220

The Evaluation of a pHOX Model 962 Hand-Held Dissolved Oxygen Meter

WRc plc

R&D 220/28/T

NRA

National Rivers Authority

THE EVALUATION OF A pHOX MODEL 962 HAND-HELD DISSOLVED OXYGEN METER

D A Neville, M M I Harman, P D Whalley and A Chappell

Research Contractor:
WRc plc
Henley Road Medmenham
PO Box 16 Marlow
Buckinghamshire SL7 2HD

National Rivers Authority
Rivers House Waterside Drive
Almondsbury Bristol BS12 4UD

Evaluation Report 220/28/T

National Rivers Authority
Rivers House
Waterside Drive
Almondsbury
BRISTOL
BS12 4UD

Tel: 0454 624400
Fax: 0454 624409

Dissemination Status
Internal: Restricted
External: Restricted

Statement of use
This evaluation report is one of a series produced by the NRA National Evaluation Facility in conjunction with WRc. The performance of an individual item of equipment is described in terms of both laboratory and field tests. Information concerning the reliability, applicability and cost of ownership of instruments is provided where possible.

Research Contractor
This document was produced under R&D Contract 220 by:

WRc plc
Henley Road Medmenham
PO Box 16 Marlow
Buckinghamshire
SL7 2HD

Tel: 0491 571531
Fax: 0491 579094

WRc Reference: NR 3432/4245

NRA Project Leader
The NRA's Project Leader for R&D Contract 220:

Tim Reeder - Thames Region

Additional Copies
Further copies of this document may be obtained from Regional R&D Co-ordinators or the R&D Section of NRA Head Office.

CONTENTS

CONTENTS (continued) Page

LIST OF TABLES

EXECUTIVE SUMMARY

This report describes the results of an evaluation of a pHOX 962 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 pHOX 962 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 unit is both compact and light and presented no difficulties during operation. The sophistication provided by the in-built software (particularly the use of the security protected menus) means that the user is required to read the manual thoroughly before operation. Once the user has become familiar with the controls the 'quick' guides provided with the documentation allow the user to follow the required switch sequences with little difficulty.

The instrument display was clear and legible and incorporates a useful backlight for use in low ambient light.

In two of the test procedures there appeared to some temperature affect on the instrument readings.

The total error (quadrature sum of random and systematic errors) for five test concentrations varied between 1.6% and 5.7%. 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 calculated against Winkler determinations was 0.77 mg l^{-1} for Lea Marston and 0.44 mg l^{-1} for Fobney Mead.

The instrument cost £695.00. No maintenance or repairs were required during the four month evaluation.

KEY WORDS

Dissolved Oxygen, Evaluation

NRA Evaluation Report 220/28/T

1. INTRODUCTION

This report describes the evaluation of a pHOX Model 962 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 pHOX Model 962 is fitted with the Mackereth electrode, 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).

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:
pHOX Systems Ltd
Iver Road
Shefford
Beds.
SG17 5JU

Supplier:
pHOX Systems Ltd
Iver Road
Shefford
Beds.
SG17 5JU

Tel: 0462 817070
Fax: 0462 814191

Instrument Description: Model 962 Hand-held Dissolved Oxygen Meter

Serial Number: 7511

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 pHOX 962 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 unit is both compact and light and presented no difficulties during operation. The sophistication provided by the in-built software (particularly the use of the security protected menus) means that the user is required to read the manual thoroughly before operation. Once the user has become familiar with the controls the 'quick' guides provided with the documentation allow the user to follow the required switch sequences with little difficulty.

The instrument display was clear and legible and incorporates a useful backlight for use in low ambient light.

When the probe is transferred from different temperature regimes the manufacturer states that the probe should be allowed 1 minute per 2°C change before a reading is taken. This was confirmed during the evaluation .

The instrument display is blanked, after a warning message, before the readings are affected by a decrease in the power supply.

Only a very low flow was required (>0.10 m S^{-1}) to achieve the expected 100% saturation reading, however, once achieved there appeared to be some instability in the reading.

There is no effect on the readings by varying the immersion depth.

The total error (quadrature sum of random and systematic errors) for five accuracy test concentrations varied between 2 and 4.5%. It should be noted that Winkler determinations of these solutions gave a total error of 2.0% to 4.7%.

The manufacturer does not state a response time. It can be seen that the response for the oxygen and temperature sensors are similar. This will mean that the response of the instrument is not limited by either parameter.

The salinity correction on this instrument produced readings that were comparable with the expected readings from published salinity tables (Weiss, 1974).

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 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.

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 (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 content of 0.00%, 8.80%, 15.30% and 28.80% respectively. By dividing these values by the percentage of oxygen in air the theoretical percentage saturation dissolved oxygen level could be calculated. These were 0.00%, 42.0%, 73.1%, and 137.5%. A fifth level, 100% air-saturation, was achieved by bubbling air through tap water.

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

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

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

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

This test sequence was repeated five times.

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

Readings were taken for each measurand provided by the instrument (e.g. mg l^{-1}, % sat. and °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 51 page A5 size instruction manual was supplied with the instrument.

The manual is very comprehensive and provides detailed information on the instrument and its controls and instructions on the use of the security protected menus, calibration of temperature and oxygen sensors, maintenance procedures, use of the in-built data logging facilities and a general specification for the meter unit and the probe assembly. The manual is well written and unambiguous and provides a very detailed description of the operational use of the instrument. The need for an index in such a large manual has been offset by the use of contents pages for each section.

A full description of the possible calibration procedures is provided for the temperature sensor and a 2-point oxygen calibration covering air calibration and air-saturated water methods, including diagrams to illustrate the apparatus recommended. Although an altitude correction table has been included no correction table has been given for atmospheric pressure correction.

No data is provided for the effects of commonly known interferents and no discussion is given, of instrument component, probe related and calibration related measurement errors.

The maintenance section of the manual provides information on cleaning and replacement of the sensor assembly. Detailed drawings are provided to enable correct re-assembly of the components.

A fault finding section is included in the manual, however, no detailed servicing instructions or list of accessories and replacement parts is included.

Other minor omissions relate to the lack of dimensions of the probe assembly in the probe specification section and the pre-determined period used for automatic cut-off of the backlight function is not stated.

The manual includes general information on Health and Safety, however, no specific information is given for the storage, use or disposal of chemicals that may be used during calibration e.g. Winkler reagents, sulphite solutions etc.

5.2 Design and Construction

The pHOX 962 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 various functions are provided by membrane switches on the front panel, some of which have multiple functions. The instrument's internal software enables the use of security protected menus (accessed via special keys) to prevent the unauthorised use of the calibration mode.

The meter weighs approximately 1 kg including batteries. The IP rating of the instrument is not stated.

A large LCD panel meter is fitted to the meter. The display incorporates a backlight facility. The backlight will automatically switch off after a pre-determined period.

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

The probe is a membrane covered galvanic type sensor incorporating a thermistor for temperature measurement and compensation, housed within the upper body of the probe assembly.

5.3 Installation

None Required

5.4 Commissioning

None Required

5.5 Maintenance and Downtime

No maintenance was required during the four months of the evaluation.

5.6 Ease of Use

The meter unit is both compact and light and presented no difficulties during operation. The sophistication provided by the in-built software (particularly the use of the security protected menus) means that the user is required to read the manual thoroughly before operation. Once the user has become familiar with the controls the 'quick' guides provided with the documentation allow the user to follow the required switch sequences with little difficulty.

The instrument display was clear and legible and incorporates a useful backlight for use in low ambient light.

6. RESULTS

Table 6.1 Instrument stabilisation readings for different temperature changes.

Temperature Change. (°C)	Time (secs)	Dissolved Oxygen Sensor
Room Temperature → 5°C	15	75
	30	90
	60	94
	120	97
	180	97
	300	99
	600	100
	1200	102
Room Temperature → 21°C	5	104
	30	104
	60	104
	120	104
	180	104
	300	104
	600	104
	1200	102
5°C → 5°C	15	88
	30	95
	60	97
	120	99
	180	99
	300	100
	600	100
	1200	102

Table 6.2a Power consumption

Meter Setting	V	mA	mW
OFF	8.51	0.61	5.19
ON	8.29	16.78	139.11
Backlight on	7.26	40.70	295.48

Table 6.2b Battery characteristics.

Battery Make	NOT STATED
Battery Type	Rechargeable Pack
Battery Voltage	7.2 V
Battery Capacity	1 Ah
Replacement Interval	NOT STATED

Table 6.3 Effects of different power supply voltages on the instrument readings.

Power Supply (Volts)	Instrument Setting		
	% sat.	mg l^{-1}	°C
8.51	106	9.8	17.3
7.99	106	9.8	17.3
7.49	106	9.8	17.4
6.99	106	9.8	17.4
6.51	106	9.8	17.4
6.01	106	9.8	17.4
5.49	-	Display Blank	-

Table 6.4 Instrument readings for different flows at the sensor surface

Water Temperature - 10.3 (°C)

Flow Rate ($m\ S^{-1}$)	Dissolved Oxygen ($mg\ l^{-1}$)	Temp. (°C)	Dissolved Oxygen (% sat.)
0.35	10.7	11.2	100
0.30	10.6	11.2	100
0.24	10.5	11.2	100
0.16	10.5	11.2	99
0.10	10.5	11.2	100
0.05	10.4	11.2	98
0.00	10.2	11.2	96
0.04	10.6	11.2	100
0.09	10.8	11.2	102
0.13	10.8	11.2	102
0.19	10.9	11.2	104
0.29	11.0	11.3	104
0.37	11.1	11.3	106

Table 6.5 Instrument readings at different immersion Depth

Water Temperature 17.9 °C

Depth (m)	Dissolved Oxygen ($mg\ l^{-1}$)	Temp. (°C)	Dissolved Oxygen (% sat.)
0.3	9.0	18.9	102
1.0	9.8	18.9	108
2.0	9.6	18.9	108
0.3	9.4	19.0	106

All Dissolved Oxygen levels were unstable

Table 6.6 Instrument readings for two different Interferents

Interferent	Level	Dissolved Oxygen (mg l^{-1})	Temp. (°C)	Dissolved Oxygen (% sat.)
Temperature	10°C	10.3	10.2	95
	30°C	7.4	30.2	102
Chlorine	0 mg l^{-1}	8.8	21.3	102
	30 mg l^{-1}	8.8	21.8	104

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	8.6	21.0	100
!	River Water	8.4	21.0	98
!	Dechlorinated Tap Water	8.3	20.7	96

* calibrated in dechlorinated tap water
! calibrated in air

Table 6.8a Instrument readings at dissolved oxygen levels -Test 1

Atmospheric Pressure - 102.0 (kPa)
Water Temperature - 19 °C

*Dissolved Oxygen (% sat.)	Dissolved Oxygen (mg l^{-1})	Temp. (°C)	Dissolved Oxygen (% sat.)
0	0.0	17.4	0
42.0	4.1	18.4	45
73.1	6.9	18.3	76
100	9.1	18.4	100
137.5	12.1	19.3	136
137.5	11.9	19.7	136
100	9.1	19.3	102
73.1	6.9	19.7	78
42.0	4.1	20.9	47
0	0.0	20.8	0

* see text for details (Section 4.8)

Table 6.8b Instrument readings at dissolved oxygen levels -Test 2

Atmospheric Pressure - 101.7 (kPa)
Water Temperature - 22.1 °C

*Dissolved Oxygen (% sat.)	Dissolved Oxygen (mg l^{-1})	Temp. (°C)	Dissolved Oxygen (% sat.)
0	0.0	21.5	0
42.0	4.2	22.5	50
73.1	6.7	21.6	79
100	8.9	21.2	104
137.5	11.9	22.4	142
137.5	12.0	22.8	144
100	9.0	21.6	106
73.1	6.8	22.5	82
42.0	4.0	23.9	49
0	0.1	22.8	1

*see text for details (section 4.8)

Table 6.8c Instrument readings at dissolved oxygen levels - Test 3

Atmospheric Pressure - 101.3 (kPa)
Water Temperature - 20.1 °C

*Dissolved Oxygen (% sat.)	Water Temp. (°C)	Dissolved Oxygen (mg l^{-1})	Temp. (°C)	Dissolved Oxygen (% sat.)
0	18.4	0.3	18.7	3
42.0		4.0	19.6	46
73.1	19.2	6.9	19.4	77
100		9.2	19.0	102
137.5	19.8	12.1	20.0	138
137.5	20.5	12.1	20.7	140
100		9.0	20.2	102
73.1	21.0	6.7	21.2	78
42.0		4.0	22.3	47
0	21.8	0.1	22.1	1

* see text for details (section 4.8)

Table 6.8d Instrument readings at dissolved oxygen levels - Test 4

Atmospheric Pressure - 101.2 (kPa)
Water Temperature - 23.9°C

*Dissolved Oxygen (% sat.)	Dissolved Oxygen (mg l^{-1})	Temp. (°C)	Dissolved Oxygen (% sat.)
0	0.2	23.0	2
42.0	3.7	24.0	46
73.1	6.4	23.3	78
100	8.7	22.5	104
137.5	11.5	24.2	142
137.5	11.3	24.4	140
100	8.7	23.1	104
73.1	6.4	24.4	79
42.0	3.6	25.8	47
0	0.0	25.2	0

* see text for details (section 4.8)

Table 6.8e **Instrument readings at dissolved oxygen levels - Test 5**

Atmospheric Pressure - 101.7 (kPa)
Water Temperature - 26.0°C

*Dissolved Oxygen (% sat.)	Water Temp. (°C)	Dissolved Oxygen (mg l^{-1})	Temp. (°C)	Dissolved Oxygen (% sat.)
0	25.3	0.1	25.5	2
42.0		3.7	26.5	48
73.1	25.2	6.3	25.5	80
100.0		8.4	24.4	104
137.5	25.6	11.1	25.8	140
137.5	26.1	11.0	26.3	142
100.0		8.3	25.3	106
73.1	26.4	6.1	26.6	79
42.0		3.7	27.1	49
0	26.9	0.1	27.1	2

* see text for details (section 4.8)

Table 6.8f **Winkler Accuracy for the Test Solutions**

*Actual Dissolved Oxygen (% sat.)	Instrument	Readings	Winkler	Readings
	Random Error	Systematic Error	Random Error	Systematic Error
0	-1.1	1.10	-5.74	2.01
42.0	-5.4	1.58	-8.42	5.98
73.1	-5.5	1.65	-3.98	4.06
100	-3.4	1.90	-1.88	4.14
137.5	-2.5	2.67	-13.42	21.43

* 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*	22.68	21.12	19.78
Step change high to low Dissolved Oxygen *	36.59	29.84	30.94

* see text for details (section 4.9)

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

	Time 1 (seconds)	Time 2 (seconds)	Time 3 (seconds)
Step change low to high Temperature (°C)*	23.37	22.75	22.63
Step change high to low Temperature (°C)*	24.50	23.91	24.28

* see text for details (section 4.9)

Table 6.11 **Instrument readings for different levels of Salinity.**

		No Saline Adjustment			Saline Adjustment		
Chlorine (mg l^{-1})	Water Temp. (°C)	Dissolved Oxygen (mg l^{-1})	Temp. (°C)	Dissolved Oxygen (% sat.)	Dissolved Oxygen (mg l^{-1})	Dissolved Oxygen (% sat.)	setting
0	18.1	9.4	18.3	100	-	-	-
5	17.9	9.5	18.1	100	9.0	100	7
10	18.2	9.4	18.4	100	8.6	100	13
20	19.0	9.4	19.1	102	8.0	102	23
40	19.4	9.2	19.6	100	7.2	100	33
20	19.9	9.3	20.1	102	7.8	102	23
10	19.9	9.3	20.1	102	8.5	102	13
5	19.9	9.4	20.1	102	8.9	102	7
0	20.7	9.2	20.9	104	-	-	-

Table 6.12a Field Data - Class 1A River

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)	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	8.6	100.8	15:53	11.48	11.4	98	8.7	18:00	11.38	11.4	98	8.7					
29/01/93	8.8	101.7	11:50	11.48	11.6	100	8.9	14:37	11.62	11.4	99	9.0	16:52	11.41	11.5	99	9.0
01/02/93	8.3	103.4	12:42	12.02	11.8	100	8.4	14:11	12.33	11.8	100	8.4	16:49	12.02	11.8	100	8.2
02/02/93	7.8	103.7	11:25	12.10	12.3	104	7.9	14:23	12.00	12.1	102	8.1	16:28	12.35	12.1	102	8.1
03/02/93	8.2	103.9	11:53	11.90	12.1	102	8.2	17:11	11.90	11.9	102	8.3	18:09	11.76	11.9	102	8.3
04/02/93	7.8	103.4	12:26	12.00	12.2	102	7.9	16:35	11.80	12.1	102	7.9	18:13	11.80	12.1	102	7.8
05/02/93	7.1	103.5	12.07	11.19	12.8	106	7.2	15:52	11.99	12.7	104	7.1	16:48	12.60	12.6	104	7.1
08/02/93	9.0	103.4	11.36	11.69	11.8	102	9.1	15:45	11.45	11.6	100	9.2	17:03	11.35	11.5	100	9.2
09/02/93	8.7	103.1	10.48	11.49	11.8	102	8.9	14:42	11.35	11.7	100	8.8	17:20	11.88	11.7	100	8.7
11/02/93	7.8	102.9	12.55	11.78	12.3	104	7.9	16:45	11.94	12.2	102	7.7					
10/02/93	7.1	103.0	12.08	11.98	12.7	106	7.2										

Table 6.12b Field Data - Class 3 River

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			15:00	7.62	8.0	70	9.1										
16/02/93		102.8	13:57	7.62	8.2	72	9.6	15:28	7.41	8.0	70	9.7					
17/02/93	10.6	102.6	13:59	6.90	7.5	67	10.3	15:12	7.04	7.5	68	10.8	16:06	6.87	7.6	68	10.9
18/02/93	10.9	101.7	15:27	7.04	7.5	68	10.7	15:48	7.21	7.5	68	10.8					
19/02/93	8.9	101.9	11:47	6.53	8.1	70	8.8	13:20	7.30	8.2	72	9.1	14:21	7.74	8.3	73	9.3
22/02/93	9.0	102.1	15:06	7.68	8.5	73	9.0	16:00	7.77	8.4	73	9.1	16:30	7.76	7.5	72	9.2
23/02/93	8.0	102.6	09:25	6.84	7.5	62	7.9	11:20	7.07	7.9	67	8.2	11:39	7.37	8.0	68	8.3
24/02/93	10.0	102.5	15:01	7.18	8.0	71	9.9	15:40	7.11	7.9	70	10.0	16:35	7.22	7.9	70	10.1
25/02/93	8.7	101.5	09:25	6.50	7.2	62	8.6	9:55	6.67	7.2	62	8.5	11:15	6.81	7.5	65	8.6
26/02/93	8.2		11:41	7.18	7.7	66	8.3	12:45	6.97	7.7	66	8.7	13:25	6.98	7.7	67	8.9
01/03/93	6.8	101.4	13:30	8.00	9.7	79	6.6										

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

Date	Time	Atmospheric Pressure (kPa)	Dissolved Oxygen (mg l^{-1})	Temp. (°C)	Dissolved Oxygen (% sat.)
28/01/93	15:46	108.8	10.3	14.5	102
29/01/93	11:43	101.7	11.1	11.7	102
01/02/93	12:34	103.4	11.0	11.9	102
02/02/93	10:45	103.6	12.1	8.5	104
03/02/93	11:45	103.9	11.3	11.5	104
04/02/93	12:20	103.4	11.2	11.8	104
05/02/93	11:59	103.5	11.5	10.8	104
08/02/93	11:29	103.4	11.3	11.7	104
09/02/93	10:40	103.1	10.0	16.2	102
10/02/93	12:49	102.9	11.4	11.1	104
11/02/93	12:00	103.0	11.5	10.4	104

Table 6.13b Instrument reading for Class 3 river - Calibration Check

Date	Time	Atmospheric Pressure (kPa)	Dissolved Oxygen (mg l^{-1})	Temp. (°C)	Dissolved Oxygen (% sat.)
16/02/93	13:47	102.8	12.0	7.6	100
17/02/93	13:47	102.6	10.9	12.9	104
18/02/93	15:17	101.7	11.3	11.5	104
19/02/93	12:26	102.0	11.0	13.8	108
22/02/93	15:00	102.1	12.2	7.4	102
23/02/93	11:11	102.7	11.8	9.3	102
24/02/93	14:55	102.5	8.7	8.7	102
25/02/93	9:50	101.5	11.9	8.2	102
26/02/93	12:30	100.4	11.4	9.7	100
01/03/93	13:25	101.4	14.3	3.8	110

Table 6.14 Random and Systematic Errors for calibration data

Test	Class 1A River	Class 3 River
Mean	103.3	103 .4
Random error	3.3	3.4
Systematic error (Bias)	1.0	3.1
Total Error	3.5	4.6
Sample size	11	10

Table 6.15 Random and Systematic Errors for field data

Test	Class 1A River	Class 3 River
Random error	-0.18	-0.68
Systematic error (Bias)	0.40	0.36
Total Error	0.44	0.77
Sample size	29	27

7. INSTRUMENT BEHAVIOUR

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

During the evaluation it was noted that all percentage saturation values above 100% were reported to a resolution of 2%.

Table 6.1 shows the stabilisation of the percentage saturation readings for different temperature regimes. It can be seen that in two of the test regimes a stable reading is not achieved until after 5 minutes. The manufacturer states that the probe should be allowed 1 minute per 2°C change before a reading is taken. A temperature change of 15°C would therefore require 7.5 minutes to stabilise. Where there was no temperature change the readings still takes up to 5 minutes to stabilise for the lower temperature regime. At the higher temperature the meter reading is stable after five seconds, although the level is higher than would be expected. This suggests that there may be a temperature effect.

Given the stated battery capacity (Table 6.2b) and the power consumption (Table 6.2a) the expected battery life can be calculated. This value, 60 hours, is well above that stated by the manufacturer (20 hours).

The instrument display is blanked, after a warning message, before the readings are affected by decreasing the power supply (Table 6.3). The manual states a shut down will occur at 5.5 volts, it was found to occur at 5.71 volts.

The effect of flow on the sensor performance is given in table 6.4. It shows that only a very low flow is required (>0.10 m s^{-1}) to achieve the expected reading, however once achieved there appeared to be some instability in the reading. The manufacturer does not state a minimum flow rate.

Table 6.7 shows the effect of immersion depth on the instrument reading. It can be seen that there is no effect on the readings, although the readings are higher than the expected 100 % saturation.

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 11.30 mg l^{-1}, whilst at 30°C there would be 7.58 mg l^{-1} dissolved oxygen present. At the higher temperature levels the meter reading is correct whereas the lower temperature is incorrect. This supports the findings in the stabilisation test that there may be some temperature effect on the readings.

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

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

The instrument accuracy was tested on 5 separate occasions and compared with a range of oxygen/nitrogen gas mixtures. These results are presented in tables 6.8a - 6.8e. The random and systematic errors for the instrument and the Winkler determinations are provided in Table 6.8f. The total error (quadrature sum of random and systematic errors) for five test concentrations varied between 2 and 4.5%. It should be noted that Winkler determinations of these solutions gave a total error of 2.0% to 4.7%.

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 manufacturer does not state a response time. It can be seen that the response for the oxygen and temperature sensors are similar. This will mean that the response of the instrument is not limited by either parameter.

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 4.6% in the Class 3 river and 3.4% 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 0.77 mg l^{-1} for the Class 3 river and 0.44 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. MANUFACTURER'S COMMENTS

The instrument loaned for assessment was supplied with the incorrect carrying case; the Model 962 dissolved oxygen meter is currently supplied with a water proof holster for use in the field.

The user manual will be amended to incorporate more specific details of the instrument's power supplies, e.g. battery packs etc.

In the section on instrument behaviour reference is made to the instrument resolution for dissolved oxygen values above 100% saturation being only 2%. This feature was in fact, a requirement in the specification for the NRA multiparameter hand-held meter which unfortunately, had been carried over into the design of the Model 962. The software is currently being changed to allow the instrument to display results to a resolution of 1% throughout its' measurement range.

We are already aware of the adverse temperature effect stated within the report and are currently re-designing the head of the oxygen electrode to relocate the temperature sensors, thereby eliminating the effect of the mass of the electrode body on the temperature stabilisation.

Furthermore, since the loan of the model 962 for assessment we have undertaken further development of the instrument which is now incorporated into the new pHOX corporate enclosure to IP67 standard.

9. COST OF OWNERSHIP

The pHOX Model 962 Hand-Held Dissolved Oxygen Meter (including carrying case, all accessories and an alternative shoulder holster).	£695.00
The electrode cartridge (One supplied, expected life, typically one year)	£32.00
Battery pack (One supplied expected life dependant on usage, typically one year)	£35.00.
Membrane kit (One supplied, expected life, typically 2 years)	£11.00.

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
- pHOX systems 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.

REFERENCES

Baldwin I G (1992) Instrument Performance Assessment Standard Test Protocols- Revision A. NRA Project Report 220/9/T.

Baldwin I G, Harman M I and van Dijk P (1992) Evaluation of Multiple Parameter Hand-held Meters. NRA Project Record 63/9/ST.

British Standards Institute (1986) Glossary of terms used in Metrology. BS5233.

British Standards Institute 1980 (1987) Methods of measurement of fluid flow: estimation of uncertainty of a flow-rate measurement. BS 5844.

Harman M M I (1992) Protocol for Investigation of Hand-held Dissolved Oxygen Meters. NRA Project Record 220/7/T.

Hitchman M L (1978) Measurement of dissolved oxygen. Chemical Analysis Vol 49.

HMSO (1981) Methods for the examination of waters and associated materials in waters.

International Standards Organisation (1985) Evaluation of the performance characteristics of gas analysers. ISO 8158-1985(E).

WAA Process Systems Committee (1992) Water Industry Specifications, Information, and Guidance notes. WSA/FWR 7-00-00.

Weiss R F (1974) Carbon Dioxide in Water and Sea water; The solubility of a non ideal Gas, Marine Chemistry, Vol 2, p203-215.

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

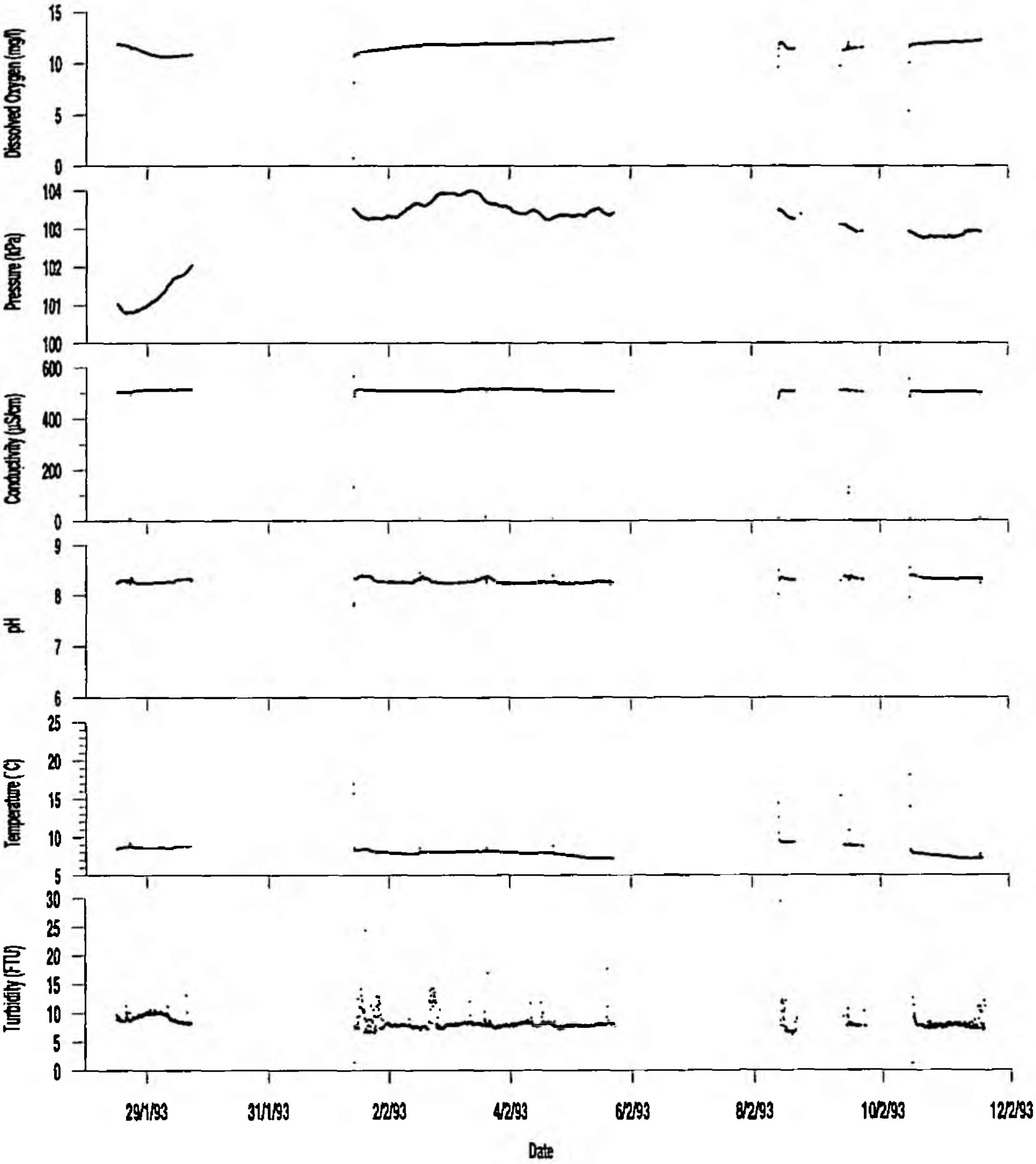

Figure B1 Water Quality Parameters Class 1A River

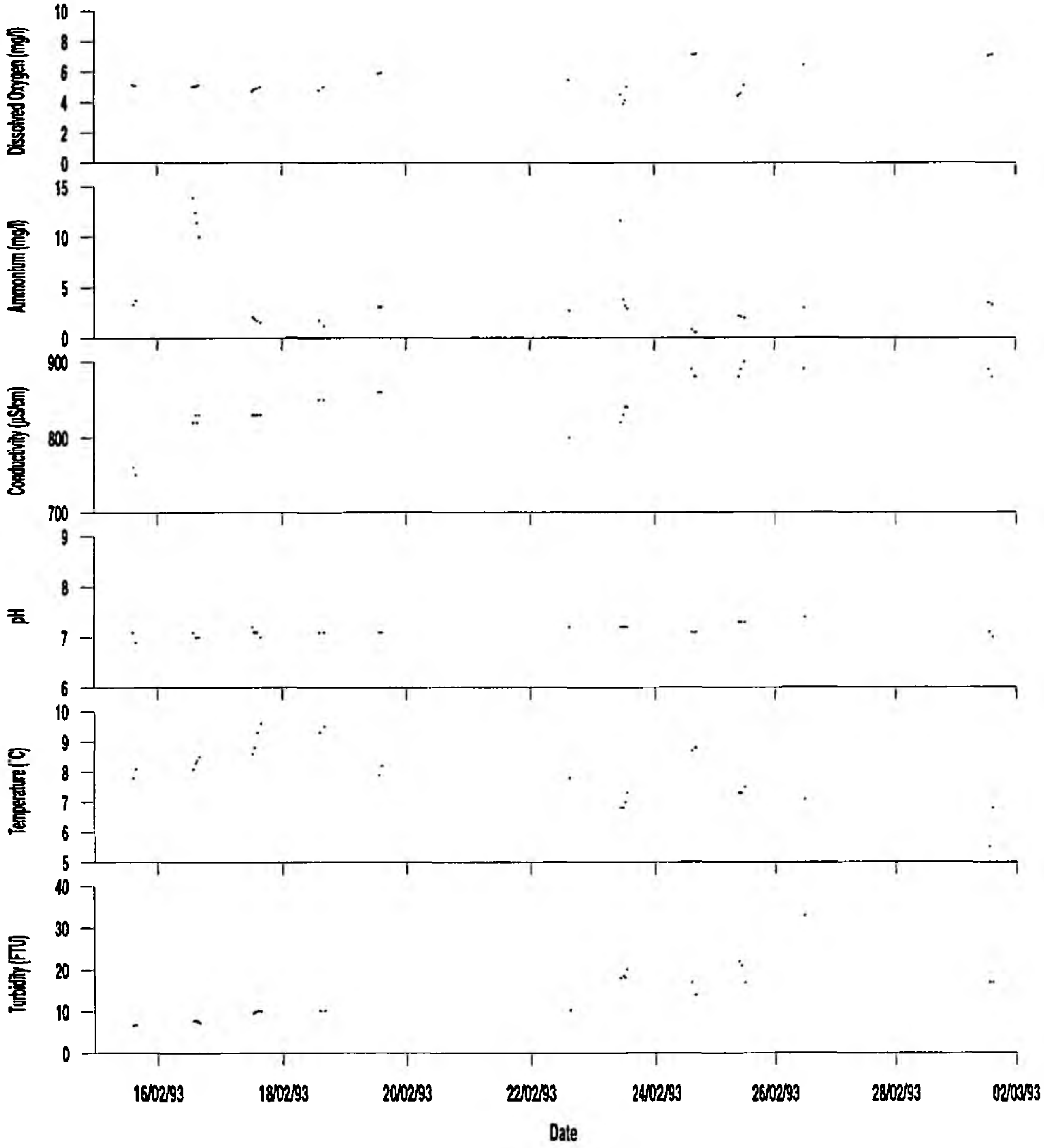

Figure B2 Water Quality Parameters Class 3 River

APPENDIX C MANUFACTURER'S SPECIFICATION

Oxygen Measurement

RANGES:	0 - 200 % sat, 0 - 20.0 mg l^{-1}
ACCURACY	±1% of FSD

Temperature Measurement

RANGE:	0 - 45.0 °C
ACCURACY	±1% of FSD

Instrument Environment

Temperature range	Not stated
Water Resistance	Not stated
Power Supply	Internal 6 x 1.2 volts re-chargeable batteries Nominal 20 hours between re-charges

Probe

Response Time (90% change)	< 35 seconds