Water Quality Monitoring - A Practical Guide to the Design and Implementation of Freshwater Quality Studies and Monitoring Programmes
Edited by Jamie Bartram and Richard Ballance
Published on behalf of United Nations Environment Programme and the World Health Organization
© 1996 UNEP/WHO
ISBN 0 419 22320 7 (Hbk) 0 419 21730 4 (Pbk)

Chapter 6 - FIELD TESTING METHODS

This chapter was prepared by R. Ballance

Analyses for many important physical, chemical and microbiological variables can be carried out in the field using apparatus made specifically for field use. A significant advantage of field analysis is that tests are carried out on fresh samples whose characteristics have not been contaminated or otherwise changed as a result of storage in a container. This is of special importance for samples that are to undergo microbiological analysis but cannot be transported to a laboratory within the time limits or under the conditions described in Chapter 5. Some variables must be measured in the field, either *in situ* or very soon after the sample has been collected. Field analysis is necessary for temperature, transparency and pH. Dissolved oxygen may be determined in the field or the sample may be treated (fixed) in the field and the remainder of the analysis completed in a laboratory. If samples are to be chemically preserved before being transported to the laboratory, conductivity (if required) must be measured before preservative chemicals are added.

Another advantage of field analysis is that samples are highly unlikely to lose the labels that identify the time and place of sampling. Loss of such identification would be disastrous if, for example, many samples had been collected to determine the water quality profile of a river.

Where there are no laboratories within a reasonable distance of the sampling stations, field analysis may be the only feasible way to obtain water quality information. Mobile laboratories are expensive to set up and maintain, while a temporary laboratory is justified only if a large sampling and analysis programme is to be carried out within a relatively compact sampling area.

The limitations of field analysis must, however, be recognised. Some of the methods used in field analysis produce less accurate results than those that can be used in a well-equipped laboratory. In addition, the limits of detection and the reproducibility of field analyses will often be less than is possible with laboratory methods. Furthermore, it is difficult to implement an analytical quality assurance programme when analyses are done in the field, although some attempt should be made to control the quality of field results.

Several manufacturers produce equipment designed specifically for use in the field (see Annex 1 for examples). This equipment, often in the form of a “kit”, almost invariably contains instruments, glassware, reagent packages and other consumables that are unique to the kit. Replacement of broken components and replenishment of reagents and consumables therefore requires re-supply from the manufacturer or an approved agent, and many developing countries experience difficulties with this. Extensive delays may be experienced in replacement and re-supply and, for various reasons, these replacements may prove

expensive. While the same problems apply to standard laboratory supplies and reagents, there is always the possibility of borrowing from another laboratory while waiting for an order to be filled.

The ease with which the procedure involved in a field analysis may be followed will depend on the complexity of the procedure and the climatic and other conditions at the time of analysis. For example, a field measurement that can be made with an electrode and a meter (temperature, pH, conductivity, dissolved oxygen) is normally very easily accomplished provided that little or no meter calibration is necessary. On the other hand, photometric or titrimetric procedures that involve the addition of two or more reagents, a reaction time of several minutes, and the observation of a colour change or a photometer reading might present difficulties under some field conditions.

In using any field kit it is essential to follow exactly the procedures specified in the manufacturer's instruction manual. Carefully measured quantities of reagents may be supplied in pre-packaged form, and use of a different concentration of a chemical from that recommended would distort the result of an analysis. Even when methods are followed exactly it is vital that they are validated before use. Method validation is discussed in Chapter 9 and is especially important where on-site testing is to be undertaken because analytical quality assurance is more difficult, as noted above. Care must also be taken to ensure that the batteries in any battery-powered apparatus (such as a photometer or a pH meter) are fresh and are supplying the correct voltage.

As an alternative to purchasing a field kit, it is possible for an analyst to assemble and package the glassware and chemicals needed to analyse for some of the variables. If this is done, plastic (as opposed to glass) bottles, burettes, pipettes, flasks and beakers should be used whenever possible, and the quantity of reagent chemicals should be no greater than is needed for one sampling expedition. The field kit thus made should be "field-tested" close to the laboratory where it is assembled. Staff should practise using the kit to identify any problems associated with its use; they should also make realistic estimates of the supplies required and the time that will be needed to conduct the planned series of analyses under field conditions. For example, they should establish how much distilled water is needed for rinsing glassware, whether paper towels or wiping cloths are needed, whether a table is needed to hold glassware during the analyses. This sort of trial run before analytical work is attempted in the field must be part of the training course for all field staff who will carry out on-site testing, regardless of the type of field test kit or portable equipment that is being used.

Appendix 1 lists some suppliers of water testing equipment, although their inclusion in this handbook is not necessarily an endorsement of these suppliers. It is worth noting that many laboratory suppliers market other companies' products under their own name. Sometimes the general laboratory suppliers are less expensive than the manufacturer because they are able to buy in bulk. Price quotations should therefore be sought from several sources. It is important to be aware of the full extent of the package when a kit is purchased for water testing: many suppliers do not mention consumable costs and there may be expensive calibration standards that must be purchased at extra cost.

The fact that field testing assays are performed away from the laboratory should not mean that less care is taken to ensure reliability of results. The use of quality assessment and internal quality control techniques to ensure and monitor quality is still possible (see Chapter 9).

6.1 Temperature

Temperature must be measured *in situ* because a water sample will gradually reach the same temperature as the surrounding air. If it is not possible to measure the temperature *in situ*, a sample must be taken from the correct location and depth of the sampling station and its temperature measured immediately it is brought to the surface.

Temperature is measured with a glass thermometer, either alcohol/toluene-filled or mercury-filled, with 0.1 °C graduations, or an electronic thermometer of the type that is usually an integral part of a dissolved oxygen meter or a conductivity meter.

Procedure

The procedure to follow depends on the type of thermometer being used and on whether direct access to the point at which the temperature is to be measured is impossible (as, for example, when the water to be tested is in a deep well or when a water sample can be taken only from a bridge).

1. When a glass thermometer is used and the testing point can be reached, immerse the thermometer in the water until the liquid column in the thermometer stops moving (approximately 1 minute, or longer if necessary). For a pumping well, immerse the thermometer in a container with water flowing through until the temperature stabilises. Record the reading to the nearest 0.1 °C.

2. When either a glass thermometer or an electronic thermometer is used and the measurement point is inaccessible, obtain a water sample of at least 1 litre. Rinse the thermometer (or the probe) with a portion of the sample and discard the rinse water. Immerse the thermometer (or the probe) in the sample. Hold it there for approximately 1 minute (longer if the temperature reading has not become constant). Record the reading to the nearest 0.1 °C.

3. When an electronic thermometer having a probe with long leads is used, lower the probe to the required depth. Hold it at that depth until the reading on the meter is constant. Record the temperature to the nearest 0.1 °C and the depth to the nearest 10cm. Lower (or raise) the probe to the next measurement point for the next reading.

6.2 Transparency

Transparency is a water quality characteristic of lakes and reservoirs and can be measured quickly and easily using simple equipment. This characteristic varies with the combined effects of colour and turbidity. Some variation may also occur with light intensity and with the apparatus used.

The apparatus used for transparency measurement is called a Secchi disc - named after Secchi, who first used it in 1865 to measure the transparency of the Mediterranean Sea. The disc is made of rigid plastic or metal, but the details of its design are variable. It may be 20 to 30 cm or even larger in diameter and is usually painted white. Alternatively, it may be painted with black and white quadrants.

The disc is suspended on a light rope or chain so that it remains horizontal when it is lowered into the water. The suspension rope is graduated at intervals of 0.1 and 1 metre from the level of the disc itself and usually does not need to be more than 30 m in length. A weight

fastened below the disc helps to keep the suspension rope vertical while a measurement is being made. Figure 6.1 shows a typical Secchi disc.

The same size and pattern of disc should be used at any given sampling station so that a series of measurements made over a number of years will be as free as possible from distortions arising from differences in apparatus.

Use of a boat to reach the measurement site is essential.

Procedure

The observation should not be made early in the morning or late in the afternoon.

1. Lower the Secchi disc, where possible, through a shaded area of water surface (glare on the water surface can distort the observation).

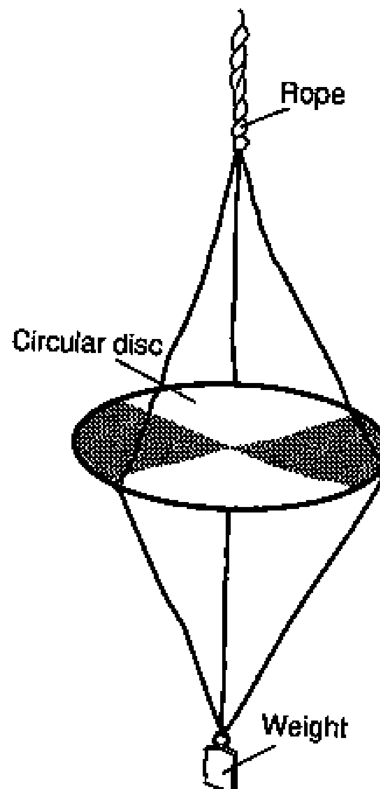
2. As the disc is lowered, note the depth at which it just disappears from view.

3. Lower the disc a little further, then raise it and note the depth at which it reappears.

Reporting

The average of the two depth readings is reported as the Secchi disc transparency. The report must also state the diameter of the disc and the pattern, if any, on the upper surface of the disc.

Figure 6.1 The Secchi disc



6.3 pH

Determination of the pH of water should, if possible, be made *in situ*. If this is not possible, for example with well water or when access to a lake or river is very difficult, the measurement should be made immediately after the sample has been obtained.

There are three different methods of pH measurement: pH indicator paper, liquid colorimetric indicators and electronic meters. The use of pH indicator paper is simple and inexpensive, but the method is not very accurate and requires a subjective assessment of colour by the user. Liquid colorimetric indicators change colour in accordance with the pH of the water with which they are mixed. The colour that develops can then be compared with a printed card, with coloured glass standards, or with a set of prepared liquid standards. Colorimetric methods are reasonably simple and accurate to about 0.2 pH units. Their main disadvantage is that standards for comparison or a com- parator instrument must be transported to the sampling station. Moreover, physical or chemical characteristics of the water may interfere with the colour developed by the indicator and lead to an incorrect measurement. The third method, electrometric pH measurement, is accurate and free from interferences. Pocket-sized, battery-powered, portable meters that give readings with an accuracy of ± 0.05 pH units are suitable for field use. Larger, more sophisticated models of portable meter can attain an accuracy of ± 0.01 pH units. Care must be taken when handling such equipment. The electrodes used for measurement generally need replacing periodically (e.g. yearly). Old or poor quality electrodes often show a slow drift in the readings.

6.3.1 Measurement of pH using colour indicators

A comparator and colour discs are required for this method of measuring pH. The instrument made by one manufacturer uses colour discs for the pH ranges and indicators listed below.

Indicator	pH range
Universal	4.0-11.0
Bromocresol green	3.6-5.2
Methyl red	4.4-6.0
Bromocresol purple	5.2-6.8
Bromothymol blue	6.0-7.6
Phenol red	6.8-8.4
Thymol blue	8.0-9.6
Phenolphthalein	8.6-10.2

Procedure

1. Fill three comparator cells to the 10-ml mark with portions of the water sample and place one of the cells in the left-hand compartment of the comparator.

2. Add 1 ml of universal indicator to one of the cells and mix well; place the cell in the right-hand compartment. Compare the colour in the right-hand cell with the glass standards of the universal disc.

3. From the above list, choose an indicator that has the mid-point of its range near to the approximate pH determined with the universal indicator. Add 0.5 ml of this indicator to the third comparator cell, mix, and place the cell in the right-hand compartment of the comparator.

4. Put the appropriate standard disc in the comparator and compare the colour of the sample with the glass standards on the disc. Record the result to the closest 0.2pH unit.

6.3.2 Measurement of pH using a pH meter

There are many models of pH meter and it is beyond the scope of this manual to describe them all. The common features are a sensing electrode and a reference electrode connected to an electronic circuit that amplifies the voltages produced when the electrodes are immersed in a solution or water sample. The amplified voltage is displayed on a meter graduated in pH units. Sensing and reference electrodes designed for field use are often combined in one element. The electronic circuitry in a portable meter is powered by either disposable or rechargeable batteries, depending on the design of the meter.

It is possible to purchase a more complex instrument that is designed for measurement of conductivity and temperature as well as pH. Some instruments offer additional features and are equipped with circuitry and probes that allow the measurement of dissolved oxygen, redox potential and/or turbidity. It is not possible to provide detailed operating instructions for all of the many makes and models of pH meter. Operating and maintenance instructions are supplied by the manufacturer. There is, however, a general procedure that should be followed. The sensing, or glass, electrode must be soaked in distilled water for several hours before use when it is new or if it has dried out during storage of more than a day. When a glass electrode is not in use for more than a few hours, its tip (the lower 1-2 cm) should be kept immersed in distilled water. The tips of glass electrodes should be carefully protected against abrasion and breakage.

The reference electrode is usually supplied with a rubber cap that protects the tip against breakage as well as preventing the crystallisation of dissolved salts on the tip. A hole in the side of the electrode is provided for filling the body of the electrode with saturated potassium chloride (KCl) solution. The correct liquid level is approximately 5 mm below the bottom edge of the hole. When the electrode is not in use the hole should be covered with a rubber sleeve that slides over the body of the electrode.

One or more buffer solutions are necessary for standardising the meter. It is usual for the manufacturer to provide a container of buffer solution with the meter, and the supply may be replenished with purchases from either the manufacturer or a chemicals supplier. Buffer solutions may also be prepared in an analytical laboratory where volumetric glassware and an analytical balance (accurate to ±1 mg) are available.

Procedure

Standardising the meter

1. Remove the protective rubber cap and slide the rubber sleeve up to expose the hole in the side of the reference electrode.

2. Rinse both electrodes with distilled water and blot them dry with soft absorbent paper.

3 Pour sufficient buffer solution into a beaker to allow the tips of the electrodes to be immersed to a depth of about 2 cm. The electrodes should be at least 1 cm away from the sides and the bottom of the beaker.

4. Measure the temperature of the buffer solution with a thermometer and set this on the temperature adjustment dial of the meter (if the meter is so equipped). Some meters have an automatic temperature adjustment feature.

5. Turn on the pH meter.

6. Adjust the needle on the pH dial to the known pH of the buffer. If the needle keeps jumping, check that the leads from the electrodes are firmly connected to the meter. When the needle stops moving, make the fine adjustment.

7. Turn the instrument to stand-by (if it is equipped for this).

8. Raise the electrodes clear of the buffer solution. Remove the buffer and rinse the electrodes with distilled water.

9. Proceed to determination of pH of the sample. If the sample is not ready, place the electrodes in distilled water.

Determination of pH of sample

1. The electrodes are either immersed in, or have been rinsed with, distilled water. Remove them from the water and blot dry.

2. Rinse the electrodes and a small beaker with a portion of the sample.

3. Pour sufficient of the sample into the small beaker to allow the tips of the electrodes to be immersed to a depth of about 2 cm. The electrodes should be at least 1 cm away from the sides and the bottom of the beaker.

4. Measure the temperature of the water sample and set the temperature adjustment dial accordingly (if the instrument does not have automatic temperature compensation).

5. Turn on the pH meter.

6. Read the pH of the water sample on the dial of the meter. Make sure that the needle has stopped moving before the pH is recorded.

7. Turn the pH meter to stand-by and raise the electrodes out of the sample. Remove the sample and discard it. Rinse the electrodes and the beaker with distilled water, and blot the electrodes with soft tissue.

8. If other samples are to be tested, repeat steps 2 to 7.

9. If no other samples are to be tested, slide the rubber sleeve down to cover the hole in the side of the reference electrode and replace the protective rubber cap on the tip.

10. Switch the meter off and pack it in its carrying case for transport.

Reporting

Report the pH and the temperature of the water at the time the measurement was made.

6.4 Conductivity (or specific conductance)

The ability of water to conduct an electric current is known as conductivity or specific conductance and depends on the concentration of ions in solution. Conductivity is measured in millisiemens per metre (1 mS m^{-1} = 10 µS cm^{-1} = 10 µmhos cm^{-1}). The measurement should be made *in situ*, or in the field immediately after a water sample has been obtained, because

conductivity changes with storage time. Conductivity is also temperature-dependent; thus, if the meter used for measuring conductivity is not equipped with automatic temperature correction, the temperature of the sample should be measured and recorded.

Many manufacturers of scientific equipment produce conductivity meters. The apparatus consists of a conductivity cell containing two rigidly attached electrodes, which are connected by cables to the body of the meter. The meter contains a source of electric current (a battery in the case of portable models), a Wheatstone bridge (a device for measuring electrical resistance) and a small indicator (usually a galvanometer). Some meters are arranged to provide a reading in units of conductance (mhos), while others are graduated in units of resistance (ohms). The conductivity cell forms one arm of the Wheatstone bridge. The design of the electrodes, i.e. shape, size and relative position, determines the value of the cell constant, K_c, which is usually in the range 0.1 to 2.0. A cell with a constant of 2.0 is suitable for measuring conductivities from 20 to 1,000 mS m^{-1}.

The cell constant K_c can be determined by using the apparatus to measure the conductivity of a standard solution (0.0100 mol l^{-1}) of potassium chloride and dividing the true conductivity of the solution (127.8 mS m^{-1} at 20 °C) by the measured conductivity, $K_c=C_t/C_m$. Care must be taken to ensure that measured and true conductivities are expressed in the same units. The temperature of the solution is critical because electrolytic conductivity increases with temperature at a rate of approximately 1.9 per cent per °C. Some meters provide a reading of resistance, which is the reciprocal of conductance. When resistance is measured, the cell constant is calculated by dividing the measured resistance by the true resistance, $K_c=R_m/R_t$.

Platinised electrodes require replating if readings become erratic or when the platinum black coating peels or flakes off. The replating procedure is not difficult but it should be done in the laboratory. Stainless steel electrodes are more appropriate for field use but they must be kept clean. If they become contaminated, for example with oily wastewater, they must be cleaned with a solvent, then with alcohol and finally be well rinsed with distilled water. When not in use the cell should be wiped dry and stored in its carrying case.

Reagents

√ Distilled water for preparing standard potassium chloride solution should have a very low conductivity. It must not contain CO_2. Use redistilled water and boil it immediately before use. Allow to cool in a hard-glass bottle fitted with a CO_2 trap.

√ Standard potassium chloride solution, 0.0100 mol l^{-1}, for the calibration of electrodes and determination of the cell constant. Dissolve 0.7456 g of anhydrous KCl (dried at 105°C and cooled in a desiccator) in CO_2-free distilled water. Make up to 1,000 ml at 20°C. Store in a hard-glass bottle fitted with a CO_2 trap. The conductivity of this solution is 127.8 mS m^{-1} at 20 °C.

Procedure

Determination of cell constant

1. Rinse out the conductivity cell with at least three portions of standard KCl solution.

2. Adjust the temperature of a fourth portion of the solution to 20 ± 0.1 °C (or as near as possible to that temperature).

3. Immerse the conductivity cell in a sufficient volume of the KCl solution for the liquid level to be above the vent holes in the cell. There should be no air bubbles clinging to the electrodes and the cell should not be closer than 2 cm to the sides and bottom of the container.

4. Observe and record the temperature of the KCl solution to the nearest 0.1 °C. Some meters have built in thermometers and/or automatic temperature compensation.

5. Turn the meter on. Follow the manufacturer's operating instructions and record the meter reading.

6. Calculate the cell constant. The formula includes a factor that compensates for the difference in temperature if the reading was taken at a temperature other than 20.0°C. The value of the temperature correction factor [0.019(*t* - 20) + 1] can be determined from the graph in Figure 6.2.

If *conductivity* was measured, the calculation is:

$$K_C = (127.8/C_{KCl}) \times [0.019(t - 20) + 1]$$

where

C_{KCl} = measured conductivity (μmhos)
t = observed temperature (°C)
K_c = the cell constant (cm^{-1}).

If *resistance* was measured, the calculation is:

$$K_C = R_{KCl} \times 0.001278 \times [0.019(t-20) + 1]$$

where

R_{KCl} = measured resistance (ohms)
t = observed temperature (°C)
K_c = the cell constant (cm^{-1})

Measurement of sample conductivity

1. Rinse the conductivity cell with at least three portions of the sample.

2. Adjust the temperature of a portion of the sample to 20 ± 0.1 °C (or as close as possible to that temperature).

3. Immerse the conductivity cell containing the electrodes in a sufficient volume of the sample for the liquid level to be above the vent holes in the cell. There should be no air bubbles clinging to the electrodes and the cell should not be closer than 2 cm to the sides and bottom of the container.

4. Observe and record the temperature of the sample to the nearest 0.1 °C. Some meters have built in thermometers and/or automatic temperature compensation.

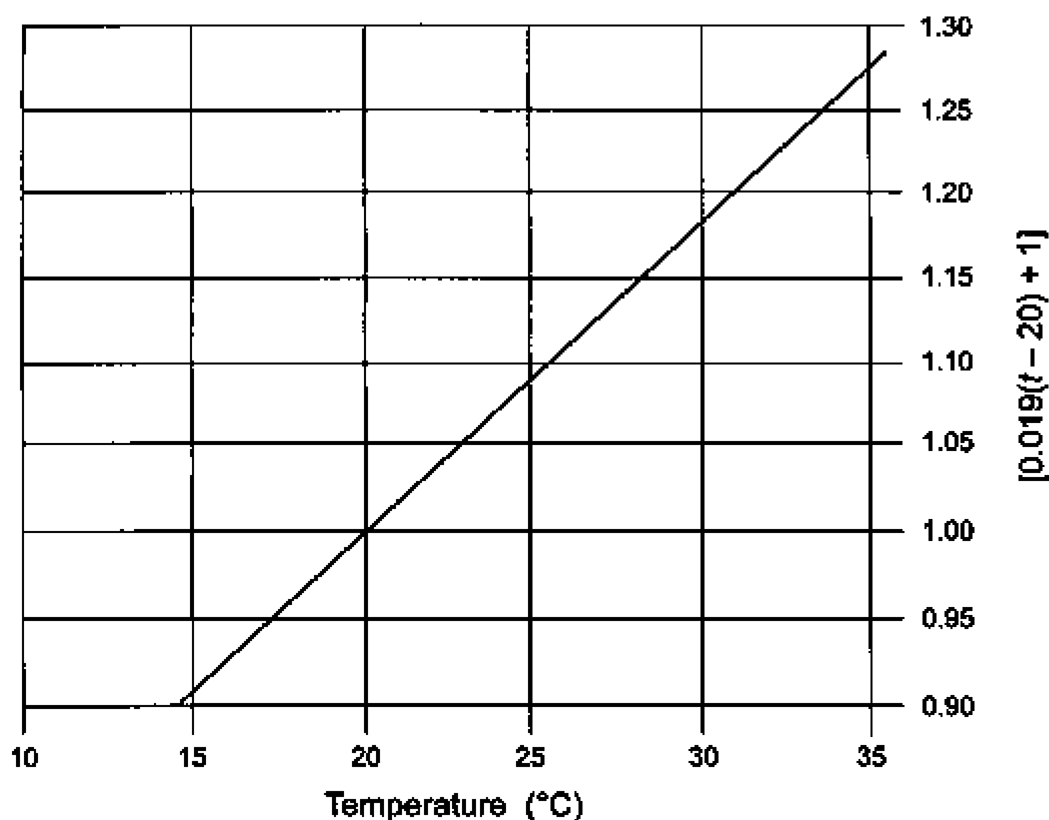
5. Turn the meter on. Follow the manufacturer's operating instructions and record the meter reading.

6. Turn the meter off and pack it and the electrode in the carrying case for transport.

Calculation

Electrolytic conductivity increases with temperature at a rate of 1.9 per cent per °C. Conductivity measurements will therefore be the most accurate when made at the same temperature as that at which the cell constant is determined. While a temperature correction factor is included in the calculation, the temperature coefficient, 0.019, is for standard (0.0100 mol l^{-1}) KCl solution: the temperature coefficient for water will usually be different. Thus, if the temperature is much higher or much lower than 20 °C, an error will be introduced into the calculation.

Figure 6.2 Values of [0.019(*t*-20) +1]



When *conductivity* of the sample has been measured, the calculation is:

$$\text{Conductivity} = \frac{C_m \times K_c}{[0.019(t-20)+1]} \ \mu\text{mhos cm}^{-1}$$

When *resistance* of the sample has been measured, the calculation is:

$$\text{Conductivity} = \frac{10^6 \times K_c}{R_m [0.019(t-20)+1]} \ \mu\text{mhos cm}^{-1}$$

where

K_c = cell constant (cm^{-1})
C_m = measured conductivity of sample at t °C (µmhos cm^{-1})
R_m = measured resistance of sample at t °C (ohms)
T = temperature of sample (°C).
Note: The value for $[0.019(t - 20) + 1]$ may be taken from the graph in Figure 6.2.
Reporting

Record the meter reading, the units of measurement, and the temperature of the sample at the time of reading. Report conductivity at 20 °C.

6.5 Dissolved oxygen

The dissolved oxygen concentration depends on the physical, chemical and biochemical activities in the water body, and its measurement provides a good indication of water quality. Changes in dissolved oxygen concentrations can be an early indication of changing conditions in the water body.

Two main methods are available for the determination of dissolved oxygen: the Winkler method and the electrometric method using membrane electrodes. Use of the Winkler method requires the addition of three chemical reagents to the sample very soon after it is obtained. The dissolved oxygen concentration (in mg l^{-1}) is then determined by titration with sodium thiosulphate solution, which may be done in the field or up to 6 hours later in a laboratory. The electrometric method is suitable for the field determination of dissolved oxygen and is simple to perform. It requires an electrically powered meter and an appropriate electrode. The result it gives requires the application of correction factors to compensate for salinity and temperature; some meters have built in temperature compensation.

6.5.1 Winkler method

Apparatus

√ BOD bottle, capacity 250 to 300 ml
√ Graduated cylinder
√ Flask
√ Burette (or other device for dispensing and measuring liquid)
√ Pipettes (or similar means of adding reagents)
Reagents
√ Distilled water in a rinse bottle.

√ Manganous sulphate solution. Dissolve 500 g manganous sulphate pentahydrate, $MnSO_4.5H_2O$, in distilled water. Filter if there is any undissolved salt, and make up to 1 litre.

√ Alkaline-iodide-azide solution. Dissolve 500 g sodium hydroxide, NaOH (or 700 g potassium hydroxide, KOH), and 135 g sodium iodide, NaI (or 150 g potassium iodide, KI), in distilled water and dilute to 1 litre. Sodium and potassium salts may be used interchangeably. Dissolve 10 g sodium azide, NaN_3, in 40 ml distilled water and add to the NaOH/NaI mixture. This reagent should not give a colour with starch when diluted 1:25 and acidified.

√ Concentrated sulphuric acid.

√ Starch indicator solution. Make a smooth paste by blending 1 g of soluble starch with a little cold distilled water in a beaker of capacity at least 200 ml. Add 200 ml of boiling distilled water while stirring constantly. Boil for 1 minute and allow to cool. Store in a refrigerator or at a cool temperature. Alternatively, thiodene powder may be used as an indicator.

√ Sodium thiosulphate solution (0.025 mol l^{-1} for 200 ml sample). Dissolve 6.3 g sodium thiosulphate pentahydrate, $Na_2S_2O_3.5H_2O$, in distilled water and make up to 1 litre. Standardise against KI. Add either 1 ml chloroform or 10 mg mercuric iodide to stabilise the solution. Store in a brown bottle.

Procedure

The procedure described here assumes that the sample has already been properly collected in a dissolved oxygen sampler and is contained in a BOD bottle.

1. Remove the BOD bottle containing the sample from the dissolved oxygen sampler and insert the matching ground-glass stopper in the neck of the bottle. Be sure that no air bubbles have been trapped under the stopper and maintain a water seal around the stopper until ready for the next step of the procedure.

2. Pour off the water seal and remove the ground glass stopper. Add 1 ml of $MnSO_4$ solution, then 1 ml of alkaline-iodide-azide solution. For both additions, hold the tip of the pipette against the inside of the bottle neck to prevent splashing.

3. Replace the ground-glass stopper, being careful to avoid trapping air bubbles under it.

4. Mix the contents by inverting the bottle several times. Keep a finger over the stopper during mixing to make sure that it does not fall out. A brown floc will form in the bottle before and during the mixing. If there was no dissolved oxygen in the sample, the floc will be white. When the bottle is set down the floc will settle, leaving a clear liquid above it.

5. Allow the floc to settle between a half and two-thirds of the way down the bottle, then mix again as in step 4 (above). Allow to settle once more, until all of the floc is in the lower third of the bottle.

6. Remove the stopper, add 1 ml of H_2SO_4 without splashing, replace the stopper and mix the contents of the bottle by inverting it several times. The floc will disappear and the liquid in the bottle will be a yellowish-brown colour. If there was no dissolved oxygen in the sample the liquid will be colourless.

Note: The dissolved oxygen in the sample is now “fixed”. The amount of iodine that has been released from the reagent (causing the yellow-brown colour) is proportional to the amount of oxygen that was in the sample. If the bottle is kept tightly stoppered it may be stored for up to 6 hours before step 8, titration with sodium thiosulphate solution.

7. Transfer a volume, V_t, corresponding to 200 ml of the original sample to the flask. Adjustment should be made to compensate for the amount by which the sample was diluted when 1 ml of $MnSO_4$ and 1 ml of the alkaline-iodide-azide solution were added. If, for example, a 300-ml BOD bottle is used, the volume would be:

$$V_t = 200 \times \frac{300}{300-2} = 201.3 \text{ ml}$$

8. Titrate with sodium thiosulphate solution (0.025 mol l^{-1}), stirring the contents of the flask until the yellow-brown colour fades to a pale straw colour. Add a few drops of starch solution and a blue colour will develop. Continue titrating a drop at a time until the blue colour disappears.

Calculation

For titration of 201.3 ml (200 ml of sample plus 1.3 ml allowance for reagents) with 0.025mol l^{-1} sodium thiosulphate:

1 ml $Na_2S_2O_3$ solution = 1 mg l^{-1} dissolved oxygen

If sodium thiosulphate is used at a strength other than 0.025 mol l^{-1}, and if the sample volume titrated is other than 200 ml (excluding the volume added to compensate for the chemical reagents as described in step 7), the dissolved oxygen in the sample may be calculated from the following formula:

$$\text{Dissolved oxygen} = \frac{\text{ml titrant} \times \text{mol l}^{-1}\ \text{titrant} \times 8{,}000}{\text{volume of sample titrated}}\ \text{mg l}^{-1}$$

6.5.2 Electrometric method

Apparatus

√ Battery-powered meter. This is a meter designed specifically for dissolved oxygen measurement. Other meters, such as a specific ion meter or an expanded scale pH meter, may also be used.

√ Oxygen-sensitive membrane electrode.

Procedure

1. Follow exactly the calibration procedure described in the manufacturer's operating instructions. Generally, electrodes are calibrated by reading against air or against a sample of known dissolved oxygen content. This "known" sample could be one for which dissolved oxygen concentration has been determined by the Winkler method or one that has been saturated with oxygen by bubbling air through it. The zero end of a calibration curve can be determined by reading against a sample containing no dissolved oxygen, prepared by adding excess sodium sulphite, Na_2SO_3, and a trace of cobalt chloride, $CoCl_2$, to the sample.

2. Rinse the electrode in a portion of the sample which is to be analysed for dissolved oxygen.

3. Immerse the electrode in the water, ensuring a continuous flow of water past the membrane to obtain a steady response on the meter.

4. Record the meter reading and the temperature, and the make and model of the meter.

5. Switch the meter off and pack it and the electrode in the carrying case for transport.

6.6 Thermotolerant (faecal) coliforms

Samples for microbiological testing are very prone to changes during transport and storage and there is therefore considerable advantage in field testing for variables such as thermotolerant (faecal) coliforms.

Almost all kits for field testing for thermotolerant coliforms are based on the membrane filtration method. This method is described in detail in Chapter 10 and is not repeated here.

An example of a kit originally developed for testing drinking water samples is provided in Figure 6.3. The kit includes equipment to test for thermotolerant coliforms, turbidity, pH, residual chlorine and (optionally) conductivity. This and some similar kits include an integral incubator and rechargeable battery which provide independence from mains electricity for up to a week.

6.6.1 Disinfecting equipment in the field

Disinfection of equipment is essential for many microbiological analytical procedures, but some of the devices used for this purpose in a laboratory are unsuitable for transporting to the field. Some of the methods for disinfecting equipment in the field are:

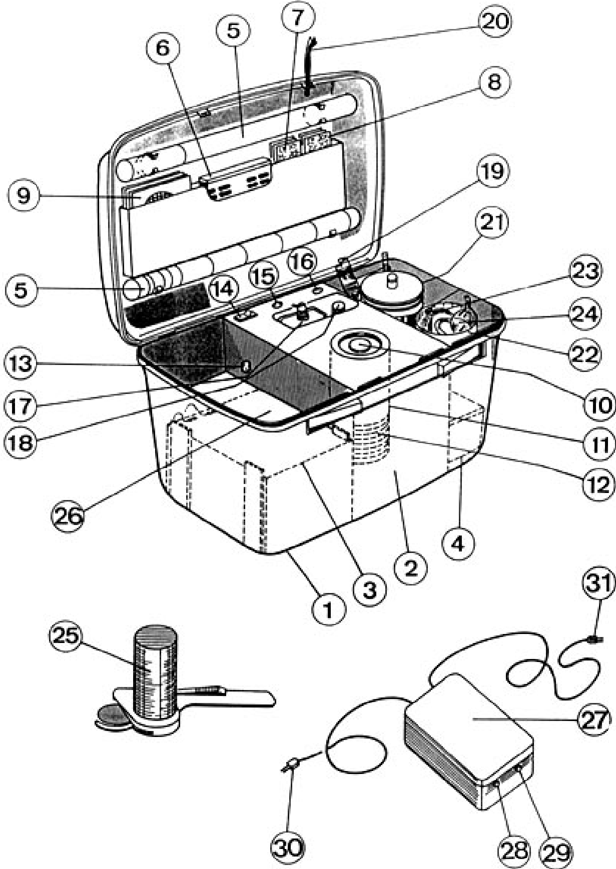
• *Dry heat:* The flame from a gas cigarette-lighter, for example, can be used to disinfect forceps for manipulation of membrane filters. It must be a butane or propane gas lighter, not one that uses gasoline or similar liquid fuel, which would blacken the forceps.

• *Formaldehyde:* This gas is a powerful bactericide. It may be generated by the combustion of methanol (but no other alcohol) in a closed space where oxygen becomes depleted. In the field, this is a convenient way to disinfect the filtration apparatus between uses. A minimum contact time of 10 minutes is recommended.

• *Disinfecting reusables:* The two main items of reusable equipment, Petri dishes (glass or aluminium) and bottles, may be disinfected by immersion in boiling water for a few minutes, by dry heat sterilisation in an oven or by heating in a pressure cooker for at least 20 minutes.

• *Disposal of contaminated material:* Autoclaving (or pressure cooking) of contaminated material is impractical in the field. Contaminated materials such as membrane filters and pads may be burned.

Figure 6.3 Example of a field kit that includes the facility to test for thermotolerant coliforms. Reproduced with the permission of the Robens Institute, Guildford, UK



1. Case
2. Incubator
3. Battery
4. Spares case
5. Turbidity tubes (pair)
6. Chlorine and pH comparator
7. Chlorine test tablets
8. pH test tablets
9. Membrane filters
10. Incubator lid
11. Incubator pot
12. Petri dishes
13. Power socket
14. On/Off socket
15. Power “On” indicator
16. Heater “On” Indicator
17. Methanol dispenser
18. Culture medium bottle
19. Lighter
20. Tweezers
21. Filtration assembly with sample cup

22. Vacuum cup
23. Sample cable
24. Vacuum pump
25. Absorbent pad dispenser
26. Storage space

Charger unit

27. Battery charger/mains power unit
28. Power “On” Indicator
29. Charged battery indicator
30. Incubator plug
31. Mains supply plug

6.7 Quality assurance in the field

Quality control of analytical procedures is as important in field testing as it is in traditional laboratory analysis. This topic is covered in detail in Chapter 9 but certain problems are peculiar to field testing. Such problems may include one or more of the following:

- Staff performing the analyses may not be fully trained in chemical or microbiological analyses.

- The conditions of sampling and analysis may vary considerably between sampling sites.

- Analytical methodology may be of limited accuracy and precision because of the need for equipment to be portable and easy to use on site.

Such problems can lead to the generation of erroneous data.

All field testing should be conducted to specified standards. Training in the proper use of the equipment and a programme of regular equipment maintenance and calibration are essential. In addition, there should be an internal quality control system, similar to those described in Chapter 9, for each analytical technique.

Ideally, field analysis should be performed under the supervision of a central laboratory. This allows the independent checking of quality control data before they are accepted into any formal data base. Quality assurance of field assays can be integrated with the quality system used by the central laboratory.

When a link with an analytical laboratory is not possible, appropriate quality control procedures should be implemented and monitored by the management of the field testing service, in particular by personnel who are not directly involved with generation of data. This again ensures independent checking of data. Often the expertise required to conduct monitoring is available only from field testing staff themselves, in which case it is advisable for management to institute some form of audit system to monitor the validity of reported data.

6.8 Source literature and further reading

APHA 1992 *Standard Methods for the Examination of Water and Wastewater.* 18th edition. American Public Health Association (APHA), American Water Works Association (AWWA) and Water Pollution Control Federation (WPCF), Washington, DC.

AWWA 1978 *Simplified Methods for the Examination of Drinking Water* American Water Works Association, Denver, CO.

Hach Company 1989 *Hach Water Analysis Handbook*. Hach Company, Loveland, CO.

Hutton, L.G. 1983 *Field Testing of Water in Developing Countries*. Water Research Centre, Medmenham.

ISO 1990 *Water Quality - Detection and Enumeration of Coliform Organisms, Thermotolerant Coliform Organisms and Presumptive Escherichia coli. Part 1: Membrane Filtration Method*. International Standard ISO 9308-1, International Organization for Standardization, Geneva.

WHO 1992 *GEMS/WATER Operational Guide*. Third edition, Unpublished WHO document GEMS/W.92.1, World Health Organization, Geneva.