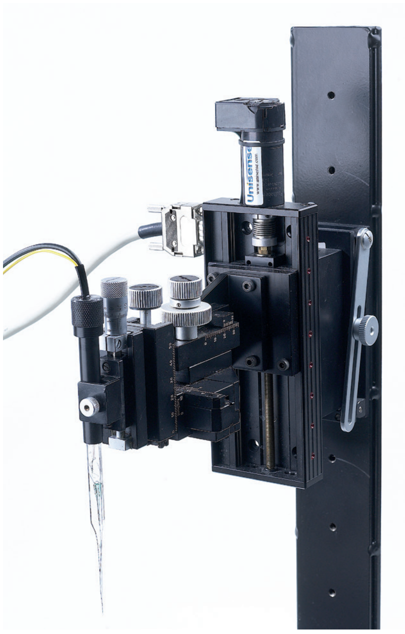
6. MEASUREMENTS

The H_2-type sensor should be used in H_2S free environments. If H_2S is expected to be present, the H_2-X-type sensor should be used.

Hydrogen sensors can be used for a wide variety of measurements (see our website for further information unisense.com). The most common use of hydrogen sensors is for making profiles in e.g. sediment or animal tissue where a high spatial resolution is wanted, or for hydrogen measurements in water samples.

6.1 Use of glass-tip microsensors

Although the Unisense microsensors are made of glass, the tip is flexible and can bend slightly around physical obstacles. The sensor is thus rather sturdy in the longitudinal direction. However, large obstacles like stones or lateral movements of the sensor when the tip is in contact with a solid substrate may cause the tip to break.
Furthermore, due to the small size of the microsensor tip and to the steepness of gradients in many environments, even a displacement of the sensor tip of few microns may change its environment.
Therefore, we recommend that measurements should be performed only in a stabilized set-up free of moving or vibrating devices. We recommend the Unisense lab stand LS and the Unisense micromanipulator MM33 (MM33-2 or MMS) for laboratory use. For in-situ use, we recommend our in situ stand (IS19) and a micromanipulator.



Micromanipulator

6.2 Use of sensors without visible glass tip

Sensors with stainless steel tubes, needles, flow through cells, etc. do not have an exposed glass tip and are, therefore, less fragile. However, these sensors still contain a glass sensor inside which can be damaged by physical shock. To protect the sensor, do not let the sensor drop onto the table or floor. If the sensor has a needle, make sure that the needle does not bend or flex. This will break the glass sensor inside.

6.3 Electrical noise

The signal of the microsensor is very small (10^{-13} to 10^{-10} ampere). Although both the Unisense amplifiers and the Unisense Hydrogen microsensors are very resistant to electrical noise from the environment, electrical fields may interfere with the sensor signal. Therefore, we recommend that unnecessary electrical/mechanical equipment is switched off and the sensor or wires are not touched during measurements and signal recording.

6.4 Interference

Sulphide in the H_2S form may interfere with the H_2 measurements. The standard hydrogen sensor, the H_2-type, is very sensitive to H_2S and other reduced sulphur gases. It should, therefore, not be used in environments where H_2S and other reduced sulphur gases are present. The H_2-X sensor type is not sensitive to H_2S up to 100 µM in solution or 1000 ppm H_2S in gas. The H_2S trap on the H_2-X sensor works by removing protons from the H_2S and the ionized forms of sulfide cannot pass through the silicone membrane into the H_2 sensing part. Other sulphur gases where protons are less easily removed may still penetrate the silicone membrane. The H_2-X sensor may, therefore, still be sensitive to other reduced sulphur gases than H_2S. It is recommended to only expose the H_2S-X sensor to H_2S when needed, to maximize the lifetime of the H_2S trap.

The H_2-X sensor may be made even more resistant to H_2S. If you need a custom built sensor, contact sales@unisense.com

6.5 Interference from H_2 or H_2S entering the rear of the sensor

Avoid exposing the rear end of the sensor to H_2 or H_2S. This is especially important for sensors for In Situ use, mounted in the In Situ Connector. H_2 or H_2S entering the sensor from rear end will affect the potential of the reference electrode, which is placed here. This will cause signal drift and give negative values.

7. ADVANCED USE

Unisense can construct hydrogen sensors for customer requested applications at additional costs. The most frequently requested construction options are described on our website www.unisense.com.

The options include for instance customer specified dimensions, response time, stirring sensitivity, pressure tolerance, range and detection limit. If your specifications for a special hydrogen sensor is not described at our web page please contact sales@unisense.com for further options and prices.

7.1 Examples of advanced applications

- Consumption/production rates of hydrogen. E.g. during enzyme assays in small samples in Unisense microrespiration chambers MRCh

- Measurements of hydrogen under high external pressure e.g. in closed pressurized systems, underwater and deep sea applications

- Long-term hydrogen monitoring

If you have questions, please contact sales@unisense.com

8. STORAGE AND MAINTENANCE

Sensors with glass tips, needles, or stainless-steel protection caps should be stored in the plastic protection tube used for shipping. Other sensor types can be stored in the sensor box used for shipping.

The hydrogen microsensor can be stored with the tip exposed to water or air. The room in which the hydrogen microsensor is stored should be dry and not too hot (10-30°C). If the sensor is used regularly it can be stored polarized.

8.1 Cleaning the sensor

Depending on which substance is present on the sensor tip or membrane, the sensor can be cleaned with different solutes. The standard method is to rinse with 96 % ethanol (NOT in the protection tube), then rinse with 0.01 M HCl and rinse with water. This will remove most substances.
Alternatively it is possible to rinse with 0.1M NaOH, isopropanol or different detergents

TROUBLESHOOTING

NOTE! Always ensure that you are using the latest version of uSense Solutions. You can always download the latest version from www.unisense.com

Problem	High and drifting signal
Possible cause	The sensor tip is broken
Solution	Replace the hydrogen sensor

Problem	The signal is very low
Possible cause	Damage to internal working electrode
Solution	Replace the hydrogen sensor

Problem	Very low sensitivity to H_2 and low signal
Possible cause 1	Bubble in the narrow parts of the sensor, often not visible to naked eye
Solution 1	Shake the sensor gently like shaking an old mercury fever thermometer. As shown in this video guide: unisense.com/video-guides/#troubleshooting
Possible cause 2	Bubble in the sensor tip, *not* visible to the naked eye
Solution 2	Soak the sensor in degassed water for at least 2 hours. Degas water by boiling it and subsequently cool it to room temperature without getting air into it

Problem	Slow response
Possible cause	Insoluble compounds deposited at the sensor tip
Solution	Rinse with 96 % ethanol, rinse with 0.01 M HCl and rinse with water

Problem	Unstable signal or the signal fluctuates if the set-up is touched or equipment is being introduced in the medium you are measuring in
Possible cause	Electrical disturbance of the sensor through the tip membrane
Solution	Ground the set-up using the blue grounding cable supplied with the amplifier. Connect the reference plug on the amplifier (blue plug) with the medium you are measuring in.

If you encounter other problems and need scientific/technical assistance, please contact sales@unisense.com for online support (we will answer you within one workday).

REFERENCES

Revsbech, N. P., and B. B. Jørgensen. 1986. Microelectrodes: Their Use in Microbial Ecology, p. 293-352. In K. C. Marshall (ed.), Advances in Microbial Ecology, vol. 9. Plenum, New York.

Itoh, T., et al. 2009. Molecular Hydrogen Suppresses FcepsilonRI-Mediated Signal Transduction and Prevents Degranulation of Mast Cells. Biochem. Biophys. Res. Commun. 389:651-656.

Kajiya, M. et al. 2009. Hydrogen From Intestinal Bacteria Is Protective for Concanavalin A-Induced Hepatitis. Biochemical and Biophysical Research Communications 386:316-321.

Kajiya, M. et al. 2009. Hydrogen Mediates Suppression of Colon Inflammation Induced by Dextran Sodium Sulfate. Biochemical and Biophysical Research Communications 386:11-15.

Vopel, K., et al. 2008. Modification of Sediment-Water Solute Exchange by Sediment-Capping Materials: Effects on O_2 and PH. Marine and Freshwater Research 59, 1101-1110.

APPENDIX

Salinity (parts per thousand)									
Temp. (°C)	**0**	**10**	**20**	**30**	**32**	**34**	**36**	**38**	**40**
-2			901,34	851,79	841,96	832,59	823,21	813,84	804,46
-1			890,18	841,52	832,14	822,77	813,84	804,46	795,54
0	982,59	929,46	879,46	832,14	822,77	813,84	804,46	795,98	787,05
1	969,64	917,86	869,2	822,77	813,84	804,91	795,98	787,5	778,57
2	957,59	907,14	858,93	813,84	804,91	796,43	787,5	779,02	770,98
3	945,54	896,43	849,55	805,36	796,43	787,95	779,91	771,43	763,39
4	934,38	886,16	840,18	796,88	788,39	780,36	771,88	763,84	755,8
5	923,66	876,34	831,7	789,29	780,8	772,77	764,73	756,7	748,66
6	912,95	866,96	823,21	781,7	773,66	765,63	757,59	749,55	741,96
8	893,3	849,11	807,14	767,41	759,38	751,79	744,2	736,61	729,46
10	875,45	833,04	792,41	754,02	746,43	739,29	731,7	724,55	717,41
12	858,93	817,86	779,02	741,96	734,82	727,68	720,54	713,39	706,7
14	843,75	804,02	766,52	730,8	723,66	716,96	710,27	703,13	696,43
16	829,46	791,52	755,36	720,54	713,84	707,14	700,45	693,75	687,5
18	816,96	779,91	744,64	711,16	704,46	698,21	691,52	685,27	679,02
20	805,36	769,64	735,27	702,68	695,98	689,73	683,48	677,23	671,43
22	794,64	759,82	726,34	694,64	688,39	682,14	676,34	670,09	664,29
24	785,27	751,34	718,75	687,5	681,7	675,45	669,64	663,84	657,59
26	776,79	743,3	711,61	681,25	675	669,2	663,39	657,59	651,79
28	768,75	736,16	704,91	675,45	669,64	663,84	658,04	652,23	646,88
30	762,05	729,91	699,55	670,09	664,29	658,48	653,13	647,32	641,96

Table 1: Equilibrium hydrogen concentrations (μmol/litre) at ambient hydrogen partial pressure of 1 atm. in water as a function of temperature.
Ref. Wiesenburg and Guinasso 1979. J.Chem Eng. Data 24(4):356-360

Note: The Unisense software has a built-in calculator, giving the solubility of H_2 at a given combination of temperature and salinity ("Tools - H_2 Calculator" or the "H_2 table" button in the calibration dialog).

For conversion between units go to the Unit Converter on Unisense website: unisense.com/unit-converter

UNISENSE
SCIENTIFIC