

The Evaluation of a Partech Model 5100 Hand-Held Dissolved Oxygen Meter

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R&D 220/26/T



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EXECUTIVE SUMMARY

This report describes the results of an evaluation of a Partech Model 5100 Hand-held Dissolved Oxygen meter. The evaluation was undertaken by the NRA (Thames Region) at the Evaluation and Demonstration Facilities at Fobney Mead, Reading and Lea Marston, Birmingham according to an evaluation protocol jointly devised by WRc and the NRA.

The Partech hand-held Dissolved Oxygen meter performed well. No comparison could be made to any manufacturer stated accuracy and reliability as this was not provided with instrument.

In order to change the batteries on this instrument it is necessary to open the case thus exposing the instrument's electronics. The instrument is not protected against installation of the battery with incorrect polarity.

The total error (quadrature sum of random and systematic error errors) for five accuracy test concentrations gave a total error of between 3.7 and 5.4 percentage saturation. Winkler determinations of these solutions gave total errors of between 6 and 25 percentage saturation.

During the field trials there was no significant (95% confidence levels) drift of the calibration at either of the evaluation sites. The total error (quadrature sum of random and systematic errors) was 0.46 mg l^{-1} for Lea Marston and 0.55 mg l^{-1} for Fobney Mead.

When operating the instrument it was found that the only convenient way to view the display was with instrument hanging from the operator's neck. No provision was included to allow the instrument to be free standing. The length of the strap made reading of the display difficult. The calibration control was found to be too near to the selector control making it very likely that the calibration could be accidentally changed.

The instrument currently costs £595.00. No maintenance was required during the four month evaluation. other than re-fitting of the selector switch, which took only a few minutes.

KEY WORDS

Dissolved Oxygen, Evaluation

NRA Evaluation Report 220/26/T

1. INTRODUCTION

This report describes the evaluation of a Partech MODEL 5100 Hand-held Dissolved Oxygen Meter.

A discussion of the chemistry of oxygen in natural waters may be found in the protocol document (Harman 1993). However a resume is given here to assist in the understanding of the evaluation methods applied.

Following the principle of Henry's Law, the concentration of dissolved oxygen in a sample of water is directly proportional to the partial pressure of oxygen in equilibrium with that water sample at a constant temperature; assuming that air has an oxygen content of 20.94% v/v (and is saturated with water vapour). In addition, the solubility of oxygen in water (or air) is dependent on the concentration of other dissolved species within the water and atmospheric pressure.

An instrumental procedure for the measurement of dissolved oxygen in water involves the use of an electrochemical cell (often called an oxygen electrode or sensor), the response of which is proportional to the thermodynamic activity of oxygen in solution.

Electrochemical sensors with membranes can be of two types; galvanic and polarographic. The Partech Model 5100 is fitted with the most commonly used galvanic electrochemical cell, the Mackereth cell. The cell consists of a perforated silver cathode in the form of a cylinder which surrounds a lead anode. An aqueous or gel potassium hydroxide solution (often saturated with potassium hydrogen carbonate to eliminate interference from carbon dioxide) acts as an electrolyte and fills the space between the cathode and the anode. The electrolyte is confined by a thin polythene or silicone membrane which is supported by the cathode. Oxygen which diffuses through the membrane is reduced at the cathode to give a current proportional to the partial pressure of oxygen. A detailed description of the theory of membrane-covered oxygen electrodes is given in (Hitchman 1978).

Generally, the current output from the cell is converted to either a reading equivalent to the percentage saturation of oxygen in water, or to the actual concentration in terms of $\text{mg O}_2 \text{ l}^{-1}$

The evaluation was undertaken by the NRA (Thames Region) at the Evaluation and Demonstration Facilities at Fobney Mead, Reading and Lea Marston, Birmingham in accordance with an evaluation protocol jointly devised by WRc and the NRA. The protocol allows the instrument to be assessed in a manner commensurate with typical use in the field.

The objectives of the assessment were as follows ;

- to assess the performance characteristics of hand-held dissolved oxygen meters currently in use within the NRA,
- to provide information on the appropriate application of the instruments, the correct method of use, and calibration and maintenance procedures, and
- to establish methods of use which optimise the performance and the quality of the data obtained for the instruments presently in use and those currently commercially available.

2. DETAILS OF EQUIPMENT EVALUATED

Manufacturer:	Partech (Electronics) Ltd Eleven Doors Charlestown St. Austell Cornwell PL25 3NN
Supplier:	Partech (Electronics) Ltd Eleven Doors Charlestown St. Austell Cornwell PL25 3NN
Tel:	0726 74856
Fax:	0726 68850
Instrument Description:	Model 5100 Hand-held Dissolved Oxygen Meter
Serial Number	105
Sensor Type	Galvanic

The manufacturer's specification for the instrument is described in Appendix C.

3. MAJOR FINDINGS AND COMMENTS

This section provides a summary of the major findings and conclusions of the evaluation.

No comparison could be made to any manufacturer stated accuracy and reliability as this was not provided with instrument.

In order to change the batteries on this instrument it is necessary to open the case thus exposing the instrument's electronics, this may be of concern under field conditions. Although a planned programme of preventative maintenance should ensure that this is not necessary.

The manufacturer stated that care should be taken when installing the battery to ensure the correct polarity otherwise the instrument could be damaged.

Due to the nature of dissolved oxygen measurement testing of the accuracy of the instrument proved difficult. By the diffusion of certificated nitrogen-oxygen mixtures a theoretical dissolved oxygen level could be achieved. Winkler titrations were performed on the test solutions to verify the dissolved oxygen level. However, this test showed large variations in the test solutions. The total error (quadrature sum of random and systematic error errors) for Winkler Determinations on the five test concentrations gave a total error of between 6 and 25 percentage saturation. Whilst the instrument total error was between 3.7 and 5.4 percentage saturation.

The response time of the dissolved oxygen probe was better than the stated response of 35 seconds however the temperature probe took considerably longer (50 seconds) which would affect the performance of the instrument.

During the field trials there was no significant (95% confidence levels) drift in the calibration at either of the evaluation sites. The total error (quadrature sum of random and systematic errors) was 0.46 mg l^{-1} for Lea Marston and 0.55 mg l^{-1} for Fobney Mead.

Residual chlorine, was found not to cause any variation in the instrument readings for the levels tested. However this test did showed that the instrument readings varied from the expected values taken from tables (Hitchman, 1978).

When operating the instrument it was found that the only convenient way to view the display was with instrument hanging from the operator's neck. No provision was included to allow the instrument to be free standing. The length of the strap also caused some difficulty in reading the display. The calibration control was found to be too near to the selector control making it very likely that the calibration could be accidentally changed.

Although the instrument did not require any maintenance during the four months of the evaluation. The selector switch needed to be re-fitted.

4. EVALUATION PROCEDURES

The evaluation and demonstration facility at Fobney Mead, Reading and Lea Marsaton, Birmingham have been previously described (Baldwin 1991) as have the test procedures (Harman 1992). A brief description of each test is provided for information.

4.1 Sensor stabilisation

The instrument was calibrated according to the manufacturer's instructions. Following calibration the instrument was switched off and the sensor assembly stored in its transit container for at least 1 hour prior to the test.

The sensor was then placed in a 100% air-saturated solution under different temperature regimes. Readings were taken after 10, 30, 60, 120, 180, 300, 600 and 1200 seconds immersion.

Three different temperature change regimes were tested:-

- Sensor stored at room temperature, test solution at 20 °C,
- Sensor stored at room temperature, test solution at 5 °C.
- Sensor stored at 5 °C, test solution at 5 °C.

4.2 Battery life

The power consumption was recorded whilst the instrument measured a 100% air-saturated sample.

In addition, note was also made of the make and type of battery fitted and the nominal battery voltage and capacity.

4.3 Effects of low battery power

The battery (or batteries) were replaced by an adjustable stabilised power supply and oxygen and temperature readings were taken at a range of reduced voltages.

The power supply voltage was adjusted downwards whilst observing the dissolved oxygen and temperature readings and a note made of the supply voltage at which the readings changed or became unstable.

The readings were taken with the instrument probe immersed in a 100% saturated sample. The instrument was allowed adequate time to discharge any capacitance before the readings were taken.

The voltage at which the 'low battery' indicator (if fitted) operates was noted.

4.4 Effect of flow at the sensor surface

The effect of flow on the sensor was investigated by taking measurements from the sensor in test solution at 100% air-saturation at a range of flow rates. The work was carried out in the outside flow tank at Fobney. Flow was measured by a water current meter accurate to $\pm 0.03 \text{ m s}^{-1}$. Two sets of measurements were taken at the following range of flow rates; 0.05 m s^{-1} , 0.13 m s^{-1} , 0.19 m s^{-1} , 0.27 m s^{-1} , 0.35 m s^{-1} and 0.37 m s^{-1} .

4.5 Effect of immersion depth

The effects of depth on the instrument sensor were measured using a specially constructed 2-metre long, 0.2 m diameter PVC tube. The construction details have been described previously (Harman 1992). The test column was filled with tap water and aerated to achieve a 100% air-saturated solution at room temperature.

The instrument was calibrated using the manufacturer's standard procedure and the sensor immersed to the specified depth and allowed five minutes to reach equilibrium before readings were taken. Continuous aeration maintained a flow of 0 to 0.03 m s^{-1} past the sensors.

Two sets of dissolved oxygen concentration, % saturation and temperature readings were taken at 0.3, 1.0 and 2.0 metres depth.

4.6 Effects of Interferents

The instrument was calibrated using the manufacturer's instructions.

The sensor was placed in twenty litres of 100% air-saturated de-ionised water. A reading was taken once it had stabilised. To produce a solution with a residual chlorine level of 30 mg l^{-1} , 7.5 ml of (8% available chlorine) sodium hypochlorite solution was added. A second reading was then taken.

For the temperature interference test the required temperatures were maintained by the control system at Fobney. The actual temperatures were recorded using type E thermocouples. After calibration of the sensor according to the manufacturer's instructions, readings were taken in 100% air-saturated water held at $10 \text{ }^\circ\text{C}$ ($\pm 0.1^\circ\text{C}$). The meter was switched off until the control system raised the test temperature to $30 \text{ }^\circ\text{C}$. The heated water was subsequently aerated to 100% saturation and the reading recorded.

4.7 Calibration.

The instrument was calibrated in air according to the manufacturers instructions. Readings were then taken in 100% air-saturated tap water and 100% air-saturated river water. The instrument was then calibrated in 100% air-saturated tap water and the measurements repeated.

4.8 Accuracy tests.

Test solutions were prepared by diffusing mixtures of the oxygen and nitrogen gas through tap water. The gas mixtures had a certified oxygen contents of 0.00%, 8.80%, 15.30% and 28.80% respectively. By dividing these values by the percentage of oxygen in air the theoretical percentage saturation dissolved oxygen level could be calculated. These were 0.00%, 42.0%, 73.1%, and 137.5%. A fifth level, 100% air-saturation, was achieved by bubbling air through tap water.

Prior to the test the dissolved oxygen concentrations were verified by Winkler determination (SCA 1979).

To reduce the effects of temperature variation between the various test solutions all tests were carried out at ambient room temperature. However, in order to allow subsequent comparison of the data, the temperature of each test solution was noted.

Prior to the test the instrument was calibrated for 100% air-saturation dissolved oxygen in distilled water in accordance with to the manufacturer's instructions.

The sensor was placed in each of the test solutions, in ascending order of dissolved oxygen concentration, and allowed to stabilise before the readings were taken. The sensor was then placed in each of the test solutions, in descending order, allowed to stabilise and further readings taken.

This test sequence was repeated five times.

The sensor was returned to its transit container for a period of at least 5 minutes between each successive set test solutions.

Readings were taken for each measurand provided by the instrument (e.g. mg l^{-1} , % sat. and $^{\circ}\text{C}$) and the temperature of the various test solutions recorded using a graduated mercury thermometer or type E thermocouple.

4.9 Response time tests

4.9.1 Oxygen sensor

The instrument was calibrated prior to the test using solutions prepared according to the standard method. The temperature of the test solutions was $20 \pm 0.1^\circ\text{C}$.

The sensor was placed in each solution, in turn, and the time taken for the instrument to register a measurement within 90% of the step change recorded, i.e. when the sensor was removed from the 0% solution; the time required for the reading to reach 90% saturation and, following stabilisation at 100%, and when the sensor was placed back into the 0% solution; the time required for the reading to reach 10% saturation.

The test cycle was repeated 3 times.

4.9.2 Temperature sensor

The instrument was calibrated prior to the test in accordance with the manufacturer's instructions.

The sensor was placed in two test solutions, $25 \pm 0.2^\circ\text{C}$ and $5 \pm 0.2^\circ\text{C}$ in turn, and the time taken for the instrument to register a measurement within 90% of the step change recorded,

The test cycle was repeated 3 times.

4.10 Salinity correction/compensation

Test solutions were prepared by the addition of 2, 5, 10, 20 and 40 g l⁻¹ NaCl in distilled water. The solutions were maintained at 100% saturation throughout the tests. The sensor was placed into each test solutions, and once stabilised, the concentration, % saturation and temperature readings were noted.

4.11 Field assessments

At the beginning of the test the sensor was calibrated in accordance with the manufacturer's instructions.

Once the instrument had been calibrated no further adjustment of the calibration took place until the end of the field test.

The sensor was immersed into the continuous sample stream of a Class 1A river three times each day for a period of 2 weeks. Percentage saturation, dissolved oxygen concentration and temperature readings were recorded manually from the meter. The sensor was returned to the

transit container and the instrument switched off between readings.

Triplicate Winkler determinations were taken to coincide with the daily readings. The time at which the Winkler samples were taken were noted to enable comparison of the results from the standard water quality monitors installed at the particular site.

Each day the sensor was immersed in 100% saturated water and the displayed result noted.

Independent temperature and atmospheric pressure readings were also taken.

The instrument battery condition was checked daily and replaced if necessary. Note was kept of any necessary battery changes.

This procedure was repeated on a Class 3 river.

During the test the water was monitored for the following parameters: temperature, dissolved oxygen, pH, conductivity, turbidity and ammonium (Class 3 river only).

Daily samples were also taken for laboratory analysis.

5. OBSERVATIONS

5.1 Documentation

An 8 page A4 size instruction manual was supplied with the instrument. The manual provides a description of the basic operational use of the instrument.

Instructions are provided both for the air-calibration method (for readings in % saturation) and for the air-saturated water method (for the mg l⁻¹ mode). The method of preparation of the calibration solution is not described. Oxygen saturation tables are provided. No salinity correction tables have been provided for the use of this instrument in an estuarine or marine environment. The manual provided states that the calibration control is a 10-turn potentiometer giving good resolution, however, the meter supplied was fitted with a three-quarter turn type.

Maintenance procedures are limited to changing of the batteries, electrode and replacement of the sensor membrane. (The manual states that the user should be careful to observe the correct polarity when changing the batteries otherwise the meter may be permanently damaged. This implies that the instrument does not incorporate in-built polarity protection). The expected life of the batteries is simply stated as 'many months'.

No advice is given on the correct or preferred procedure for the removal of foulant from the surface of the membrane itself.

A very brief fault finding table is included.

The general specification provides data only for response time of the dissolved oxygen sensor.

No data is given for accuracy, stability or the effects of specific common interferences, including the effects of flow past the sensor.

No advice is given for the interpretation or significance of the readings obtained.

5.2 Design and Construction

The instrument is based around a cylindrical watertight plastic housing with two controls mounted in a recess at one end. A shoulder strap is provided for use in the field. The meter does not include a stand for bench use. The meter unit is approximately 200 mm x 80 mm and weighs 1.5 kg. The manual states that the unit is sealed to IP67 and is capable of withstanding short-term immersion.

A LCD panel meter is fitted to the meter, however the display does not incorporate a backlight facility.

The various functions provided are all selected by knobs. The calibration control knob does not incorporate a locking mechanism. Furthermore the calibration control lies very close to the rotary mode selector control, giving rise to the possibility of inadvertent operation of the

calibration control during normal operation in the field without the operator's knowledge.

No means is provided for adjusting temperature calibration or zeroing the dissolved oxygen reading.

The probe is a galvanic membrane covered sensor incorporating thermistors for temperature measurement and compensation.

No facility is provided for housing the probe or lead during transit.

5.3 Installation

None Required

5.4 Commissioning

None Required

5.5 Maintenance and Downtime

During the assessment the mode selector switch became loose and had to be re-tightened.

5.6 Ease of Use

The instrument cannot be stood upright on the work bench as the oxygen sensor cable protrudes from the lower face of the cylindrical plastic housing. This means that the meter's display may only be conveniently viewed whilst the instrument is hanging from the neck strap provided.

The various functions provided are all selected by knobs. The calibration control knob does not, however, incorporate a locking mechanism. Furthermore the calibration control lies very close to the rotary mode selector control, giving rise to the possibility of inadvertent operation of the calibration control during normal operation in the field without the operator's knowledge.

The instrument has to be opened in order to change the batteries and, as a consequence, the internal electronics are exposed. This may cause problems if the user needs to change the batteries in the field during damp or wet weather.

The manufacturer recommends setting the calibration after leaving the sensor in air for 10 minutes. This period may be too long since as it may allow the membrane to surface to become dry.

6. RESULTS

Table 6.1 Instrument Stabilisation readings for different temperature changes

Temperature Change	Time (secs)	Dissolved Oxygen (%sat.)
Room Temperature → 5°C	10	91
	30	94
	60	96
	120	97
	180	97
	300	98
	600	99
	1200	100
Room Temperature → 20°C	10	97
	30	100
	60	99
	120	98
	180	98
	300	99
	600	99
	1200	99
5°C → 5°C	10	90
	30	96
	60	97
	120	97
	180	97
	300	97
	600	97
	1200	99

Table 6.2a Power consumption

Meter Setting	V	mA	mWatts
OFF	9.16	0.00	0.0
% sat.	9.09	2.81	25.5
mg l ⁻¹	9.09	2.81	25.5
°C	9.08	3.11	28.2

Table 6.2b Battery characteristics

Battery Make	Ever Ready
Battery Type	6LF22 Alkaline
Battery Voltage	NOT STATED
Battery Capacity	0.52 Ah
Replacement Interval	NOT STATED

Table 6.3 Effects of different power supply voltages on instrument readings

Power Level (Volts)	Instrument Setting			Low Battery Indicator
	% sat.	mg l ⁻¹	°C	
9.00	100	10.1	16.0	NO
8.52	101	10.3	15.9	NO
7.99	102	10.5	15.9	NO
7.49	103	10.5	15.9	NO
7.01	101	10.4	15.9	YES
6.51	101	10.4	13.7	YES
5.99	99	10.1	10.4	YES
5.50	81	8.2	8.2	YES
5.00	59	6.0	5.8	YES

Table 6.4 Instrument readings for different Flows at sensor surface

Water Temperature 10.3 °C

Flow Rate (m s ⁻¹)	Dissolved Oxygen (mg l ⁻¹)	Temp. (°C)	Dissolved Oxygen (% sat.)
0.35	11.7	10.6	103
0.30	11.7	10.6	102
0.24	11.6	10.6	102
0.16	11.5	10.6	101
0.10	11.4	10.6	100
0.05	11.0	10.6	96
0.00	9.8	10.6	86
0.04	11.0	10.6	96
0.09	11.2	10.6	98
0.13	11.5	10.6	101
0.19	11.6	10.6	102
0.29	11.6	10.6	102
0.37	11.8	10.6	104

Table 6.5 Instrument readings at different Immersion Depth

Water Temperature - 12.0 °C

Depth (m)	Dissolved Oxygen (mg l ⁻¹)	Temp. (°C)	Dissolved Oxygen (% sat.)
0.3	9.4	12.6	86
1.0	9.4	12.5	86
2.0	9.5	12.7	87
0.3	9.8	13.0	90

During this test the Dissolved Oxygen (% sat.) readings were unstable

Table 6.6 Instrument readings for two Interferents

Interferent	Level	Dissolved Oxygen (mg l ⁻¹)	Temp. (°C)	Dissolved Oxygen (% sat.)
Temperature	10°C	10.7	10.8	95
	30°C	7.8	31.1	102
Chlorine	0 mg l ⁻¹	9.1	23.7	104
	30 mg l ⁻¹	9.2	23.9	105

Table 6.7 Instrument readings for commonly employed Calibration techniques

	Sample (100% saturation)	Dissolved Oxygen (mg l ⁻¹)	Temp. (°C)	Dissolved Oxygen (% sat.)
*	Chlorinated Tap Water	9.2	20.5	99
*	River	9.2	20.7	100
!	River Water	8.8	20.9	95

* Calibrated in Air

! Calibrated in Dechlorinated Tap Water

Table 6.8a Instrument readings for different dissolved oxygen levels - Test 1

Atmospheric Pressure - 98.8 kPa
Water Temperature - 21.2 °C

*Dissolved Oxygen (% sat.)	Dissolved Oxygen (mg l ⁻¹)	Temp. (°C)	Dissolved Oxygen (% sat.)
0	0.7	21.9	8
42.0	3.9	22.9	44
73.1	6.7	22.3	74
100	8.8	21.5	96
137.5	12.4	22.3	137
137.5	12.0	22.3	133
100	9.0	21.6	99
73.1	6.7	22.8	75
42.0	3.8	23.9	44
0	0.4	23.3	4

* see text for details (section 4.8)

Table 6.8b Instrument readings for different dissolved oxygen levels - Test 2

Atmospheric Pressure - 98.7 kPa
Water Temperature - 23.5 °C

*Dissolved Oxygen (% sat.)	Dissolved Oxygen (mg l ⁻¹)	Temp. (°C)	Dissolved Oxygen (% sat.)
0	0.3	23.5	3
42.0	3.7	24.6	43
73.1	6.6	23.8	76
100	8.9	22.1	99
137.5	12.2	23.9	140
137.5	12.0	24.0	137
100	8.9	22.7	100
73.1	6.5	24.6	75
42.0	3.9	26.0	46
0	0.3	25.2	4

* see text for details (section 4.8)

Table 6.8c Instrument readings for different dissolved oxygen levels - Test 3

Atmospheric Pressure - 10.2 kPa
Water Temperature - 17.3 °C

*Dissolved Oxygen (% sat.)	Dissolved Oxygen (mg l ⁻¹)	Temp. (°C)	Dissolved Oxygen (% sat.)
0	0.2	17.1	2
42.0	4.9	17.7	49
73.1	7.9	17.6	80
100	10.3	17.0	103
137.5	14.2	17.9	144
137.5	14.2	18.3	146
100	10.4	17.9	106
73.1	7.8	19.0	81
42.0	4.6	19.7	49
0	0.5	19.2	5

* see text for details (section 4.8)

Table 6.8d Instrument readings for different dissolved oxygen levels - Test 4

Atmospheric Pressure - 102.3 kPa
Water Temperature - 20.3°C

*Dissolved Oxygen (% sat.)	Dissolved Oxygen (mg l ⁻¹)	Temp. (°C)	Dissolved Oxygen (% sat.)
0	0.5	19.5	5
42.0	4.7	20.8	50
73.1	7.4	20.6	79
100	10.0	20.0	106
137.5	13.5	20.8	146
137.5	13.4	21.1	145
100	9.8	20.6	105
73.1	6.9	21.6	75
42.0	4.3	22.5	48
0	0.3	21.5	3

* see text for details (section 4.8)

Table 6.8e Instrument readings for different dissolved oxygen levels - Test 5

Atmospheric Pressure - 100.9 kPa
Water Temperature - 17.5°C

*Dissolved Oxygen (% sat.)	Dissolved Oxygen (mg l ⁻¹)	Temp. (°C)	Dissolved Oxygen (% sat.)
0	0.4	16.6	4
42.0	4.4	17.3	44
73.1	7.2	17.4	72
100	10.2	16.9	102
137.5	13.6	17.9	139
137.5	13.4	18.7	139
100	9.7	18.6	101
73.1	7.4	18.6	77
42.0	4.2	20.5	45
0	0.2	20.2	2

* see text for details (section 4.8)

Table 6.8f Summary of Accuracy Data

*Actual Dissolved Oxygen (% sat.)	Instrument Accuracy		Winkler Accuracy	
	Systematic Error	Random Error	Systematic Error	Random Error
0	-4.0	1.8	-5.7	2.0
42.0	-4.2	2.6	-8.4	6.0
73.1	-3.3	2.8	-4.0	4.1
100	-1.7	3.3	-1.9	4.1
137.5	-3.1	4.5	-13.4	21.4

* see section 4.8 for details

Table 6.9 Response time tests - Oxygen Sensor

	Time 1 (seconds)	Time 2 (seconds)	Time 3 (seconds)
Step change low to high Dissolved Oxygen*	13.03	21.06	9.22
Step change high to low Dissolved Oxygen*	12.81	15.66	12.90

* see text for details (section 4.9)

Table 6.10 Response time Test - Temperature Sensor

	Time 1 (seconds)	Time 2 (seconds)	Time 3 (seconds)
Step change low to high Temperature (°C)*	56.60	41.56	39.88
Step change high to low Temperature (°C)*	56.91	58.63	48.35

* see text for details (section 4.9)

Table 6.11 Instrument readings for different Salinity levels

Chlorine (mg/l)	Water Temp. (°C)	Dissolved Oxygen (mg l ⁻¹)	Temp. (°C)	Dissolved Oxygen (% sat.)
0	14.5	10.5	15.1	101
5	14.6	10.5	15.2	102
10		10.3	15.7	100
20	15.4	10.5	16.1	103
40	15.6	10.4	16.3	102
20	16.5	10.1	17.2	102
10	17.1	10.0	17.8	102
5	17.8	10.2	18.6	105
0	18.4	10.1	19.3	105

Table 6.12a

Field Data Class 1A River

Date	Water Temp. (°C)	Pressure (kPa)	Time	Winkler (mg l ⁻¹)	Dissolved Oxygen (mg l ⁻¹)	Dissolved Oxygen (% sat.)	Temp. (°C)	Time	Winkler (mg l ⁻¹)	Dissolved Oxygen (mg l ⁻¹)	Dissolved Oxygen (% sat.)	Temp. (°C)	Time	Winkler (mg l ⁻¹)	Dissolved Oxygen (mg l ⁻¹)	Dissolved Oxygen (% sat.)	Temp. (°C)
28/01/93	8.6	100.8	15:30	11.48	11.8	100	9.1	17:42	11.38	11.8	101	9.1					
29/01/93	8.8	101.7	11:38	11.48	11.8	101	9.2	14:45	11.62	11.9	101	9.2	17:19	11.41	11.9	101	9.3
01/02/93	8.2	103.4	11:55	12.02	12.1	102	8.6	14:40	12.33	12.2	103	8.8	16:22	12.02	12.2	102	8.5
02/02/93	7.8	103.7	11:48	12.10	12.3	103	8.3	14:15	12.00	12.3	104	8.4	15:49	12.35	12.3	103	8.4
03/02/93	8.2	104.0	11:25	11.90	12.4	104	8.5	17:00	11.90	12.3	103	8.6	18:32	11.76	12.2	103	8.6
04/02/93	7.8	103.4	12:00	12.00	12.3	103	8.2	16:52	11.80	12.4	103	8.1	18:23	11.80	12.4	103	8.1
05/02/93	7.1	103.5	12:24	11.19	12.5	103	7.6	15:36	11.99	12.6	103	7.5	16:39	12.60	12.6	104	7.5
08/02/93	9.0	103.4	11:22	11.69	12.1	104	9.5	16:05	11.45	12.1	104	9.5	16:44	11.35	12.1	104	9.6
09/02/93	8.7	103.2	11:21	11.49	12.1	104	9.6	14:24	11.35	12.2	104	9.1	16:51	11.53	12.1	103	9.2
10/02/93	7.8	102.8	13:10	11.78	12.3	103	8.3	16:21	11.94	12.4	103	8.1					
11/02/93	7.1	102.9	12:41	11.93	12.4	102	7.5										

Table 6.12b

Field Data Class 3 River

Date	Water Temp. (°C)	Pressure (kPa)	Time	Winkler (mg l ⁻¹)	Dissolved Oxygen (mg l ⁻¹)	Dissolved Oxygen (% sat.)	Temp. (°C)	Time	Winkler (mg l ⁻¹)	Dissolved Oxygen (mg l ⁻¹)	Dissolved Oxygen (% sat.)	Temp. (°C)	Time	Winkler (mg l ⁻¹)	Dissolved Oxygen (mg l ⁻¹)	Dissolved Oxygen (% sat.)	Temp. (°C)	
15/02/93			15:23	7.62	8.0	68	9.5											
16/02/93			14:17	7.62	8.2	71	9.9	15:35	7.41	8.1	70	9.9						
17/02/93	10.7	102.6	14:24	6.90	7.5	66	10.8	15:00	7.04	7.4	66	11.0	15:51	6.87	7.5	67	11.1	
18/02/93	10.8	101.8	14:35	7.04	7.2	64	10.8	16:00	7.21	7.6	67	11.0						
19/02/93		101.9	11:30	6.53	7.2	61	9.0	13:10	7.30	7.8	66	9.3	14:10	7.74	7.8	66	9.4	
22/02/93	9.2	102.1	15:35	7.68	8.2	70	9.3	16:10	7.77	8.2	70	9.4	16:40	7.76	8.3	71	9.4	
23/02/93	7.9	102.7	9:40	6.84	7.0	58	8.1	10:36	7.07	7.3	61	8.1	11:51	7.37	7.7	65	8.5	
24/02/93	10.0	102.5	14:37	7.18	7.7	67	10.2	15:55	7.11	7.6	66	10.3	16:20	7.22	7.7	67	10.4	
25/02/93	8.7	101.5	9:15	6.50	6.6	55	8.8	10:30	6.67	7.0	59	8.8	11:30	6.81	7.3	61	8.8	
26/02/93	8.1	100.4	11:32	7.18	7.3	62	8.4	12:32	6.97	7.4	62	8.8	13:01	6.98	7.5	64	9.1	
01/03/93	7.1	101.4	14:15	8.00	8.4	68	7.1											

Table 6.13a Instrument readings for Calibration Data - Class 1A

Date	Time	Pressure (kPa)	Dissolved Oxygen (mg l ⁻¹)	Temp. (°C)	Dissolved Oxygen (% sat.)
28/01/93	15:25	100.8	10.7	13.9	101
29/01/93	11:30	101.7	11.3	11.4	101
01/02/93	11:47	103.4	11.4	10.3	100
02/02/93	11:43	103.7	11.4	11.5	102
03/02/93	11:19	104.0	11.7	10.7	103
04/02/93	11:53	103.4	11.6	11.1	103
05/02/93	12:16	103.5	11.4	11.9	103
08/02/93	11:15	103.5	11.3	11.7	102
09/02/93	11:21	103.1	10.4	17.7	106
10/02/93	13:05	102.8	11.3	12.1	103
11/02/93	12:32	102.9	11.4	12.1	103

Table 6.13b Instrument readings for Calibration Data - Class 3

Date	Time	Pressure (kPa)	Dissolved Oxygen (mg l ⁻¹)	Temp. (°C)	Dissolved Oxygen (% sat.)
16/02/93	14:05	102.8	11.7	8.6	98
17/02/93	14:15	102.6	11.0	14.1	103
18/02/93	14:27	101.8	11.4	9.9	99
19/02/93	12:24	102.0	10.8	13.3	100
22/02/93	15:30	102.1	11.8	9.1	100
23/02/93	10:30	102.7	12.2	7.5	100
24/02/93	14:30	102.5	12.1	7.9	100
25/02/93	10:25	101.5	11.5	9.8	99
26/02/93	12:02	100.4	11.5	9.0	97
01/03/93	14:10	101.4	12.2	6.1	97

Table 6.14 Systematic and Random Error for calibration data

Test	Class 1A River	Class 3 River
Mean	102.5	99.3
Random error	2.5	0.7
Systematic error (Bias)	1.5	1.7
Total Error	2.9	1.8
Sample size	11	10

Table 6.15 Systematic and Random Errors for field data

Test	Class 1A River	Class 3 River
Random error	-0.43	-0.42
Systematic error (Bias)	0.35	0.18
Total Error	0.55	0.46
Sample size	11	10

7. INSTRUMENT BEHAVIOUR

This following section describes the general performance of the instrument during the various test procedures.

Table 6.1 shows that a stable reading is achieved after about three minutes. This does not appear to be affected by the stabilisation of the temperature sensors

The battery is a standard 9V PP3. The expected battery life is simply stated as 'many months', however, given the current drain (Table 6.2a) and the battery capacity (Table 6.2b) it can be calculated that the battery would last approximately 170 hours.

The instrument readings are affected by decreasing the power supply (Table 6.3) however the low battery indicator is illuminated before the lower power has an effect.

The effect of flow on the sensor performance is given in table 6.4. It shows that even at very low flows (0.10 m s^{-1}) a stable reading is achieved. The manufacturer does not state a minimum flow requirement.

Table 6.7 shows the effect of immersion depth on the instrument reading. It can be seen that there is no effect on the readings. More importantly, the low percentage saturation values would indicate that there was inadequate flow at the sensor surface.

Table 6.6 demonstrates the effect of the presence of two possible interferences on the meter readings. At a temperature of 10°C 100% air-saturation (corrected for pressure) would be achieved at a dissolved oxygen level of 11.30 mg l^{-1} , whilst at 30°C there would be 7.58 mg l^{-1} dissolved oxygen present. At both temperature levels the meter reading is incorrect.

The addition of sodium hypochlorite, to achieve a concentration of 30 mg l^{-1} of residual chlorine, had no effect on the displayed values.

Only minor disparities were noted between the different calibration techniques used (Table 6.7).

The instrument accuracy was tested on 5 separate occasions and compared with a range of oxygen nitrogen gas mixtures. These results are presented in tables 6.8a - 6.8e. The random and systematic errors for the instrument and the Winkler determinations are provided in Table 6.8f. The total error (quadrature sum of random and systematic errors) for five test concentrations varied between 3.7 and 5.4%. It should be noted that Winkler determinations of these solutions gave a total error of 6% to 25%.

The variation in the Winkler titration for the nominal zero dissolved oxygen concentration means that it is not possible to establish if hysteresis is an important factor with this instrument.

The response time for the oxygen sensor (Table 6.9) is within the 35 seconds stated by the manufacturer, however, the temperature sensor (Table 6.10) takes on average 50 seconds to respond which will effect the displayed output of the instrument.

There is no salinity correction provided on this instrument.

Table 6.13a shows the calibration check data for the Class 1A river. A correlation coefficient calculated for this data against time shows that there is no significant (95% confidence limits) drift with time. Table 6.13b shows the calibration check data for the Class 3 river. A correlation coefficient calculated for this data against time shows that there is no significant (95% confidence limits) drift with time.

Table 6.14 shows the systematic and random errors for the calibration check data for the Class 1A and 3 river. This test should show if there is any drift in the calibration of the instrument. It shows that the total error was 1.8% in the Class 3 river but rose to nearly 2.9% in the Class 1A river. If this is compared to the Winkler determinations for the 100% saturation solution, it can be seen that thier total error is 4.5%. This would indicate that there is more variability in the Winkler determinations than the instrument readings. The same statistical test was applied to the river water results (Table 6.12a and 6.12b). In this case the readings were made in mg l^{-1} . The mean of the readings is not stated since there will be naturally occurring variation in dissolved oxygen concentration over the test period. The results describe the variation of the readings given by the test instrument as compared to that made by the Winkler determinations. The total error was 0.46 mg l^{-1} for the Class 3 river and 0.55 mg l^{-1} for the Class 1A river. It can be seen that the variations are small, particularly if the variability in the Winkler measurements are assumed to be simliar to those seen in the accuracy tests.

Data from automatic water quality instrumentation for the Class 1A and Class 3 river are show in figures B1 and B2 respectively. Other water quality parameters were monitored by daily sampling and laboratory analysis. These results are provided in tables A1 and A2.

8. MANUFACTURER'S COMMENTS

The manufacture did not make any comment on the contents of this report.

9. COST OF OWNERSHIP

Model 5100 Dissolved Oxygen Monitor c/w sensor	£595.00
CHX15 Dissolved Oxygen cartridge	£195.00
DO-AH Active head Dissolved Oxygen Sensor	£595.00
Exchange CHX15 cartridge	£ 65.00
OE15 Dissolved Oxygen sensor (2m cable)	£395.00
OME2/4007 Dip type Dissolved Oxygen Electrode	£450.00

All prices nett ex works.

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- the analysis staff at WRc for providing calibration solutions, and
- Partech Instruments for the loan of the instrument.

DEFINITIONS AND ABBREVIATIONS

Error (of indication) of a measuring instrument (BS 5233): The indication of a measuring instrument minus the true value of the measurement.

Response time (WSA/FWR 7-00-02): The time interval from the instant a step change occurs in the value of the property to be measured to the instant when the change in the indicated value passes (and remains beyond) 90% of its steady state amplitude difference.

Random Error: describes the way in which repeated measurements are scattered around a central value. It therefore defines the precision of the instrument.

Systematic Error (Bias): is present when results are consistently greater or smaller than the true value. The magnitude and direction of systematic error will depend on the properties of the sample (pH, temperature, turbidity and interfering species).

Drift: Change of the indicators of an instrument, for a given level of concentration over a stated period of time under reference conditions which remain constant.

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Table A1 **Water Quality Laboratory Analysis Class 1A River**

Date	Time	pH	Sulphate as SO ₄ mg l ⁻¹	Conductivity µS cm ⁻¹	Copper as Cu µg l ⁻¹	Ammoniacal N as N mg l ⁻¹	Nitrite as N mg l ⁻¹	Chloride as Cl mg l ⁻¹	Calcium as Ca mg l ⁻¹	Magnesium as Mg mg l ⁻¹	Sodium as Na mg l ⁻¹	Potassium as K mg l ⁻¹	Nitrate as N mg l ⁻¹
28/01/93	16:15	8.0	35	538	<5	<0.05	<0.05	23	117	3	12	3	5.7
29/01/93	11:45	8.0	36	519	<5	<0.05	<0.05	24	118	3	12	2	5.1
01/02/93	12:40	8.1	35	535	<5	<0.05	<0.05	22	120	3	12	2	5.7
02/02/93	16:25	8.1	34	542	<5	<0.05	0.06	22	118	3	12	2	5.7
03/02/93	12:30	8.0	33	539	<5	<0.05	<0.05	5	114	3	11	2	4.7
05/02/93	12:30	7.9	44	534	<5	<0.05	<0.05	22	117	3	11	2	5.7
08/02/93	10:50	8.1	45	535	<5	<0.05	0.05	23	115	3	11	2	5.6
09/02/93	11:30	8.0	26	536	<5	<0.05	<0.05	23	118	3	11	2	5.8
10/02/93	14:15	8.1	31	538		<0.05	<0.05	31					5.5
11/02/93	14:05	8.1	31	539	<5	<0.05	<0.05	23	3	3	11	2	6.0

Table A2 Water Quality Laboratory Analysis - Class 3 River

Date	Time	pH	Sulphate as SO ₄ mg l ⁻¹	Conductivity µS cm ⁻¹	Copper as Cu µg l ⁻¹	Ammoniacal N as N mg l ⁻¹	Nitrite as N mg l ⁻¹	Chloride as Cl mg l ⁻¹	Calcium as Ca mg l ⁻¹	Magnesium as Mg mg l ⁻¹	Sodium as Na mg l ⁻¹	Potassium as K mg l ⁻¹	Nitrate as N mg/l mg l ⁻¹
15/02/93	16:00	7.1	128	835	30.4	1.45	0.27	100	74	18	72	15	15.5
16/02/93	15:00	7.0	135	911	45.7	1.51	0.39	123	85	21	90	16	15.0
17/02/93	14:45	7.2	148	908	40.5	1.63	0.36	124	81	20	89	15	12.4
18/02/93	14:10	7.3	148	936	40.6	1.40	0.37	130	81	19	87	14	12.7
23/02/93	10:30	7.6	154	936	40.3	1.90	0.33	114	84	19	95	16	14.1
24/02/93	15:50	7.0	140	956	42.3	1.70	0.29	127	74	17	98	16	13.6
25/02/93	10:00	7.1	148	979	43.0	2.60	0.34	129	85	19	93	15	11.7
26/02/93	11:57	7.2	144	993	66.0	3.70	0.27	142	89	20	96	14	10.5
01/03/93	14:20	7.2	135	971	47.0	3.90	0.25	141	80	18	102	15	14.3

APPENDIX B

FIGURES

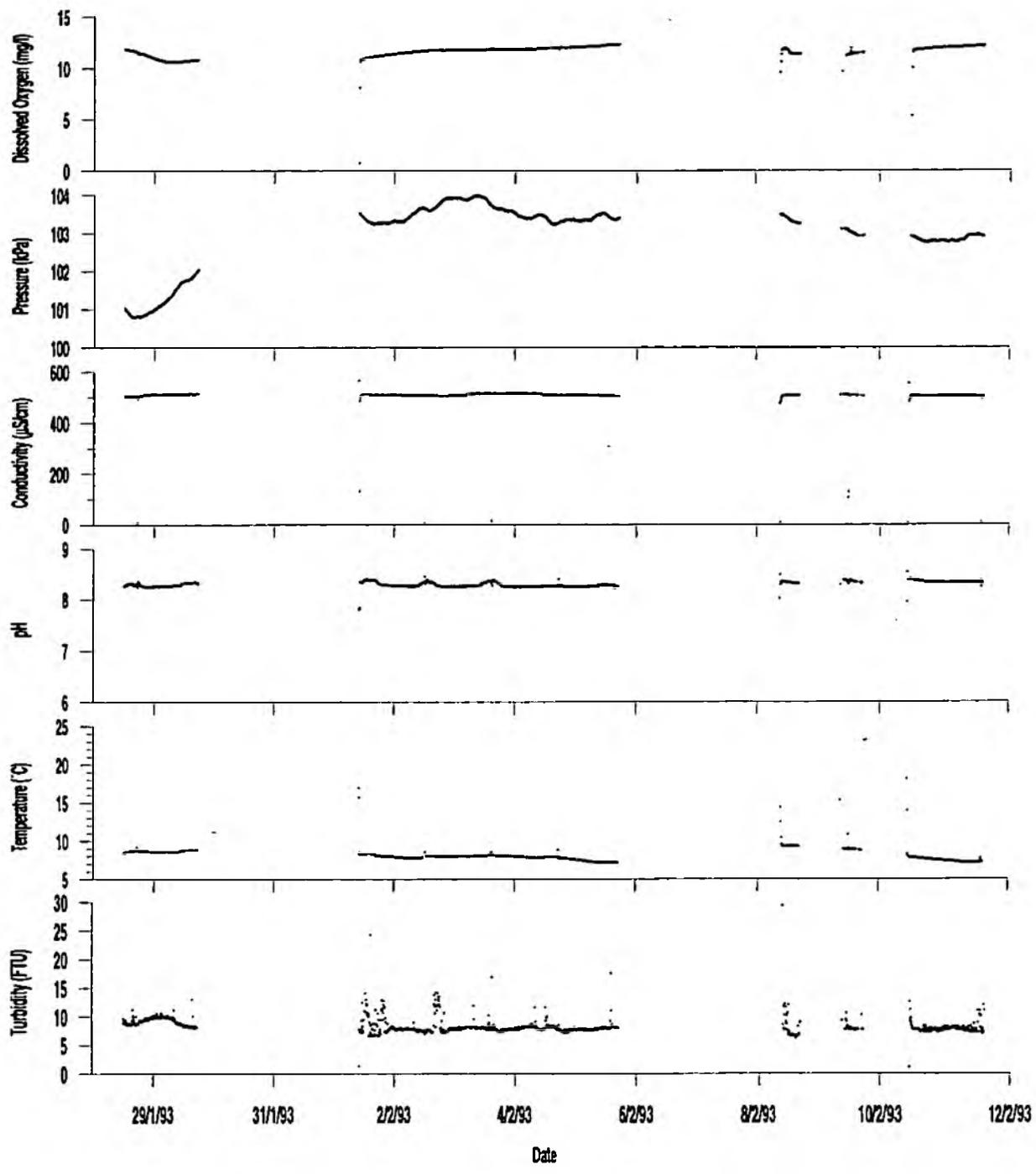


Figure B1 Water Quality Parameters Class 1A River

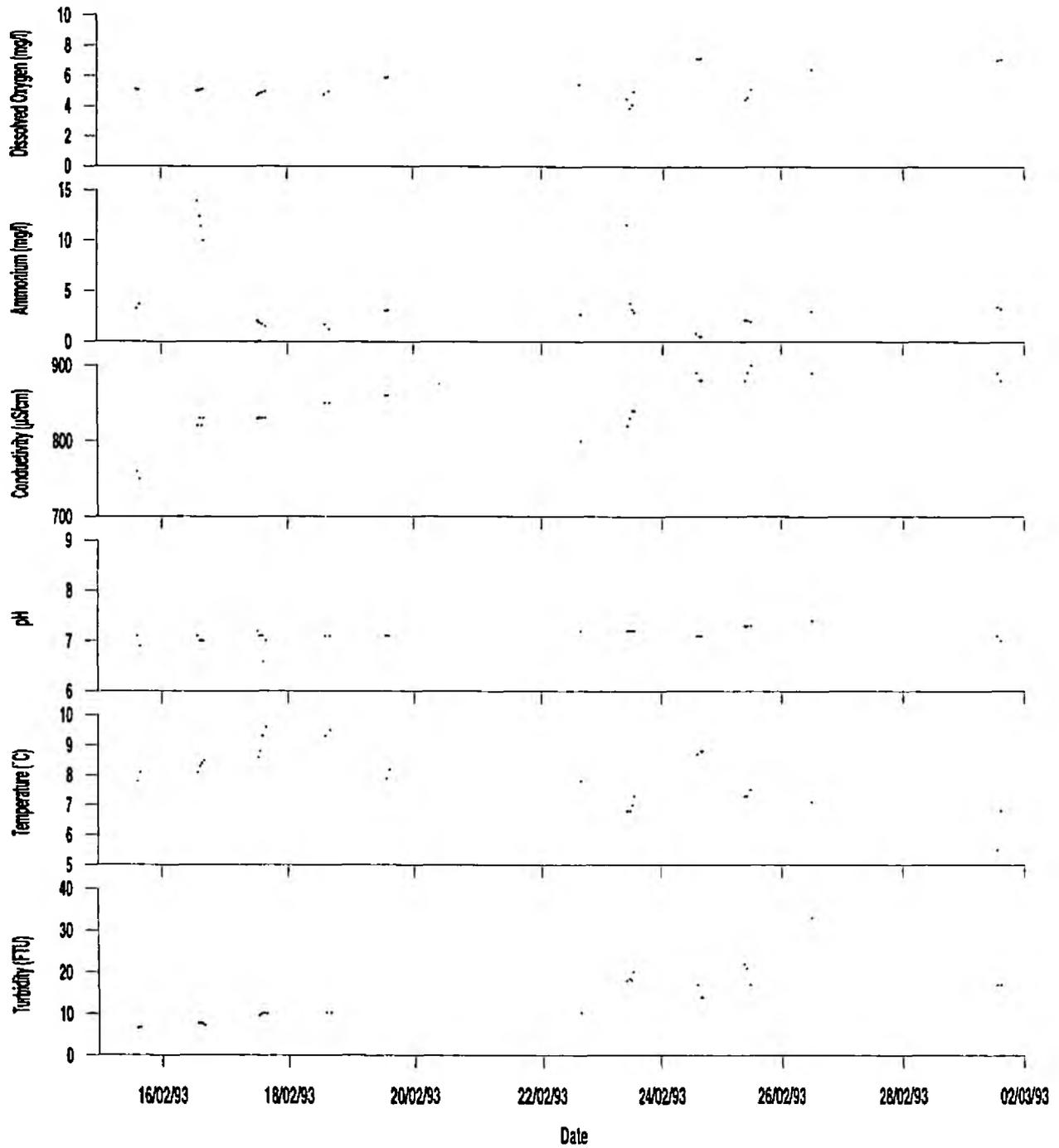


Figure B2 Water Quality Parameters Class 3 River

APPENDIX C MANUFACTURER'S SPECIFICATION

Oxygen Measurement

RANGES: 0 - 200 % sat,
 0 - 20.0 mg l⁻¹

ACCURACY Not stated

Temperature Measurement

RANGE: 0 - 50.0 °C

ACCURACY Not stated

Temperature Compensation Automatic over 5 °C to 35 °C

Salinity Compensation None

Instrument Environment

Temperature range Not stated

Water Resistance IP67 (Short term immersion)

Power Supply PP3 (Battery life stated as 'many months')

Probe

Type Galvanic Mackereth Cell
Cathode Silver
Anode Lead
Membrane 0.025 mm polythene
Electrolyte Half-saturated KHCO₃ gel

Temperature Sensor
Accuracy Not stated

Pressure Compensation Not stated

Response Time
(90% change) < 35 seconds