INTRODUCTION TO METERING DEVICES

INTRODUCTION

In this experiment, several physical and physiochemical properties of aqueous samples will be measured using various metering devices. In particular, you will measure the specific conductivity, turbidity, pH and dissolved oxygen of several supplied samples.

CONDUCTIVITY

The conductivity of an aqueous sample is a reflection of the total ion concentration present. Since ions carry a charge, they reduce the resistance of a solution and increase the conductivity. The specific conductivity takes into account the geometry and separation of the inert metal electrodes used to measure the conductivity. Conductivity is often used to estimate the amount of total dissolved solids (TDS) that would have the same charge carrying capacity.

TURBIDITY

Turbidity is an optical property detected by the scattering of incident light by suspended or dispersed solids in solution. Turbid water contains particles in suspension. The particles may be present naturally (e.g. clay, plankton, algae) or may be the result of human activity (e.g. increased erosion, mine tailings or pulp mill effluent).

pH

pH is a measure of the concentration of the [$\mathbf{H}^+$] or more precisely the activity of the H^+ (a_{H+}) ion. The pH scale is logarithmic and is defined as follows:

$pH = - \log a_{H+}$ or $pH \cong -\log [\mathbf{H}^+]$

DISSOLVED OXYGEN

Dissolved oxygen is important in the support of aquatic species as it is a key parameter in water pollution and wastewater treatment control.

Part A: CONDUCTIVITY

Conductivity is defined as the ability of a solution to carry an electric current and is inversely related to resistance. Although 'pure' water is a poor conductor, the presence of various ions increases conductivity considerably. When a voltage is applied between two metallic electrodes, a current is carried by the migration of the dissolved ions. The conductance of a solution depends on the concentration of ionic species as well as their charge and mobility (dissolved neutral molecules are not detected). Conductance is the reciprocal of resistance and it's basic unit of measure is the Siemen, formerly called mho (or ohm^{-1}). Conductivity is reported as the conductance per cm (known as the specific conductivity) to compensate for differences in electrode geometry (see figure 1). The units microsiemens per cm (μS/cm) and milliseimens per cm (mS/cm) are commonly encountered in aqueous solutions.

Solutions	**Specific Conductivity Ranges**
Deionized water	0.1 – 10 μS/cm
Distilled water	~0.5 μS/cm
Tap water	0.3 – 1 mS/cm
Seawater	~53 mS/cm

Conductivity is a non-specific indicator of all ionic species and is often employed to estimate the total dissolved solids (TDS) in a water sample. The specific conductivity of a water sample (μS/cm) can be multiplied by an empirical factor ranging from ~0.5 to ~0.9 depending on the water source to convert the reading into an equivalent mass in mg of **NaCl** per liter that would have the same conductivity. (For surface waters, a factor of 0.65 is often employed).

Conductivity is measured directly using a self-contained conductivity meter and conductivity cell or probe (see figure 2). The conductance of a solution is measured between two spatially fixed inert metal electrodes. The measured conductance will depend on exact electrode geometry, being directly proportional to electrode surface area and inversely proportional to distance between electrodes. The cell constant is determined for a given electrode by measuring the conductance of a standard solution and comparing this observed value to the known conductance. The specific conductance (or specific conductivity) is the product of the measured conductance and the cell constant.

Specific Conductivity(μS/cm) = Conductance(μS) x cell constant (cm^{-1})

Where the cell constant is determined for a given conductivity probe.

cell constant = known conductance of standard soln/observed conductance of standard soln

Many conductivity meters store the cell constant entered as part of a calibration procedure. This value is then applied to all subsequent conductance measurements. Because the conductivity of a solution increases with temperature, conductivity is measured at 25°C or corrected to a value at 25°C. Temperature corrections can be applied provided the sample temperature is recorded or an automatic temperature compensation algorithm is used. Typically, a correction of +2% for each Celsius degree below 25°C or a -2% correction for each Celsius degree above 25°C is employed.

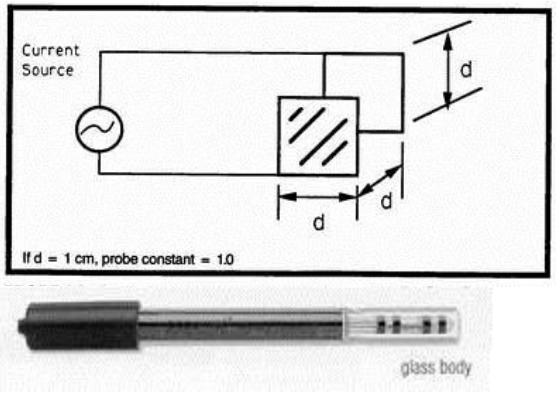


Figure 1: Schematic illustrating a hypothetical conductivity probe with cell constant = 1.0 cm^{-1}
Figure 2: A four cell conductivity probe.
Taken from: Electrochemistry Handbook, Fisher Scientific, 2002

EXPERIMENTAL PROCEDURE for CONDUCTIVITY

Sample collection and handling: measure specific conductivity on-site if possible or collect samples and store at 4°C until analysis. Holding time 28 days.

Method No. 2510 (Standard Methods, 18th edition)

Operating Instructions for AR20 Conductivity Meter
The conductivity cell should be stored in distilled water for at least 10 minutes prior to use. Always rinse cell thoroughly with distilled water between samples. Rinse cell with a small portion of sample to be measured prior to immersion in sample. Dip cell up and down to completely wet surface and allow air bubbles to escape.

In the instrument Setup mode set or confirm the following values:

Conductivity units = µS/cm
Cell constant = 1.0 cm^{-1}
Conductivity reference temperature = 25°C
Conductivity temperature co-efficient = 2%/°C
Conductivity significant figures = 3

Standardization (measuring and storing the cell constant)
Following the general operating instructions outlined above complete the following:

- enter the std mode
- transfer ~20 mL of 1409 µS/cm conductivity standard solution to clean pre-rinsed beaker
- immerse the conductivity cell into the standard solution and stir gently to remove air bubbles
- clear previous standardization value
- enter std again
- use keypad to enter known value of conductivity standard
- enter

Record the actual cell constant from the data box on the screen.
Measure the conductivity of the supplied aqueous samples in triplicate by transferring ~20 mL of sample each time and immersing the conductivity cell until a stable reading appears.
Tabulate recorded conductivity values in an excel spreadsheet and calculate the associated mean value and standard deviation for each sample measured. Report the cell constant, reference temperature and temperature co-efficient with your data tables.

Part B: TURBIDITY

Turbidity is caused by suspended and colloidal matter that reduces water clarity and gives rise to a cloudy or murky appearance. Turbidity may be caused by clay, silt, finely divided organic and inorganic matter, plankton and other microscopic organisms. Turbidity is an expression of an optical property that causes light to be scattered rather than transmitted through a sample. It is quantified by measuring the intensity of scattered light using a turbiditimeter also called a nephelometer. The greater the intensity of scattered light, the higher the turbidity. Turbidity measurements can vary tremendously depending on local conditions. It is best to collect several representative samples and measure the turbidity at the time of collection to avoid changes due to particulate settling. Land-use such as agriculture, forestry, mining and urbanization increase erosion and sediment loads to surface waters and can contribute to turbidity. Some typical turbidity values are summarized below.

Sample	**Nephelometric Turbidity Ranges**
Distilled water	≤ 0.5 NTU
Tap water	0.1 – 1 NTU
Creek water	1 – 20 NTU
Stagnant pond water	≥ 50 NTU

An optical instrument used to measure turbidity is known as a nephelometer and reports turbidity as nephelometric turbidity units, NTU's. This is another example of an aggregate parameter since there is not a single analyte being measured but rather an assemblage of species which contribute to the overall lack of clarity of a solution. The nephelometer or turbidity meter is essentially a spectrophotometer that illuminates the sample with a light beam and monitors the intensity of light scattered by the suspended particles at an angle of 90° from the incident light.

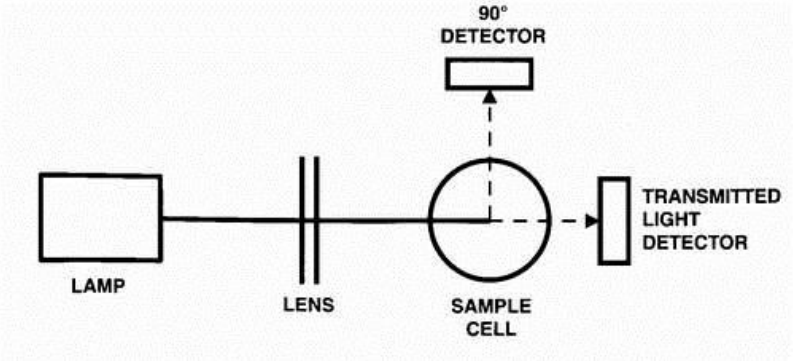


Figure 3: Schematic of the components of a Nephelometer used to measure turbidity. Taken from: 2100P Turbidimeter Manual, Hach Company,1998

The instrument has been factory calibrated with primary standards of foramzin suspensions. Since these standards are difficult to work with, secondary standards (permanently suspended in a polymer gel) are used periodically to ensure that the instrument is still operating within

specified limits. The absolute turbidity values generated by turbidimeters from different manufactures are notoriously inaccurate, since the signal depends on a number of specific optical configurations which are difficult to reproduce. Because of this, the manufacturer and instrument model number should be reported with turbidity data.

EXPERIMENTAL PROCEDURE for TURBIDITY

Sample collection and handling: collect samples directly in sample cells and measure immediately on site.

Method No. 2130 (Standard Methods, 18th edition)

Operating Instructions for HACH 2100 Turbidimeter
The sample is collected into glass sample cells. (If samples are supplied in the lab, shake thoroughly before 'collecting' into sample cell). Handle sample cells with tissues to avoid fingerprints and scratches on the glass. The outside of samples cells must be cleaned of dirt or moisture prior to recording turbidity. Use soft felt cloth to remove lint and add thin coat of silicone oil to the outer glass surface just prior to placing into the cell compartment. Rotate sample cell to align arrow with raised mark, close lid and push 'Read'. Always rinse cell thoroughly with distilled water between samples. Rinse cell with a small portion of sample to be measured prior to next measurement.

In the instrument Setup Mode, set or confirm the following values:
Signal averaging = ON

Checking Factory Calibration with Secondary Gel Standards
Following the general operating instructions outlined above, measure and record the turbidity readings of the secondary standards supplied with the turbidimeter. Check that the observed values are within 3% of the recorded values marked on each secondary standard.

Measure the turbidity of the supplied water samples in triplicate transferring a fresh portion of sample each time.

Tabulate recorded turbidity values in an excel spreadsheet and calculate the associated mean value and standard deviation for each sample measured. Report the observed and known turbidity values of the secondary standards along with your data table.

Part C: pH

The measurement of pH with a glass pH electrode involves the most common ion selective electrode (ISE) measurement. The $\mathbf{H^+}$ ion is detected by the accumulation of a potential (voltage) difference across a thin (and fragile!) glass membrane. For every change of 1.00 pH unit (corresponding to a 10 fold change in [$\mathbf{H^+}$]), a 0.05916 V potential is developed. A typical pH combination electrode actually consists of two electrodes in one probe: a glass membrane electrode and a reference electrode. The cell diagram is:

Ag (s)/**AgCl** (s)/$\mathbf{Cl^-}$(aq)//$\mathbf{H^+}$(aq, outside)||$\mathbf{H^+}$(aq, inside), $\mathbf{Cl^-}$(aq)/**AgCl**(s)/**Ag**(s)

NB: salt bridge // glass membrane ||

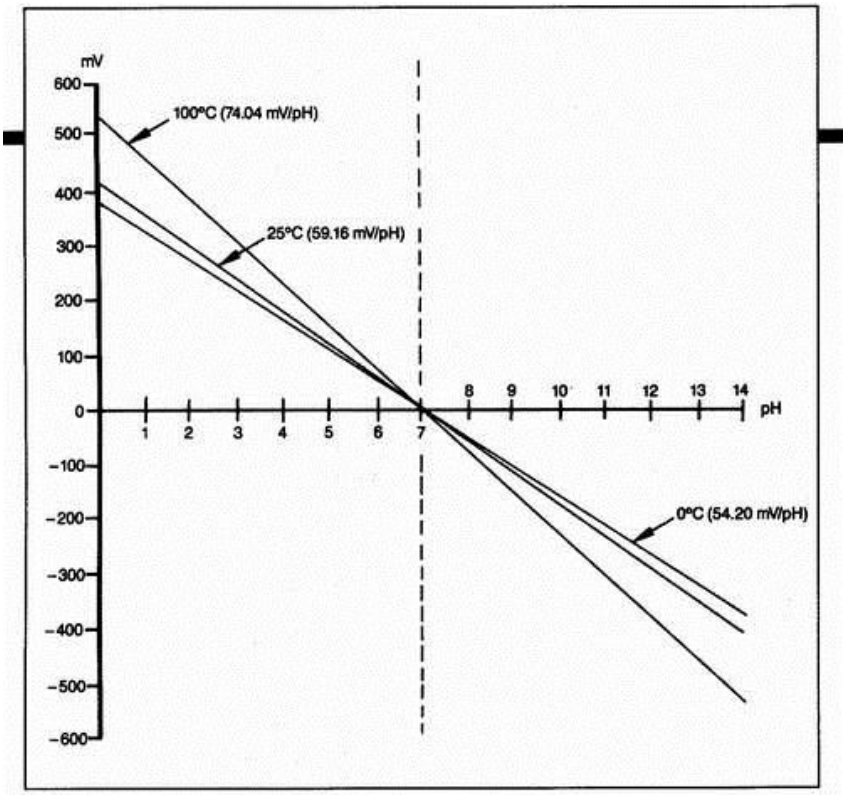
The pH sensing bulb on the end of a typical pH electrode (see figure) is a very thin layer of imperfectly networked $\mathbf{SiO_4}$ tetrahedra. This solid has open structures that allow the limited diffusion of $\mathbf{Na^+}$ ions through the glass structure. Exposed -$\mathbf{O^-}$ sites on the glass surface of the bulb allow $\mathbf{H^+}$ to bind with the membrane surfaces (inner and outer). The $\mathbf{Na^+}$ ions within the solid membrane migrate from whichever surface is accumulating more $\mathbf{H^+}$ ions in an effort to reduce the resulting (positive) charge buildup. This creates the measureable potential difference. The pH meter is essentially a high impedence voltmeter which has been factory calibrated to report measured pH directly. The measurement of pH by a "real" glass electrode is given by:

$$E\ (V) = \beta\ (0.05916V)\ \Delta pH + \text{constant} \qquad (\text{at } 25^oC)$$

where β varies from 0.98 to 1.00, ΔpH is the pH difference between the analyte solution and that inside the bulb. The constant is referred to as the "asymmetry potential", arising because the inner and outer surfaces of the glass membrane are not exactly identical. As can be seen by the above equation, the measured potential is a linear function of ΔpH. The equation is in the form of $y = mx + b$, where y represents the measured voltage and β represents the slope. The effects of asymmetry potential are corrected by calibrating the pH electrode with solutions of known pH. Benchtop and field portable pH meters need to be calibrated frequently to compensate for small changes which occur to the electrode potential over time. Calibration generally involves two or three standards (in this case pH buffers solutions). The first calibration point involves pH = 7.00 buffer and sets the isopotential point. The second calibration solution (usually pH = 4.00 or 10.00) is then used to set the slope of the calibration curve (and is temperature dependent).

Figure 4: Theoretical calibration curves for a typical pH electrode showing Nernstian slopes at several different temperatures.

Taken from: The pH and Conductivity Handbook, Omega Engineering Inc. 1992



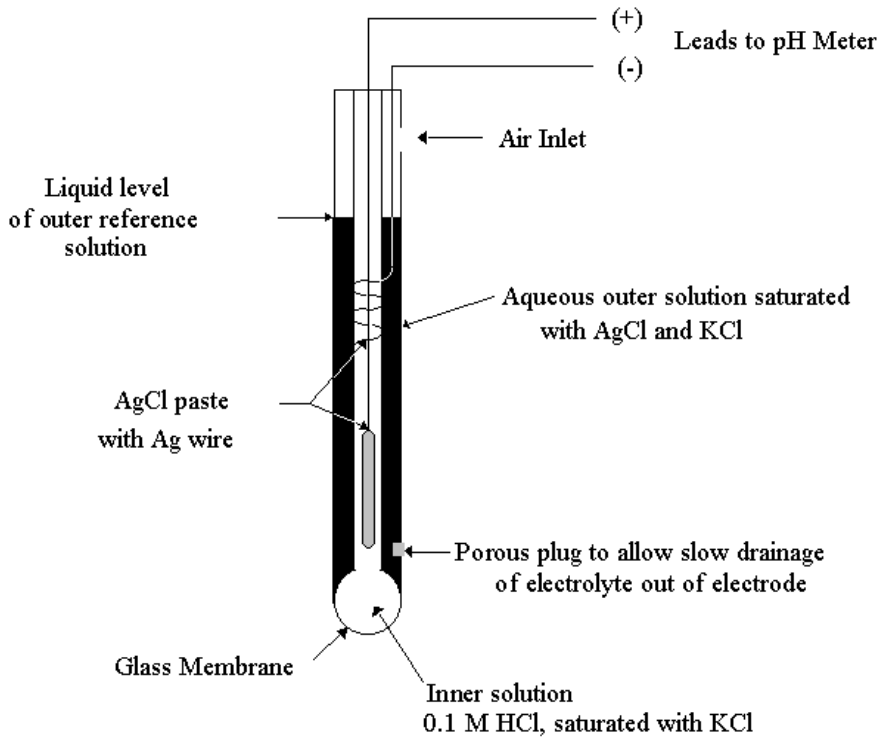


Figure 5: Illustration of a typical pH combination electrode, showing the internal Ag/AgCl reference electrode and glass membrane interface.

Taken from: www.ecs.umass.edu/cee/reckhow/courses/572/572bk18/572BK18.html

EXPERIMENTAL PROCEDURE for pH

Sample collection and handling: Measure pH on-site if possible with gentle stirring. If necessary, collect sample into glass or plastic bottles and analyze for pH within 24 hours.

Method No. 4500-H+ (Standard Methods, 18th edition)

Operating Instructions for pH meters
See individual operating instructions that accompany each instrument.

Handle pH electrodes with care, the thin glass membrane is very fragile. Always rinse electrode thoroughly with distilled water between samples. Rinse electrode with a small portion of sample to be measured prior to next measurement. Do not store electrodes for prolonged periods (> 24 hrs) in distilled water.

Calibration with pH buffers
Following the general operating instructions outlined with individual instruments.

Measure the pH of the supplied aqueous samples in triplicate transferring a fresh portion of sample each time.

Soil samples: weigh ~20g of soil into beaker and add ~20mL of deionized water. Let stand for 15 min mixing at 5 min intervals. Carefully place electrode into supernatant solution with gentle swirling. Carefully clean electrode with distilled water after use.

Tabulate recorded pH values in an excel spreadsheet and calculate the associated mean value and standard deviation for each sample measured. Report the calibration buffers used along with your data.

Part D: DISSOLVED OXYGEN

When gaseous molecular oxygen comes into contact with water, a small portion will dissolve and an equilibrium will be established. The solubility of **O_2** increases with increasing atmospheric pressure and decreasing water temperature.

$$O_2\,(g) \rightleftharpoons O_2\,(aq)$$

The amount of dissolved oxygen (DO) will depend on a number of biotic and abiotic factors. The DO concentration may be expressed in absolute terms such as mole/L or mg/L or relative to the solubility limit under a given set of conditions, i.e., the % saturation. For example, the maximum solubility of **O_2** in freshwater at 5 ^oC and 760 torr (1.00 atmosphere) is 12.8 mg/L. If a sample were observed to contain 6.4 mg/L under these conditions it would be 50% saturated.

DO can be determined chemically (i.e., Winkler titration) or monitored instrumentally using an **O_2** specific electrode or a DO meter. Most DO meters are ammeters that measure the current produced in a probe or sensor device. The current is proportional to the **O_2**(aq) concentration. The probe is an electrolytic cell containing two electrodes, an electrolyte solution (**KCl**) and a semi-permeable membrane that is permeable to **O_2**.

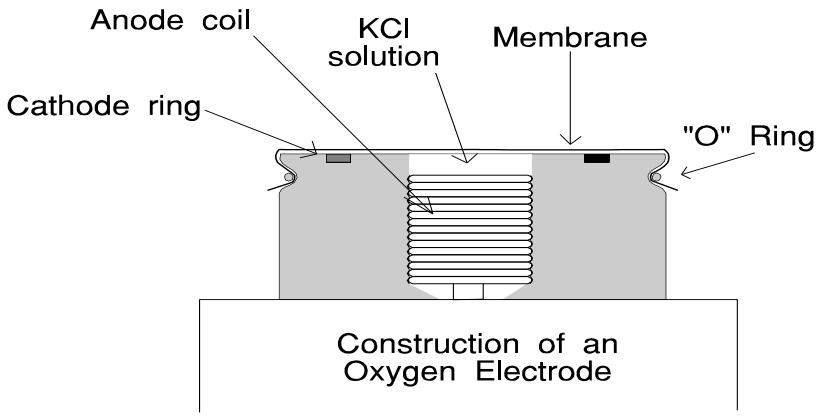


Figure 6: Schematic of typical DO probe.

O_2 from the sample being tested enters the cell through the membrane. The voltage between the electrodes is such that the electrolysis reaction **$O_2 + 4\,H^+ + 4\,e^- \rightarrow 2\,H_2O$** occurs. The current flowing through the cell changes as the **H^+** ions are removed. This change in current is proportional to the amount of **O_2** that has entered the cell from the solution being tested. The meter, once calibrated, displays the dissolved **O_2** in units of mg/L and %saturation. The meter is calibrated by exposure of the probe to samples containing a known **O_2** content, typically a humid air sample. Corrections for temperature, atmospheric pressure (or altitude) and salinity can be made. Some meters have built in algorithms to automatically compensate for some or all of these factors.

EXPERIMENTAL PROCEDURE for DISSOLVED OXYGEN

Sample collection and handling: DO should be measured on –site with gentle stirring.

Method No. 4500-O (Standard Methods, 18th edition)

Operating Instructions for ORION Dissolved Oxygen Meter
The DO probe can be used directly in the original sample. Move the electrode around or gently agitate the sample to ensure a fresh supply of sample in contact with the membrane. Handle the electrode with care to avoid scratches and tears on the membrane. Always rinse probe thoroughly with distilled water between samples.

DO membranes have to be frequently replaced and the **KCl** filling solution rejuvenated. Care must be taken to exclude air bubbles from the sensing cell when changing the membrane.

Calibration with water saturated air
Follow the calibration instructions outlined by the manufacturer.

Calibration Check
Set up two gas bubblers to sparge one sample of distilled water with $\mathbf{N_2}$ and another with 'medical air' for ~30 mins. Record the DO and temperature by inserting the probe into each sample. Check your values with the DO saturation concentration at your recorded temperature in the accompanying table.

Measure the DO of the supplied aqueous samples in triplicate transferring a fresh portion of sample each time.

Tabulate recorded dissolved oxygen values in an excel spreadsheet and calculate the associated mean value and standard deviation for each sample measured. Report the observed and theoretical DO values of the sparged samples along with your data table.

Note: In a seawater sample corrections for salinity may be required, both during calibration and measuring. See manufacturers instructions for these corrections.

Saturated Concentrations of Dissolved Oxygen at Several Temperatures in Freshwater*

T (^oC)	DO (mg/L)	T (^oC)	DO (mg/L)	T (^oC)	DO (mg/L)	T (^oC)	DO (mg/L)
0	*14.62*	10	*11.29*	20	*9.09*	30	*7.56*
1	*14.22*	11	*11.03*	21	*8.92*	31	*7.43*
2	*13.83*	12	*10.78*	22	*8.74*	32	*7.31*
3	*13.46*	13	*10.54*	23	*8.58*	33	*7.18*
4	*13.11*	14	*10.31*	24	*8.42*	34	*7.07*
5	*12.77*	15	*10.08*	25	*8.26*	35	*6.95*
6	*12.45*	16	*9.87*	26	*8.11*	36	*6.84*
7	*12.14*	17	*9.67*	27	*7.97*	37	*6.73*
8	*11.84*	18	*9.47*	28	*7.83*	38	*6.62*
9	*11.56*	19	*9.28*	29	*7.69*	39	*6.52*

* values quoted are at sea-level

Altitude Correction Factor for DO Saturation Values**

Altitude (m)	Correction Factor	Altitude (m)	Correction Factor**
0	1.00	1643	0.82
170	0.98	1843	0.80
343	0.96	2047	0.78
519	0.94	2256	0.76
698	0.92	2469	0.74
880	0.90	2687	0.72
1066	0.88	2909	0.70
1254	0.86	3137	0.68
1447	0.84	3371	0.66

** multiply the saturation values at sea-level by the correction factor to obtain saturation value at given altitude

Submit Data Tables for Conductivity, Turbidity, pH and Dissolved Oxygen

Notes;

1. Include a descriptive table title.

2. Report individual readings, estimated reading errors, mean values, sample standard deviation (s), percent relative standard deviation (%RSD) and 95% confidence interval (95%CI).

3. Round off your final reported value to the appropriate number of significant figures along with the 95% CI (Appendix 2).

4. Include footnotes to specify sample information, instruments used and calibration techniques.

See further comments in Appendix 3, Page 2