

A GUIDE TO CONDUCTIVITY AND DISSOLVED OXYGEN

- the theory and practice of conductivity and dissolved
oxygen measurement

INTRODUCTION

This guide to conductivity and dissolved oxygen measurement is one of a series produced over the past few years, covering analytical techniques such as pH and ion selective electrode Analysis.

As well as an insight into the theoretical aspects of the techniques, sections covering applications and troubleshooting have been included to make this a comprehensive review of the measurement of these important parameters.

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SECTION 1 Conductivity

Introduction

Conductivity is measured in a wide range of industries and gives a readout of total ionic concentration within the sample solution.

In some industries the nature of the ions is known and may be present as one molecular species. In food manufacturing processes, the conductivity meter becomes a salt meter and is used for quality control measurement.

By contrast, industrial effluent and the resultant polluted waterways may contain many ionic species. Conductivity is used to give total ionic strength readings. It gives a means of monitoring the build-up of contaminants and also the success of water treatment programmes. Industrial cleaning and sterilising processes use conductivity to monitor their effectiveness and also the strength of residual, spent solutions. Depending on their ionic strength readings, they may be recycled for further use, or replenished.

The plating industry will also use conductivity in a similar way, to monitor the strength of etching, cleaning and waste solutions.

In general the measurement of conductivity is rapid and an inexpensive way of determining the ionic strength of a solution. The main drawback is that it is a non-specific technique.

Various ions in solution contribute to a total conductivity reading. Some ions contribute more than others. The presence of organic alcohols and sugars will give unusable conductivity results. Some materials also reduce the accuracy of the technique by coating the sensor. Temperature effects also contribute to experimental inaccuracies.

Total Dissolved Solids (TDS) is a measurement of the total concentration of ionic species in a sample. The measurement of solution conductivity gives a method by which a TDS value for the sample solution can be determined. The microprocessor controlled meter carries conversion factors, which are user selectable, in order to give a TDS value referenced to a calibration standard (usually KCl or CaCO_3).

Theory of conductivity measurement

Electricity is a flow of electrons. This indicates that charged particles (ions) will conduct electricity.

Conductivity is the ability of a solution to pass current. It follows that the amount of current flowing is proportional to the number of ions present in the conducting solution. Therefore, a measure of the conductivity will give a direct reading of the solution concentration.

All substances conduct to some extent. In solution the level of ionic strength varies from the low conductivity of ultra pure water to the high conductivity of concentrated chemical samples.

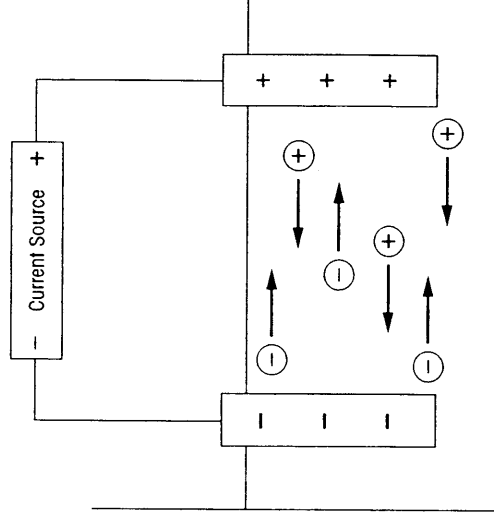


Fig. 1: Ionic mobility in solution

Historically, the measurement of conductivity was made between two platinum plates (1 cm x 1 cm in size) placed one centimetre apart. This method simplifies the theoretical interpretation of results. However, in practice it results in a plating effect when current flows, and reduces the conductivity electrode performance. This type of sensor is relatively expensive to manufacture and fragile.

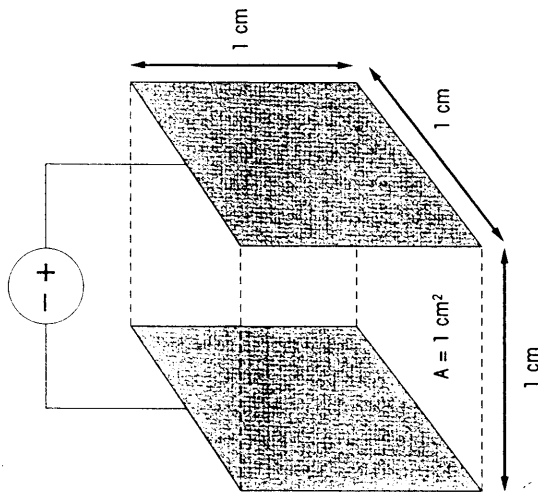


Fig. 2: Traditional 2-plate cell

Because conductivity values are affected by cell geometry, specific conductivity (C) should be used. This compensates for cell geometry and standardises conductivity measurements.

If the cell is filled with a solution of conductance, G , the conductivity between the electrodes is given by the expression

$$C = \frac{G \cdot L}{A}$$

where: C = conductivity in Siemens per cm (S/cm)
 G = conductance in Siemens (S)
 L = distance between electrodes (cm)
 A = plate area of the electrodes (cm²)

As the cell dimensions change, the cell constant varies as the ratio of L to A .

In the traditional cell using 1 cm squares of platinum, 1 cm apart, the cell constant (L/A) is 1.0 and the conductance reading in microsiemens is numerically equal to the conductivity in $\mu\text{S/cm}$.

For low conductivity solutions, the electrode can be placed closer together (reducing L) to give cell constants of 0.1 and 0.01 cm⁻¹.

This raises the conductance between the platinum plates and makes it easier for the electronic circuitry to obtain a result. Similarly, for high conducting solutions, L can be increased to give a cell constant of 10.0 or more.

Alternative sensors have been developed to overcome the problems associated with traditional cells. They operate on a four ring principle. These are arranged concentrically, one above the other, on the probe.

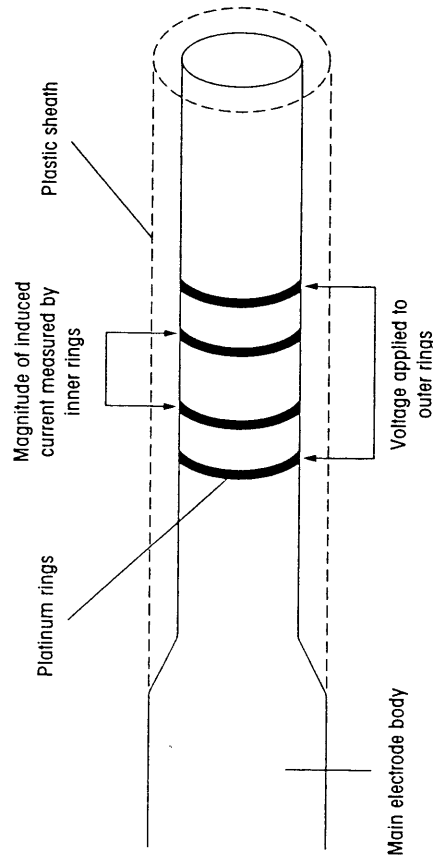


Fig. 3: 4 ring conductivity cell

An alternating voltage is applied to the two outer rings. In the sample solution, the voltage induces a current, whose magnitude is dependent upon the number of ions in solution. Therefore, the current measured by the inner sensing rings gives a direct value for the conductivity of the solution.

The AC current measured is converted to a DC value by the electronic circuitry within the sensor. It is the DC value that is converted to a sample result by the meter. These measurements are volume dependent. The outer sheath of the probe ensures that the volume of sample solution remains constant for all analyses.

By relating the conductivity of a standard solution to its concentration, a value for Total Dissolved Solids (TDS) can also be determined.

Temperature effects

The conductivity of a solution will increase with temperature. The effect is usually expressed by a change of conductivity (as a percentage) per degree Celsius.

This is often called the 'slope' or temperature coefficient (α) of the solution.

For example, ultra pure water has a slope of 5% / °C whereas concentrated samples may be at the 1% / °C level. (See table 1 for further examples of α values).

Temperature sensors, whose characteristics are similar to those of the sample solutions, are used in conjunction with the meter circuitry to determine the exact solution temperature and to display a conductivity reading at a chosen reference temperature (usually 20°C or 25°C).

For accurate measurements, samples and standards should be at a similar temperature, preferably at the chosen reference temperature.

Substance @ 25°C	Concentration %	Temperature coefficient (α)
HCl	10	1.56
KCl	10	1.88
NaCl	10	2.14
HF	1.5	7.20

Table 1: α values

Applications

Industrial heating and cooling systems use recirculating water. Evaporation can lead to a high level of dissolved solids resulting in precipitation and scaling within the plant. Conductivity measurements can monitor the effectiveness of these systems and in particular the status of boilers and cooling towers. Swimming pools and other closed water systems are also monitored.

In the chemical industry, the conductivity of effluent streams can quickly indicate spillage or leakage problems. Similarly, the environmental sector can use conductivity measurements to highlight pollution problems caused by industrial outflows.

Chemical processes using high purity, low conductivity water can be monitored for contaminants with conductivity measuring equipment.

In solutions, H^+ and OH^- ions give high conductivity readings and this forms the basis for using conductivity as an endpoint detector in acid-based neutralisation systems.

The preference for a conductivity system over the use of pH electrodes is the robustness of the conductivity probes and the fact that they can operate at higher pressures and temperatures than conventional pH electrodes.

Sample type	Conductivity @ 25°C ($\mu S/cm$)
Pure water	0.055
Distilled water	0.5
Boiler feed water	1.0
Natural streams	1.0
Mains water supply	50.0
Portable water	1060
0.01 M KCl standard	1413
Sea water	50,000
10% NaOH	355,000
31% HNO_3	865,000

Table 2: Conductivity values

Measurement of conductivity

Equipment

1. Meter and conductivity electrode
2. Standard solution (84 μ S/cm, 1413 μ S/cm, 12.88mS/cm or 80mS/cm)

Calibration of System

1. Fit sensor to meter module, ensuring outer sheath is in place.
2. Switch on meter module.
3. Calibrate as instructed in the manual.
4. Wash the probe thoroughly with distilled water to prevent carryover to sample solution.

Measurement of Sample

Immerse sensor in sample solution. Measure the sample as instructed. The result in milli or microsiemens per centimetre will be displayed.

For TDS readout, select the required factor and follow the instructions to obtain a TDS reading on the meter display.

Troubleshooting guide

Installation

The 4-ring conductivity cell has a robust, solid state design. Fit the cell to the meter.

For optimum performance:

1. Make sure the clear plastic sheath is in place when measuring.
2. Ensure that the solution is above the cell chamber rings and below the vent hole before measuring.
3. To prevent carryover from high to low conductivity solutions rinse with distilled water between measurements.
4. Make sure the cell chamber is bubble free when measuring. To reduce air bubbles, immerse the probe in the solution at an angle and then raise to a vertical position.
5. Allow sufficient time for the sensor to stabilise when measuring samples of different temperatures. Manual endpointing is advised with these samples.
6. Clean the probe and sheath with distilled water after use.

Glossary of terms

Automatic temperature compensation

Automatic instrumental adjustment of displayed conductivity to correct for temperature variations. This is achieved by using thermistor built into the conductivity probe.

Calibration

A means of maintaining the accuracy of the electrode by fixing a zero point and one other point of reference using a standard calibrant that is closest to the expected range of sample readings. Calibration should be performed regularly to obtain optimum performance.

Cell constant

This defines the volume (of solution) between the electrodes of a conductivity cell. Solutions with a high conductivity require a sensor with a cell constant greater than 1.0. For low conductivity samples a sensor with a constant less than 1.0 is needed.

Conductivity

Electricity is the flow of electrons. This indicates that ions in solution will conduct electricity. Conductivity is the ability of a solution to pass current. The conductivity reading of a sample will change with temperature.

Endpoint (Automatic/Manual)

If the automatic mode is selected for sample measurement, the meter waits for the reading to stabilise. The display is then frozen to give the sample result. The manual mode requires the operator to freeze the display, via a keypad function, when stabilisation is reached.

Reference temperature

Each conductivity reading is referenced to a specific temperature, typically 20°C or 25°C, for comparative purposes.

Resistivity

This is the reciprocal of the conductivity value and is measured in ohms. It is generally limited to the measurement of ultrapure water whose conductivity is very low.

Response time

The time taken for an electrode to reach a stable reading when it is removed from one solution and placed in another of a differing conductivity. This depends on the magnitude of the change as well as the electrode condition and temperature variation.

Standard solution

A solution of known concentration that is used to standardise or calibrate an analytical instrument.

Total Dissolved Solids (TDS)

This is the measure of the total concentration of ionic species of a sample. Its magnitude is relative to the standard solution used to calibrate the meter. For example, a high TDS value means a high concentration of dissolved solids which may indicate pollution by ionic chemical species.

TDS factor

Conductivity readings are converted to TDS readings by multiplication with a known mathematical factor. The meter has a range of factors based upon the reference material used to prepare the calibration standard. Commonly, KCl and CaCO_3 are used.

Units of measure

The conductivity of a solution is given in $\mu\text{S}/\text{cm}$ or mS/cm . TDS is expressed in mg/L or g/L .

SECTION 2 Dissolved oxygen

Theory of dissolved oxygen measurement

Introduction

Oxygen, making up one-fifth of the Earth's atmosphere, is one of the most important elements. Combination of oxygen with other substances is the means by which energy is released in living cells. However, life can only be supported when the concentration of oxygen is within certain limits, hence the importance of oxygen measurements.

Oxygen was not identified in science until 200 years ago, while methods of analysis have only been available during this century.

Before the advent of polarography, methods for the analysis and measurement of oxygen were slow and laborious. In the early days of polarography, when dropping mercury electrodes were used, oxygen was considered an undesirable interference because the current resulting from its easy reduction could mask the reduction of other substances.

Solid cathodes, usually of platinum rather than dropping mercury, were employed when physiologists began to use polarography to measure oxygen tension in living tissues in the 1940's. Electrodes had to be designed for an analytical situation, since the sample could not be processed to meet the requirements of the electrodes. There was no satisfactory means of treating or purifying the living tissue sample, nor of controlling or evaluating the stirring effects taking place. Electrode materials were changed, however, by direct exposure to the complex chemicals found in blood and tissues, and many ingenious methods were invented to handle specific measurement situations. The problem of protecting the electrodes from the analytical environment was generally solved by Dr Leland Clark's development of the membrane-covered electrode which provided a more uniform diffusion layer for oxygen and largely prevented the entrance of unwanted substances.

Operating Principles

Oxygen probes have a noble metal cathode and a silver anode. The noble metal can be silver, gold or platinum. These elements are electrically connected in a potassium chloride solution separated from the sample medium by a gas permeable membrane.

The physical properties of oxygen are related to temperature, so a thermistor is often fitted in the probe to give temperature compensation. A constant voltage is placed across the cathode and anode. Molecular oxygen diffuses through the membrane and is reduced at the cathode by the applied voltage. This electrical process results in a current flow.

The instrument detects this current which is proportional to the PARTIAL PRESSURE of oxygen. The IDEAL GAS LAW expresses the proportional relationship between gas pressure P and n, the number of gas molecules present.

$$PV = nRT$$

(where R = Gas Constant, T = Temperature in Kelvin)

This relationship, and the ability of the meter to compensate for temperature changes, allows results to be expressed as percentage oxygen or mg/L O₂.

Relationship between Partial Pressure and % Oxygen

Air is a mixture of gases in which oxygen contributes 21% of the total pressure. Consider a volume of air at atmospheric pressure, 760 mm. 21% of this pressure 160 mm, is contributed by oxygen.

If the total pressure on this system is doubled to 1520 mm, the partial pressure also doubles to 320 mm. The relative percent of the oxygen is still 21%. However, the sensor and instrument would see a two fold increase in the oxygen concentration since the sensor is only responding to the partial pressure of oxygen.

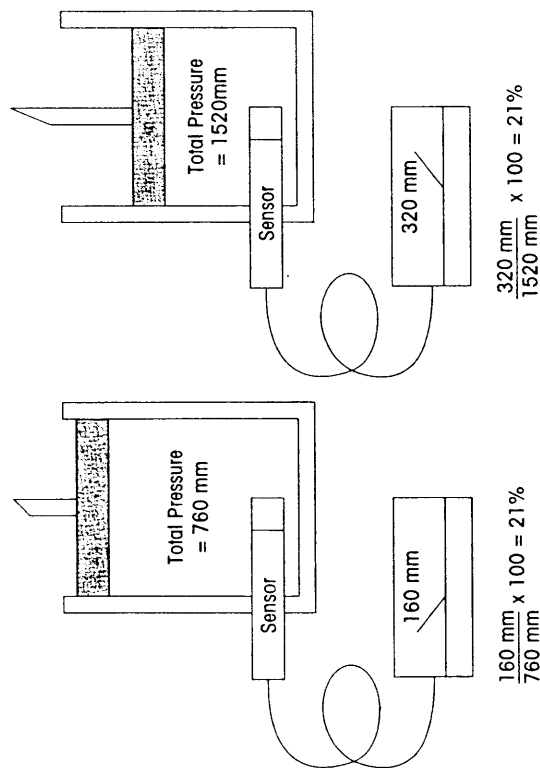


Fig. 4: Relationship between partial pressure and % oxygen

For this reason, air calibration of this system in the percent oxygen mode is valid only if the gas mixture is under a total pressure of one atmosphere. Sample correction can be made to convert oxygen partial pressure values to percent oxygen at other pressures as follows:

$$\begin{aligned} \text{Actual } \% \text{ O}_2 &= \frac{\text{Indicated Percent Oxygen} \times \text{Atmospheric pressure (mm Hg)}}{\text{System Pressure (mm Hg)}} \\ &= \frac{\text{Instrument Reading} \times \text{Atmospheric pressure (mm Hg)}}{\text{System Pressure (mm Hg)}} \end{aligned}$$

Gases are soluble in liquid to varying degrees. This solubility, expressed as a molefraction, is proportional to the partial pressure of the gas over the liquid (Henry's law). For most dissolved oxygen applications, the desired units are parts per million, ppm (when liquid density is 1 g/cm³, ppm equals mg/L O₂). The molefraction is easily converted to these units.

Percent Saturation

Percent Saturation is another parameter that is frequently used. This is the amount of oxygen the liquid can hold at that temperature. For a given liquid, a constant relationship holds between percent saturation and concentration at various temperatures. This relationship must be determined experimentally.

To illustrate this relationship, consider a container of 100% air saturated water. As the container is heated and the water begins to boil, bubbles of air form in the container. These bubbles would eventually rise to the surface and then leave the liquid.

One would intuitively conclude that the concentration of air in the solution has decreased, however, the water would still be 100% saturated with air at that temperature.

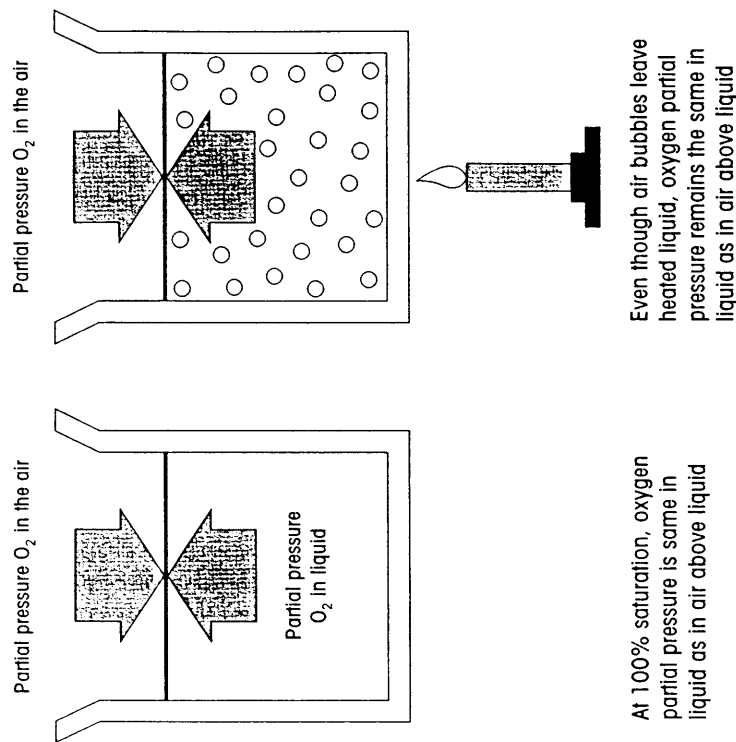


Fig. 5: Relationship between % saturation and concentration

Salinity

The ionic strength (salt content) of natural and waste waters has a considerable effect on dissolved oxygen levels. In order to obtain dissolved oxygen results, correction for salting-out effects have to be made. Such effects greatly reduce electrode sensitivity.

Salinity has been defined traditionally as the total solids in water after all carbonates have been converted to oxides, all bromide and iodide to chloride and all organic compounds oxidised. However, for practical purposes, the definition of salinity is based upon the conductivity of seawater relative to a specified potassium chloride solution. Therefore, the measurement of solution conductivity greatly simplifies the calibration and usage of dissolved oxygen measuring systems.

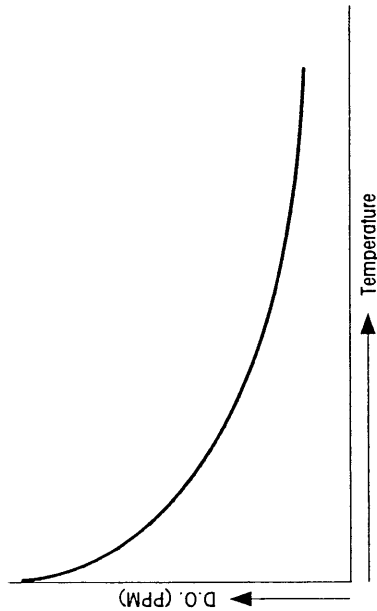


Fig. 6: Relationship between dissolved oxygen and temperature

PPM Dissolved Oxygen Versus Temperature

This phenomenon of decreasing solubility of gases at increasing temperature can be accounted for by the thermodynamic relationship between free energy and entropy. If the temperature were held constant, then the relationship between percent saturation and concentration (ppm) may be established. It can be seen that percent saturation is linearly proportional to concentration. As mentioned before, the exact relationship between percent saturation and concentration must be determined experimentally for each different sample.

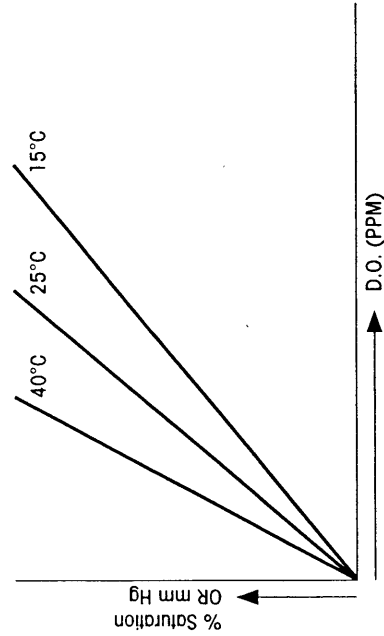


Fig. 7: Temperature dependence of relationship between % saturation and concentration

Oxygen probes

The three types of oxygen sensors in common use are the oxygen balance, the polarographic and the galvanic probe. They are more convenient than chemical titration methods, and each is capable of accurate measurement.

The Oxygen Balance Probe

The oxygen balance sensor has three electrodes. The electrolyte is typically potassium hydroxide. A reference electrode senses the voltage applied to the cathode and anode and feeds this signal to a separate amplifier which drives these electrodes by providing a varying current sufficient to maintain the flow of oxygen. When the sensor is immersed in a sample, oxygen diffuses through the membrane and is reduced at the cathode while an equivalent amount of oxygen is generated at the anode. The diffusion continues until the oxygen tension on both sides of the membrane is equal. The current necessary to maintain this balance is converted to a read-out of the partial pressure of dissolved oxygen.

While the oxygen balance cell consumes oxygen, it also generates an approximately equal amount, thereby reducing the need for stirring; though experiments have shown that sample flow does affect readings to some degree.

Commercially available units are supplied with permanent membranes, essentially eliminating the need for probe maintenance, but necessitating replacement of the sensor if the membrane is torn or becomes fouled. When the sensor is replaced, the instrument must be recalibrated.

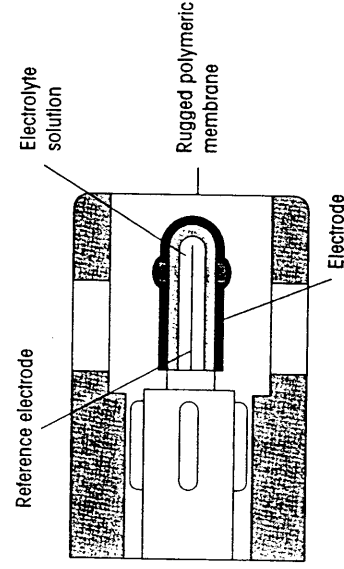


Fig. 8: Oxygen balance probe

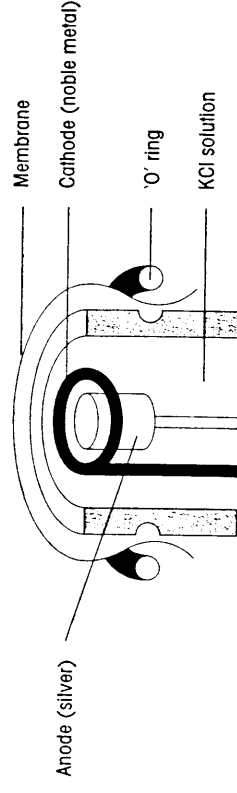


Fig. 9: Polarographic probe

The Polarographic Probe

In a typical polarographic probe the silver anode is surrounded by a noble metal cathode. Temperature sensing elements provide both temperature compensation and temperature measurement. A potassium chloride electrolyte is contained by a membrane held in place with a rubber O-ring. The sensor end of the probe is normally covered by a guard to protect the working elements from damage.

For each oxygen molecule that comes in contact with the cathode, a proportional current travels through the circuit. This provides the basis for an oxygen analyser.

The Galvanic Probe

The galvanic probe is the simplest, because it produces its own electric current. However, it needs a power source to operate the temperature compensating circuitry. The electrodes are usually silver and lead, and the electrolyte potassium hydroxide. As with the Clark electrode, galvanic potential is developed by the reduction of oxygen on a surface that acts as both catalyst and cathode. The current produced is proportional to the quantity of oxygen reduced.

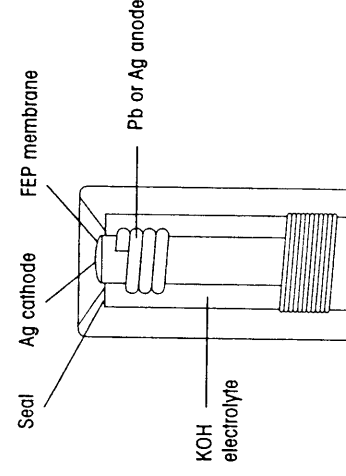


Fig. 10: Galvanic probe

The ruggedness of the galvanic sensor, combined with its high current output, makes it reliable for long-term monitoring of dissolved oxygen in heavy-duty applications such as aeration basins. Since the sensor consumes oxygen, a continuous flow of sample past the sensor is necessary to remove the oxygen-depleted sample in front of the membrane.

Commercially available galvanic sensors are typically provided in physical configurations which allow membrane changing and other probe maintenance by the user to prolong probe life.

Choosing an oxygen probe: Polarographic or Galvanic?

In practice, a choice has to be made between a polarographic and galvanic probe. Both types of sensor operate on the same electrochemical principle with molecular oxygen being reduced at the cathode. The current resulting from this reduction is proportional to the partial pressure of dissolved oxygen and therefore the concentration of dissolved oxygen can be determined.

In the galvanic probe the electrode and electrolyte system is chosen in order to generate its own potential. The polarographic type uses a polarising voltage. Both types use a membrane to separate the electrochemical cell from the test solution.

The polarographic sensor has the advantage that an optimal polarisation voltage can be chosen. A barrier between the cathode and silver anode is necessary to avoid plating of the cathode by silver diffusion. The anode can be poisoned by hydrogen sulphide diffusing through the gas permeable membrane causing a shift of anode potential.

Poisoning of the zinc or lead anode in a galvanic cell is also a problem. However, the generated voltage may not be ideal and any carbon dioxide that may be present will precipitate zinc or lead carbonate and reduce the active electrode surface and lower the output current.

Several important design features make the polarographic sensor the preferred type. The large cathodes of galvanic sensors require high rates of sample flow to achieve stable readings. Without sufficient agitation readings will be unstable. The polarographic sensor can operate reliably for long periods with minimal output noise due to its small cathode.

The membranes of polarographic sensors are typically thicker than the galvanic type and therefore have a longer working life. This is because the membranes of galvanic sensors must be relatively thin to give reasonable response times.

Insoluble reaction products quickly deactivate a galvanic cell but cathode precipitation is eliminated by the design of the polarographic sensor.

Galvanic sensors are active at all times and will degrade in storage as well as during use. Polarographic sensors are only active when polarised and by definition have a longer working lifetime.

Applications

The level of dissolved oxygen in natural waters is often a direct indication of quality, since aquatic plants produce oxygen, while micro-organisms generally consume it as they feed on pollutants. At low temperatures the solubility of oxygen is increased, so that in winter concentrations as high as 20 ppm may be found in natural waters while saturation levels in the summer may be as low as 4 or 5 ppm.

Dissolved oxygen is essential for the support of fish and other aquatic life and aids in the natural decomposition of organic matter. Waste treatment plants which employ digestion techniques must maintain a level of at least 2 ppm dissolved oxygen. This is usually accomplished by some form of mechanical aeration.

At elevated temperatures, oxygen is highly corrosive to metals, causing "pitting" in ferrous systems such as high pressure boilers and deep well oil recovery equipment. To prevent costly corrosion damage, the liquids in contact with the metal surfaces must be treated, usually by a combination of physical and chemical means. Deaeration can reduce the dissolved oxygen concentration of boiler feedwater from several ppm to a few ppb (parts per billion).

Chemical reducing agents such as hydrazine or sodium sulphite are sometimes used instead of deaeration but more often are used to react with residual oxygen which remains after the deaeration process.

A common application is the five day Biochemical Oxygen Demand (BOD) test. This measures the oxygen required for the biochemical degradation of organic material and that used to oxidise inorganic compounds such as sulphide and ferrous ions. It will also measure the oxygen needed to oxidise the reduced form of nitrogen (nitrogenous demand). The BOD test indicates the pollution strength of wastewaters and is used to measure the status of domestic as well as industrial supplies.

Factors influencing dissolved oxygen measurement

Calibration of system

With modern instrumentation a single air calibration should be employed on a regular daily basis. A standard solution, prepared from sodium sulphite, is occasionally used to check the zero oxygen calibration point.

It is a quick, simple and highly reliable procedure. The air layer outside the membrane, covering the cathode, does not become oxygen depleted, and therefore provides the ideal standard solution.

Correction for Salinity and Barometric Pressure

The correction for these parameters is carried out automatically by modern, microprocessor driven instruments.

Measuring samples

Place the probe in the sample and allow the temperature to stabilise. Stir for 30 to 60 seconds and take the meter reading when the display is stable. Depending on probe condition, temperature and oxygen level, the response time for oxygen measurement may vary from 30 seconds to 2 minutes.

Interferences

Any coating of the membrane will affect readings. It is better to store probes in moist air rather than water to reduce the possibility of algae growth.

The measurement of oils and slurries will also increase the frequency of probe cleaning. Strong solvents, acids and alkalis may also damage the probe materials. The presence of other gases, such as chlorine, nitrous oxide and nitric oxide, may also interfere with measured oxygen levels.

Sulphur based molecules such as H_2S and SO_2 are also known to interfere with oxygen measurements, along with the inert gases such as neon.

Electrode tarnishing

The cathode can be tarnished by extended exposure to H_2S and SO_2 . As the anode tarnishes it will get darker. This poisoning will reduce sensitivity and even prevent system calibration. A tarnished silver anode can be rejuvenated by soaking the probe overnight in 3% ammonium hydroxide. The anode and cathode can be polished with cleaning compound. After washing with distilled water and DO electrolyte, the probe, fitted with a new membrane cap, is fully reconditioned.

Measurement errors

These may be due to :

1. Instrument related errors such as meter non-linearity, incorrect salinity or temperature compensation.
2. User errors resulting from calibration and measurement procedures.
3. Probe related errors due to non-linearity, background interference and incorrect set-up of the membrane cap.
4. Calibration errors caused by using incorrect standard solutions, and non-allowance for temperature and barometric pressure fluctuations.

Measurement of dissolved oxygen

Equipment

1. Meter and DO electrode
2. Zero oxygen solution

Setting Up DO Sensor

The sensor may be supplied dry and must be filled before use.

1. Unscrew the membrane cap from sensor and fill using the manufacturer's DO electrolyte.
2. Tap membrane cap gently to remove air bubbles. Gently screw cap onto probe body allowing surplus electrolyte to run out. (Caution: Do not overtighten)
3. Fit sensor to meter module.
4. Allow 1 hour for polarisation of electrode.

Calibration

For greater accuracy, calibrate the meter daily.

1. Remove wetting cap from tip of sensor. Switch on meter.
2. Calibrate the instrument as instructed using the air calibration method. Correct for salinity and barometric pressure if required.

Measuring Sample

Place sensor in sample. Measure the sample as instructed. The sample result will be displayed on the meter.

Troubleshooting guide

Installation

DO membrane caps are fragile. Handle with care to prevent damage. Sensors shipped dry must be filled before use. Unscrew the membrane cap from the sensor. If the electrode tip is tarnished clean carefully using electrode cleaning compound or silver polish, paying particular attention to the cathode.

Rinse tip with DO electrolyte, and fill membrane cap, avoiding air bubbles. Hold the sensor vertically and gently screw the membrane cap onto the sensor, allowing surplus electrolyte to run out. Fit sensor to the meter and allow a minimum of 1 hour for polarisation. Calibrate as instructed.

For optimum performance

1. Before use remove wetting cap from tip of sensor.
2. To maintain polarisation and to enable immediate use, the sensor should be kept connected to the meter. For extended storage remove the membrane cap and rinse with water, and clean the sensor tip. Store dry with the membrane cap loosely fitted. Do not fit wetting cap.
3. When making measurements the sample should be stirred at a constant speed i.e. approximately 20 cm/second (8 inches/second).
4. Allow sufficient time for the sensor to stabilise when measuring samples of different temperatures - in some cases this can be several minutes. Manual endpointing is advised with these samples. Make sure the sensor is immersed to a depth that covers the temperature sensing element.
5. After use replace wetting cap containing 1 or 2 drops of distilled water to prevent electrolyte from drying out.
6. Regular maintenance is important to ensure optimum performance. Replacement of membrane caps depends on usage - we recommend replacement when the response time at room temperature exceeds two minutes.

Maintenance and Troubleshooting

If the sensor will not calibrate, or becomes sluggish or erratic:

1. The sensor tip may become tarnished with time. For optimum performance clean the tip and refill the cap every 2 weeks as described in the installation section.
2. The zero oxygen solution will absorb oxygen if left exposed to air and this will cause inaccurate calibration. Use fresh zero oxygen solution.
3. Make sure there are no air bubbles inside the membrane cap when filling with DO electrolyte.
4. Check the membrane for damage and replace with new cap as necessary.

Glossary of terms

Automatic Temperature Compensation

Automatic instrumental adjustment of displayed dissolved oxygen to correct for variations in temperature. This is achieved by using a thermistor built into the dissolved oxygen probe.

Barometric Pressure

Dissolved oxygen levels vary with barometric pressure. Modern meters automatically compensate for changing air pressure values. Older instruments are manually adjusted with reference to the following table.

Pressure (mm)	Setting	Pressure (mm)	Setting
600	79	680	90
620	82	700	92
640	84	720	95
660	87	740	97
		820	108

BOD

Biochemical oxygen demand, a test which determines the amount of dissolved oxygen used by aerobic organisms and chemical action in a sample of water over a five day period.

BOD Bottle

A glass bottle, usually with a ground glass neck and of 250 mL capacity, used to hold the sample of water during the BOD test. However, many variants are found, often with differing capacities.

Calibration

A means of maintaining the accuracy of the electrode by fixing a zero point and one other point of reference (100% saturation / 100 mg/L). Calibration should be performed regularly to obtain optimum performance. It must be remembered that the second point of the calibration should be adjusted for variations in barometric pressure and also for variations in the salinity of the sample. In practice better results will be obtained when the temperature of the calibrants is similar to that of the sample under test.

D.O.

The amount of molecular oxygen (O₂) dissolved in aqueous solution measured either as a percentage saturation (% O₂) or as mg/L (ppm).

Drift

Slow changes in the reading from the electrode while maintained in a solution at constant temperature.

Electrolyte

Solution placed in membrane cap prior to analysis.

Endpoint (Automatic/Manual)

If the automatic mode is selected for sample measurement, the meter waits for the reading to stabilise. The display is then frozen to give the sample result. The manual mode requires the operator to freeze the display, via a keypad function, when stabilisation is reached.

Membrane

Polymeric membrane, which permits passage of oxygen molecules to cathode/anode. The membrane is stretched over the electrode elements and should not be overtightened or it will puncture. When filled, the membrane cap should be slowly screwed onto the electrode body, allowing the electrolyte to seep out at the top, and adjusted to the correct tension.

Polarisation

Procedure ensuring that cathode and anode give optimum reduction of oxygen molecules during analysis.

Response Time

The time taken for an electrode to reach a stable reading when it is removed from one solution and placed in another of differing dissolved oxygen content. This depends on the magnitude of the change as well as the electrode condition and temperature variation.

Salinity

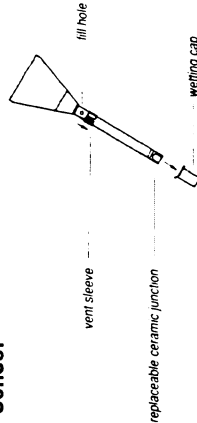
Dissolved oxygen levels vary with salinity. Modern meters automatically compensate for variations in sample salinity. Older meters are adjusted manually with reference to the following table.

Conductivity (mS)	Salinity (g/L)	Setting	Conductivity (mS)	Salinity (g/L)	Setting
—	0.0	100	24	12.5	88
6	2.5	97	27	15.0	85
11	7.5	93	31	17.5	82
20	10.0	90	34	20.0	81

Sensor Information

for direct fitting and leaded pH, DO and Conductivity Sensors

• pH Sensor



For optimum performance:

1. Before use remove wetting cap from tip of sensor, and slide the vent sleeve to expose the fill hole.
2. Make sure that the fill solution is not more than 25 mm (1 inch) below the fill hole. Add KCl solution if necessary.
3. Gently tap the sensor to remove any air bubbles at the ceramic junction.
4. Condition the new sensor by soaking the tip in 1-2 cm of pH 7 buffer for 2 hours. Prolonged soaking is not recommended.
5. Calibrate and measure samples as described in the M90 instructions. Allow sufficient time for the sensor to stabilize when measuring samples of different temperatures, or of low ionic strength. Manual endpointing is advised with these samples.
6. After use, check the level of fill solution, reposition the vent sleeve to cover the fill hole, and replace the wetting cap containing pH 7 buffer (if the sensor will not be used again for more than 2 days, we recommend using saturated KCl in the wetting cap).

Precautions and Limitations:

1. Do not wipe the sensor tip - blot dry with a lint-free tissue.
2. Do not use KCl solution saturated with AgCl as this may damage the reference element.
3. Do not leave the sensor in organic solvents or strong basic solutions for extended periods. Measurements made in these solutions should be taken quickly and the sensor rinsed immediately with distilled water. After rinsing, soak in 7.0 buffer for two hours.
4. Do not measure solutions that exceed a temperature range of 0-100°C.
5. Do not allow the electrode to go dry. Always maintain the fill solution level within one inch (2.5 cm) of the fill hole.

Maintenance and Troubleshooting

Prolonged use and aging may reduce performance i.e. slow response, low slope values, continuous drift or erratic readings. These may be caused by:

Air in junction - remove air bubbles by gentle tapping

Excess KCl crystals - KCl crystals may build up and settle on the sensor tip, or the KCl may become discolored. Remove the old fill solution and use warm distilled water to dissolve the crystals. Remove water and refill using fresh KCl solution.

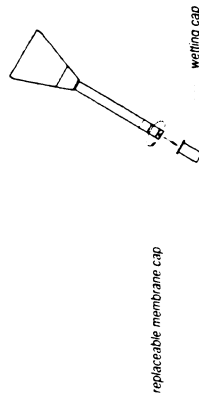
Blocked junction - some samples can block the junction. To test for this, blot the tip dry using a lint-free tissue, and air dry for 20 minutes. If no KCl appears at the tip of the sensor the junction is blocked. Remove the ceramic junction using tweezers, and insert new junction (Cat. 477269). Tap gently to remove any air bubbles.

Contaminated pH bulb - i.e. protein/oil contamination.

- Protein: soak the sensor in 10% pepsin solution adjusted to pH 2 with HCl for 30 minutes. Rinse with distilled water and soak tip in 1-2 cm of pH 7 buffer for 2 hours.

- Oil: wash sensor tip with 50% water-acetone solution. Do not soak the sensor in acetone solution as this may cause the seals to deteriorate. Rinse with distilled water and soak in pH 7 buffer for 2 hours.

• Dissolved Oxygen Sensor



Installation:

DO membrane caps are fragile. Handle with care to prevent damage. The sensor is shipped dry and must be filled before use. Unscrew the membrane cap from the sensor. Polish the silver/gold tip carefully using electrode cleaning compound or silver polish, paying particular attention to the gold cathode. Rinse tip with DO electrolyte, and fill membrane cap, avoiding air bubbles. Hold the sensor vertically and gently screw the membrane cap onto the sensor, allowing surplus electrolyte to run out. Fit sensor to the meter and allow 30 minutes minimum for polarization. Calibrate as described in M90 instructions.

For optimum performance:

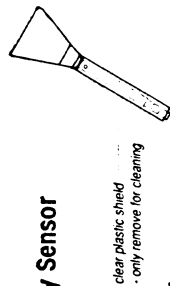
1. Before use remove wetting cap from tip of sensor.
2. For immediate use the sensor should be kept connected to the meter. The sensor may be removed for up to 3 hours as a rechargeable battery in the sensor will maintain polarization. For extended storage remove the membrane cap and rinse with water, and clean the sensor tip. Store dry with the membrane cap loosely fitted. Do not fit wetting cap.
3. When making measurements the sample should be stirred at a constant speed i.e. approximately 20 cm/second (8 inches/second).
4. Allow sufficient time for the sensor to stabilize when measuring samples of different temperatures - in some cases this can be several minutes. Manual endpointing is advised with these samples. Make sure the sensor is immersed to a depth of at least 40 mm (1.5 inches) to cover the temperature sensing element.
5. After use replace wetting cap containing 1 drop of distilled water to prevent electrolyte from drying out.
6. Regular maintenance is important to ensure optimum performance. Replacement of membrane caps depends on usage - we recommend replacement every 2 to 4 weeks.

Maintenance and Troubleshooting

If the sensor will not calibrate, or becomes sluggish or erratic:

1. The silver/gold sensor tip will become tarnished. For optimum performance polish the silver / gold tip and refill cap every week as described in Installation.
2. The zero oxygen solution will absorb oxygen if left exposed to air and this will cause inaccurate calibration. Use fresh zero oxygen solution.
3. Make sure there are no air bubbles inside the membrane cap when filling with DO electrolyte. Check by looking up through the membrane from the bottom of the sensor.
4. Check the membrane for damage and replace with new cap (Cat. 473626) as necessary.

• Conductivity Sensor



For optimum performance:

1. Make sure the clear plastic shield is in place when calibrating or measuring.
2. When measuring make sure the solution is above the cell chamber rings and below the vent hole.
3. To prevent carry over from high to low conductivity solutions rinse with distilled water between measurements.
4. Make sure the cell chamber is bubble free when measuring. To reduce air bubbles, immerse probe in the solution at an angle and then raise to a vertical position.
5. Allow sufficient time for the sensor to stabilize when measuring samples of different temperatures. Manual endpointing is advised with these samples.
6. Sensor is not recommended for low ionic strength solutions (<5 mg/L).
7. Clean the probe and shield with distilled water after use.

General Troubleshooting for all Sensors:

1. To verify meter is working check using the test plug.
2. If the sensor connector becomes damaged or wet the display may read E4 when a sensor is connected.
3. If the temperature sensing element becomes damaged the temperature display may read E1 when a sensor is connected.

Ordering Information:

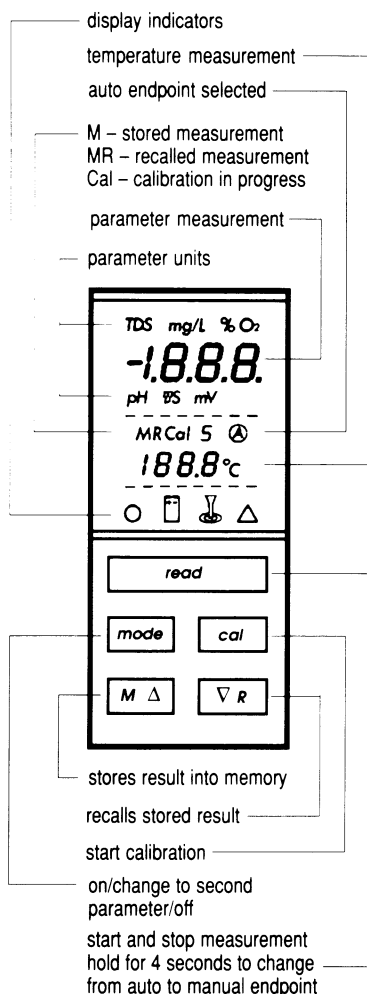
Item	Cat.
pH Sensor	473619
3M KCl 6 x 125 mL Pack	477006
pH 7 buffer sachet (pack of 30)	473650
pH 4 buffer sachet (pack of 30)	473651
pH 10 buffer sachet (pack of 30)	473652
pH multipack, pH 4, 7, and 10 (pack of 32 assorted sachets)	473676
Buffer solution pH 4.00, 2 x 500 mL (red)	478540
Buffer solution pH 7.00, 2 x 500 mL (yellow)	478570
Buffer solution pH 10.01, 2 x 500 mL (blue)	478510
Buffer rainbow pack, pH 4.00, 7.00 and 10.01 (2 x 500 mL of ea)	478574
Replaceable ceramic junctions (pH), pack of 3	477269
DO sensor	473620
DO electrolyte, 3 x 5 mL	474594
Zero oxygen solution, 500 mL	473625
Zero oxygen solution sachet (pack of 30)	473739
DO membrane replacement kit, pack of 2	473626
pO ₂ electrode cleaning compound	477656
Conductivity/TDS sensor	473621
1413uS conductivity standard, 500 mL	473623
12.88 mS conductivity standard, 500 mL	473624
1413uS conductivity standard sachet (pack of 30)	473738
12.88 mS conductivity standard sachet (pack of 30)	473737
Rinse solution sachet (pack of 30)	473653

Corning Incorporated
Corning, New York 14831
USA
1-800-222-7740 or 1-607-974-0353

090 91 002C Rev. E, 11/95

M90 Operating Instructions

The M90 is a portable, microprocessor based, pH, conductivity and dissolved oxygen meter.



Installing the Battery . . .

Remove rubber battery door on the rear of the meter.
Fit battery - alkaline type 9V or equivalent. Make sure polarity is correct when fitting. The meter must be calibrated after replacing the battery.

Installing a Sensor . . .

Locate the pins of the sensor in the meter and push firmly into the meter. The sensor is removed by squeezing down the catch at the rear and pulling the sensor away from the meter.

Making a Measurement . . .

pH – remove the sensor wetting cap and slide the vent sleeve to expose the fill hole.

D.O. – remove the sensor wetting cap. Move the sensor in a gentle circular motion when measuring.

Cond – immerse probe to halfway point in solution.

Press **mode**, **read**, **cal** or **M** to turn meter on and start measurement. Place sensor into solution. Automatic endpoint detection freezes the display when plateau is reached; to manually endpoint press **read**. Press **read** again to start new measurement.

Continuous measurement may be selected by pressing and holding **read** for 4 seconds. (In this mode battery consumption is higher and the meter will not automatically switch off when not in use.)

Return to auto endpoint by pressing and holding **read** for 4 seconds.

After use, close the fill hole (pH) and replace the wetting cap (pH and DO).

Calibrating . . .

For greater accuracy, calibrate the meter regularly.

First Cal Point

Place the sensor in the calibrating medium:

pH pH 7 buffer 7.00 pH (at 25°C)
Cond Hold in free air 0.00 μ S
TDS Hold in free air 0.00 mg/L
DO Zero oxygen solution 0. %O₂
(mg/L O₂ is calibrated in %O₂ mode).

Press **cal** – cal 1 is displayed. After endpointing the display automatically updates to the calibrated value shown, or the temperature compensated value.

If **read** is pressed after Cal 1 update, the meter assumes one point calibration only is required. Samples can now be measured.

Second Cal Point

Place the sensor in the second calibration medium:
pH pH 4 or 10 buffer 4.00 or 10.01 pH (at 25°C)
Cond Cond std. A or B 1413 μ S or 12.88 mS
TDS Cond std. A or B 706 mg/L or 6.44 g/L
DO Hold in air 10 mm
above fresh water 100 %O₂

Press **cal** – cal 2 is displayed. After endpointing the display automatically updates to the calibrated value shown or the temperature compensated value.

Dissolved oxygen only

In practice, cal 2 is required more frequently than cal 1, this is achieved by pressing **cal** twice to advance directly to cal 2.

In mg/L O₂ mode, correction may be made for salinity and barometric pressure. Press **cal** – 100 is displayed. Use $\blacktriangle$ and $\blacktriangledown$ to adjust the display according to these tables:

Cond (mS)	Salinity (g/L)	Setting
–	0.0	100
6	2.5	97
11	5.0	95
15	7.5	93
20	10.0	90
24	12.5	88
27	15.0	85
31	17.5	82
34	20.0	81

Barometric Pressure (mm)	Setting	Barometric Pressure (mm)	Setting
600	79	720	95
620	82	740	97
640	84	760	100
660	87	780	103
680	90	800	105
700	92	820	108

e.g. if salinity = 5 g/L setting = 95
if pressure = 740 mm setting = 97
for both parameters, setting will be 95 x 97% = 92.

Using the Memory . . .

5 measurements can be stored in the memory.

Entering a reading into memory

Press **M** when measurement has endpointed.

M 1 (or M 2 – M 5 if readings have already been stored) is displayed indicating that the reading has been saved. Flashing M indicates memory is full.

Recalling memory

Press **R** – the last saved measurement is displayed. Press **R** again to recall the previously saved measurement. MR 1 to MR 5 indicates which saved measurement is being displayed.

Clearing last memory

In memory recall mode (MR) press **M** to clear the measurement being displayed. Only the last entered measurement can be cleared, i.e. if 4 measurements are saved, the M 2 cannot be cleared without first clearing M 4 and M 3.

Clearing all memory

Press **R** until M C is displayed, then press **M**. All memory will be cleared.

Changing Mode . . .

Press **mode** to enter the second function of the sensor, i.e. pH to mV, conductivity to TDS, %O₂ to mg L O₂.

Press **mode** again to turn the meter off.

Display Codes/Problem Solving . . .

Using the Test Plug

The test plug is provided to test the meter.

Replace the sensor with the test plug and press **read**. The display should read:

7.00 pH $\pm$ 0.5 25°C $\pm$ 2

E1 – measurement out of range: check that sensor is immersed in solution and the wetting cap is removed (if applicable)

E2 – calibration out of range: check correct calibration

E3 – calibration out of range: medium is used.

Condition/renew sensor

E4 – sensor disconnected



low battery voltage



low electrode slope: condition/renew sensor (pH only)



Default calibration values in memory. Sensor not calibrated (2 point), or battery replaced since last calibration



manual endpoint selected (continuous measurement)



auto endpoint selected

keypad not responding - replace battery and recalibrate.

Operating Hints . . .

1. Use distilled water when transferring from one solution to another.
2. Response time is a function of the sensor and the solution. If the solutions are at different temperatures (or ionic strength – pH only) allow more time for the sensor to respond.
3. Avoid handling the sensor tip.
4. Make sure no large air bubbles are trapped under the sensor when making measurements.
5. Do not use calibration standards after the expiration date.
6. Wetting caps should contain:
pH – pH 7 buffer; DO – distilled water.
7. For greatest accuracy calibrants and samples should be at the same temperature.
8. pH – keep the electrode filled with the appropriate fill solution to prevent reading drift.
9. Conductivity – the sensor shield and probe should be kept clean. Make sure no air bubbles are in the cell chamber during measurement.
10. Dissolved oxygen – the sensor can be removed for several hours as a rechargeable battery in the sensor will maintain polarization. For longer periods the sensor should remain connected to the meter to maintain polarization and recharge the sensor battery.

Reordering Information . . .

Item	Cat.
Meter only	473617
pH sensor	473619
DO sensor	473620
Conductivity/TDS sensor	473621
Hard carrying case	473622
1413 μ S conductivity standard (A), 500 mL	473623
12.88 mS conductivity standard (B), 500 mL	473624
Zero oxygen solution, 500 mL	473625
DO membrane replacement kit	473626
pH 7 buffer sachet (pack of 30)	473650
pH 4 buffer sachet (pack of 30)	473651
pH 10 buffer sachet (pack of 30)	473652
pH multipack, pH 4, 7, 10, (pack of 30 assorted)	473676
pH electrode fill solution, 3 x 5 mL	473654
DO electrolyte, 3 x 5 mL	474594
Buffer solution pH 4.00, 2 x 500 mL (red)	478540
Buffer solution pH 7.00, 2 x 500 mL (yellow)	478570
Buffer solution pH 10.01, 2 x 500 mL (blue)	478510
Replaceable ceramic junctions (pH), pack of 3	477269

Meter Specification . . .

Temperature compensation:

pH	0 – 100°C
Conductivity/TDS	0 – 50°C
Oxygen	0 – 40°C

	Range	Resolution
Temp	–0.5°C – 100°C	0.1°C
pH	0 – 14 pH	0.01 pH
mV	0 – $\pm$ 1000 mV	1 mV
Cond	0.00 – 19.99 μ S	0.01 μ S
	20.00 μ S – 199.9 μ S	0.1 μ S
	200 – 1999 μ S	1 μ S
	2.00 – 19.99 mS	0.01 mS
TDS	0.00 – 10.00 mg/L	0.01 mg/L
	10.0 – 100.0 mg/L	0.1 mg/L
	100 – 1000 mg/L	1 mg/L
	1.00 – 10.00 g/L	0.01 g/L
DO	0 – 200% O ₂	1%
	0 – 20.0 mg/L	0.1 mg/L

Auto switch off: if not operated for 10 minutes after endpoint.

Memory: up to 5 measurements can be stored.

Coming Incorporated
Science Products Division
Coming, New York 14831
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Tel: 1-800-222-7740

473655 Rev. B, 10/93

HACH COMPANY

PORTABLE
DISSOLVED OXYGEN
METER
MODEL 16046

MANUAL



GENERAL DESCRIPTION

The Hach Model 16046 Portable Dissolved Oxygen Meter (Figure 1) measures dissolved oxygen (DO) in water in the field as well as in the laboratory. The instrument uses a Clark-type polarographic electrode as the oxygen sensor and can measure DO in the ranges of 0-10 and 0-20 mg/L with the standard membrane. With a high-sensitivity membrane, the instrument will operate in the 0-5 and 0-10 mg/L ranges. Rechargeable batteries provide operating power. Automatic temperature and pressure compensation capabilities are incorporated, and a recorder output in the 0-100 mV range is included. The instrument case has a hinged lid that can be detached for convenience in the laboratory by removing the retaining clip from the hinge pin and sliding the lid to the right.

The electrode method of measuring dissolved oxygen content is desirable when testing polluted, turbid or colored waters or waters that contain free chlorine, thiosulfate and organic chemicals which interfere when using the popular modified Winkler titration method.

PRINCIPLE OF OPERATION

The Clark-type dissolved oxygen sensor is a polarographic system composed of a gold cathode and a silver anode surrounded by a Potassium Chloride electrolyte solution. *See Figure 2.* A thin teflon membrane stretched over the sensor isolates the sensor from the environment while allowing gases to enter. Oxygen is consumed at the cathode and an oxygen pressure gradient is formed across the membrane, with the pressure on the inside near the cathode being zero and the pressure on the outside being equal to the ambient oxygen pressure. The Teflon membrane offers a resistance to the diffusion of oxygen to the inside and the amount which does diffuse through it is proportional to the oxygen pressure on the outside. The application of a polarizing potential to the gold-silver electrode system produces a current which is proportional to the amount of

oxygen being reduced at the cathode. Since the amount of oxygen available for reduction is directly proportional to the ambient oxygen pressure, the cell current will also be directly proportional to the ambient oxygen pressure. The proportionality constant includes factors of cell construction and the thickness, purity, and permeability of the membrane. Because the oxygen permeability of the membrane varies with temperature, the oxygen probe requires calibration at the measurement site if the highest degree of accuracy is to be obtained. Because of the nature of the Teflon membrane, ions of dissolved solids which could affect the performance of the electrode do not diffuse into the cell. Potential interferences are limited to reactive gases which are able to diffuse through the membrane.

Agitation of either the sample or the probe is required to avoid oxygen depletion at the ambient side of the membrane. Failure to provide this agitation will result in low readings or the inability to achieve a stable reading.

The current that is produced by the electro-chemical reaction ($O_2 + 2H_2O + 4Ag + 4KCl \rightarrow 4KOH + 4AgCl$) in the sensor is amplified by a thermistor compensated operational amplifier. The compensating effect of the thermistor probe allows the temperature of the solution being sampled to change without effecting the absolute value of the oxygen that is measured. The output of the operational amplifier is then used to drive the internal meter and supply a recorder output.

OPERATION

Instrument Controls

ZERO CONTROL - Used to zero the meter. OPERATION switch must be in ZERO position and probe connected. The zero adjustment should be checked before each measurement and the ZERO CONTROL adjusted as necessary.

MODE SWITCH - Used to select mode of

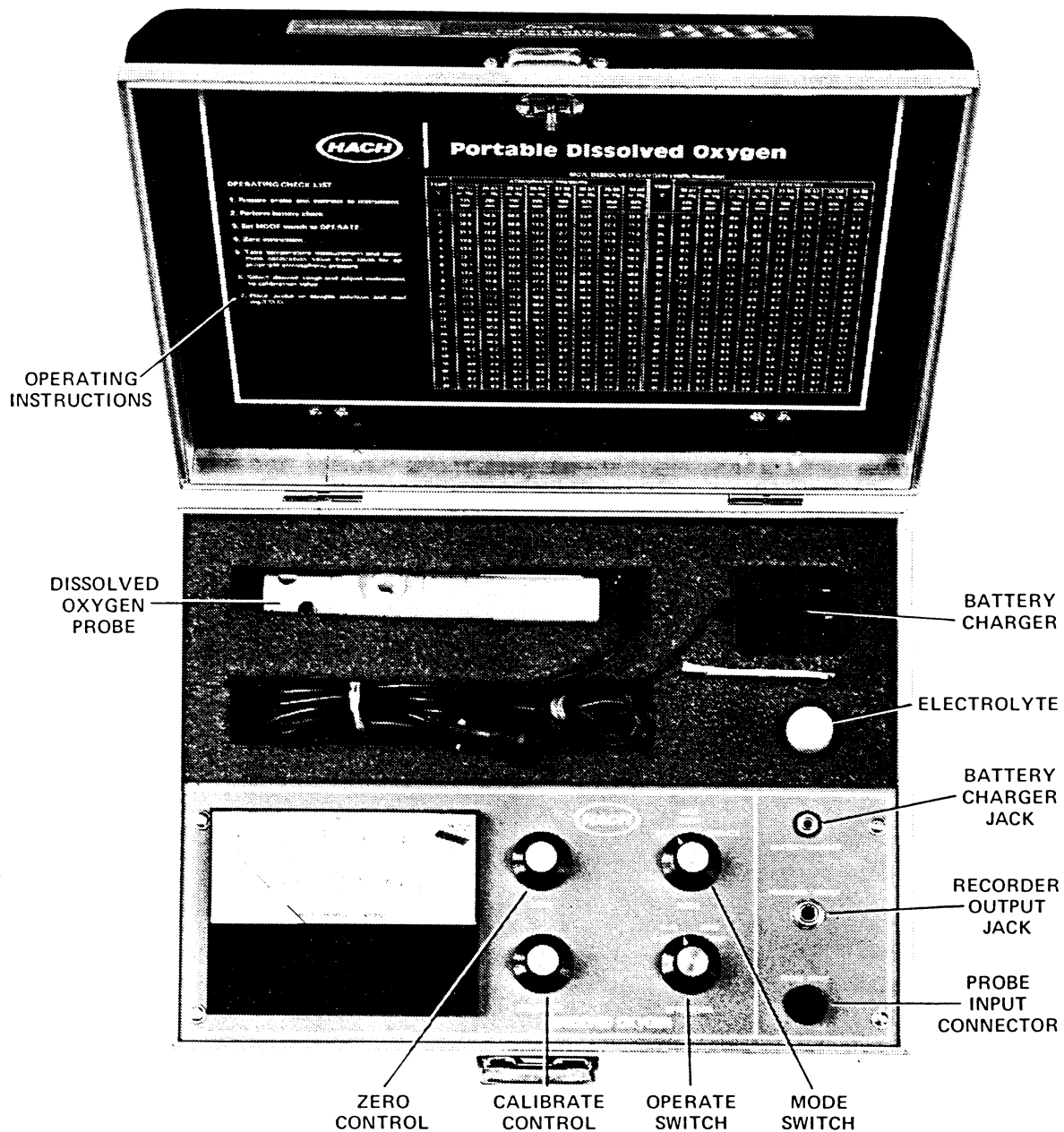
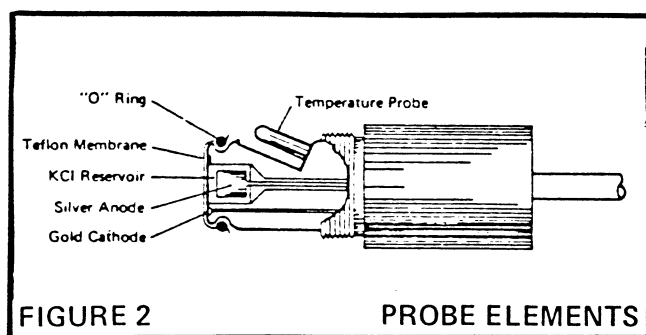


FIGURE 1

PORTABLE DISSOLVED OXYGEN METER



operation. BATT CHECK position is used only when checking the condition of the batteries. Instrument is zeroed and all temperature and DO measurements are made with the switch in the OPERATE position. In the OFF position, primary power is removed from the circuit board.

CALIBRATE CONTROL - Used to standardize the instrument to compensate for variations in atmospheric pressure and temperature. A calibration value is determined from Table 1 for the appropriate temperature and pressure and then the CALIBRATE control is adjusted to obtain a meter reading equal to the calibration value.

OPERATION SWITCH - Used to select high or low DO range, ZERO function when zeroing the instrument and TEMP function when taking a temperature measurement.

BATTERY CHARGER JACK - Used to connect converter/charger to the battery pack.

RECORDER OUTPUT JACK - Outlet jack for 0-100 mV recorder output signal. Mating recorder plug is supplied.

PROBE INPUT CONNECTOR - Eight-pin connector used to connect DO probe cable to the instrument. Plug retainer ring is tightened one-half revolution clockwise for proper connection.

Operating Procedure, Dissolved Oxygen

The following steps comprise the operating check list as shown inside the carrying case cover. For additional details on each of the steps, read the paragraphs that follow.

1. Prepare probe and connect to instrument.

Refer to Preparing the Probe for Operation.

2. Perform battery check. *Refer to Battery Check.*
3. Set MODE switch to OPERATE.
4. Zero instrument. *Refer to Zeroing the Instrument.*
5. Take temperature measurement and determine calibration value from Table 1 for appropriate atmospheric pressure. *Refer to Taking the Temperature Measurement for Standardization and Determining the Calibration Value.*
6. Select desired range and adjust instrument to calibration value (determined in Step 5). *Refer to Standardizing the Instrument.*
7. Place probe in sample solution and read mg/l DO.

Operating Procedure, Temperature

The temperature of the test sample can be measured using the dissolved oxygen probe as follows:

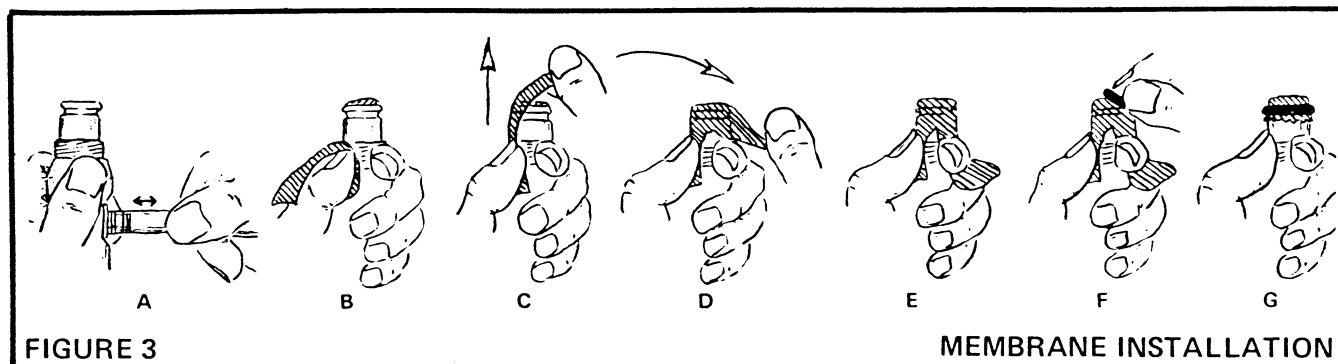
1. Perform steps 1 through 4 of the above procedure in the same manner as you would for a DO measurement.
2. Set the OPERATION switch to TEMP.
3. Place the probe in the test sample and read the temperature from the bottom scale.

Preparing Probe for Operation

The Hach Oxygen Probe is a sensitive device that requires proper treatment if measurements of high accuracy are to be obtained. Only membranes and filling solution supplied by Hach Company should be used to ensure proper electrode performance. Only demineralized water should be used to wash out the cell to avoid contaminating the cell with iron and other salts that will downgrade the performance of the electrode.

1. Remove the sensor guard by unscrewing it

- from the probe.
2. Remove the o-ring and the membrane from the tip of the probe.
 3. Flush out the sensor cell with KCl solution several times. It should be noted that some gases can be reduced at the cathode along with oxygen. The reaction of SO_2 and chlorine, bromine, etc., poisons the cell and shows up as a tarnish on the gold. This poisoning can usually be overcome by periodic wiping of the gold surface with a clean, lint-free cloth or a hard paper. Do not use any form of abrasives to polish the surface of the gold and plastic.
 4. Support the probe in a vertical position.
 5. Successively fill the sensor body with the KCl solution while pumping the diaphragm with the eraser end of a pencil or similar soft, blunt tool. See A, Figure 3. Continue pumping and filling until no more air bubbles appear and the gold cathode is completely covered.
 6. Select a membrane from the membrane kit and with one thumb secure one end of the membrane to the side of the probe—**handle the membrane only by the ends**. See Figure 3.
 7. With the thumb and forefinger of your other hand, grasp the free end of the membrane.
 8. Using a continuous motion, stretch the membrane up, over, and down the other side of the sensor. Stretching helps form the membrane to the contour of the probe.
 9. Secure the end of the membrane under the forefinger of the hand that is holding the probe.
 10. Stretch an o-ring into place. Strive for a taut, smooth membrane surface. A lax membrane or one with wrinkles will result in erratic performance, slow response, and poor response to mechanical shock. Trim the excess membrane about 1/8" beyond the o-ring with scissors. Check to see that the stainless steel temperature sensor is not covered by excess membrane.
 11. Due to the porosity of the anode, a small air bubble may appear under the membrane. New probes or probes that have been allowed to dry out will continue to develop bubbles until the porous anode is completely filled. This is normal, however, strive for a bubble-free probe. Tapping the body of the probe is helpful in removing bubbles. After the air has been driven from the anode, remove the membrane refill with KCl solution, and install another membrane.
 12. Remove excess KCl solution and replace the sensor guard.
- A bottomless plastic bottle is provided with the probe to help keep the KCl solution from drying out. Place a small piece of moist towel or sponge in the bottle and insert the probe into the open end. Depending upon usage the membranes should be replaced at least every 2-4 weeks. If an excessive amount of bubbles form under the membrane, if



erratic readings are observed, or if calibration is not stable, the membrane should be replaced.

Battery Check

The battery pack consists of six 1.25-volt nickel-cadmium batteries. Before using the instrument, the batteries should be charged for 12 to 24 hours with the charging unit provided. After the initial charge, the instrument should not be operated more than 50 hours between charging periods, and duration of charges should be 12 to 24 hours. Do not leave the charger connected to the instrument when the charger has been disconnected from the AC receptacle.

Check the battery pack by connecting the probe to the instrument and setting the MODE switch to BATT CHECK for at least 15 seconds. The meter needle should remain in the green area.

Zeroing the Instrument

The instrument (with probe connected) should be zeroed before each new sample measurement as follows:

1. Set the OPERATION switch to ZERO
2. Set the MODE switch to OPERATE
3. Adjust the ZERO control for a 0 mg/L reading on the instrument meter.

Taking Temperature Measurement for Standardization

When the instrument is to be standardized with the probe in air rather than in a sample with known dissolved oxygen content, the ambient temperature must also be considered in order to select a calibration value from Table 1. Take the temperature measurement as follows:

Table 1. Calibration Values vs Temperature and Atmospheric Pressure

MG/L DISSOLVED OXYGEN (100% Humidity)

TEMP °C	ATMOSPHERIC PRESSURE								TEMP °C	ATMOSPHERIC PRESSURE							
	30.51 in. Hg	29.92 in. Hg	29.53 in. Hg	28.54 in. Hg	27.56 in. Hg	26.57 in. Hg	25.59 in. Hg	24.60 in. Hg		30.51 in. Hg	29.92 in. Hg	29.53 in. Hg	28.54 in. Hg	27.56 in. Hg	26.57 in. Hg	25.59 in. Hg	24.60 in. Hg
	775 mm	760 mm	750 mm	725 mm	700 mm	675 mm	650 mm	625 mm		775 mm	760 mm	750 mm	725 mm	700 mm	675 mm	650 mm	625 mm
0	14.9	14.6	14.4	13.9	13.4	13.0	12.5	12.0	23	8.9	8.7	8.6	8.3	8.0	7.7	7.4	7.1
1	14.5	14.2	14.0	13.5	13.1	12.6	12.1	11.7	24	8.7	8.5	8.4	8.1	7.8	7.5	7.2	6.9
2	14.1	13.8	13.6	13.2	12.7	12.3	11.8	11.3	25	8.6	8.4	8.3	8.0	7.7	7.5	7.1	6.9
3	13.8	13.5	13.3	12.9	12.4	12.0	11.5	11.1	26	8.4	8.2	8.1	7.8	7.5	7.3	7.0	6.7
4	13.4	13.1	12.9	12.5	12.1	11.6	11.2	10.8	27	8.3	8.1	8.0	7.7	7.5	7.2	6.9	6.6
5	13.1	12.8	12.6	12.2	11.8	11.4	10.9	10.5	28	8.1	7.9	7.8	7.5	7.3	7.0	6.7	6.4
6	12.7	12.5	12.3	11.9	11.5	11.1	10.7	10.3	29	8.0	7.8	7.7	7.4	7.2	6.9	6.6	6.4
7	12.4	12.2	12.0	11.6	11.2	10.8	10.4	10.0	30	7.8	7.6	7.5	7.2	7.0	6.8	6.5	6.2
8	12.1	11.9	11.7	11.3	11.0	10.6	10.2	9.8	31	7.7	7.5	7.4	7.1	6.9	6.7	6.4	6.1
9	11.8	11.6	11.4	11.1	10.7	10.3	9.9	9.5	32	7.6	7.4	7.3	7.0	6.8	6.6	6.3	6.0
10	11.5	11.3	11.2	10.8	10.4	10.0	9.6	9.3	33	7.5	7.3	7.2	6.9	6.7	6.5	6.2	5.9
11	11.3	11.1	11.0	10.6	10.2	9.9	9.5	9.1	34	7.3	7.2	7.1	6.9	6.6	6.4	6.1	5.9
12	11.0	10.8	10.7	10.3	9.9	9.6	9.2	8.9	35	7.2	7.1	7.0	6.8	6.5	6.3	6.0	5.8
13	10.8	10.6	10.5	10.1	9.8	9.4	9.0	8.7	36	7.1	7.0	6.9	6.7	6.4	6.2	5.9	5.7
14	10.6	10.4	10.3	9.9	9.6	9.2	8.9	8.5	37	7.0	6.9	6.8	6.6	6.4	6.1	5.8	5.6
15	10.4	10.2	10.1	9.7	9.4	9.1	8.7	8.4	38	6.9	6.8	6.7	6.5	6.3	6.0	5.7	5.5
16	10.2	10.0	9.9	9.5	9.2	8.9	8.5	8.2	39	6.8	6.7	6.6	6.4	6.2	6.0	5.7	5.4
17	9.9	9.7	9.6	9.2	8.9	8.6	8.3	7.9	40	6.7	6.6	6.5	6.3	6.1	5.9	5.6	5.3
18	9.7	9.5	9.4	9.1	8.7	8.4	8.1	7.8	41	6.6	6.5	6.4	6.2	6.0	5.8	5.5	5.2
19	9.6	9.4	9.3	9.0	8.7	8.3	8.0	7.7	42	6.5	6.4	6.3	6.1	5.9	5.7	5.4	5.2
20	9.4	9.2	9.1	8.8	8.5	8.1	7.8	7.5	43	6.4	6.3	6.2	6.0	5.8	5.6	5.3	5.1
21	9.2	9.0	8.9	8.6	8.3	8.0	7.7	7.4	44	6.3	6.2	6.1	5.9	5.7	5.5	5.2	5.0
22	9.0	8.8	8.7	8.4	8.1	7.8	7.5	7.2	45	6.2	6.1	6.0	5.8	5.6	5.4	5.1	4.9

1. Place the probe in the plastic moisture cap containing a moist towel or sponge.
2. Set the OPERATION switch to TEMP. Allow the meter to stabilize and take the reading from the bottom scale.

Determining Calibration Value

When the instrument is air calibrated, the atmospheric pressure influences the DO measurement and must be considered. Table 1 is included to simplify the means of compensating for pressure differences by providing calibration values for a wide range of pressures over the operating temperature range of the instrument.

1. Find the current atmospheric pressure for your locale. *Remember that the barometric pressure readings reported via radio and TV are usually corrected to an equivalent sea level value. This is not suitable unless reconverted back to the true pressure for your locale. Table 2 or 3 can be used for the reversion. To use the tables, find the temperature and altitude which fits the sampling location most accurately, and locate the proper correction factor. The true atmospheric pressure is arrived at by reducing the reported barometer reading by this amount for each 100 feet (30.5 meters) of elevation, i.e.: Divide the elevation in feet by 100 (in meters, by 30.5) and multiply the resulting number by the proper correction factor. Subtract this final amount from the reported barometric pressure to obtain the true atmospheric pressure. Use this pressure when selecting the*

Table 2. Correction Factors For Conversion To True Atmospheric Pressure (Metric System)

CORRECTIONS IN mmHg/30.5 METERS ALTITUDE						
Temp °C	Altitude in Meters					
	300	600	900	1200	1500	1800
-16	3.01	2.95	2.90	2.85	2.78	2.73
- 8	2.92	2.87	2.81	2.76	2.72	2.66
0	2.85	2.78	2.73	2.67	2.63	2.59
10	2.73	2.68	2.63	2.59	2.54	2.50
20	2.63	2.58	2.53	2.49	2.45	2.41
28	2.56	2.51	2.47	2.44	2.39	2.35

Table 3. Correction Factors For Conversion To True Atmospheric Pressure (U.S. System)

CORRECTIONS IN inches Hg/100 ft. ALTITUDE						
Temp °F	Altitude in Feet					
	1000	2000	3000	4000	5000	6000
0	.119	.117	.115	.113	.111	.108
10	.117	.115	.113	.111	.109	.106
20	.115	.113	.110	.108	.106	.104
30	.112	.110	.108	.106	.104	.102
40	.109	.107	.106	.104	.101	.100
50	.107	.106	.104	.102	.100	.098
60	.105	.103	.101	.100	.098	.096
70	.103	.101	.099	.097	.096	.094
80	.101	.099	.098	.096	.094	.093

calibration value from Table 1.

The error in estimating the atmospheric pressure by this method is negligible at altitudes of less than 6000 ft. (1800m). At altitudes greater than this, or temperatures beyond the extremes of Tables 2 and 3, the true uncorrected atmospheric pressure must be obtained from a Weather Bureau station, or from a barometer.

2. Using the temperature reading taken for standardization and the atmospheric pressure for your locale, refer to Table 1 and determine the calibration value. For example, if the temperature reading was 20° C and the barometric pressure is closest to 30.31 inches of mercury, the calibration value would be 9.4 mg/L DO. This factor is used to standardize the instrument before measuring the test sample.

Standardizing Instrument

1. Select the appropriate range for the sample to be tested with the OPERATION switch.
2. Place the probe in the plastic moisture cap containing a moist towel or sponge and adjust the CALIBRATE control to obtain a reading equal to the calibration value taken from Table 1. The instrument is now ready to measure the DO of the test sample.

Laboratory Calibration

Calibration may be accomplished by placing the

oxygen probe into a water sample of known dissolved oxygen concentration. Such a sample can be obtained by saturating water with air by bubbling or by vigorous stirring. By knowing the temperature of the water and the atmospheric pressure, Table 1 can be used to obtain the dissolved oxygen concentration value. Care must be taken to ensure that saturation of the water with air has occurred. Approximately 15-30 minutes of vigorous stirring will cause the water to become saturated with air. When performing a laboratory calibration, Hach recommends that the calibration solution be divided into three separate portions and the three measurements averaged.

BOD Bottle Probe (optional accessory)

An optional BOD bottle probe is available for the Portable Dissolved Oxygen Meter which can be used to measure dissolved oxygen or temperature in a standard 300-ml BOD bottle. The probe is equipped with an agitator for stirring the sample solution continuously. The agitator motor operates on ac power, and the probe is available in either 115V or 230V models. Probes with convenient snap-on membranes also are available. *Refer to the Installation Instructions in the back of this manual.*

The BOD bottle probe should be prepared for operation and standardized according to the instructions for the preparation and standardization of the standard probe. When replacing the o-ring, be sure to use the one specified for the BOD bottle probe.

To use the bottle probe, plug the agitator power cable into a line receptacle and connect the probe cable to the PROBE INPUT plug on the instrument panel. With the agitator turned off, insert the probe into the bottle until an air tight seal is formed. The probe must be operated with no trapped air in the BOD bottle. Fill the bottle to overflowing and then carefully insert the bottle probe in the bottle. After the o-ring is past the narrow part of the neck, gently oscillate the probe clockwise and counterclockwise until it becomes seated in the neck of the bottle. This twisting action will expel any air bubbles trapped by the blunt end

of the probe. The BOD bottle probe has been designed to provide a snug fit in the neck of a standard 300-ml BOD bottle.

Since the temperature-measuring circuitry of the DO instrument was originally calibrated using the standard probe, it will be necessary to recalibrate the temperature circuitry using the BOD bottle probe. Do this according to the temperature control adjustment instructions contained in the *Maintenance Section*.

Stirrer Boot - The probe uses a flexible stirring boot to transmit motion from the sealed motor housing to the sample. If the boot shows signs of cracking or other damage likely to allow leaking into the motor housing, the boot must be replaced.

In fresh water applications boot life is normally several years, but this may be shortened by exposure to hydrocarbons, moderate to strong acids or bases, ozone, or direct sunlight. For maximum life, rinse the boot with demineralized water after use in contaminated samples.

Boot replacement is as follows:

1. Pull off old assembly and clean shaft.
2. Slide on new assembly making sure the top spring is on the grooved area of the shaft. A small amount of rubber cement may be used.
3. Check that there is sufficient clearance between the stirrer boot tip and the end of the shaft to permit turning without binding. The end of the shaft should extend approximately midway between the two springs.

Dissolved Oxygen Measurements In Saltwater

The sensitivity of the electrode varies with the salt content of the test solution. As a result it is necessary to know the salt concentration and what the oxygen solubility is at that concentration for a given temperature and atmospheric pressure in order to accurately measure the dissolved oxygen content. The nomogram* shown in Figure 4 can be

*Nomogram courtesy of Orbisphere Corporation, York, Maine