



Combination pH, ORP, T Electrode with Transmitter

Technical Information and Manual

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General Information

The combination electrode consists of the housing with electrodes and the transmitter that amplifies and converts the sensor analog signals into a digital format that it transmits via Ethernet. Each transmitter has its unique MAC address. The IP address can be assigned to the transmitter by a DHCP server, or can be assigned as a static address at set-up. The data can be accessed via Internet, provided the transmitter is connected to an Internet line, and an IP address has been assigned.

The electrode is connected to the transmitter with a special cable. The transmitter itself requires a power outlet. The power cable has an integrated low-voltage power supply. Electrode, transmitter, connecting cable and power supply cable are included in the set.

Application

- Municipal water and wastewater
- Industrial water and wastewater
- Aquaculture

Measuring Ranges

Values	Units	Range	Accuracy
pH		0 - 14 pH ¹	0.1 pH
ORP	mV	- 1,000 mV - + 1,000 mV	4 mV
T	°C	- 20 °C - + 60 °C	0.1 °C

Measuring Principles

pH Measurement

Basic Theory

The pH value is used as a unit of measurement of the acidity or alkalinity of a liquid or partially liquid medium. The acidity or alkalinity of medium is determined by number of hydrogen (H⁺) and hydroxyl (OH⁻) ions. Acidic solutions have a higher concentration of H⁺ ions, while alkaline (or basic) solution has higher number of OH⁻ ions. The concentration of H⁺ ions and OH⁻ ions is equal at pH = 7 when the solution has a temperature of 25 °C.

pH is an inverse logarithmic measurement of the concentration of hydronium ions, as the H⁺ ions are correctly called, per litre of solution:

$$\text{pH} = -\log_{10} [\text{H}^+]$$

The abbreviation pH originates from Latin *potentia hydrogenii*, meaning the power (exponent) of hydrogen. This concept was introduced by Søren Peter Lauritz Sørensen, a Danish chemist, in 1909.

The pH value of the medium can be measured chemically by colour changes of certain indicators. Continuous measurement of pH is done with a glass electrode, in which hydronium ions in the solution exchange partially

1 The range given is the actual measuring range of the instrument. However, all pH electrodes have a non-linear deviation towards the end of their measurement range. Further, strongly alkaline solutions can rapidly and irreversibly degrade electrodes. It is advisable not to use these electrodes in strongly alkaline solutions for more than a few seconds, and to immediately wash them afterwards.

with alkali cations of a selective (glass) barrier and produce a measurable difference of potentials proportional to the solution's pH.

It is important to understand that this “active” half-electrode works in conjunction with another half-electrode, the built-in reference electrode. The calibration process described below correlates the voltage differential between these two half-electrodes with the pH scale.

In aqueous solutions, the pH depends strongly on the temperature. It is often overlooked that the neutral point of water itself depends on the temperature of the solution, owing to the temperature dependence of the self-dissociation “constant” of water, commonly denoted as K_w ; the K_w table of water is shown in Appendix A.

Historically, pH values were determined by the pH-dependent change of the colour of some dyes (“indicators”). The use of glass electrodes has become the dominant measurement technology. However, glass electrodes require regular calibration², and degrade slowly with age³. Electrode degradation is caused by the minute internal electrical current, and accelerates when external electronics increase the current through the electrode.

Measurement Electronics

Owing to the extreme resistance of glass, the electronics to which a glass electrode is attached offers a significant challenge. As a rule of thumb, transmitters for glass electrodes are expected to have an input resistance (impedance) of $> 1 \text{ G}\Omega$. Osorno's electronic transmitter has only about 5 fA^4 input bias current. Despite this current optimization, the response time of the transmitter electronics is less than a second.

Calibration

As pointed out above, pH electrodes require regular re-calibration. Usually, quarterly re-calibration will suffice. Standard calibration solutions are available from various vendors for pH values 4, 7, and 10. A two point calibration is required; it makes little differences which one of the three standard solutions is used.

In the calibration process, the transmitter also re-calculates the “slope”, which is the slope coefficient of the linear dependance between electrode differential voltage and pH. This value is ideally $-59.2 \text{ mV per pH unit}^5$, but as a theoretical value never reached even by new and unused electrodes. As a rule of thumb, electrodes with a slope of -53 mV , or 90% of the theoretical slope, are still usable. As an effect of ageing, the slope will decrease over time. Unused electrodes also age, although slowly.

ORP Measurement

Basic Theory

ORP stands for oxidation-reduction potential (also called redox potential), typically measured in millivolt (mV), and indicates the ability of the substance to either release or accept electrons in a chemical reaction. When electrons are accepted, it is an oxidizing system. When electrons are released, it is a reducing system. The ORP is a very sensitive and dynamic parameter. It depends on the changes of the internal chemical equilibrium, or the introduction of new chemical substances to a solution.

The ORP sensor is a two-electrode system consisting of a measuring and a reference electrode. The measuring electrode serves as an electron donor or electron acceptor, depending upon the test solution.

For most substances capable of undergoing oxidation-reduction reactions, ORP is a pH dependant parameter⁶;

2 Osorno recommends quarterly recalibration with appropriate calibration solutions.

3 The lifetime can be extended significantly when the electrodes are stored in the appropriate electrode storage solution. Never expose electrodes for an extended period of time to distilled water, or any other liquid of low ionic strength.

4 $1 \text{ fA} = 10^{-15} \text{ A}$ current.

5 This follows from the Nernst equation, see below in the ORP section.

6 Only for substances where the underlying redox reaction does neither consume nor generate either H^+ or OH^- ions, is

for an increase by one pH unit, 59.2 mV are to be subtracted from the measured ORP value when one chooses a single pH reference⁷. This value of 59.2 mV can be calculated from the Nernst equation:

$$E = E_0 - R \cdot T / n \cdot F * \ln(c_{oxidized} / c_{reduced})$$

with

E - actual potential (mV);

E₀ - standard potential (mV);

R - universal gas constant (R = 8.314 J mol⁻¹ K⁻¹)

T - absolute temperature (K), T = 273.15 + t, where t is temperature of the solution in °C;

F - Faraday constant (96,485 C mol⁻¹);

n - number of moles of electrons transferred in the redox reaction;

c_{oxidized} - oxidant concentration in mol l⁻¹

c_{reduced} - reductant concentration in mol l⁻¹

If to compare pH and ORP measurement results, the pH value indicates a system's relative state for receiving or donating hydronium ions, while the ORP value characterizes a system's relative state for gaining or losing electrons. Unlike pH values with their direct relation of the concentration of hydronium ions, ORP values are significantly more difficult to interpret: they are likely the result of several independent redox reactions, often with unknown concentrations. Further, these redox reactions are not necessarily reversible, which is a required condition to apply Nernst's equation. Despite these restrictions, ORP has gained much ground in monitoring disinfection quality in water treatment and in the food processing industries, in environmental monitoring, and has become indispensable in monitoring biochemical processes.

For the ORP electrode itself, commonly used material are either gold, or platinum, or graphite. Osorno uses platinum electrodes.

As any other electrode, ORP electrodes require that the potential be measured as the difference against a reference electrode. In electrochemistry, all potentials are referenced against the standard hydrogen electrode (SHE); the SHE potential is by definition 0 V. Unfortunately, there is no practical solution to apply SHE outside of the settings of specialized laboratories, so that secondary references are always used in practical applications. Osorno's transmitter calculates the ORP that it reports on the basis of SHE, as required in electrochemistry. It must be pointed out that not all commercially available equipment follow this rule, so that **the comparison of ORP values of different equipment may require to apply an offset** to correct for the voltage of the reference electrode against SHE.

Table 1: ORP offset for Reference Electrodes.

	SCE ⁸	Ag/AgCl - 1 M KCl	Ag/AgCl - 4 M KCl	Ag/AgCl - sat. KCl
Electrode potential ⁹	+241 mV	+192 mV	+228 mV	+236 mV

Osorno's transmitter applies Nernst's equation to adjust for the solution temperature, although equipment of others usually do not apply this temperature correction. It is important to keep this in mind when comparing ORP

ORP pH independent.

7 This value is the factor RT/F in the Nernst equation, calculated for the electrochemical reference temperature of 25 °C, and multiplied by the factor 2.303 for conversion of the natural logarithm into a decadic (common) logarithm. For temperatures other than 25 °C, this value requires recalculation. It must be pointed out that this value is valid only for cases of n = 1, i.e. single electron transfer reactions, which covers most of the practical applications.

8 Standard calomel electrode.

9 Relative to SHE.

values of different equipment.

Measurement Electronics

Although the internal resistance of an ORP electrode is not nearly as high as that of a pH electrode, it is still well above 10 M Ω . The circuitry used internally in the transmitter is therefore modelled after that used for the pH electrode (see above).

Calibration

Unlike pH electrodes, ORP electrodes typically are not re-calibrated because there is no need to recalculate the measured voltage into any other value. ORP solutions available commercially are not true “calibration solutions”, owing to their limited stability, and their wide tolerances¹⁰. This serves the purpose of checking the electrode, but is rather useless for calibration. Realistically, ORP measurement is the measurement of a voltage, and as such is intrinsically absolute and calibration-free.

Temperature

Basic Theory

The built-in temperature sensor is a semiconductor¹¹ with low thermal resistance, and therefore short response time. The temperature can be read by external devices, and is also used internally for temperature corrected values according to the Nernst equation (above).

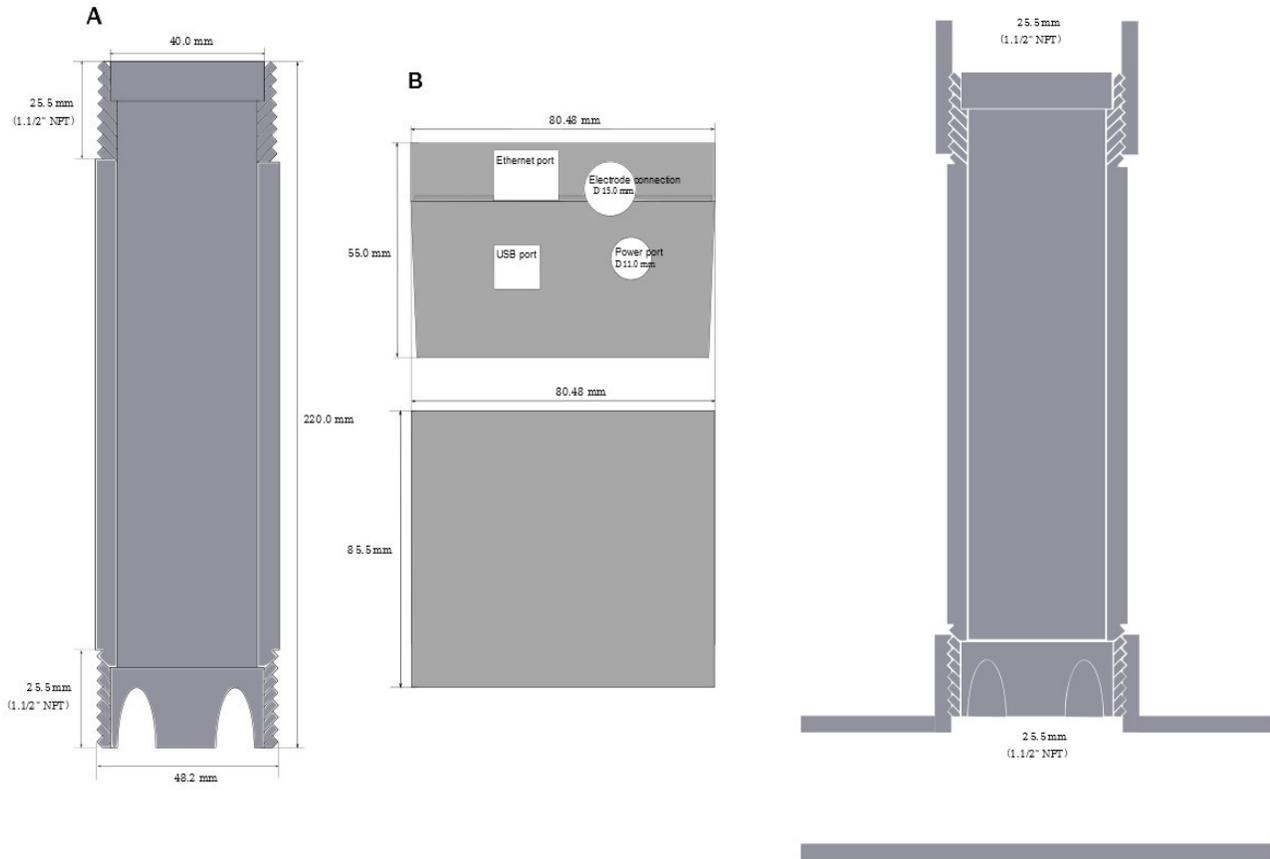
Measurement Electronics

The circuitry to which the temperature sensor is connected, is designed for fast response and low noise.

¹⁰ A tolerance of ± 35 mV is a reasonable assumption.

¹¹ Semiconductor of the TMP36 series, manufacturer Analog Devices.

Dimensional Drawings



A. Dimensions

B. Installation

Material

Components	Material
Electrode housing	PVC
pH electrode	epoxy general purpose electrode with polypropylene junction platinum plates Ag/AgCl reference
ORP electrode	epoxy general purpose electrode with polypropylene junction platinum plates Ag/AgCl reference

Connecting Information

The 25.5 mm (1 1/2" NPT) thread is available on both ends of the electrode housing (see "Dimensional Drawings" - B. Installation).

Ordering Information

The electrode can be ordered in following combinations:

1. pH, ORP, T - code OCS-pH-Eh-T
2. pH, T - code OCS-pH-T
3. ORP, T - code OCS-Eh-T

Calibration Procedures

pH Calibration in Buffer Solutions

Requirements for pH calibration:

- Computer with network connection capability.
- Two pH calibration solution; frequently used solutions are pH 4, 7, or 10.
- Distilled water (if distilled water is not available, use tap water although this is a poor replacement).
- Paper towel or dry cloth.

Calibration Steps:

1. Assure that the sensor unit is connected to the transmitter.
2. Assure that the transmitter is turned on and connected to a network that includes a DHCP server.
3. Obtain the IP address of the transmitter. The IP address can found either on the transmitter enclosure, if it is a static address, or is assigned by the DHCP server if a dynamic address assignment is used.
4. Connect your computer to the network where the transmitter is connected.
5. Once connected to the network, open a web browser (preferably Mozilla Firefox; Google Chrome is problematic).
6. Enter the IP address of the transmitter to load the website of the electrode transmitter.
7. Clean the electrodes/sensor with distilled water and wipe carefully with a paper or cloth – do not use force.
8. Submerge the electrodes/sensor into the one of the calibration solution (**solution must have a temperature of approximately 25 °C**) and allow 3 - 5 minutes for the value to stabilize.
9. When the value has stabilized, click on the calibration button for the buffer solution used (for example, if a calibration solution with pH 4 has been used, click the calibration button pH = 4, etc.).
10. When calibration with current solution is finished, repeat procedure from step 7 with a different calibration solution.
11. The transmitter accepts new calibration values with the click of the calibration button, and uses the last two entered values for the calculation of the slope. This concludes the calibration procedure.

NOTE: Always complete a two point calibration. Otherwise, the internally calculated values may not be correct, and as a result, transmitted measurement values may be faulty.

Calibration of ORP Electrode

As laid out above, ORP electrodes do not require calibration. For testing the reliability of an ORP electrode, ZoBell's solution or Light's solution are frequently used¹².

¹² Available from Osorno or other manufacturers.