220

The Evaluation of a WTW Model OXI 196 Hand-Held Dissolved Oxygen Meter

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R&D 220/29/T

NRA

National Rivers Authority

THE EVALUATION OF A WTW MODEL OXI 196 HAND-HELD DISSOLVED OXYGEN METER

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EXECUTIVE SUMMARY

This report describes the results of an evaluation of a WTW MODEL OXI 196 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 WTW OXI 196 dissolved oxygen meter is both small and light and is relatively simple and convenient to use. The dual indication of the chosen oxygen measurand (% saturation or mg l^{-1}) and temperature obviates the need to continually change ranges during use, since both values will be displayed whilst the meter is switched on.

There was a tendency for air bubbles to remain trapped under the probe shield when the probe is inserted into water. These air bubbles remained at the surface of the membrane during measurements even at relatively high sample flow rates. The manufacturer states that a minimum flow rate of 0.15 ms^{-1} is required. However, it was found that even allowing for the accuracy stated by the manufacturer the instrument requires a flow rate of approximately 0.30 m s^{-1}.

The total error (quadrature sum of random and systematic errors) for five accuracy test concentrations varied between 2.1% and 14.0%. It should be noted that Winkler determinations of these solutions gave a total error of 6% to 25%. During the field trials there was no significant (95% confidence levels) drift at either of the evaluation sites. The total error (quadrature sum of random and systematic errors) was 0.3 mg l^{-1} for Lea Marston and 0.8 mg l^{-1} for Fobney Mead.

The instrument sensor failed once during the tests. The supplier enabled us to solve the problem within three days.

The instrument currently costs £865.00. No maintenance or repairs other than the problem previously mentioned were required during the duration of the evaluation. Repair of the instrument was about an hour.

KEY WORDS

Dissolved Oxygen, Evaluation

NRA Evaluation Report 220/29/T

1. INTRODUCTION

This report describes the evaluation of a WTW MODEL OXI 196 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 WTW hand-held meter is fitted with a polarographic (voltametric) electrode. This electrode comprises an inert cathode (platinum or gold) and a reference electrode which is usually silver/silver chloride. Both the anode and cathode are separated from the sample by a thin PTFE membrane. The membrane also serves to retain a KCl solution which acts as the electrolyte. Oxygen diffuses through the PTFE membrane and is reduced at the cathode. It is necessary to apply a potential difference to the two electrodes (usually between 0.7 V and 0.8 V) in order to reduce oxygen. The reduction current is 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 mg O^2 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:	Wissenschaftlich-Technische Werkstätten GmbH D-8120 Weilheim Germany
Supplier:	SEMAT Technical (UK) Ltd 1 Executive Park Hatfield Road St. Albans Herts AL1 4TA
Tel:	0727 41414
Fax:	0727 43965

Instrument Description:	Model OXI 196 Hand-held Dissolved Oxygen Meter
Serial Number	19030169
Sensor Type	Polarographic

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 for the evaluation.

The WTW Oxi 196 dissolved oxygen meter is both small and light and is relatively simple and convenient to use. The dual indication of the chosen oxygen measurand (% saturation or mg l^{-1}) and temperature obviates the need to continually change ranges during use, since both values will be displayed whilst the meter is switched on.

It is difficult to upset the calibration, but possible since 'cal' is an option available when moving between %sat and mg l^{-1} measurements. Selection is carried out by holding the 'mode' button until the required range (including the calibration mode) is displayed. Specific selection of the calibration mode, using an independent control, would be better.

There is a tendency for air bubbles to remain trapped under the probe shield when the probe is inserted into water. These air bubbles may remain at the surface of the membrane during measurements even at relatively high sample flow rates.

The instrument readings were affected by decreasing the power supply before the low battery indicator was illuminated.

The manufacturer states that a minimum flow rate of 0.15 ms^{-1} is required. However, it was found that even allowing for the accuracy stated by the manufacturer the instrument requires a flow rate of approximately 0.30 m s^{-1}.

The total error (quadrature sum of random and systematic errors) for five accuracy test concentrations varied between 2.1 and 14.0%. It should be noted that Winkler determinations of these solutions gave a total error of 6% to 25%.

The response times for the oxygen and the temperature sensor were in agreement with the manufacturer's stated times.

The salinity correction on this instrument produced readings that are within the tolerance limits of the instrument.

During the field trials there was no significant (95% confidence levels) drift at either of the evaluation sites. The total error (quadrature sum of random and systematic errors) was 0.3 mg l^{-1} for Lea Marston and 0.8 mg l^{-1} for Fobney Mead.

4. EVALUATION PROCEDURES

The evaluation and demonstration facility at Fobney Mead, Reading and Lea Marston, 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 ± 0.03 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 °C (± 0.1°C). The meter was switched off until the control system raised the test temperature to 30 °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 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 a 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 °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 ± 0.1°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 ± 0.2 °C and 5 ± 0.2°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 Solinity 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. Readings were then made after adjusting the salinity compensation control to the appropriate setting.

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

A 16 page A5 size instruction manual is provided with the instrument. The manual describes the operation of both the Oxi-196 dissolved oxygen meter and the EOT-196 oxygen sensor. A separate 10 page manual was also provided which describes solely the operation of the EOT-916 oxygen electrode and its accessories. The only additional information provided in the second manual relates to the use of an optional battery stirrer mechanism. Both manuals include an index and a list of accessories and replacement parts.

Instructions are provided only for air-calibration of the sensor using the meter unit's so-called quiver or the separate sheath device. No procedure is given for calibrating the instrument using air-saturated water.

The manual describes the method of adjusting the instrument to give salinity corrected results.

The instrument incorporates in-built salinity correction over the range of 0 to 40 ‰. A table showing conductivity values and the equivalent salinity is provided to enable the user to make adjustments to the salinity correction factor based on readings obtained from a separate conductivity meter.

Since the instrument incorporates an in-built air-pressure correction in the range 80.0 to 108.0 kPa ± 0.2 kPa no atmospheric pressure or altitudes correction tables are provided.

Servicing instructions are limited to the exchange of the oxygen sensor membrane, and cleaning of the silver anode and gold cathode. A simple sketch shows the relative position of the oxygen sensor components. No specific instructions are provided for the removal of foulant from the sensor surface.

No specific Health and Safety information is provided for any chemicals or reagents which may be required by the instrument.

In summary, both manuals appear to be provide adequate instructions on the use of the instrument. No serious omissions and few typographical errors were noted. In some sections of the manual the style of writing appears rather idiosyncratic, presumably, as a result of literal translation.

5.2 Design and Construction

The WTW Oxi 196 dissolved oxygen meter comprises a meter unit and separate oxygen probe assembly. The meter unit is a neat and functional design based in a plastic case. The external surface of the meter is finished in a rubberised coat, intended to keep the unit watertight. The meter is fitted with a carrying handle which also serves as a prop when the instrument is used on the bench.

The meter unit incorporates an in-built air-pressure sensor to provide automatic correction over the range 80 kPa to 108 kPa. In addition, the instrument incorporates an in-built salinity correction facility over the range of 0 to 40 %o.

The instrument front panel features two separate 3 1/2 digit LCD displays; one provides oxygen readings as either % saturation or mg l^{-1}, the other indicates the sample temperature in °C. However, neither display incorporates a backlight facility. The various modes of operation are selected using pressure-sensitive membrane switches mounted on the instrument front panel.

The front panel also includes a so-called 'quiver'. This feature serves as an air-calibration pot into which the oxygen sensor is inserted during the calibration procedure. The 'quiver' also provides a means of holding the sensor whilst the unit is being carried between sites. Calibration of the instrument is achieved by placing the sensor into either the meter's in-built 'quiver' or into a specially constructed separate air-calibration sheath. A moist sponge contained within these devices ensures that the oxygen sensor membrane remains damp during air-calibration.

The meter is approximately 185 x 165 x 80 mm and weighs approximately 1000 g. The IP rating of the instrument is not stated in the user manual.

The probe is a Clark-type membrane covered polarographic sensor incorporating thermistors for temperature measurement and compensation. The oxygen probe is approximately 145 mm long and 16 mm in diameter.

5.3 Installation

None Required

5.4 Commissioning

None Required

5.5 Maintenance and Downtime

The instrument sensor failed once during the tests. The suppliers responded very promptly to this problem. A new meter and probe were supplied to in about two days to enable us to diagnose the problem. The cause of the failure was believed to have been the ingress of water at the joint between the sensor head and the connecting cable.

5.6 Ease of Use

The WTW Oxi 196 dissolved oxygen meter is both small and light and is relatively simple and convenient to use. The dual indication of the chosen oxygen measurand (% saturation or mg l^{-1}) and temperature obviates the need to continually change ranges during use, since both values will be displayed whilst the meter is switched on.

Calibration of the instrument is achieved by placing the sensor into either the meter's in-built 'quiver' or into a specially constructed separate air-calibration sheath. Both these devices serve to maintain the oxygen sensor at 100% air-saturation level; an internal moist sponge ensures that the oxygen sensor membrane remains damp during air-calibration.

This continual probe conditioning method, in conjunction with the meter's calibration routine, permits the user to carry out a very quick single-point calibration at any time.

It is difficult, but possible, to upset the calibration, since 'cal' is an option available when moving between %sat and mg l^{-1} measurements. Selection is carried out by holding the 'mode' button until the required range (including the calibration mode) is displayed. Specific selection of the calibration mode, using an independent control, would be better.

There is a tendency for air bubbles to remain trapped under the probe shield when the probe is inserted into water. These air bubbles may remain at the surface of the membrane during measurements even at relatively high sample flow rates.

6. RESULTS

Table 6.1 Instrument stabilisation readings for different temperature changes

	Time (secs)	Dissolved Oxygen (% sat.)
Room Temperature → 5°C	10	103
	30	104
	60	106
	120	105
	180	106
	300	106
	600	106
	1200	105
Room Temperature → 20°C	10	95
	30	95
	60	95
	120	95
	180	95
	300	95
	600	
	1200	
5°C → 5°C	10	104
	30	104
	60	103
	120	104
	180	103
	300	103
	600	103
	1200	104

Table 6.2a Power Consumption

Meter Setting	Volts	mA	mW
OFF	5.29	0.14	0.74
ON	5.26	2.24	11.78

Table 6.2b Battery Characteristics

Battery Make	Unknown
Battery Type	Unknown
Battery Voltage	Unknown
Battery Capacity	Unknown
Replacement Interval	Unknown

Table 6.3 Effects of different power supply voltages on instrument readings

Power Supply (Volts)	Instrument Setting			Low Battery Indicator
	% sat.	$mg\ l^{-1}$	°C	
5.99	99	9.4	17.1	NO
5.49	98	9.4	17.1	NO
5.01	98	9.4	17.1	NO
4.50	81	9.4	17.1	NO
4.00	63	7.3	17.1	YES

Table 6.4 Instrument readings for different flow at sensor surface

Water Temperature 10.0 °C

Flow Rate ($m\ s^{-1}$)	Dissolved Oxygen ($mg\ l^{-1}$)	Temp. (°C)	Dissolved Oxygen (% sat.)
0.37	11.0	9.8	98
0.35	10.9	9.8	98
0.27	10.8	9.8	97
0.19	10.8	9.7	97
0.13	10.8	9.7	97
0.05	10.4	9.7	93
0.00	9.3	9.6	85
0.04	10.3	9.6	93
0.08	10.6	9.6	95
0.16	10.7	9.7	96
0.20	10.7	9.7	96
0.29	10.5	10.3	96
0.36	6.3	43.3	105

Table 6.5 Instrument readings at different depths

Water Temperature 12.8 (°C)

Depth (m)	Dissolved Oxygen ($mg\ l^{-1}$)	Temp. (°C)	Dissolved Oxygen (% sat.)
0.3	8.5	12.7	81
1.0	9.5	13.2	98
2.0	9.4	17.5	90
0.3	7.8	17.3	81
2.0	7.5	17.3	81
0.3	8.8	13.7	86
2.0	9.9	13.7	94
0.3	7.8	17.4	81

Table 6.6 Instrument Readings for two interferents

Interferent	Level	Dissolved Oxygen (mg l^{-1})	Temp. (°C)	Dissolved Oxygen (% sat.)
Temperature	10°C	11.9	9.5	102
	30°C	7.1	29.7	92
Chlorine	0 mg l^{-1}	8.3	21.4	97
	30 mg l^{-1}	8.3	21.4	96

Table 6.7 Instrument readings for commonly employed calibration techniques

	Sample (100% saturation)	Dissolved Oxygen (mg l^{-1})	Temp. (°C)	Dissolved Oxygen (% sat.)
*	River Water	-	-	-
!	River Water	-	-	-
!	Dechlorinated Tap Water	-	-	-

* calibrated in tap water
! calibrated in air

Table 6.8a **Instrument readings at different Dissolved Oxygen levels - Test 1**

Water Temperature 18.8
Atmospheric Pressure 102.1 kPa

*Actual Dissolved Oxygen (% sat.)	Dissolved Oxygen (mg l^{-1})	Temp. (°C)	Dissolved Oxygen (% sat.)
0	0.0	16.2	0
42.0	4.0	17.8	43
73.1	6.7	17.9	72
100	9.2	18.0	98
137.5	12.8	18.9	139
137.5	11.9	19.9	132
100	8.7	19.6	97
73.1	6.5	20.0	72
42.0	3.5	21.5	40
0	0.1	21.1	1

*see section 4.8 for details

Table 6.8b **Instrument readings at different Dissolved Oxygen levels - Test 2**

Atmospheric Pressure 101.7 (kPa)
Water Temperature 22.4 °C

*Actual Dissolved Oxygen (% sat.)	Dissolved Oxygen (mg l^{-1})	Temp. (°C)	Dissolved Oxygen (% sat.)
0	0.1	21.8	1
42.0	3.3	22.9	39
73.1	6.3	21.9	72
100	8.6	21.4	98
137.5	12.2	22.7	142
137.5	12.1	23.1	141
100	8.2	21.9	95
73.1	6.1	22.8	71
42.0	3.6	24.2	43
0	0.1	23.1	2

*see section 4.8 for details

Table 6.8c: Instrument readings at different Dissolved Oxygen levels -Test 3

Atmospheric Pressure 101.3 (kPa)
Water Temperature 19.8°C

Actual Dissolved Oxygen (%sat.)	Dissolved Oxygen (mg l^{-1})	Temp. (°C)	Dissolved Oxygen (% sat.)
0	0.1	18.2	1
42.0	3.9	18.8	42
73.1	7.1	19.1	77
100	9.2	18.6	100
137.5	12.7	19.7	140
137.5	12.4	20.6	140
100	8.8	20.0	101
73.1	6.2	20.9	70
42.0	3.6	22.0	41
0	0.2	21.7	2

*see section 4.8 for details

Table 6.8d Instrument readings for different Dissolved Oxygen levels - Test 4

Atmospheric Pressure 101.2 kPa
Water Temperature 24.3 °C

*Actual Dissolved Oxygen (% sat.)	Dissolved Oxygen (mg l^{-1})	Temp. (°C)	Dissolved Oxygen (% sat.)
0	0.3	23.4	3
42.0	3.2	24.4	39
73.1	5.9	23.7	70
100	8.3	22.8	97
137.5	11.4	24.3	138
137.5	11.4	24.6	137
100	8.2	23.3	98
73.1	5.8	24.7	70
42.0	3.2	26.1	39
0	0.1	25.3	2

*see section 4.8 for details

Table 6.8e Instrument readings for different Dissolved Oxygen levels - Test 5

Atmospheric Pressure 101.4 (kPa)
Water Temperature 26.1°C

*Actual Dissolved Oxygen (% sat.)	Dissolved Oxygen (mg l^{-1})	Temp. (°C)	Dissolved Oxygen (% sat.)
0	0.2	25.9	3
42.0			
73.1	5.7	25.9	70
100	8.1	24.8	98
137.5	11.2	26.2	139
137.5	11.2	26.2	142
100	7.8	25.2	96
73.1	5.6	26.5	70
42.0	3.2	27.8	42
0	0.2	27.1	3

*see section 4.8 for details

Table 6.8f Summary of Accuracy Data

*Actual Dissolved Oxygen (% sat.)	Instrument	Accuracy	Winkler	Accuracy
	Systematic Error	Random Error	Systematic Error	Random Error
0	-1.8	1.0	-5.7	2.0
42.0	5.2	13.0	-8.4	6.0
73.1	1.7	2.2	-4.0	4.1
100	2.2	1.6	-1.9	4.1
137.5	-1.5	2.9	-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 (% sat.)*	6.59	8.94	8.72
Step change high to low Dissolved Oxygen (% sat.)*	8.37	7.62	9.66

* see text for details

Table 6.10 Response time Test - Temperature Sensor

	Time 1 (seconds)	Time 2 (seconds)	Time 3 (seconds)
Step change low to high Temperature (°C)*	7.13	6.13	6.40
Step change high to low Temperature (°C) *	5.46	8.25	6.28

* see text for details

Table 6.11 Instrument readings for different salinity levels

Water Temperature 19.8 °C

Chlorine (mg l^{-1})	Dissolved Oxygen (mg l^{-1})	Temp. (°C)	Dissolved Oxygen (% sat.)	After Adjustment Dissolved Oxygen (mg l^{-1})	After Adjustment setting
0	8.9	19.1	97	8.9	-
5	9.1	18.9	98	8.5	3
10	8.8	19.3	96	7.9	6
20	8.7	19.9	96	7.5	16
40	8.5	19.9	94	7.9	23
20	8.6	20.4	97	7.5	16
10	8.6	20.4	96	7.9	6
5	8.6	20.5	96	8.3	3
0	8.4	21.3	97	8.5	-

Table 6.12a Field Data - Class 1A River

Date	Water Temp. (°C)	Pressure (kPa)	Time	Winkler (mg l^{-1})	Instrument Dissolved Oxygen (mg l^{-1})	Instrument Dissolved Oxygen (% sat.)	Instrument Temp. (°C)	Time	Winkler (mg l^{-1})	Instrument Dissolved Oxygen (mg l^{-1})	Instrument Dissolved Oxygen (% sat.)	Instrument Temp. (°C)	Time	Winkler (mg l^{-1})	Instrument Dissolved Oxygen (mg l^{-1})	Instrument Dissolved Oxygen (% sat.)	Instrun Tem (°C
28/1/93	8.5	100.8	14:58	11.48	11.5	101	8.8	17:43	11.38	11.5	100	8.8					
29/1/93	8.8	101.7	11:20	11.48	11.6	101	8.9	14:42	11.62	11.6	102	9.1	17:07	11.41	11.5	101	9.0
1/2/93	8.2	103.4	12:00	12.02	12.2	104	8.4	14:37	12.33	12.0	102	8.4	16:36	12.02	12.0	102	8.2
2/2/93	7.8	103.7	11:46	12.10	12.1	100	7.9	14:13	12.00	12.2	103	8.1	15.58	12.35	12.1	101	8.1
3/2/93	8.2	104.0	11.17	11.90	11.9	99	8.2	17:03	11.90	11.7	98	8.3	18:27	11.76	11.8	99	8.2
4/2.93	7.9	103.4	12:10	12.00	12.2	102	8.0	16:50	11.80	12.2	101	7.9	18.22	11.80	12.2	101	7.8
5/2/93	7.1	103.5	12:17	11.19	12.4	102	7.2	15:35	11.99	12.5	102	7.1	16:40	12.60	12.3	101	7.2
8/2/93	9.0	103.5	11:16	11.69	9.2	101	11.8	15:52	11.45	11.7	101	9.3	16:45	11.35	11.8	102	9.3
9/2/93	8.7	103.1	10:59	11.49	8.9	101	11.8	14:25	11.35	12.0	103	8.8	16:53	11.88	12.0	102	8.8
10/2/93	7.8	102.9	13:02	11.78	12.2	103	7.9	16:22	11.94	12.4	104	7.8					
11/2/93	7.1	102.9	12:30	11.98	12.6	104	7.2										

Table 6.12b Field Data - Class 3 River

Date	Water Temp. (°C)	Pressure (kPa)	Time	Winkler (mg l^{-1})	Instrument Dissolved Oxygen (mg l^{-1})	Instrument Dissolved Oxygen (% sat.)	Instrument Temp. (°C)	Time	Winkler (mg l^{-1})	Instrument Dissolved Oxygen (mg l^{-1})	Instrument Dissolved Oxygen (% sat.)	Instrument Temp. (°C)	Time	Winkler (mg l^{-1})	Instrument Dissolved Oxygen (mg l^{-1})	Instrument Dissolved Oxygen (% sat.)	Instrument Temp. (°C)
15/2/93			15:45	7.62	7.6	67	9.6										
16/2/93			14:07	7.62	7.7	68	9.7	15:30	7.41	7.4	66	9.7					
17/2/93	10.6	102.6	14:17	6.90	7.0	62	10.5	15:00	7.04	6.9	62	10.8	15:50	6.87	6.9	63	10.9
18/2/93	10.8	101.7	14:45	7.04	6.7	61	10.7	16:01	7.21	7.0	64	10.8					
19/2/93	8.7	101.9	11:35	6.53	6.7	58	8.8	13:06	7.30	6.9	61	9.1	14:05	7.74	7.2	63	9.4
22/2/93	9.2	102.1	15:29	7.68	7.8	68	9.2	16:10	7.77	7.8	69	9.3	16:40	7.76	7.8	69	9.3
23/2/93	7.9	102.7	09:35	6.84	7.0	59	8.0	10:45	7.07	7.1	61	8.0	11:50	7.37	7.1	64	8.4
24/2/93	10.0	102.5	14:48	7.18	7.3	65	10.0	15:55	7.11	7.2	65	10.2	16:20	7.22	7.3	65	10.2
25/2/93	8.7	101.5	09:15	6.50	6.3	55	8.6	10:25	6.67	6.7	58	8.5	11:30	6.81	6.9	60	8.8
26/2/93	8.2	100.4	11:39	7.18	7.2	62	8.2	12:41	6.97	7.1	63	8.8	13:16	6.98	7.2	64	9.0
1/3/93	7.0	101.4	14:08	8.00	8.3	70	6.9										

Table 6.13a Instrument Readings for Class 1A River - Calibration Check

Time	Time	Pressure (kPa)	Dissolved Oxygen (mg l^{-1})	Temp. (°C)	Dissolved Oxygen (% sat.)
28/1/93	14:50	100.8	10.5	12.3	99
29/1/93	11:10	101.7	11.4	10.2	102
01/2/93	11:52	103.4	11.5	10.0	101
02/2/93	11:39	103.7	11.4	11.2	103
03/2/93	11:10	103.9	11.5	10.1	101
04/2/93	12:02	103.4	11.1	11.2	101
05/2/93	12:10	103.5	11.2	11.4	102
08/2/93	11.10	103.5	11.5	10.8	103
09/2/93	10:50	103.1	9.6	16.4	97
10/2/93	12:56	102.9	11.5	11.5	105
11/2/93	12:18	103.0	11.3	11.3	103

Table 6.13b Instrument Readings for Class 3 River - Calibration Check

Time	Time	Pressure (kPa)	Water Temp (°C)	Dissolved Oxygen (mg l^{-1})	Temp. (°C)	Dissolved Oxygen (% sat.)
16/2/93	14:00	102.8		11.8	8.0	100
17/2/93	14:07	102.6	13.7	10.2	13.6	98
18/2/93	14:37	101.8	10.1	11.0	10.1	99
19/2/93	12:35	102.0	14.5	9.8	14.6	99
22/2/93	15:20	102.1	8.5	11.8	8.5	102
23/2/93	10:38	102.7	7.8	12.2	7.8	103
24/2/93	14:40	102.5	8.0	12.0	8.0	102
25/2/93	10:15	101.5	9.4	11.4	9.4	102
26/2/93	12:21	100.5	9.5	11.4	9.7	101
01/3/93	14:01	101.4	7.0	2.8	5.6	103

Table 6.14 Systematic and Random Errors for daily calibration check

Test	Class 1A River	Class 3 River
Mean	101.5	100.9
Random error	2.1	1.7
Systematic error (Bias)	-1.5	-0.9
Total Error	2.6	1.9
Sample size	11	10

Table 6.15 Systematic and Random Errors for field data

Test	Class 1A River	Class 3 River
Random error	0.8	0.2
Systematic error (Bias)	0.0	0.0
Total Error	0.8	0.2
Sample size	29	27

7. INSTRUMENT BEHAVIOUR

This following section describes the general performance of the instrument during the evaluation.

The first tests made on the instrument were preliminary tests designed to give a guide to the performance of the instrument before more detailed tests were carried out.

Table 6.1 shows the stabilisation of the instrument readings when the instrument probe is transferred between different temperature regimes. It shows that there is no drift in the results throughout the test period. The stabilisation period for the oxygen sensor appears to be unaffected by equilibration of the temperature sensor.

The instrument readings were affected by decreasing the power supply (Table 6.3). As the power supply reached the level of the battery indicator being illuminated there was some affect on the readings. This could mean that erroneous readings would be displayed before the operator was aware of the battery condition.

The effect of flow on the sensor performance is given in table 6.4. The manufacturer states that a minimum flow rate of 0.15 m s^{-1} is required. The readings shows that even allowing for the accuracy stated by the manufacturer the instrument requires a flow rate of approximately 0.30 m s^{-1}.

This meter has an in-built pressure compensation system. The system is intended to compensate for atmospheric pressure changes. Table 6.5 shows the instrument readings at different depths. There is a large fluctuation in readings taken at particular depths. This is due to the low flow rates achieved in the test configuration. Due to this variability it is impossible to conclude if there is any effect due to the depth.

Table 6.6 demonstrates the effect of the presence of two possible interferents on the meter readings. At a temperature of 10°C (at standard pressure) 100% air-saturation would be achieved at a dissolved oxygen level of 11.11 mg l^{-1}, whilst at 30°C there would be 7.44 mg l^{-1} present. It can be seen that at both levels the meter reading is correct and the percentage saturation is also within the manufacturer's specified accuracy.

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

The instrument accuracy was tested on five 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 2.1% and 14.0%. It should be noted that Winkler determinations of these solutions gave a total error of 6% to 25%.

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

The response times for the oxygen and the temperature sensor (tables 6.9 and 6.10) are in agreement with the manufacturer's stated times.

The salinity correction on this instrument can be seen to produce readings that are within the tolerance limits of the instrument (Table 6.11 and Appendix C). The accuracy of these readings can be confirmed by referring to previously published salinity tables (Weiss, 1974).

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 shows the accuracy of the instrument calibration. This shows that the total error was approx. 2% over the test period for the two sites. The variability in the readings was only 1.9% in the Class 3 river and 2.6% in the Class 1A river. If this is compared to the Winkler determinations for the 100% saturation solution, it can be seen that their 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 0.2 mg l^{-1} for the Class 3 river and 0.8 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 similar 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. COST OF OWNERSHIP

OXI 196	£865.00
EOT196-4	£529.00
ZBK90/190	£ 96.00
Battery pack	£ 39.00

9. MANUFACTURER'S COMMENTS

The manufacturer did not make any comments on this report.

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- the analysis staff at WRc for providing calibration solutions.
- SEMAT 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, 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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APPENDIX A LABORATORY ANALYSIS OF WATER QUALITY PARAMETERS

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

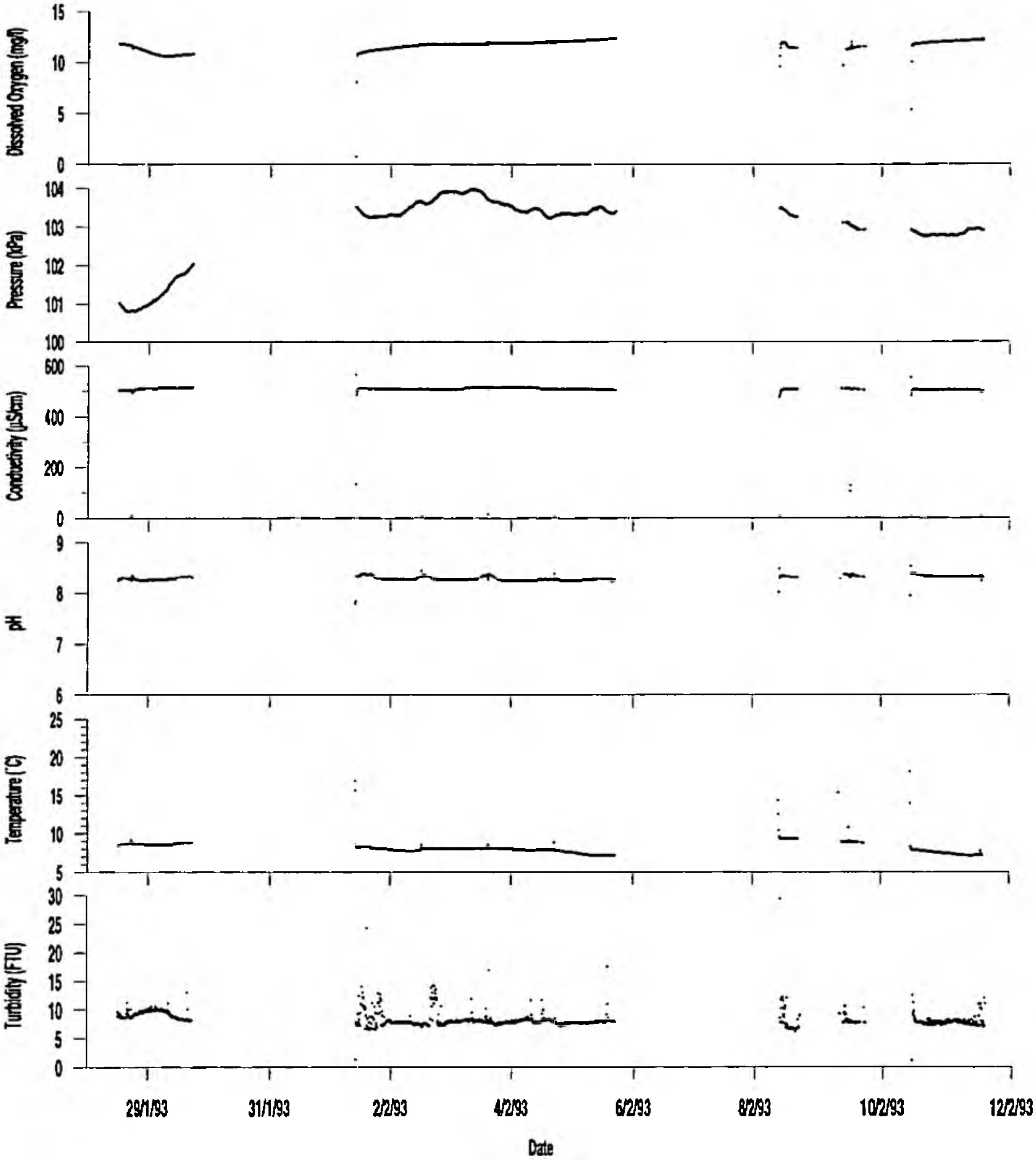

Figure B1 Water Quality Parameters Class 1A River

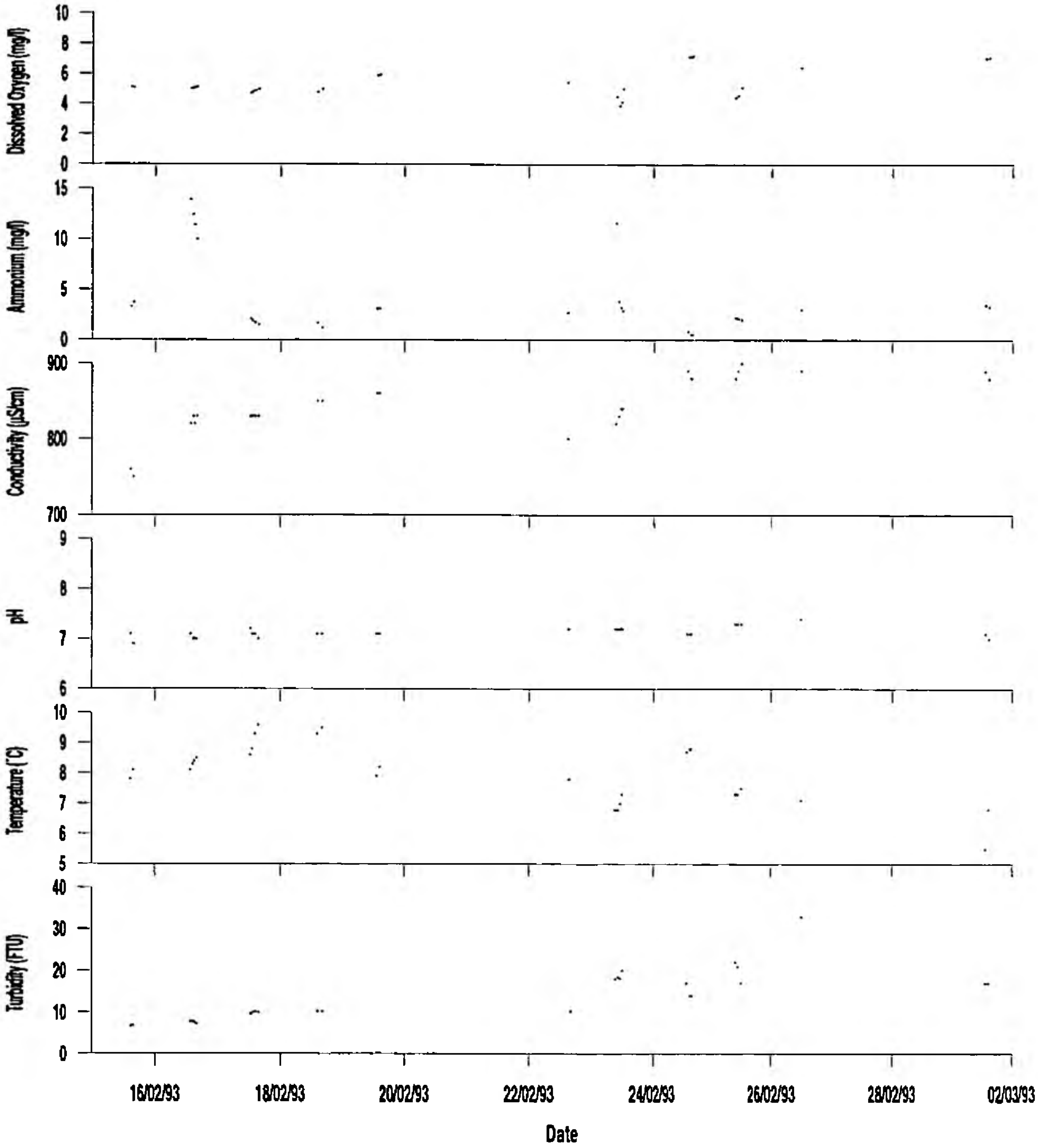

Figure B2 Water Quality Parameters Class 3 River

APPENDIX C - MANUFACTURER'S SPECIFICATIONS

Oxygen Measurement

RANGES:	0 to 60.0 mg l^{-1} dissolved oxygen 0 to 600.0 % air saturation
ACCURACY	± 1% of the measuring value ± 1 digit mg l $^{-1}$ ± 1% of the measuring value ± 1 digit % air saturation

Temperature Measurement

RANGE:	0 to +50°C
ACCURACY	± 0.2 K ± 1 digit

Salinity Compensation

RANGE	0 to 40 parts per thousand
ACCURACY	NOT STATED

Pressure Compensation

Automatic built-in pressure sensor

RANGE	80.0 to 108.0 kPa
ACCURACY	±0.2 kPa

Instrument Environment

Power Supply	Built-in accumulator for approx 40 operating hours, mains supply, charging via mains transformer

Probe

Cathode	Gold
Anode	Silver
Membrane	12.5 µm
Electrolyte	NOT STATED
Response Time (90% change)	<10 seconds at 20°C
Minimum Flow	15 cm s^{-1}