



OxyGuard[®]

CO2 Portable

Carbon Dioxide Analyser

USER MANUAL

Ser. Nr.:

Range: 0-50 mg/l

Output: 0-1 V

Delivery

Checked by:

1. DESCRIPTION

The OxyGuard CO2 is an analyser designed to measure the gaseous dissolved carbon dioxide content of water in fish farms and similar. The range of the instrument is as standard set to 0-50 mg/l. The instrument can be delivered with other ranges.

The OxyGuard CO2 Portable consists of a Probe, a Transmitter with display, a battery charger, an output lead and calibration accessories. The transmitter has a 0-1VDC signal as output. This 0-1V signal corresponds to 0-50 mg/l. Calibration accessories consist of a calibration beaker with stirrer, calibration solution, pH conditioner dosing syringe for use during calibration and a measure for dosing pH conditioner.

The OxyGuard CO2 is calibrated both in zero and span. Zero calibration is performed in water that does not contain any free dissolved CO2. Span calibration is performed in the same water to which a precise amount of CO2 has been added. Since it is difficult to add a precise amount of CO2 in gaseous form to water, a precise amount of a chemical is added and then the chemical is treated with pH conditioner to make it release CO2.

Using the OxyGuard CO2 is easy - just switch on, put the probe in the water and measure. It will take a few minutes to obtain the correct value. The display shows the milligram per litre free carbon dioxide in the water.

When the probe is in the water the instrument MUST ALWAYS be switched ON. Charge the batteries fully before leaving the instrument to make measurements in the field, and do not leave it to measure for more than 3 days.

We would like to add that tests with the OxyGuard CO2 analyzer have shown that the traditional methods of determining CO2 by titration have their limitations. These methods were designed for boiler feed water analysis. Boiler feed water is - or should be - quite pure, and does not contain dissolved solids that can affect a titration. The water found in fish farms, however, contains many compounds that can interfere with titrations. Ammonia, ammonium, phosphates, humic acids, urea, silicates and chlorides are examples. More information on this subject is found later in this manual.

The OxyGuard CO2 is temperature compensated in a similar way to a dissolved oxygen meter. The compensation range is from 3 to +35°C.

The OxyGuard CO2 measures only free dissolved carbon dioxide. It does not consume CO2 for its measurement and does not change the pH or any other property of the water.

Carbon dioxide dissolves in water both chemically and physically.

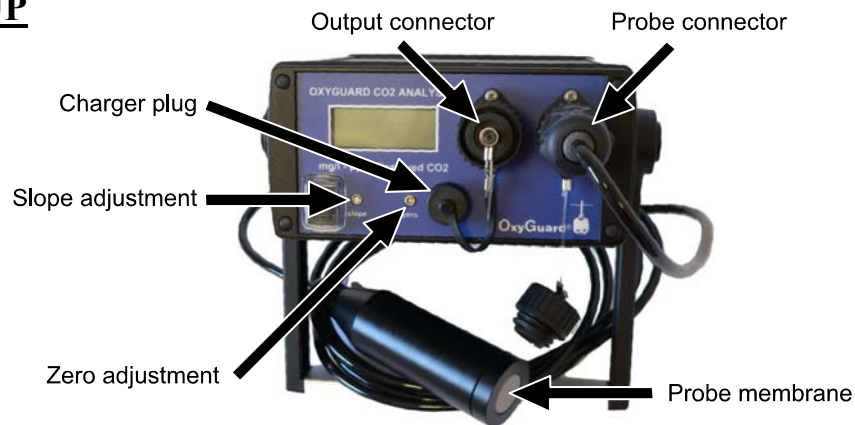
The chemically dissolved CO2 is part of the carbonate system in the water and is as such harmless.

The physically dissolved CO2 is the CO2 that affects the fish, and is the CO2 that is measured by the OxyGuard CO2 analyzer.

IMPORTANT

If you try to measure the CO2 content of aquaculture water by titration, you will not only measure CO2, but also any other substance in the water that can affect the titration. You will obtain a result that is too high

2. STARTING UP



Please note the following:

2.1.1 THE ANALYZER IS DELIVERED CALIBRATED AND READY FOR USE. WE RECOMMEND THAT YOU USE IT AND BECOME FULLY FAMILIAR WITH ITS USE BEFORE YOU CHECK THE CALIBRATION FOR THE FIRST TIME.

2.1.2 THE PROBE HAS A RELATIVELY LONG RESPONSE TIME. TYPICAL VALUES ARE A FEW MINUTES IN MOVING WATER AND 15 MINUTES IN STILL WATER.

2.1.3 WHEN THE PROBE IS IN WATER THE INSTRUMENT MUST BE SWITCHED ON.

2.1.4 THE COVER OVER THE CHARGER PLUG SHOULD BE PULLED OFF, NOT TURNED.

2.1.5 THIS IS A SENSITIVE INSTRUMENT. KEEP POINTED OBJECTS AWAY FROM THE PROBE MEMBRANE.

2.1.6 DO NOT ATTEMPT TO OPEN THE PROBE – THIS WILL DAMAGE IT AND VOID ANY GUARANTEE.

Keep the probe reasonably clean - wipe it or wash in household detergent if necessary. If carbonate deposits appear on the membrane add 1 tsp. of the pH conditioner supplied to a small cup of water and leave the probe in it until the deposits have gone. Remember to keep the instrument switched on when the probe is in water.

2.2 Charging

The unit is shipped ready for use, but may need charging before being taken into use. Chargers can differ - for example, the charger for use in North America differs from the charger for use in Denmark. Some chargers have an indicator that lights when charging is complete, others indicate when charging is taking place. Please see the charger for information of the actual type of charger.

NB. The OxyGuard CO2 transmitter is splash-proof, NOT immersion-proof.

CHARGE THE BATTERIES FULLY BEFORE LEAVING THE INSTRUMENT TO MEASURE IN THE FIELD, AND DO NOT LEAVE IT TO MEASURE FOR MORE THAN 3 DAYS.

Do NOT measure after an ozone treatment unit. Ozone treatment forms CO2 in the water, and active ozone can damage the probe. Measure before the ozone treatment unit.

2.3 Switch On Sequence

When you switch the Portable CO₂ analyzer on it will perform a switch-on sequence lasting about a minute. The display can show various values during this time. We advise that you simply switch on and wait two minutes and then use the instrument.

2.4 Analogue Output.

The 0-1V analogue output is obtained by inserting the plug of the output lead into the output connector. The brown lead is plus (connector pin 2), the blue lead is minus (connector pin 3).

2.5 Use as a Bench Top Instrument

If you need to make measurements in more than one tank or body of water we recommend that the OxyGuard CO₂ is used as a bench top instrument, where the analyser remains in the laboratory and samples are taken to it. This enables the instrument to remain switched on continuously, and avoids subjecting it to changing temperatures etc. and the mechanical stress of being moved from one place to another. Tests show that water with about 50 mg/l carbon dioxide remains stable in the calibration beaker with the stirrer switched on for almost 30 minutes, and that the error introduced by removing the sample and measuring in the laboratory rather than on-the-spot can, with care, be kept to one or two mg/l.

We recommend that samples are taken in glass bottles with tight fitting stoppers (e.g. screw caps). The samples should be transferred to the calibration beaker and the CO₂ content measured. For the greatest accuracy let the samples attain the same temperature as that the calibration water had during calibration. The samples should, however, preferably be measured within an hour or two.

Care must be used when taking the samples and when pouring them into the calibration beaker. Tilt the beaker and pour so that the sample runs smoothly down the side of the beaker with as little aeration as possible.

Make sure that the stirrer magnet is in place, tilt the beaker a little and insert the probe. Make sure that there are no air bubbles trapped under the probe - if there are, lift the probe a little and tilt the beaker to let the bubbles escape. Start the stirrer.

When the reading is steady, which normally takes about 5 minutes, note the value. You can then stop the stirrer and discard the sample.

NB. The voltage on the analogue output can go above 1 V and below 0V.

For example, during the switch on sequence -0.4V is likely, and if the probe is not connected -3V can appear. The output can source about 50 mA. Please ensure that connected equipment can tolerate this.

3. CALIBRATION

NB THE ANALYZER IS DELIVERED CALIBRATED AND READY FOR USE. WE RECOMMEND THAT YOU USE IT AND BECOME FAMILIAR WITH ITS USE BEFORE YOU CHECK THE CALIBRATION FOR THE FIRST TIME.

Note that the analyser will normally display "0" or "1" in the air. You can easily check that it is working by breathing out on the probe - the value will rise.

For calibration you need the following:

As supplied with the analyser: -Calibration beaker with stirrer.
-pH conditioner.
-Calibration fluid in bottle.
-Dosing syringe.
-Measure for pH conditioner.

Obtained locally: "Calibration water" -distilled or demineralised water that has been checked as described below.

NB It is very important that the cap of the calibration fluid bottle is kept tightly closed.

Calibration is a two-step process where the OxyGuard CO2 is adjusted in Zero and Slope.

Distilled or demineralised water is used during calibration. The quality of such water can vary greatly; it can contain both free dissolved carbon dioxide and carbonate. It is therefore necessary to check the water and, if necessary, obtain water from another source.

The calibration procedure thus has the following steps:

- 3.1) Check the distilled water.
- 3.2) Zero check/adjust the OxyGuard CO2
- 3.3) Check and note the total CO2 and carbonate content of the water.
- 3.4) Add a known amount of CO2. and note the new measurement.
- 3.5) Calculate the correct reading and adjust the OxyGuard CO2.

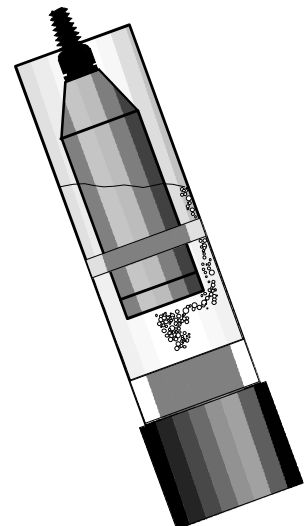
3.1 Check the distilled water

3.1.1) Make sure that the OxyGuard CO2 is switched on. Pour approximately 100 ml of the distilled water into the calibration beaker, place the probe in the beaker and start the stirrer. The stirrer is started and stopped by inserting/removing the power connector.

3.1.2) After approx. 5 minutes check the value on the OxyGuard CO2. If it is higher than 10 mg/l the distilled water cannot be used. Obtain water from another source and repeat the process.

3.1.3) If the value is under 10 mg/l note it in the "Raw Water" column of the table. The distilled water is now approved as calibration water.

NB to remove bubbles stop stirrer and tilt.



3.2 Zero adjust the OxyGuard CO2

3.2.1) Fill the dosing syringe with 1 ml calibration solution. Replace the cap on the solution bottle immediately. Lift the probe and inject the 1 ml fluid into the water in the beaker. The fluid will absorb all the free CO2 in the water. Replace the probe

3.2.2) When the reading is stable you can adjust the "Zero" adjustment until the analyser displays "0". Stop the stirrer.

3.3 Check the total CO2 content of the water.

3.3.1) Remove the probe and empty the beaker. Rinse the probe, beaker and stirrer magnet thoroughly with calibration water.

3.3.2) Pour calibration water into the beaker up to the top of the black ring in the middle of the beaker.

3.3.3) Add one measuring spoonful of pH conditioner. Stir until the powder has dissolved. Stop the stirrer, place the probe in the beaker and start the stirrer again.

3.3.4) When the reading is stable, after about five minutes, note the reading in column "A". If it is greater than 20 mg/l the water cannot be used and water from another source must be obtained.

If the value is less than 20 mg/l proceed with the water in the beaker.

3.4) Add a known amount of CO2

3.4.1) Fill the dosing syringe with 1ml calibration fluid. Tighten the cap of the bottle firmly.

3.4.2) Lift the probe from the water without spilling. Add the fluid from the syringe. Stir without the probe for 10 seconds. Replace the probe and start the stirrer again. When the reading is stable note the value in column "B". Keep the stirrer running.

3.5 Calculate the calibration value and adjust the analyser

3.5.1) Calculate "U"; $U=50 \times A / (B-A)$ Note this in the table.

3.5.2) Calculate the calibration value "K"; $K = 50 + U$

3.5.3) Note "K" in the table and adjust the "Slope" screw until the display shows this value.

Calibration is now completed. Stop the stirrer, remove the probe, discard the water in the beaker, rinse and dry the parts.

If you measure in salt water add the necessary amount of salt (NaCl - ordinary table salt can be used) when you add the pH conditioner in 3.3.3.

Add g to beaker	for salinity ppt
1	5
2	10
3	15
4	20
5	25
6	30
7	35
8	40

$$U = \frac{50A}{B - A}$$

$$K = U + 50$$

How often should calibration be performed?

This depends on the actual conditions, how the analyzer is used and the accuracy wanted. Start by calibrating once every 2 months. When you have become familiar with the instrument you will be able to extend the interval as desired.

3.6 Calibration for Optimum Accuracy

Whatever the measuring apparatus, the greatest accuracy is obtained when the measurement values are close to the calibration value. The above calibrates the OxyGuard CO₂ at 50 mg/l, measurements at this value have the greatest accuracy.

If you measure at lower values you can obtain greater measurement accuracy by calibrating close to the actual measurement value.

To calibrate to 25 mg/l use distilled water that has max. 5 mg/l free CO₂ as measured in 3.1.2, and max. 10 mg/l in 3.3.4.

Add only 0.5 ml calibration fluid in 3.4.

Calculate "U" as $U = 25 \times A / (B - A)$

Calculate "K" as $K = 25 + U$

You can also calibrate to other CO₂ concentrations in a similar manner. For lower calibration values even purer distilled water is needed.

4. SPECIFICATIONS

Size:	Probe: 40mm dia. x 140 mm. Cable length 3m. Meter: 120 x 120 x 58 mm Calibration beaker 65mm dia. x 260 mm
Weight	Approx. 7 kg including charger, calibration fluid, calibration conditioner, calibration beaker and dosing syringe.
Supply (to charger)	230VAC (115VAC on request).
Range	0 - 50 mg/l dissolved carbon dioxide. Temperature compensated range 3-35°C.
Output:	Analogue signal 0-1VDC
Operating conditions:	Electronics -10 to +60°C, splashproof.
Accuracy	Depends on calibration. Expected practical accuracy +/- 1 mg/l when calibration temperature = measuring temperature.
Response time	Typically 5 minutes at 20°C depending on flow velocity past probe. In still water up to 15 minutes.
Flow requirements	The instrument does not use carbon dioxide for its measurement, but a certain flow is necessary to ensure that the sensing element of the probe is in equilibrium with the surrounding water, and to avoid "spot" measurements.
Operating time:	Approximately 70 hours on fully charged batteries.
Charging time:	Approximately 24 hours to charge batteries fully.

Analyser comprises: Transmitter and probe with 3m cable, charger, analogue output lead.

Calibration accessories comprise: Beaker with stirrer & magnet, 75 g calibration conditioner, 100 ml calibration solution, dosing syringe, measure, adjustment screwdriver.

Spares and accessories:

G02ST	Calibration beaker with stirrer and magnet. For 12VDC.
G02STC	Charger for battery pack for 230VAC, other on request.
G02XCT	75 g calibration conditioner.
G02XCS	100 ml calibration solution.
G02XCD	Dosing syringe.

Changing the Fuse

The fuse is found inside the unit, on top of the battery. The front panel with the electronics must be removed. Start by removing the 4 small plugs over the screws at the corners of the front panel. Then unscrew the screws and carefully lift the front with the electronics. Unplug the battery leads. The fuse, a 2A slow-blow, can now be changed. A spare fuse is found in the plastic bag taped to the battery.

Use a small screwdriver to remove the fuse.

Brug en lille skruetrækker til at løsne sikringsholderen



Spare fuse in plastic bag

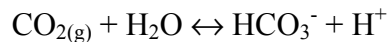
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ABOUT THE MEASUREMENT OF CO₂

General

CO₂, both naturally occurring and from piscine respiration, dissolves in the water in two ways, chemically and physically. The chemically dissolved part forms hydrogen carbonate and hydrogen ions, and this is balanced by the physically dissolved part which is present as CO₂ gas dissolved in the water just as oxygen is dissolved in the water.

The equilibrium has the form:



The CO_{2(g)} is in gas form; **it is this CO₂ that the fish are subjected to and react to.** The CO_{2(g)} exerts as such a gas pressure, so if this pressure is measured the gaseous CO₂ content of the water in mg/l can be determined.

With the OxyGuard CO₂

The probe of the OxyGuard CO₂ contains a pressure sensor that is selectively sensitive to the gas pressure of CO₂. It is completely insensitive to oxygen, nitrogen, argon, water vapour or any dissolved gas found in the water other than CO₂. The sensor is located behind a gas permeable membrane that does not allow any ionic species to pass, so the OxyGuard CO₂ only reacts to the CO_{2(g)}.

The OxyGuard CO₂ thus measures the CO₂ that affects the fish.

By Titration

Chemical methods for the determination of dissolved CO₂ are based on titration of a sample, either with base to pH 8.2 or by acid to pH 4.3. Both methods work well, but only on pure water such as boiler feed water, for which the methods were developed probably as long as a hundred years ago. If the water contains anything else that can affect a titration then a titration will give a too high result.

Aquaculture water contains many different substances that interfere with the above mentioned titrations, either by consuming base or by consuming acid. Phosphates, ammonia and ammonium interfere strongly, but silicates, borates, humic acid, urea and other substances also interfere. Titrations on aquaculture water will thus always react both to the CO_{2(g)} and to other substances in the water.

When CO₂ in aquaculture is measured with the OxyGuard CO₂, therefore, one obtains lower values than those obtained by chemical methods.

The only easy way of measuring the CO_{2(g)} in aquaculture water accurately is to use the OxyGuard CO₂.

A Comparison of methods to determine Dissolved CO₂: Direct measurement versus Chemical Determination.

The OxyGuard CO₂ analyzer is an instrument for the measurement of dissolved gaseous CO₂ in water. The measuring principle of this instrument is based on selective partial pressure measurement. It responds only to CO₂ and it is completely insensitive to any other gas that can be dissolved in water, such as oxygen, nitrogen, argon, etc.

The construction therefore makes the instrument very accurate. Problems, however, arise when comparisons are made between measured and analytically determined values.

Users of the OxyGuard CO₂ are surprised by the fact that measurements obtained with this instrument are much lower than values obtained by chemical analysis, and over and over again we have been asked: Why do I measure much lower values than those I obtain by chemical analysis?

The answer is the same every time: The reason is that the chemical methods are strongly affected by naturally occurring interferences such as ammonium, phosphates, etc. etc. - and there are also technical problems involved.

The following outlines in a fairly simple way in more detail why the chemical methods fail.

The two commonly used methods are based on adding base or acid to a known volume of water until a certain pH is reached - either to end-point pH 8.2 or to pH 4.3. By measuring the amount of base or acid used the CO₂ content can be found.

The 8.2 method is the easiest to understand, so let us start here:

By adding hydroxide to water containing CO₂ the following chemical reaction takes place:
 $\text{CO}_2 + \text{OH}^- = \text{HCO}_3^-$

At pH 8.2 all of the CO₂ has been converted to HCO₃⁻ so by “counting” how much hydroxide was added it is fairly easy to calculate how much CO₂ the sample originally contained. There are several chemical test kits available for this method. Generally they consist of a 50 ml sample beaker, a small size syringe, a bottle of dilute sodium hydroxide and a bottle of colour pH indicator: total value a couple of EURO. The technique is that you take a sample of a known volume, add 2 drops of colour indicator and add sodium hydroxide by using the syringe until the indicator changes its colour. By looking at the syringe you can see how much sodium hydroxide was consumed and a quick calculation gives you the answer. This works quite well on very pure water in a warm laboratory, but unfortunately is not so well suited for aquaculture water! The reasons are many:

It is very difficult in the field to take an exact volume small size sample. Typical variation is often +/- 1 ml. Relative to 50 ml., this is an error of +/-2%.

The titration end-point 8.2 is only valid at 25 degrees Celsius. At other temperatures the end-point is different. Not much aquaculture is operated at 25 degrees Celsius!

A colour pH indicator is never a good thing in turbid and/or coloured water, and it can be very difficult to observe exactly when the colour change happens. Of course, this can be overcome by using a pH meter but also this is not without problems as we shall learn later.

Chemical interferences! There are many things dissolved in the water that interfere with the titration method by consuming base (sodium hydroxide). A list of many of them is found later on this page.

Ammonium is one of the more important ones: 1 mg/l of ammonium (NH_4^+) counts as approximately 0.2 mg/l of CO_2 . So if you have 50 mg/l of ammonium then your CO_2 determination is automatically 10 mg/l too high.

Phosphates, such as H_2PO_4^- interfere too, and even stronger: 1 mg/l of H_2PO_4^- corresponds to almost 0.5 mg/l of CO_2 !

Ammonium and phosphates are, of course, inevitable by-products formed when fish digest the feed they are given....

The 4.3 method is a little more complex but equally unsuitable. It is based on the determination of the total alkalinity combined with an initial pH measurement. The trick is that if you know the pH of the sample, then it is possible from a so-called Bjerrum diagram (Bjerrum, Danish chemist 1879 to 1958) to find out what the ratio of CO_2 to HCO_3^- is, and by determining what the amount of HCO_3^- is by titrating the sample to pH 4.3, you get the amount of CO_2 . Again an elegant method – but not suitable for use in aquaculture water because:

The method only works at 25 degrees Celsius.

This method also has the same problems of taking a precise small size sample as described above.

The pH measurement has to be very precise. This is in fact a lot more difficult than most people imagine, especially in salt water. A modern pH meter displays pH with 2 decimals, and the value displayed is seldom questioned. It is, however, far from that simple; and in practice the accuracy of such a measurement is probably ± 0.2 pH.

This uncertainty affects the CO_2 determination by some $\pm 10\%$.

The picture with regard to chemical interference is almost the same as before except that ammonium does not interfere here but phosphates certainly do. Any component that reacts with acid interferes in fact – so depending on the actual water quality the error is variable, but it is always positive, thus again leading to too high CO_2 numbers.

The complete list of whatever interferes with either the 8.2 or the 4.3 method is very long. Indeed, anything that reacts with either base or acid or both will interfere. We can name ammonium, phosphates, silicates, borates, nitrites, humic acids, fat, amino acids, urea, and dissolved iron, but there are many more.

Both the two methods described above were originally designed for steam boiler feed water. Their use on aquaculture water for many years has led to the belief that this water contains more CO_2 than it actually does.

Maybe some of the text books about how the different species of fish tolerate CO_2 need to be rewritten