The Evaluation of a LTH BOM 1 Hand-Held Dissolved Oxygen Meter

WRc plc

R&D 220/25/T

NRA

National Rivers Authority

THE EVALUATION OF A LTH BOM 1 HAND-HELD DISSOLVED OXYGEN METER

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Evaluation Report 220/25/T

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EXECUTIVE SUMMARY

This report describes the results of an evaluation of a LTH BOM 1 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 LTH hand-held Dissolved Oxygen meter performed in good agreement to the manufacturer's stated response and reliability.

It was found that the instrument readings were affected by a reduction in the power supply and even though the low battery indicator had been activated the only means to check this was by a manual test button. The non-mirrored analogue meter fitted to the meter required careful interpretation. The calibration adjustment was found to be particularly sensitive making precise adjustments difficult. Where the dissolved oxygen level was close to the '100 %' and '200 %' ranges a discrepancy between the readings of approximately 2% were noted.

The total error (quadrature sum of random and systematic errors) for five accuracy test concentrations varied between 2.4 and 6.2%. It should be noted that Winkler determinations of these solutions gave a total error of 6% to 25%. For the field evaluation the total error was 0.35 mg l^{-1} for Lea Marston and 0.30 mg l^{-1} for Fobney Mead.

The instrument currently costs £495.00. No maintenance or repairs were required during the four month evaluation.

KEY WORDS

Dissolved Oxygen, Evaluation

NRA Evaluation Report 220/25/T

1. INTRODUCTION

This report describes the evaluation of an LTH BOM 1 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 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 Mackereth electrode is the most commonly used galvanic electrochemical 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).

The polarographic (voltametric) oxygen 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.

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:	LTH Electronics LTD Eltelec Works Chaul End Lane Luton Beds LU4 8EZ
Supplier:	LTH Electronics LTD Eltelec Works Chaul End Lane Luton Beds LU4 8EZ
Tel:	0582 593693
Fax:	0582 598036
Instrument Description:	Model BOM 1 Hand-held Dissolved Oxygen Meter
Serial Number:	OE15 3m
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 for the evaluation.

The LTH hand-held Dissolved Oxygen meter performed in good agreement to the manufacturer's stated response and reliability.

There appeared to be some variation in the current when the instrument was used at the lower settings (0-3 ppm or 0-30 % saturation) it could therefore be expected that there would be a reduction in the battery life as the instrument was continually used at this setting. At other settings the battery should last the 100 hours stated by the manufacturer.

It was found that the instrument readings were affected by a reduction in the power supply (Table 6.3) and even though the low battery indicator had been activated the only means to check this was by a manual test button. Care would therefore be needed at all times to ensure that the battery contained an adequate charge.

The instrument readings were very susceptible to changes in flow at the sensor surface (Table 6.4). It was also found that even at the highest flow rate tested (0.37 m s^{-1}) the readings did not appear to be stable.

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 titrations are provided in Table 6.8f. The total error (quadrature sum of random and systematic errors) for five test concentrations varied between 2.4 and 6.2%. It should be noted that Winkler determinations of these solutions gave a total error of 6% to 25%.

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

Although the manufacturer states a response time for the oxygen sensor as 35 seconds, it was found that the it actual responded faster (10 seconds). However, the temperature probe took approximately 50 seconds to respond which would effect the response of the instrument.

The interferents tested, temperature and residual chlorine, were found not to cause any unexpected variation in the readings for the levels tested.

The instrument does not provide any means of correcting for salinity changes in the water. Salinity tables were not provided to allow a manual correction.

There was no significant (95% confidence limits) drift of the calibration during the field evaluation.. The total error (quadrature sum of random and systematic errors) for the calibration check data was approximately 2% over the test period for the two sites. The Winkler determinations for the 100% saturation solution showed a total error of 4.5%. For the field data the total error was 0.35 mg l^{-1} for the Class 3 river and 0.30 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.

The non-mirrored analogue meter fitted to the meter required careful interpretation.

The calibration adjustment was found to be particularly sensitive making precise adjustments difficult.

Where the dissolved oxygen level was close to the '100 %' and '200 %' ranges a discrepancy between the readings of approximately 2% was noted.

The instrument did not require any maintenance during the four months of the evaluation.

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. Measurements were also taken using the display backlight where fitted.

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 operated 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 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 actual dissolved oxygen concentrations were determined by Winkler titrations (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 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

Information on the operation of the BOM-1 was provided in the form of a label fixed to the inside of the meter carrying case. A single A5 sheet provided details of probe membrane replacement. The instruction label provides brief details of the basic operating sequence.

Calibration instructions state the use of air-saturated water, however, the method of preparation of the air-saturated solution is not stated. No oxygen solubility tables are provided.

No information has been included on the use of the instrument in saline waters; no salinity correction tables are provided. Furthermore, no data is given on the response of the instrument in the presence of other common interferents.

Maintenance information is limited to routine inspection of the batteries; no methods have been given for the removal of foulant from the sensor, or for checking the operational performance of the instrument. The absence of manufacturer's data on such parameters as response time and accuracy, means that the user is unable to devise their own check of instrument performance.

No guidance is given on the interpretation or significance of the readings obtained by the instrument.

The environmental rating of the instrument is not stated.

Clear diagrams are included on the sheet detailing replacement of the probe membrane, however, additional information on the replacement of the oxygen sensor itself are not included.

5.2 Design and Construction

The BOM-1 portable oxygen meter provides measurement of temperature and dissolved oxygen as both % saturation or concentration. The instrument is housed in a die cast case incorporating an analogue meter. A black 'Texon' leatherette carrying case is provided. The oxygen probe assembly is supplied with a 5 meter cable. The meter unit is approximately 196 mm x 120 mm x 57mm and weighs approximately 3 kg including probe and carrying case.

Selection of the measurement mode and range setting is by means of a multi-position switch. Calibration adjustment is made using a three-quarter turn non-locking knob.

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

In order to change the batteries the instrument has to be opened thus exposing the electronics, this would be a problem under field conditions.

5.3 Installation

None Required

5.4 Commissioning

None Required

5.5 Maintenance and Downtime

During the four months of the evaluation this instrument did not require any maintenance.

5.6 Ease of Use

The non-mirrored analogue meter fitted to the meter requires more careful interpretation than a digital display of an equivalent size.

Adjustment of the calibration control is provided by a 270° potentiometer, fitted to front panel, which allows a range of adjustment of approximately ±40% oxygen saturation. As a consequence this control appears to be rather sensitive; precise minor adjustment is difficult to achieve.

Changing between the '100 %' and '200 %' ranges at a threshold concentration of, say, 100 % oxygen saturation reveals a discrepancy between the readings of approximately 2 %. To reduce systematic error the user should therefore, if practicable, secure readings without changing between ranges.

To change the battery the instrument needs to be opened, thereby exposing the electronics. This may cause problems if the unit is opened in damp or wet field conditions.

6. RESULTS

Table 6.1 Instrument stabilisation readings for different temperature changes

Temperature (°C)	Time (secs)	Dissolved Oxygen Sensor
Room Temperature → 5°C	5	106
	30	104
	60	103
	120	102
	180	100
	300	99
	600	97
	1200	95
Room Temperature → 20°C	5	112
	30	108
	60	106
	120	105
	180	104
	300	101
	600	99
5 °C →5°C	5	115
	30	105
	60	104
	120	102
	180	101
	300	100
	600	98
	1200	96

Table 6.2a Battery life

	Power Consumption		
	Volts	mA	mWatt
OFF	9.12	0.00	0.00
°C	9.04	5.45	49.3
Range 3 mg l^{-1}	8.98	8.79	78.9
Range 10 mg l^{-1}	9.02	5.81	52.4
Range 20 mg l^{-1}	9.03	5.26	47.5
Range 30 %sat.	8.97	8.94	80.2
Range 100 %sat.	9.01	5.86	52.8
Range 200 %sat.	9.02	5.25	47.3

Table 6.2b Battery Characteristics

Battery Make	NOT STATED
Battery Type	MN1604
Battery Voltage	NOT STATED
Battery Capacity	NOT STATED
Replacement Interval	NOT STATED

Table 6.3 **Effects of Low battery power**

		Instrument Setting		Low Battery Indicator
	% sat.	mg l $^{-1}$	°C	
9.00	100.0	9.95	16.8	NO
8.54	102.0	9.99	16.8	NO
7.99	100.0	9.90	16.8	NO
7.51	100.0	9.95	16.8	NO
7.00	101.0	9.90	16.8	NO
6.50	101.0	10.00	16.8	YES
6.00	101.0	9.90	16.8	YES
5.49	101.0	9.90	15.5	YES
5.01	100.0	9.82	14.0	YES
4.51	99.5	9.78	12.2	YES
4.00	99.5	9.80	10.8	YES
3.52	98.0	9.75	9.5	YES
2.99	85.0	8.40	9.0	YES

Low battery indicator appeared at 6.96V

Table 6.4 Flow at sensor surface

Water Temperature 10.0 °C			
Flow Rates (m/S)	Dissolved Oxygen (mg l $^{-1}$)	Temp. (°C)	Dissolved Oxygen (% sat.)
0.37	10.8	10.1	97
0.35	10.4	10.1	94
0.27	10.3	10.1	92
0.19	10.3	10.1	92
0.13	10.2	10.0	91
0.05	9.8	10.0	86
0.00	8.0	10.0	71
0.04	9.9	10.0	87
0.08	10.6	10.0	90
0.16	10.8	10.1	93
0.20	10.5	10.2	93
0.29	10.6	10.1	95
0.36	10.8	10.1	98

Table 6.5 Effect of Immersion Depth

Water Temperature 12.5°C			
Depth (m)	Dissolved Oxygen (mg l $^{-1}$)	Temp. (°C)	Dissolved Oxygen (% sat.)
0.3	7.4	12.9	72
1.0	8.2	12.5	76
2.0	7.6	13.0	72
0.3	7.4	13.5	70

Table 6.6 Interference

Interferent	Level	Dissolved Oxygen (mg l^{-1})	Temp. (°C)	Dissolved Oxygen (% sat.)
Temperature	10°C	10.4	10.8	94.5
	30°C	7.65	31	102
Chlorine	0 mgl^{-1}	8.7	21.9	97
	30 mgl^{-1}	8.7	22.2	98

Table 6.7 Instrument readings for commonly employed calibration techniques

	Calibration Technique	Dissolved Oxygen (mgl^{-1})	Temp. (°C)	Dissolved Oxygen (% sat.)
*	River Water	8.6	19.2	92
!	Dechlorinated Tap Water	7.9	18.1	82
!	River Water	8.0	19.5	86

* Calibrated in Dechlorinated tap water
! Calibrated in Air

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

Water Temperature 19.6°C
Atmospheric Pressure 102.0 kPa

* Dissolved Oxygen (% sat.)	Dissolved Oxygen (mg l $^{-1}$)	Temp. (°C)	Dissolved Oxygen (% sat.)
0	0.11	18.2	2
42.0	4.2	19.3	45
73.1	6.9	19.1	74
100	9.4	19.1	101
137.5	13.4	20.0	145
137.5	13.2	20.8	146
100	9.1	20.8	100
73.1	6.8	21.2	76
42	4.2	22.5	48
0	0.18	21.9	2

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

Atmospheric Pressure 101.7 kPa
Water Temperature - 22.2 °C

*Dissolved Oxygen (% sat.)	Dissolved Oxygen (mg l $^{-1}$)	Temp. (°C)	Dissolved Oxygen (% sat.)
0	0.19	22.1	2
42.0	4.3	23.2	49
73.1	6.8	22.3	77
100	9.3	21.9	106
137.5	12.0	23.1	138
137.5	12.2	23.5	142
100	9.0	22.3	100
73.1	6.7	23.2	77
42.0	4.2	24.7	49
0	0.3	23.7	4

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

Water Temperature - 20.7 °C
Atmospheric Pressure 101.3 kPa

* Dissolved Oxygen (% sat.)	Dissolved Oxygen (mg l^{-1})	Temp. (°C)	Dissolved Oxygen (% sat.)
0	0.3	20.0	3.4
42.0	4.1	20.9	45
73.1	6.9	20.7	76
100	9.2	20.1	100
137.5	12.1	20.9	133
137.5	12.5	21.8	140
100	9.2	21.3	102
73.1	6.8	22.2	76
42.0	4.1	23.4	47
0	0.3	23.1	4

Table 6.8d Instrument Readings at different Dissolved Oxygen levels - Test 4

Atmospheric Pressure 101.2 kPa
Water Temperature 23.6 °C

*Dissolved Oxygen (% sat.)	Dissolved Oxygen (mg l^{-1})	Temp. (°C)	Dissolved Oxygen (% sat.)
0	0.36	23.4	4.2
42.0	4.1	24.1	47.5
73.1	6.6	23.5	77
100	9.2	22.8	103
137.5	12.3	24.5	146
137.5	12.2	25.3	148
100	9.0	24.1	104
73.1	6.7	25.7	81
42.0	3.9	26.8	49
0	3.8	26.1	4.5

Table 6.8e Instrument Readings at different Dissolved Oxygen levels - Test 5

Atmospheric Pressure 101.6 kPa
Water Temperature - 25.6°C

* Dissolved Oxygen (% sat.)	Water Temp. (°C)	Dissolved Oxygen (mg l^{-1})	Temp. (°C)	Dissolved Oxygen (% sat.)
0	25.4	0.4	26.2	4.8
42.0		4.0	27.2	49.5
73.1	25.3	6.6	26.4	81
100		9.3	25.2	106
137.5	25.7	12.6	26.8	155
137.5	24.6	12.8	26.7	157
100		9.1	25.7	108
73.1	25.9	6.7	26.9	82.5
42.0		3.9	28.2	49
0	26.6	0.2	27.5	2.6

Table 6.8f Summary of Accuracy Data

*Actual Dissolved Oxygen (% sat.)	Instrument	Accuracy	Winkler	Accuracy
	Systematic Error	Random Error	Systematic Error	Random Error
0	-3.21	1.08	-5.7	2.0
42.0	-4.85	1.94	-8.4	6.0
73.1	-3.20	2.31	-4.0	4.1
100	-0.90	2.18	-1.9	4.1
137.5	-4.1	4.65	-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 *	10.84	10.25	9.22
Step change high to low Dissolved Oxygen *	10.46	10.94	13.18

* see text for details (Section 4.10.1)

Table 6.10 **Response time Test - Temperature Sensor**

	Time 1 (seconds)	Time 2 (seconds)	Time 3 (seconds)
Step change low to high Temperature(°C)	48.72	57.00	54.56
Step change high to low Temperature(°C)	51.38	54.00	56.50

* see text for details (Section 4.10.2)

Table 6.11 **Instrument readings for different levels of salinity**

Chlorine (mg l^{-1})	Water Temp. (°C)	Dissolved Oxygen (mg l^{-1})	Temp. (°C)	Dissolved Oxygen (% sat.)
0	20.0	9.1	20.5	100
5	20.7	9.6	20.2	103
10	20.0	9.7	20.7	105
20	20.6	9.7	21.2	106
40	20.6	10.0	21.2	110
20	20.9	9.9	21.6	108
10	20.8	9.8	21.5	107
5	20.7	9.7	21.3	106
0	21.5	9.3	22.2	104

Table 6.12a Field Data - Class 1A

Date	Water Temp. (°C)	Atmospheric 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)
28/01/93	8.5	100.8	15:35	11.48	11.4	99.5	8.8	17.51	11.38	11.6	102/100	9.0					
29/01/93	8.8	101.7	11:40	11.48	11.4	101/99	8.9	14:58	11.62	11.5	101/99	9.0	16:40	11.41	11.4	100/98	9.0
01/02/93	8.2	103.4	12:13	12.02	11.6	100/98	8.3	14:31	12.33	11.7	>100/101	8.3	16:35	12.02	11.6	100/98	8.2
02/02/93	7.8	103.7	11.36	12.10	11.8	>100/99	7.9	14:04	12.00	12.0	>100/102	8.2	15:59	12.35	12.2	>100/103	8.2
03/02/93	8.2	103.9	11:08	11.90	11.9	>100/102	8.3	17:32	11.90	11.8	>100/101	8.2	18:25	11.76	11.8	>100/100	8.2
04/02/93	7.8	103.4	11:43	12.00	11.8	>100/100	7.9	17:04	11.80	12.2	>100/103	8.0	18:02	11.80	11.8	>100/100	7.8
05/02/93	7.1	103.6	11:37	11.19	12.0	>100/100	7.1	16:03	11.99	12.2	>100/102	7.3	16:50	12.60	12.0	>100/100	7.0
08/02/93	9.0	103.5	11:07	11.69	11.3	100/98	9.1	16:14	11.45	11.6	>100/102	9.4	16:35	11.35	11.6	>100/101	9.1
09/02/93	8.7	103.1	11:10	11.49	11.3	100/99	9.0	14:34	11.35	11.6	>100/101	8.9	17:03	11.53	11.6	>100/101	8.6
10/02/93	7.8	102.9	12:30	11.78	11.5	99/97	8.1	17:00	11.94	11.7	100/98	7.8					
11/02/93	7.1	102.9	12:59	11.93	11.6	99/97	7.3										

Table 6.12b Field Data - Class 3

Date	Water Temp. (°C)	Atmospheric 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)
15/02/93			15:35	7.62	7.6/7.6	66.5/66	9.4										
16/02/93		102.8	14:30	7.62	7.9/7.8	69/68	9.7	15:45	7.41	7.8/7.8	68.5/68	9.8					
17/02/93	10.6	102.6	13:49	6.90	7.1/7.1	61.5/62	10.4	15:20	7.04	7.3/7.2	65.5/65	10.8	15:47	6.87	7.15/7.1	64/64	10.9
18/02/93	10.8	101.8	14:56	7.04	7.0/6.9	63/62	10.7	15:59	7.21	7.1/7.1	64/63	10.8					
19/02/93	8.9	102.0	11:54	6.53	7.1/7.0	61/60	9.0	13:00	7.30	8.0/7.8	66/64	10.0	14:00	7.74	7.8/7.6	66/64	9.0
22/02/93	9.0	102.1	14:50	7.68	7.9/8.0	69/68	8.8	16:10	7.77	7.7/7.7	67/66	9.1	16:40	7.76	7.8/7.7	67/68	9.2
23/02/93	7.9	102.7	9:35	6.84	6.9/6.9	58.5/58	8.0	11:02	7.07	7.2/7.1	61/61	8.1	11:49	7.37	7.3/7.3	62.5/62	8.3
24/02/93	10.0	102.5	15:10	7.18	7.7/7.6	68/66	10.0	15:55	7.11	7.3/7.3	65/64	10.1	16:20	7.22	7.5/7.4	66/66	10.2
25/02/93	8.7	101.5	9:15	6.5	6.5/6.6	56/56	8.7	10:55	6.67	6.95/6.9	59/59	8.7	11:30	6.81	7.05/7.0	60/60	8.7
26/02/93	8.1	100.4	11:35	7.18	7.35/7.3	63/63	8.1	12:37	6.97	7.35/7.3	62.5/62	8.6	13:05	6.98	7.4/7.4	63.5/63	8.8
01/03/93	7.0	101.3	13:56	8.00	8.3/8.35	68.5/68	6.9										

Table 6.13a Calibration Data - Class 1 River

Date	Time	Atmospheric Pressure (kPa)	Dissolved Oxygen (mg l^{-1})	Temp. (°C)	Dissolved Oxygen (% sat.)
28/01/93	15:29	100.8	10.4	13.9	100
29/01/93	11:35	101.7	11.0	11.5	100
01/02/93	12:03	103.4	11.0	10.6	98
02/02/93	11:26	103.7	11.2	10.5	99
03/02/93	11:03	103.9	11.8	9.7	104
04/02/93	11:37	103.4	11.4	10.1	100
05/02/93	11:26	103.5	11.9	9.5	104
06/02/93	10:59	103.4	11.4	10.5	102
07/02/93	10.50	103.1	>10/9.9	17.0	101
08/02/93	12:24	102.9	11.2	10.0	99/101
11/02/93	12:53	102.9	10.6	12.8	100

Table 6.13b Calibration Data - Class 3 River

Date	Time	Atmospheric Pressure (kPa)	Dissolved Oxygen (mg l^{-1})	Temp. (°C)	Dissolved Oxygen (% sat.)
16/02/93	14:25	102.8	11.5	9.0	>100/100
17/02/93	13:35	102.6	11.2	12.2	>100/104
18/02/93	14:48	101.8	11.2	10.4	>100/100
19/02/93	12:36	102.0	10.4	10.8	>100/104
22/02/93	14:45	102.1	12.0	6.9	>100/100
23/02/93	10:54	102.7	11.6	8.7	>100/99
24/02/93	15:03	102.5	11.6	9.1	>100/101
25/02/93	10:45	101.5	11.1	10.5	100/99
26/02/93	12:12	100.4	11.1	9.0	98/98
01/03/93	13:49	101.3	12.3	5.1	99/97

Table 6.14 Systematic and Random Errors for Calibration Check Data

Test	Class 1A River	Class 3 River
Mean	100.8	100.2
Random error	0.8	-0.2
Systematic error (Bias)	1.8	2.2
Total Error	2.0	2.2
Sample size	11	10

Table 6.15 Systematic and Random Errors for Field Data

Test	Class 1A River	Class 3 River
Random error	0.05	-0.21
Systematic error (Bias)	0.35	0.21
Total Error	0.35	0.30
Sample size	29	27

7. INSTRUMENT BEHAVIOUR

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

Throughout this section references are made to the specification of the instrument given in Appendix C. It should be noted that this specification was not provided with the instrument but was taken from a promotional brochure.

Table 6.1 shows readings taken during the sensor stabilisation test. The sensor readings appear to reach stability (given 2% accuracy as stated by the manufacturer) after approximately 3 minutes, however, there then appears to be slight downward drift in the values. The different temperature regimes do not appear to have any affect on the stabilisation time.

The specification of the battery type (Table 2b) permits an estimate of the battery life to be calculated given the instrument power consumption (Table 6.2a). This shows that the manufacturer's stated life of 100 hours would be achieved at the lower currents. However, the increased currents when the meter is used in the 3 mg l^{-1} and 30 % ranges would decrease the expected battery life and therefore not meet the 100 hours specification.

By decreasing the power supply to the instrument it can be seen that the readings are not affected until the supply voltage becomes low. Before this point a low battery is indicated. However, to check the state of the battery a button has to be pushed. This could mean that the readings are being affected without the operator being aware.

The effect of flow on the sensor performance is given in table 6.4. It would appear that the readings are being affected by the flow rate. A calculated correlation coefficient for percentage saturation against flow rate gave a significant (95% confidence) relationship. It can also be noted that even at the highest flow rate the reading did not reach 100% saturation. It must therefore be concluded that a flow rate in excess of that tested is required by this instrument.

There does not appear to any affect on the readings by increasing the immersion depth (Table 6.5). 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 interferents 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 11.08 mg l^{-1}, whilst at 30°C there would be 7.42 mg l^{-1} present. It can be seen that at both levels the meter reading is outside the manufacturers stated 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.

There would appear to be large disparities between the different calibration techniques (Table 6.7). However, this may be due to the large effect of flow past the sensor since up to 10% changes could be induced by varying the amount of agitation of the sensor in the sample.

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. In general the performance of the instrument is within that stated by the manufacturer. However, for some specific test solutions there are much larger variations. Since these effects are not seen throughout all the tests at a specific concentration it can be concluded that there are local flow effects which cause variability in the readings, especially as it has already been noted how sensitive the instrument is to flow. 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 2.4 and 6.2 %. 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 hysterisis is an important factor with this instrument.

The response time for the oxygen sensor is considerable better than the 35 seconds stated by the manufacturer (Table 6.9). However the temperature sensor (Table 6.10) response is very slow, around 50 seconds, which means that the early response of the sensor could be dependant on any temperature changes.

This instrument does not provide any salinity correction. To correct the readings salinity tables are required which were not provided in the manual.

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 rivers. This test should show if there is any drift in the calibration of the instrument. The result show that the total error was approximatley 2% over the test period for the two sites. 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 0.35 mg l^{-1} for the Class 3 river and 0.30 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 shown 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

BOM 1 Battery operated dissolved oxygen meter complete with carrying case, OE15 probe with 3 metres of connection cable and membrane kit comprising 1 metre of membrane, 1 set of 'O' rings and applicator. Code 4005	£495.00 ea.
OE15 Dissolved Oxygen probe with 3 metres of cable. Code 4008	£265.00 ea.
CHX15 Replacement cartridge for the OE15 probe. Code 4009	£150.00 ea.
CHX15G Replacement cartridge with gold cathode for the OE15 probe. Code 4024	£207.00 ea.
OE15 Membrane kit comprising 1 metre of membrane , 1 set of 'O' rings and applicator. Code 4011	£ 19.50 ea.
Membrane	£ 1.75 /m
Applicator	£ 4.25 ea.
Extra 54C cable fitted to the OE15 probe. Code 700/701	£ 2.60 /m
Cartridge regeneration (replacement of gel electrolyte and lead anode).	£ 47.00 ea.

Note:

All prices are ex-works, carriage, packing and insurance are extra.

9. MANUFACTURER'S COMMENTS

Some small modifications are proposed following the comments in the report as follows;

- The analogue display is replaced by an LCD digital panel meter. This will also include a low battery warning on the display.

- The calibration potentiometer is replaced by a multi-turn potentiometer with a locking facility

- A more comprehensive handbook is supplied with the instrument with the following information:

    - Salinity tables for correction,
    - Pressure tables for correction,
    - Full operational instructions,
    - Full specification,
    - Minimum flow rate for stable operation and
    - Probe and instrument maintenance.

We would envisage these modifications being introduced before the end of 1993.

We would like to take this opportunity to thank all those involved in compiling the report which we found of value and will enable us to improve the specification of the product.

ACKNOWLEDGEMENTS

The authors would like to thank;

- the NRA staff at Fobney Mead and Lea Marston for their help in providing laboratory and water quality data,
- the analysis staff at WRc for providing calibration solutions, and
- LTH 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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APPENDIX A LABORATORY ANALYSIS OF FIELD DATA

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

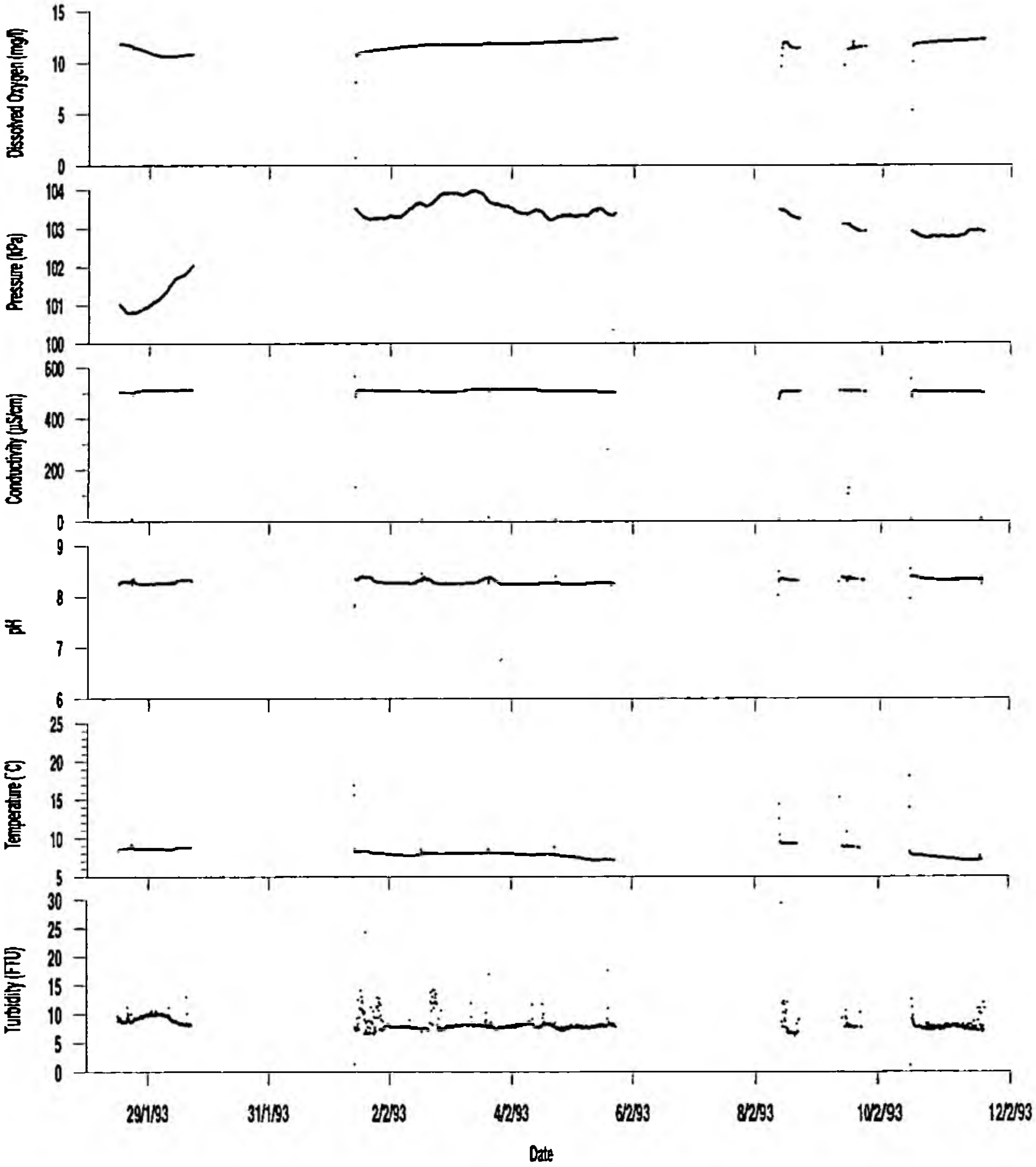

Figure B1 Water Quality Parameters Class 1A River

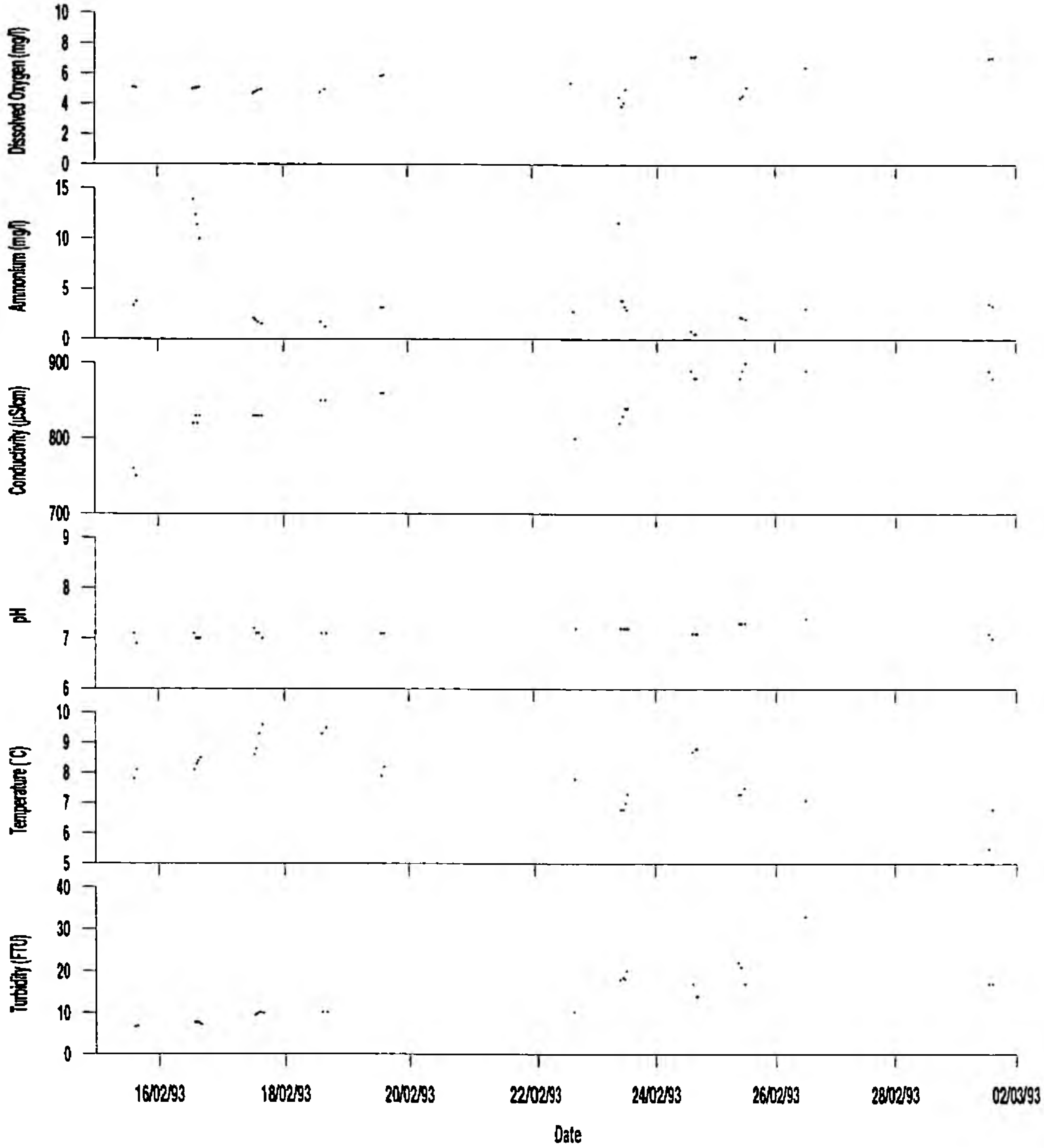

Figure B2 Water Quality Parameters Class 3 River

APPENDIX C MANUFACTURER'S SPECIFICATION

Oxygen Measurement

Range	0-3, 0-10, 0-100 ppm 0-30, 0-100, 0-200% saturation in six switched ranges.
Accuracy	Better than 2% of scale length on all ranges.
Temperature Compensation	Automatic temperature compensation effective over the range °5°C to 35°C.

Temperature Measurement

Range	0 to 50°C
Accuracy	± 1°C including probe
Meter Scale	Linear 0-30 and 0-100 for oxygen Parallel 0-50°C scale for temperature

Environment

Probe Response	0 to 90% of value within 35 seconds for a step change in oxygen level.
Recorder Output	0-1 mA corresponding to the meter span into a maximum load of 500 ohms. Output is via a standard ¼" jacket socket.
Ambient Temperature	0 to 40°C for full specification.
Power Supply	Standard PP3 type alkaline manganese battery providing approx. 100 hours continuous use.
Dimensions	196 x 120 x 57 mm
Weight	3000g including probe, carrying case and accessories