The Evaluation of a YSI Model 58 Hand-Held Dissolved Oxygen Meter

WRc plc

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NRA

National Rivers Authority

THE EVALUATION OF A YSI MODEL 58 HAND-HELD DISSOLVED OXYGEN METER

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Evaluation Report 220/24/T

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CONTENTS Page

CONTENTS (continued) Page

LIST OF TABLES

Page

EXECUTIVE SUMMARY

This report describes the results of an evaluation of a YSI Model 58 Hand-held Dissolved Oxygen Meter. The evaluation of this instrument was undertaken by the NRA (Thames Region) at the Evaluation and Demonstration Facilities at Fobney Mead, Reading and Lea Marston, Birmingham according to a protocol jointly devised by WRc and the NRA.

The YSI hand-held Dissolved Oxygen meter performed in good agreement to the manufacturer's stated response and reliability. The manufacturer states that a fifteen minute 'warm-up' time is required prior to use of the instrument. The instrument was found to be easy to operate, although the installation of the membrane was found to require a high degree of manual dexterity and would be very difficult to perform under field conditions. Similarly, the necessity to open the case of the instrument to replace the batteries could cause problems in the field. The total error (quadrature sum of random and systematic errors) for five test concentrations varied between 2 and 4.5%. It should be noted that Winkler Titrations of these solutions gave a total error of 6% to 25%. For the field evaluation the total error was 0.19 mg l^{-1} for Lea Marston and 0.31 mg l^{-1} for Fobney Mead.

The instrument cost £1045.00, it required 1 hour to install. No maintenance or repairs were required during the four month evaluation.

KEYWORDS

Dissolved Oxygen, Evaluation

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1. INTRODUCTION

This report describes the evaluation of a YSI MODEL 58 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 YSI MODEL 58 Hand-held Dissolved Oxygen Meter sensor is a polarographic sensor.

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:	YSI Incorporated Yellow Springs Instrument Co. Inc. Yellow Springs Ohio 45387 USA
Supplier:	YSI Ltd Lynchford House Lynchford Lane Farnborough Hants GU14 6LT
Tel:	0252 514711
Fax:	0252 511855

Instrument Description:	Model 58 Hand-held Dissolved Oxygen Meter
Electrochemical Sensor Type:	Polarographic
Serial Number:	92F 039453

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

3. MAJOR FINDINGS AND COMMENTS

This section provides a summary of the major findings and conclusions for the evaluation of a YSI hand-held Dissolved Oxygen meter.

The YSI hand-held Dissolved Oxygen meter performed in good agreement to the manufacturer's stated response and reliability. The manufacturer states that a fifteen minute 'warm-up' time is required prior to use of the instrument. This needs to be considered carefully as by the nature of hand-held instruments, measurements are made intermittently.

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 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 2 and 4.5 percentage saturation.

The instrument was sensitive to flow changes, requiring a flow rate of greater than 0.30 $m\ s^{-1}$ to achieve a stable reading.

The response times were in agreement with those specified by the manufacturer.

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

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 0.19 $mg\ l^{-1}$ for Lea Marston and 0.31 $mg\ l^{-1}$ for Fobney Mead.

The instrument was found to be easy to operate, although the installation of the membrane was found to require a high degree of manual dexterity and would be very difficult to perform under field conditions. Similarly, the necessity to open the case of the instrument to replace the batteries could cause problems in the field which may effect the long term reliability. These difficulties are unlikely to be encountered in the field if a planned programme of preventative maintenance is undertaken.

The instrument did not require any maintenance during the four months of the evaluation. Overall the instrument was found to be excellent with only a few minor concerns regarding the battery changing procedure and the method for changing the membrane. Care must be taken to insure that there is adequate flow past the sensor when readings are being taken.

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 (for comparison with the manufacturer's documentation) 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 was maintained at a flow rate 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.

Atmospheric pressure was monitored continuously throughout the test.

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 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 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. 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 29 page A5 size instruction manual was supplied with the instrument. The manual appears to be well written and unambiguous and provides a very detailed description for the commissioning and operational use of the instrument. No serious omissions or obvious typographical errors were noted. A comprehensive index is included. Detailed servicing instructions are provided which are supported by diagrams and a full circuit diagram.

A separate service manual was also provided in addition to the user manual. This includes detailed circuit description, PCB layout drawings and schematic diagrams and diagnostic tests to enable the tracing of faults to component level. A full parts list is included.

A brief summary of the instrument operating procedures is reproduced on the back of the instrument itself. The documentation states that a brief summary is also included on the back of the user manual, however, the manual provided did not include this information.

Instructions are provided separately for the air-calibration method (for readings in % saturation) and using air-saturated water (for the mg l^{-1} mode). Additional advice is given on the calibration of the instrument against Winkler oxygen determinations and, furthermore, a calibration method is described to allow the instrument to display oxygen partial pressure in mm Hg.

Saturation tables are provided which incorporate values for various atmospheric pressures and operating altitudes. As the instrument incorporates in-built salinity correction from 0 to 40 parts per thousand, no separate salinity correction table is provided in the manual. Similarly, no data on hydrostatic pressure correction is deemed necessary as the probe incorporates an in-built pressure correction system to minimise depth error.

Detailed maintenance procedures are included. However, the only advice on cleaning the probe refers to cleaning the anode and cathode; no advice is given on the correct or preferred procedure for the removal of foulant from the surface of the membrane itself.

The manual states that the probe should be replaced every 2 weeks of operation, although it is unclear if this refers to intermittent or continuous immersion. A very useful probe performance check is, however, provided which is based on the following criteria;

(a) speed of response,
(b) background current, and
(c) calibration stability.

No special instructions have been given for the long-term storage of the probe.

Full details of both the instrument and probe specification are given. Additional information on factors such as temperature sensitivity and response time of the probe, and % to mg l^{-1} 'mode to mode' accuracy data is provided.

Health and Safety information is not provided for the chemicals or reagents required during use of the instrument.

A detailed discussion is given, and examples provided, of instrument component, probe related and calibration related measurement errors.

A description of the use of different thickness membranes to optimise measurement of dissolved oxygen at both low temperature and low oxygen saturation conditions, and for robust long-term monitoring is included.

The description of the low-battery test function in the Care and Maintenance section of the manual does not make it clear that the low-battery warning of the meter's principal power supply will be displayed automatically whenever the instrument is switched on. The documentation implies that the spring-loaded 'LOBAT' test function should be used. However, other sections of the manual, provide further notes on this feature, which is more clearly explained.

5.2 Design and Construction

The YSI Model 58 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 meter is approximately 280 x 216 x 95 mm and weighs approximately 1900 g including batteries.

Battery replacement requires the casing to be opened exposing the electronics. This could be a problem if the batteries are to be replaced under field conditions.

An optional mains power supply (battery eliminator) is available for long term laboratory use. The meter is fitted with a carrying handle which also serves as a prop when the instrument is used on the bench.

The IP rating of the instrument is not stated. All case openings are gasketed; the instrument is described in the manual as able to resist the entry of water, provided that the recorder output, battery eliminator and stirrer connectors are capped.

A large 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 salinity range selector incorporates a detent and may be adjusted in 1 part per thousand increments. The oxygen calibration knob is fitted with a locking mechanism to prevent inadvertent adjustment. No facility is provided for housing the probe or lead during transit.

The probe is a Clark-type membrane covered polarographic sensor incorporating thermistors for temperature measurement and compensation. The probe assembly may be combined with detachable leads which are available in lengths from 0.3 m to 61 m.

5.3 Installation

None required

5.4 Commissioning

The probe was supplied in a dry state. The electrolyte was prepared by dissolving the potassium chloride crystals in distilled water using the dropper bottle provided. The probe reservoir was then filled with the electrolyte. Subsequently, the membrane was installed. Although the diagrams provided in the documentation suggest a straightforward operation, installation required a high degree of manual dexterity.

5.5 Maintenance and Downtime

The instrument performed satisfactorily thoughout the four months of the evaluation. No maintenance was required during this period.

5.6 Ease of Use

The YSI Model 58 dissolved oxygen meter features large switches for the various controls and provides a large display which is very legible in both high and low lighting conditions. The legends are clear and unambiguous. The large ABS plastic case is easy to handle and appears to sufficiently robust for routine field operation.

The dissolved oxygen reading can be presented at two resolutions; 0 to 20.0 mg l^{-1} or 0 to 20.00 mg l^{-1}, with an accuracy of $\pm$ 0.03 mg l^{-1}. The instrument can also measure % air-saturation and water temperature. Salinity correction is easily adjusted using a large incremental selector switch.

Adjustment of the 100 % air-saturation value is performed using a 10-turn potentiometer which is fitted with a lockable collar. This control provides fine adjustment of the upper calibration value whilst preventing accidental or inadvertent operation. However, adjustment of the zero calibration value is made using a single-turn, non-lockable, potentiometer providing adjustment over the range of $\pm$ 3 % of dissolved oxygen. The absence of a locking-collar means that the user may unknowingly change the zero calibration setting of the instrument, thereby significantly affecting the actual measured oxygen value.

It is necessary to open the meter unit to change the internal batteries, thereby exposing the electronics to the elements and compromising the IP rating of the instrument. The replacement of the internal batteries in the field, during harsh weather conditions, may allow water to enter the electronics and cause the instrument to fail.

6. RESULTS

Table 6.1 Instrument stabilisation readings for different temperature changes

Temperature Change	Time (secs)	Dissolved Oxygen (% sat.)
Room Temperature → 5°C	10	126.0
	30	101.7
	60	98.0
	120	96.6
	180	96.1
	300	95.8
	600	95.3
	1200	94.7
5°C	5	150.0
	30	101.1
	60	96.0
	120	95.5
	180	94.2
	300	94.8
	600	93.9
	1200	94.2
Room Temperature → 20°C	5	130.0
	30	103.1
	60	100.1
	120	98.1
	180	97.9
	300	99.1
	600	98.2
	1200	98.6

Table 6.2a Power consumption

Meter Function	Volts	mA	mW
Off	6.43	0.00	00.0
Zero	6.33	3.66	23.2
°C	6.32	4.50	28.4
0.1 mg l^{-1} Range	6.35	3.65	23.2
0.01 mg l^{-1} Range	6.35	3.50	22.2
% sat.	6.35	3.50	22.2

Table 6.2b Battery Characteristics

Battery Make	Panasonic
Battery Type	4 D cells Extra Heavy Duty
Battery Voltage	1.5 V per cell
Battery Capacity	Not Stated
Replacement Interval	Not Stated

Table 6.3 Effects of different power supply voltages on instrument readings

Voltage	% sat.	0.1 (mg l^{-1}) Range	0.01 (mg l^{-1}) Range	°C	Low Battery Indicator
5.99	100.0	9.9	9.89	15.6	NO
5.01	99.7	9.8	9.83	15.9	NO
4.49	99.7	9.8	9.82	15.9	YES
4.00	99.4	9.8	9.79	15.9	YES
3.52	99.6	9.8	9.78	16.0	YES
2.99	100.2	9.8	9.83	16.0	YES
2.88		Blank	Display		

Table 6.4 Instrument readings for different Flows at the sensor surface

Water Temperature 10.0 °C

Flow Rate ($m\ s^{-1}$)	Dissolved Oxygen ($mg\ l^{-1}$)	Temp. (°C)	Dissolved Oxygen (% sat.)
0.37	11.21	10.1	100.0
0.35	11.15	10.1	99.5
0.27	11.08	10.1	98.9
0.19	10.94	10.1	97.5
0.13	10.80	10.0	96.4
0.05	10.36	10.0	91.8
0.00	9.09	10.0	80.8
0.04	10.29	10.0	91.7
0.08	10.64	10.0	94.7
0.16	10.74	10.0	95.8
0.20	10.80	10.0	96.2
0.29	10.90	10.1	97.3
0.36	11.05	10.1	98.5

Table 6.5 Instrument readings at different Depths

Water Temperature 17.7 °C

Depth (m)	Dissolved Oxygen ($mg\ l^{-1}$)	Temp. (°C)	Dissolved Oxygen (% sat.)
0.3	7.5	17.8	75
1.0	8.2	17.8	79
2.0	7.3	17.8	81
0.3	7.5	17.9	81

Table 6.6 **Instrument Readings for two Interferents**

Atmospheric Pressure - 101.8 kPa

Interferent	Level	Dissolved Oxygen ($mg\ l^{-1}$)	Temp. (°C)	Dissolved Oxygen (% sat.)
Temperature	10°C	10.98	10.2	98.2
	30°C	7.42	30.0	98.7
Chlorine	0 $mg\ l^{-1}$	8.41	22.6	97.8
	30 $mg\ l^{-1}$	8.40	23.0	98.2

Table 6.7 **Instrument readings for commonly employed Calibration techniques**

Atmospheric Pressure 101.5 kPa

	Sample (100% Saturation)	Dissolved Oxygen ($mg\ l^{-1}$)	Temp. (°C)	Dissolved Oxygen (% sat.)
+	Dechlorinated tap water	9.00	19.3	98.2
+	River water	8.83	19.8	97.3
!	Dechlorinated tap water	9.00	19.4	98.3
!	River water	9.00	19.9	99.2

+ Calibrated in Air

! Calibrated in Dechlorinated tap water

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

Atmospheric Pressure - 98.9 kPa
Water Temperature - 20.8 °C

Dissolved Oxygen Concentration (% sat.)*	Dissolved Oxygen (mg l^{-1})	Temp. (°C)	Dissolved Oxygen (%sat.)
0.0	0.29	20.6	3.2
42.0	3.92	21.5	44.6
73.1	6.48	21.0	73.1
100.0	8.74	20.5	97.8
137.5	12.23	20.9	137.4
137.5	11.95	21.2	135.0
100.0	8.65	20.6	96.7
73.1	6.45	21.7	73.7
42.0	3.63	22.7	42.3
0.0	0.27	22.0	3.1

* See Section 4.8 for details

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

Atmospheric Pressure - 98.9 kPa
Water Temperature - 20.8 °C

Dissolved Oxygen Concentration (% sat.)*	Dissolved Oxygen (mg l^{-1})	Temp. (°C)	Dissolved Oxygen (% sat.)
0.0	0.20	22.2	2.4
42.0	3.39	23.1	39.7
73.1	6.36	22.4	73.8
100.0	8.62	20.9	96.9
137.5	11.55	22.5	133.9
137.5	11.30	22.8	132.1
100.0	8.67	21.2	98.3
73.1	6.10	23.3	71.8
42.0	3.63	24.5	43.7
0.0	0.28	23.7	3.4

* See Section 4.8 for details

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

Atmospheric Pressure - 102.4 kPa
Water Temperature - 16.9 °C

Dissolved Oxygen Concentration (% sat.)*	Dissolved Oxygen (mg l^{-1})	Temp. (°C)	Dissolved Oxygen (% sat.)
0.0	0.22	15.4	2.2
42.0	4.52	16.8	46.7
73.1	7.15	16.7	74.0
100.0	9.57	16.1	97.7
137.5	13.12	17.0	135.9
137.5	12.88	17.6	135.6
100.0	9.20	17.0	95.1
73.1	6.99	18.2	74.4
42.0	3.76	18.8	40.8
0.0	0.31	18.3	3.3

* See Section 4.8 for details

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

Water Temperature 18.7 °C
Atmospheric Pressure 102.3 kPa

Dissolved Oxygen Concentration (% sat.)*	Dissolved Oxygen (mg l^{-1})	Temp. (°C)	Dissolved Oxygen (% sat.)
0.0	0.27	18.8	2.9
42.0	4.02	19.7	44.0
73.1	6.81	19.4	74.3
100.0	8.83	18.9	95.5
137.5	11.98	19.8	131.5
137.5	12.05	20.1	133.5
100.0	8.69	19.5	95.1
73.1	6.17	20.7	69.1
42.0	3.74	21.6	42.6
0.0	0.20	20.5	2.3

* See Section 4.8 for details

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

Atmospheric Pressure -101.0 kPa
Water Temperature - 18.1 °C

Dissolved Oxygen Concentration (% sat.)*	Dissolved Oxygen (mg l^{-1})	Temp. (°C)	Dissolved Oxygen (% sat.)
0.0	0.27	16.8	2.8
42.0	3.97	17.5	41.8
73.1	6.54	17.6	68.9
100.0	9.05	17.0	94.3
137.5	12.30	17.9	130.2
137.5	12.32	18.4	131.8
100.0	8.88	18.4	95.0
73.1	6.51	18.4	69.7
42.0	3.80	20.2	42.1
0.0	0.34	19.7	3.8

* 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	-2.9	0.5	-5.7	2.0
42.0	-0.8	2.0	-8.4	6.0
73.1	0.8	2.2	-4.0	4.1
100	3.8	1.4	-1.9	4.1
137.5	3.8	2.3	-13.4	21.4

see section 4.8 for details

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

Atmospheric Pressure -101.0 kPa
Water Temperature - 18.1 °C

Dissolved Oxygen Concentration (% sat.)*	Dissolved Oxygen (mg l^{-1})	Temp. (°C)	Dissolved Oxygen (% sat.)
0.0	0.27	16.8	2.8
42.0	3.97	17.5	41.8
73.1	6.54	17.6	68.9
100.0	9.05	17.0	94.3
137.5	12.30	17.9	130.2
137.5	12.32	18.4	131.8
100.0	8.88	18.4	95.0
73.1	6.51	18.4	69.7
42.0	3.80	20.2	42.1
0.0	0.34	19.7	3.8

* 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	-2.9	0.5	-5.7	2.0
42.0	-0.8	2.0	-8.4	6.0
73.1	0.8	2.2	-4.0	4.1
100	3.8	1.4	-1.9	4.1
137.5	3.8	2.3	-13.4	21.4

see section 4.8 for details

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.)	Instrument Temp. (°C)
28/1/93	8.5	100.8	15:03	11.48	11.65	100.5	8.7	17:48	11.38	11:58	100.0	8.7					
29/1/93	8.8	101.7	11:25	11.48	11.51	99.8	8.8	15:03	11.62	11.62	101.0	9.0	16:50	11.41	11.63	100.5	8.9
1/2/93	8.2	103.4	12:20	12.02	11.94	102.0	8.3	14:15	12.33	12.01	102.9	8.4	16:46	12.02	11.95	101.6	8.2
2/2/93	7.7	103.7	11:24	12.10	12.20	103.2	7.8	14:02	12.00	12.20	103.5	8.0	16:19	12.35	12.15	103.1	8.0
3/2/93	8.2	103.9	11:35	11.90	12.13	103.5	8.2	17:30	11.90	11.93	101.7	8.2	18:16	11.76	12.05	102.8	8.2
4/2/94	7.8	103.4	11:40	12.00	12.13	102.6	7.9	17:04	11.80	12.06	101.9	7.8	18:03	11.80	12.12	102.4	7.8
5/2/93	7.1	103.5	11:43	11.19	12.33	102.6	7.1	16:02	11.99	12.36	102.7	7.1	16:51	12.60	12.44	103.1	7.1
8/2/93	9.0	103.5	11:00	11.69	11.68	101.6	9.1	16:04	11.45	11.72	102.1	9.2	16:36	11.35	11.68	102.0	9.2
9/2/93	8.7	103.1	10:38	11.49	11.58	100.3	8.8	14:33	11.35	11.73	101.6	8.8	17:06	11.88	12.07	101.6	8.7
10/2/93	7.7	102.9	12:23	11.78	12:07	102.1	7.8	17:02	11.94	12.11	102.1	7.7					
11/2/93	7.1	102.9	12:50	11.93	12:39	103.0	7.1										

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			16:00	7.62	7.71	67.9	9.6										
16/2/93		102.8	14:24	7.62	7.58	67.0	9.7	15:45	7.41	7.56	66.8	9.7					
17/2/93	10.5	102.6	13:37	6.90	7.00	62.7	10.2	15:20	7.04	7.01	63.5	10.7	15:49	6.87	6.87	62.4	10.8
18/2/93	10.8	101.7	15:06	7.04	6.92	62.6	10.7	15:56	7.21	7.04	63.8	10.8					
19/2/93	8.9	102.0	11:50	6.53	6.96	60.8	8.8	12:50	7.30	7.66	65.9	9.0	13:55	7.74	7.70	67.1	9.3
22/2/93	9.0	102.1	15:00	7.68	7.86	68.2	8.9	16:10	7.77	7.72	67.6	9.2	16:40	7.76	7.63	66.6	9.2
23/2/93	7.9	102.7	9:35	6.84	6.93	58.7	7.9	10:55	7.07	7.16	60.8	8.0	11:48	7.37	7.38	63.1	8.3
24/2/93	10.1	102.5	15:17	7.18	7.34	65.2	10.0	15:55	7.11	7.25	64.7	10.1	16:20	7.22	7.27	64.9	10.1
25/2/93	8.7	101.5	9:15	6.50	6.32	65.2	8.5	10:45	6.67	6.73	57.9	8.5	11:30	6.81	6.93	59.8	8.7
26/2/93	8.2	100.4	11:41	7.18	6.95	59.1	8.2	12:42	6.97	6.97	60.2	8.7	13:18	6.98	7.05	61.2	8.9
1/3/93	6.8	101.3	13:45	8.00	8.56	70.5	6.8										

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

Date	Time	Pressure (pKa)	Dissolved Oxygen (mg l^{-1})	Temp. (°C)	Dissolved Oxygen (% sat.)
28/1/93	14:55	100.8	10.61	12.4	99.8
29/1/93	11:17	101.7	11.27	10.5	101.6
1/2/93	12:10	103.4	11.31	10.8	102.7
2/2/93	10:50	103.6	12.21	8.8	105.6
3/2/93	11:27	103.9	11.29	10.7	102.4
4/2/93	11:34	103.4	11.48	9.9	101.8
5/2/93	11:36	103.6	11.64	9.8	103.1
8/2/93	10:54	103.5	11.54	9.9	102.5
9/2/93	10:31	103.1	9.62	15.8	97.6
10/2/93	12:12	102.9	11.51	9.5	101.6
11/2/93	12:42	102.9	10.78	12.2	100.9

Table 6.13b Instrument Readings for daily calibration check - Class 3 River

Date	Time	Pressure (kPa)	Dissolved Oxygen (mg l^{-1})	Temp. (°C)	Dissolved Oxygen (% sat.)
15/2/93	15:50		11.60	9.5	102.1
16/2/93	14:15	102.8	11.87	8.6	102.3
17/2/93	13:26	102.6	10.53	11.9	97.9
18/2/93	14:58	101.8	10.88	10.9	98.8
19/2/93	12:40	102.0	10.07	15.0	99.9
22/2/93	14:55	102.1	12.19	7.0	100.9
23/2/93	10:47	102.7	11.79	8.2	100.5
24/2/93	15:12	102.5	11.29	9.4	99.0
25/2/93	10:35	101.5	10.86	10.1	96.6
26/2/93	12:26	100.4	10.98	9.7	97.0
1/3/93	13:40	101.4	13.32	4.6	104.0

Table 6.14 Systematic and Random Errors for daily calibration check

Test	Class 1A River	Class 3 River
Mean	101.8	99.9
Random error	1.8	-0.1
Systematic error (Bias)	1.9	2.2
Total Error	2.6	2.2
Sample size	11	11

Table 6.15 Systematic and Random Errors for field Data

Test	Class 1A River	Class 3 River
Mean	-	-
Random error	-0.16	-0.06
Systematic error (Bias)	0.27	0.18
Total Error	0.31	0.19
Sample size	29	27

7. INSTRUMENT BEHAVIOUR

This section describes the general performance of the YSI Dissolved Oxygen meter during the various test procedures.

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 drift in the results throughout the test period. The manufacturer recommends that the readings should not be taken until the instrument has been allowed at least fifteen minutes to settle. The stabilisation period for the oxygen sensor appears to unaffected by equilibration of the temperature sensor.

The expected battery life (table 6.2) cannot be calculated since the battery capacity is not stated. However, to achieve the manufacture specification of 1000 hours a battery of 3.8 Ah capacity would be required.

The instrument readings are not affected by decreasing the power supply (Table 6.3). Indeed even after the low battery warning is given, further reduction of the voltage does not affect the reading up to the point where the display is lost.

The effect of flow on the sensor performance is given in table 6.4. It shows that a flow of greater than 0.30 m s^{-1} is required to achieve a stable reading. This is in broad agreement with the manufacturer's specification. It should be noted that throughout this test the percentage saturation readings were unstable ($\pm$ 0.3 % dissolved oxygen).

This meter has an in-built pressure compensation system. The manufacturer states that the readings are compensated to an accuracy of 0.5% at depths of up to 70 m. Clearly the depths tested in this procedure could not be expected to affect the recorded values. More importantly, the values were low and gave unstable percentage saturation values. This would indicate that there was inadequate flow through the test system.

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.

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 titrations are provided in Table 6.8f. The total error (quadrature sum of random and systematic errors) for five test concentrations varied between 2 and 4.5%. It should be noted that Winkler titrations 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 broad agreement with the that stated by the manufacturer.

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 should show if there is any drift in the calibration of the instrument. This shows that the total error was approx. 2% over the test period, for the two sites. The variability in the readings was only 0.1% in the Class 3 river but rose to nearly 2% in the Class 1A river. If this is compared to the Winkler titrations 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 exposure of the sensor to the water was only for a short period. The same statistical test was therefore 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 titrations. The total error was 0.19 mg l^{-1} for the Class 3 river and 0.31 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

Model 58 Dissolved Oxygen Meter		£1045.00
Probe 5739 (requires cable)		£ 176.40
Cables - 10 ft		£ 100.80
- 25 ft		£ 131.25
- 50 ft		£ 149.10
- 100 ft		£ 183.75
- 150 ft		£ 215.25
- 200 ft		£ 247.80
Submersible Stirrer includes Cable connector		£ 432.95
Membrane Kits	(Standard)	£ 12.00
Membrane Kits	(High sensitivity)	£ 12.00
S718 Budget Probe 12 ft c/w probe		£ 168.00

9. MANUFACTURER'S COMMENTS

The manufacturer did not have any comments to make on this report.

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- the analysis staff at WRc for providing calibration solutions.
- YSI Ltd 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 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^{-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

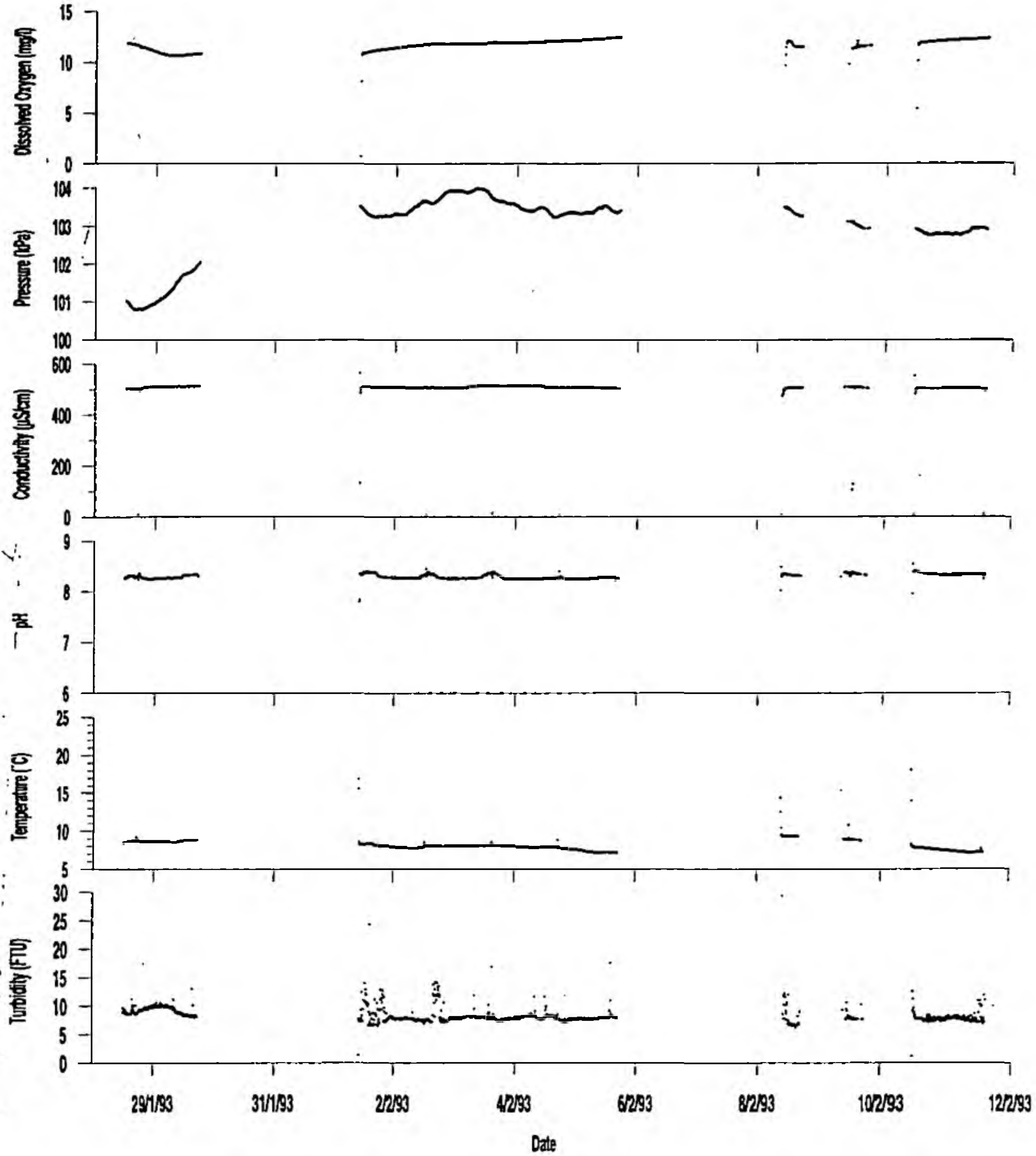

Figure B1 Water Quality Parameters Class 1A River

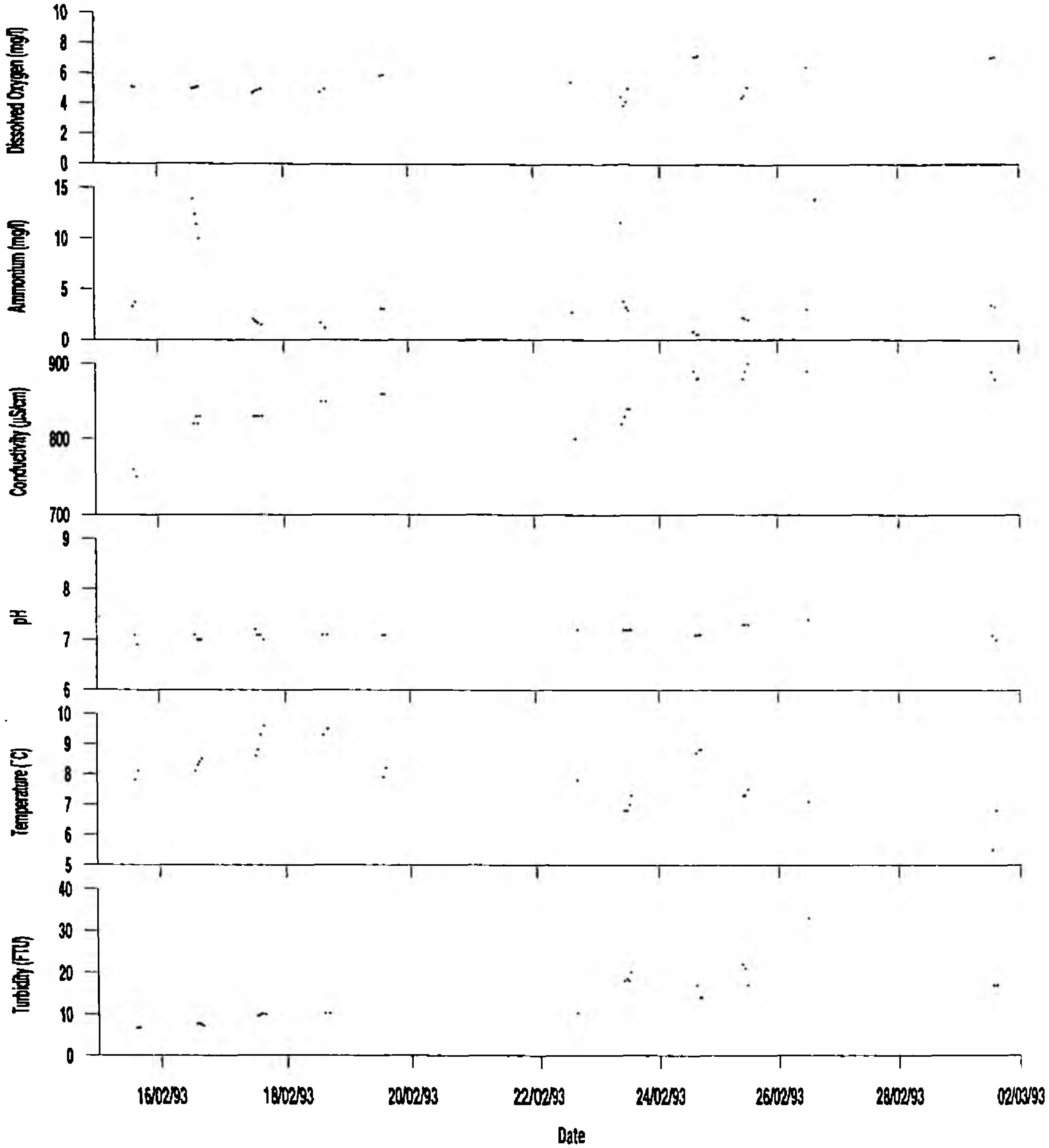

Figure B2 Water Quality Parameters Class 3 River

APPENDIX C - MANUFACTURERS SPECIFICATIONS

Oxygen Measurement

RANGES:	0 to 20.0 mg l^{-1} dissolved oxygen
	0 to 20.00 mg l^{-1} dissolved oxygen
	0 to 200.0 % air saturation
ACCURACY	± 0.03 mg l^{-1} (0 to 20.00 mg/l range)
	± 0.3% air saturation

Temperature Measurement

RANGE:	-5 to +45°C
ACCURACY	± 0.3°C (plus probe interchangeability)

Temperature Compensation

mg l^{-1} mode	5°C - 45°C	± 1%	Dissolved Oxygen Reading
	0°C - 5°C	± 2%	Dissolved Oxygen Reading
% sat mode	5°C - 45°C	± 1%	Dissolved Oxygen Readings
	0°C - 5°C	± 1.5%	Dissolved Oxygen Readings

Salinity Compensation

RANGE	0 to 40 parts per thousand
ACCURACY	± 0.3% of reading ± 1 digit

Instrument Environment

Temperature range	0 to 45°C
Water Resistance	with receptacles capped every case opening is gasketed to resist entry of water.
Power Supply	4 D size batteries or battery eliminator Approx. 1000 hours battery life Low Battery indicator (LOBAT) appears automatically when approximately 50 hours of battery life remain

Probe

Cathode	Gold
Anode	Silver
Membrane	0.001" FEP Teflon (YSI 5775)
Electrolyte	Half-saturated KCL with Kodak Photo-Flo

Temperature Sensor Accuracy	± 0.2°C
Pressure Compensation	0.5% (up to 100 psi)
Response Time (90% change)	10 seconds at a constant 30°C 30 seconds at low temperature and Dissolved Oxygen