220

The Evaluation of an ABB Kent-Taylor Model 7135 Hand-Held Dissolved Oxygen Meter

WRc plc

R&D 220/30/T



THE EVALUATION OF AN ABB KENT-TAYLOR MODEL 7135 HAND-HELD DISSOLVED OXYGEN METER

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Evaluation Report 220/30/T

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EXECUTIVE SUMMARY

This report describes the results of an evaluation of a Kent Hand-held Dissolved Oxygen meter The methods used during the evaluation are briefly described and a summary of the conclusions provided. The evaluation was undertaken by the NRA (Tharnes 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.

Considerable care must be taken to ensure that all surfaces within the probe body are completely dry before fitting a replacement oxygen sensor capsule. Failure to do this will result in erroneous readings from the instrument.

The miniature impeller inside the stirrer bar attachment is positioned too close to the membrane. If the probe assembly is stood on its end damage to the membrane may occur.

A small plastic shield is provided for protection of the membrane and which should be fitted to the probe during use in the field. The connection between the shield and the probe is not secure; the shield frequently became dislodged during normal use.

Even at the highest flow rate tested (0.33 ms -1) a stable result was not achieved.

The total error (quadrature sum of random and systematic errors) for five accuracy test concentrations varied between 3.0 and 5.1%. It should be noted that Winkler determinations of these solutions gave a total error of 6% to 25%. There was no significant (95% confidence limits) drift with time in the calibration of the instrument during the month field trial. The total error was 2.3% in the Class 3 river and 3.5 in the Class 1A river. Winkler determinations showed a total error of 4.5%.

The instrument cost is £870.00. The oxygen capsule required replacement during the course of the evaluation, however, no repairs were necessary during the evaluation.

KEY WORDS

Dissolved Oxygen, Evaluation

NRA Assessment Report 220/30/T

1. INTRODUCTION

This report describes the evaluation of a ABB Kent-Taylor MODEL EIL 7135 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 ABB Kent-Taylor Model EIL 7135 is fitted with a galvanic electrochemical cell. This cell consists of a membrane covered silver cathode which forms the end face of a replaceable cylindrical capsule. 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 O² 1⁻¹

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: ABB Kent-Taylor Ltd

Oldends Lane Stonehouse Gloucestershire GL10 3TA

Supplier: ABB Kent-Taylor Ltd

Oldends Lane Stonehouse Gloucestershire GL10 3TA

Tel: 0453 826661 Fax: 0453 826358 0453 827856

Instrument Description: Model EIL 7135 Hand-held Dissolved Oxygen Meter

Serial Number L/50139/5/4

Sensor Type Galvanic

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

MAJOR FINDINGS AND COMMENTS

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

The Model 7135 dissolved oxygen meter comprises a meter unit and separate oxygen probe assembly. The unit is intended for operation both in the laboratory and in the field. The meter unit is housed in a robust plastic case which is fitted with an adjustable neck strap. The external power socket and recorder output socket are fitted with splash-proof caps.

The calculated expected battery life was 600 hours. The manufacturer does not state an expected battery life.

The instrument readings were affected by decreasing the power supply. However the low battery indicator appeared before this occurred.

Even at the highest flow rate tested (0.33 m s⁻¹) a stable result was not achieved. The manufacturer specifies a minimum recommended flow rate of 0.30 m s⁻¹.

The total error (quadrature sum of random and systematic errors) for five accuracy test concentrations varied between 3.0 and 5.1%. It should be noted that Winkler determinations of these solutions gave a total error of 6% to 25%.

The response time for the oxygen sensor was in agreement with that stated by the manufacturer. However the temperature sensor response was over twice the twenty seconds stated by the manufacturer.

There was no significant (95% confidence limits) drift with time in the calibration of the instrument during the month field trial. The total error was 2.3% in the Class 3 river and 3.5% in the Class 1A river. Winkler determinations showed a total error of 4.5%.

There is a delay of up to 10 seconds for the display to stabilise after selecting the required measurand. Furthermore, the temperature reading is only displayed whilst the pressure sensitive switch is being operated. The temperature reading also requires approximately 10 seconds to attain stability, this was found to be frustrating when a sequence of readings were being taken.

The shelf-life of the oxygen sensor capsules appears to be only about 2 months.

Considerable care must be taken to ensure that all surfaces within the probe body are completely dry before fitting a replacement oxygen sensor capsule. Failure to do this will result in erroneous readings from the instrument.

The miniature impeller inside the stirrer bar attachment is positioned too close to the membrane. If the probe assembly is stood on its end damage to the membrane may occur.

A small plastic shield is provided for protection of the membrane and which should be fitted

to the probe during use in the field. The connection between the shield and the probe is not secure; the shield frequently became dislodged during normal use.

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 <u>Battery life</u>

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

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

4.3 Effects of low bottery 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 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 (\pm 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 according to the manufacturers instructions. Readings were then taken in 100% air-saturated river water. The instrument was then calibrated in 100% air-saturated tap water and the measurements repeated.

4.8 Accuracy tests.

Test solutions were prepared by diffusing mixtures of the oxygen and nitrogen gas through tap water. The gas mixtures had a certified oxygen contents of 0.00%, 8.80%, 15.30% and 28.80% respectively. By dividing these values by the percentage of oxygen in air 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 1-1, % 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 were 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.

OBSERVATIONS

5.1 Documentation

A 21 page A4 size instruction manual was supplied with the instrument which provided instructions for setting up and operation of the dissolved oxygen meter and probe. The manual appears to be generally well written and unambiguous and provides an adequate description of the operational use of the instrument. A detailed specification is provided. No serious omissions or obvious typographical errors were noted.

A combined table showing oxygen solubility in both pure and saline waters is provided. An appendix describes a method for calculating the effect of barometric pressure on oxygen saturation. Useful examples are given with tabulated data of saturated water vapour pressure and correction for altitude variation. One section of the manual describes the use of the instrument for its intended laboratory application; the measurement of oxygen consumption in BOD bottles.

Servicing instructions are limited to those describing the replacement of batteries and replacement of the sensor capsule. No specific instructions are given for fault-finding or the removal of foulant from the probe assembly.

A full list of accessories including part numbers and the address of the supplier is given.

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

5.2 Design and Construction

The Model 7135 dissolved oxygen meter comprises a meter unit and separate oxygen probe assembly. The unit is intended for operation both in the laboratory and in the field. The meter unit is housed in a robust plastic case which is fitted with an adjustable neck strap. The external power socket and recorder output socket are fitted with splash-proof caps.

The unit has three modes of operation; oxygen % saturation, concentration and temperature. Selection between the various modes is made using pressure sensitive switches fitted to the front panel. Adjustment of the oxygen probe calibration is carried out using two screwdriver-adjustable controls fitted to the front panel. A purpose-built screwdriver is attached to the meter strap. Calibration of the temperature mode is set internally and cannot be adjusted by the user.

The instrument display is in the form of a 3 1/2 digit LCD. A low-battery indicator is included on the LCD panel, however, the display does not incorporate a backlight facility.

The meter unit is approximately 220 x 203 x 90 mm and weighs approximately 2000 g including batteries. The probe assembly (specially designed to measure oxygen consumption in standard BOD bottles) is approximately 170 mm in length and 13 mm diameter.

The probe assembly consists of a membrane covered silver/lead galvanic cell and incorporates a thermistor for temperature measurement and compensation.

5.3 Installation

None Required

5.4 Commissioning

After a new sensing module has been installed the instrument must be switched on for 1 hour to charge the new module.

5.5 Maintenance and Downtime

None Required

5.6 Ease of Use

There is a delay of up to 10 seconds for the display to stabilise after selecting the required measurand. Furthermore, the temperature reading is only displayed whilst the pressure sensitive switch is being operated. As the temperature reading also requires approximately 10 seconds to attain stability, even when the probe assembly has been allowed to reach thermal equilibrium, this procedure can be frustrating when a sequence of readings are being taken.

The shelf-life of the oxygen sensor capsules appears to be only about 2 months. As a consequence, the user is likely to experience some difficulty in maintaining a stock of viable replacement oxygen sensor capsules.

Considerable care must be taken to ensure that all surfaces within the probe body are completely dry before fitting a replacement oxygen sensor capsule. Failure to do this will result in erroneous readings from the instrument.

The miniature impeller inside the stirrer bar attachment is positioned so close to the membrane that if the probe assembly is stood on its end in, say, a beaker of aerated water during calibration, the impeller rests against the membrane. As a consequence, damage to the membrane may occur.

No facility is provided for housing the probe or lead during transit. The optional carrying case does not allow the probe to be connected to the meter during transit; the probe must be disconnected from the meter and plugged into a special short-circuit socket.

A small plastic shield is provided for protection of the membrane and which should be fitted to the probe during use in the field. The connection between the shield and the probe is

unfortunately not secure; the shield frequently became dislodged during normal use.

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6. RESULTS

Table 6.1 Instrument stabilisation readings for different temperature changes

Water Temperature 5.0 °C

Pressure 100.5 kPa Time Dissolved Oxygen (secs) (% sat:) Room Temperature → 5°C 10 . 83.8 30 87.8 60 88.6 120 88.4 88.7 180 300 89.1 89.0 600 1200 89.1 Room Temperature → 20°C 10 30 60 120 180 300 600 1200 $5^{\circ}C \rightarrow 5^{\circ}C$ 86.0 10 30 86.4 60 86.7 120 86.7 180 86.8 300 86.8 600 86.8 1200 87.0

Table 6.2a Power Consumption

	•	Meter Setting		. v	mA	mW
_		Y 4 2 2	_	7.		
	i.	Off		9.26	0.00	0.00
		°C	•	9.24	0.88	8.13
		ppm		9.24	0.83	6.75
		% sat.		9.24	0.83	6.75

Table 6.2b Battery Characteristics

		+	
Battery Make		Ever Ready	
Battery Type		6LF22 Gold Seal	
Battery Voltage		9 V	
Battery Capacity		0.52 AH	
Replacement Interval		NOT STATED	
	er .		

Table 6.3 Effects of different power supply voltages on instrument readings

Voltage		Instrument Setting		Low Battery Indicator
	% sat.	mg I-1	°C	
9.00	99.9	9,33	18.0	NO
8.50	99.8	9.31	17.9	NO
8.02	99.7	9.30	17.9	NO
7.52	99.1	9.29	17.9	NO
7.02	99.1	9.29	17.9	NO
6.52	106.6	9.94	17.9	NO
5.99	114.8	10.73	17.9	YES
5.49	53.5	4.60	17.9	YES
4.98	-1	-1	18.1	YES

Table 6.4 Instrument readings for different flow at sensor surface

Water Temperature 9.5°C Pressure 103.4 pKa

Flow	Dissolved	Temp.	Dissolved
Rate	Oxygen	(°C)	Oxygen
ms -1	(mg l^{-1})	A 14.00 E	(% sat.)
	19	9 4	
0.33	11.31	. 8.6	99.4
0.30	11.16	8.6	98.2
0.21	11.13	8.6	97.7
0.09	11.04	8.6	96.6
0.04	10.70	8.5	93.6
0.03	10.30	8.5	90.5
-0.01	7.93	8.4	69.4
0.04	10.15	8.3	89.6
0.10	10.89	8.3	95.6
0.17	11.16	8.2	97.5
0.24	11.25	8.2	97.8
0.29	11.21	8.2	97.7
0.33	10.95	8.1	95.0

Note All readings at nominal zero flow rate were unstable

Table 6.5 Instrument readings at different depths

Atmospheric Pressure - 101.3 kPa

Depth	Dissolved	Temp.	Dissolved
(m)	Oxygen	(°C)	Oxygen
	$(mg l^{-1})$		(% sat.)
T.			
0.3	7.5	9.6	69
1.0	7.1	9.7	64
2.0	7.3	9.9	68
0.3	7.3	10.3	55

Note All Dissolved Oxygen readings were unstable (±3%)

Instrument Readings for two Interferents Table 6.6

Interferent	Level	Dissolved	Temp.	Dissolved
		Oxygen	(°C)	Oxygen
		$(mg l^{-1})$	1.2	(% sat.)
Temperature	9.6°C	11.33	8.6	99.5
	29.7°C	7.40	29.9	95.4
Chlorine	0 mg 1-1	8.50	23.8	100.1
	30 mg 1 ⁻¹	8.51	23.8	100.5
- 1			10.00	

Instrument readings for commonly employed Calibration techniques Table 6.7

	Conditions (100% saturation)	Dissolved Oxygen (mg l-1)	Temp.	Dissolved Oxygen (% sat.)
			0	
*	River Water		15.1	99.8
!	River Water		15.4	96 .1
!	Dechlorinated Tap Water		15.5	97.8
-				2

^{*} Calibrated in Dechlorinated tap water ! Calibrated in Air

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

Atmospheric Pressure 101.9 kPa

*Actual	D	issolved	Temp.	Dissolved
Dissolved		Oxygen:	(°C)	Oxygen
Oxygen	• (:	mg l ⁻¹)		(% sat.)
(% sat)				
*				
0		-0.55	18.0	-5.9
42.0		3.61	18.9	39.3
73.1		6.54	18.5	70.7
. 100		8.95	18.4	96.4
137.5		12.16	19.2	139.9
137.5		13.01	19.8	144.3
100		8.91	19.3	97.5
73.1		.6.26	20.1	69.6
42.0	9	3.40	21.5	38.9
0		-0.50	20.9	-0.55

^{*} see text section 4.8 for details

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

Atmospheric Pressure 101.7 kPa Water Temperature 22.0 °C

*Actual	Dissolved	Temp.	Dissolved
Dissolved	Oxygen	(°C)	Oxygen
Oxygen	$(mg l^{-1})$		(% sat.)
(% sat.)			
0	-0.51	21.2	-5.7
ŭ			
42.0	3.40	22.1	39.2
73.1	6.04	21.1	68.3
100	8.52	20.7	95.5
137.5	12.08	21.9	138.5
137.5	12.08	22.5	138.8
100	8.34	21.2	94.3
73.1	5.78	22.1	66.0
42.0	3.18	23.6	37.4
0	-0.35	22.4	-4.2

^{*} see text (section 4.8) for details

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

Atmospheric Pressure 101.3 kPa Water Temperature 20.5 °C

*Actual	Dissolved	Temp.	Dissolved	
Dissolved	Oxygen	(°C)	Oxygen	
Oxygen	(mg l^{-1})		(% sat.)	
(% sat.)		. 0		
			<u>. </u>	
0	-0.1	18.8	-1.0	
42.0	3.71	19.6	40.9	
73.1	6.67	19.3	73.7	
100	8.72	18.9	94.9	
137.5	12.67	20.1	140.0	
137.5	12.50	20.7	140.3	
100	8.65	20.1	96.1	
73.1	6.99	21.1	67.8	
42.0	3.45	22.2	39.7	
.0	-0.06	22.0	-0.6	
· ·				

^{*} See text (section 4.8) for details

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

Atmospheric Pressure 101.2 kPa

Water Temperature 23.5 °C

Actual Dissolved Oxygen (% sat.)	Water Temp. (°C)	Dissolved Oxygen (mg l ⁻¹)	Temp.	Dissolved Oxygen (% sat.)
		<u></u>		
0	22.4	0.05	22.4	0.6
42.0		3.28	23.3	38.3
73.1	22.5	5.93	22.5	68.6
100		8,38	21.8	95.6
137.5	23.3	11.52	23.3	134.6
137.5	24.1	11.60	24.2	137.7
100		8.26	22.8	95.8
73.1	24.1	5.57	24.2	65.9
42.0		3.17	25.5	38.1
0	24.7	-0.06	24.8	-0.8

^{*} See text (section 4.8) for details

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

Atmospheric Pressure 101.6 kPa Water Temperature 26.0 °C

*Actual	Dissolved	Temp.	Dissolved
Dissolved	Oxygen	(°C)	Oxygen
Oxygen	$(mg l^{-1})$		(% sat.)
(% sat.)			1
		1	4
		2.1	
0	0.05	25.8	0.7
42.0	2.94	26.9	36.2
73.1	5.45	25.8	66.2
100	7.96	24.6	95.3
137.5	11.16	26.1	136.3
137.5	11.37	26.3	140.1
100	8.00	24.9	95.9
73.1	5.61	26.5	68.7
42.0	3.12	27.9	39.2
0	-0.01	27.0	-0.1
	11.4		3.5

^{*} see text for (section 4.8) details

Table 6.8f Summary of Accuracy Data

*Actual Dissolved	Instrument	Accuracy	Winkler	Accuracy
Oxygen				
(% sat.)				
	Systematic	Random	Systematic	Random
	Error	Error	Error	Error
				1
)	
0	1.8	2.5	-5.7	2.0
42.0	3.3	1.3	-8.4	6.0
73.1	4.6	2.4	-4.0	4.1
100	4.3	0.9	-1.9	4.1
137.5	-1.6	2.6	-13.4	21.4

see section 4.8 for details

Table 6.9 Response time tests - Oxygen Sensor

		0 10	Time 1	Time 2	Time 3
			(seconds)	(seconds)	(seconds)
				4 3	
Step change	low to high Dis	solved Oxygen (% sat.)	18.59	22.91	19.50
Step change	high to low Dis	solved Oxygen (% sat.)	20.47	19.53	18.66

Table 6.10 Response time Test - Temperature Sensor

	1.00		Time 1	Time 2	Time 3
·			(seconds)	(seconds)	(seconds)
Step chan	ge of low to high Ten	nperature (°C)	48.81	48.03	44.69
Step chan	ge of high to low Ten	nperature (°C)	41.31	42.66	44.72
	**	1			

Table 6.11 Instrument Readings for different levels of salinity

		No	Saline	Adjustment
Chlorine	Temperature	Dissolved	Temp.	Dissolved
$(mg l^{-1})$	Thermometer	Oxygen	(°C)	Oxygen
	(°C)	$(mg l^{-1})$		(% sat.)
		2		
0	21.3	8.85	21.2	100.1
5	20.7	9.07	20.8	101.8
10	21.1	9.01	21.0	101.6
20	21.8	8.92	21.7	101.7
40	21.8	8.74	21.8	99.8
20	22.1	8.84	22.1	101.4
10	21.7	8.81	21.7	100.5
5	21.6	8.85	21.6	100.8
0	22.4	8.64	22.4	99.6

Table 6.12a Field Data - Class 1A River

Date	Water Temp. (°C)	Pressure (kPu)	Time	Winkler (mg l ⁻¹)	Instrument Dissolved Oxygen (mg l ⁻¹)	Instrument Dissolved Oxygen (% sat.)	Instrument Temp. (°C)	Time	Winkler (mg 1 ⁻¹)	Instrument Dissolved Oxygen (mg l ⁻¹)	Instrument Dissolved Oxygen (% sat.)	Instrument Temp. (°C)	Time Wink (mg l	ler Instrument Dissolved Oxygen (mg l ⁻¹)	Instrument Dissolved Oxygen (% sat.)	Instrument Temp. (°C)
28/01/93	8.6	1008	15:59	11.48	11.83	102.1	7.8	17:37	11.38	11.80	101.0	7.8			24	
29/01/93	8.8	1017	11;11	11,48	12.0	103	7.8	14:55	11.62	11.52	99,6	8.0 ,	16:35 11.4	11.63	101	8.0
01/02/93	8.3	1034	12:30	12.02	. 11.83	100.6	7.4	14:09	12.33	11.68	99,4	7.5	17:06 12.0	11.51	97.8	7.2
02/02/93	7.8	1036	10:41	12.10	11.88	99.9	6.9	14:31	12.00	11.93	100.9	7.1	15:50 12.3	11,72	99.1	7.1
03/02/93	8.2	1039	11:05	11,90	11.77	99.9	7.2 ·	17:40	11.90	11.27	95.8	7.3	18:07 11.7	11.52	97.8	7.3
04/02/93	7.8	1034	11:52	12.00	11.60	97.6	6.9	17:13	11,80	11,50	96.9	6.9	17:49 11.8	30 11.49	96.3	6.8
05/02/93	7.1	1035	11:56	11,19	11.76	96.8	6.2	15:43	11.99	11.73	96.4	6.2	16:23 12.6	50 11.78	97.0	6.2
08/02/93	9.0	1034	11:43	11.69	11.44 -	99.5	8.2	15:44	11.45	11.30	98.8	8.2	16:55 (1.3	35 11.03	96.2	. 8.2
09/0293	8.7	1031	11:19	11,49	11.25	97.2	7.9	14:51	11.35	11.21	96.6	7.8	17:12 11.8	38 11.32	97.5	7.7
10/02/93	7.8	1029	12:41	11.78	11.62	97.6	6.9	16:32	11,94	11,66	. 97.6	6.8				
11/02/93	7.1	1030	12:01	11.93	11.70	96.2	6.2				+					6

Table 6.12b Field Data - Class 3 River

Date	Water Temp. (°C)	Pressure (kPa)	Тіте	Winkler (mg l ⁻¹)	Instrument Dissolved Oxygen (mg 1 ⁻¹)	Instrument Dissolved Oxygen (% sat.)	Instrument Temp. (°C)	Time	Winkle r (mg l	Instrument Dissolved Oxygen (mg [1])	Instrument Dissolved Oxygen (% sat.)	Instrument Temp. (°C)	Time	Winkler (mg 1 - 1)	Instrument Dissolved Oxygen (mg 1 ⁻¹)	Instrument Dissolved Oxygen (% sat.)	Instrument Temp, (°C)
15/02/93		102.8	14:50	7.62	7.51	65.2	8.1										
16/02/93		102.8	13:39	7.62	7.58	66.6	8.6	15:15	7.41	7.29	64.4	8.7				1	
17/02/93	10.4	102.6	13:28	6.90	6.67	59.5	9.2	15:01	7.04	6.73	60.9	9.8	16:04	6.87	6.75	61.4	9.9
18/02/93	10.7	101.8	14:25	7.04	6.84	61.8	9.6	15:47	7.21	6.81	61.8	9.8					
19/02/93	9.5	102.0	12:00	6.53	6.33	54.1	7.8	13:20	7.30	6.87	60.2	8.1	14:25	7.74	6.94	, 61.1	8.5
22/02/93	9.1	102.1	15:20	7.68	7.70	67.0	8.1	16:00	7.77	7.72	67.3	8.2	16:30	7.76	7.56	66.1	8.2
23/02/93	8.0	102.7	9:25	6.84	6.55	55.0	6.9	10:30	7.07	6.71	56.5	7.0	11:38	7.37	7.06	60.0	7.3
24/02/93	10.0	102.5	14:28	7.18	7.02	62.5	9.0	15:40	7.11	7.15	63.7	9.1	16:35	7.22	7.10	63.5	9.1
25/02/93	8.7	101.5	9:25	6.50	6.15	52.6	7.6	10:05	6.67	6.29	· 53.7	.7.5	11:15	6.81	6.51	56.1	7.6
26/02/93	8.2	100.4	11:48	7.18	6.93	58.8	7.2	12:39	6.97	6.68	57.2	7.7	13:15	6.98	8.14	59.5	7.9
01/03/93	6.7	101.4	13:21	8.00	8.14	65.9	5.7 .										

Table 6.13a Instrument readings for daily calibration check - Class 1A River

						•
Date		Time	Pressure (kPa)	Dissolved	Temp.	Dissolved
			(KFa)	Oxygen (mg l ⁻¹)	(°C)	Oxygen (% sat.)
	de V					
28/01/93		15:52	100.8	10.08	14.0	100.0
29/01/93		11:05	101.7	11.59	9.0	103.1
01/02/93	:	12:23	103.4	11:08	10.5	102.1
02/02/93		10:34	103.6	12:08	7:0	102.2
03/02/93		10:56	103.9	11:57	8.4	101.3
04/02/93		11:46	103.4	10.77	.9.5	96.9
05/02/93		11.51	103.6	10.65	9.5	96.0
08/02/93	-	11:35	103.5	10.38	11.1	97.2
09/0293		11:11	103.1	8.94	16.4	93.1
10/02/93		12:32	102.9	11.14	9.4	100.1
11/02/93		11:53	103.0	10.51	9.2	93.7
					·	

Table 6.13a Instrument readings for daily calibration check - Class 3 River

		•			
Date	Time	Pressure (kPa)	Dissolved Oxygen (mg l ⁻¹)	Temp.	Dissolved Oxygen (% sat.)
		100.0	10.10		100.1
16/02/93	13:33	102.8	12.49	6.1	102.1
17/02/93	13:20	102.6	10.72	10.6	99.1
18/02/93	14:20	101.8	11.39	8.4	99.7
19/02/93	12:20	102.0	9.94	12.8	96.4
22/02/93	15:15	102.1	11.78	7.1	99.5
23/02/93	10:20	102.7	12.05	5.9	98.1
24/02/93	14:23	102.5	11.96	6.3	98.8
25/02/93	09:55	101.5	11.27	7.6	96.4
26/02/93	12:30	100.4	11.12	8.8	98.7
01/03/93	13:15	101.4	13.16	2.7	95.9

 Table 6.14
 Systematic and Random Errors for daily calibration check

Test		Class 1A River	Class 3 River				
		*	1				
Mean	*	98.7	98.5				
Random e	error	3.3	1.8				
Systematic err	or (Bias)	1.3	1.5	*			
Total Er	ror	3.6	2.3				
Sample s	size	11	10				
				7-1			

Table 6.15 Systematic and Random Errors for field data

Test	Class 1A River	Class 3 River			
	- 1				
Random error	0.3	0.3			
Systematic error (Bias)	0.2	0.2			
Total Error	0.4	0.4			
Sample size	29	27			

7. INSTRUMENT BEHAVIOUR

This section describes the general performance of the ABB Kent-Taylor 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 the stabilisation period for the oxygen sensor appears to be unaffected by equilibration of the temperature sensor.

The expected battery life can be calculated from the battery capacity (Table 6.2b) and the power consumption (Table 6.2a). This gives an approximate battery life of 600 hours. The manufacturer does not stated an expected battery life.

The instrument readings are affected by decreasing the power supply (Table 6.3). However the low battery indicator appears before this occurs (6.33V). Further reduction is the supply voltage the display becomes "-1" at 5.37V.

The effect of flow on the sensor performance is given in table 6.4. It shows that even at the highest flow rate tested (0.33 m s⁻¹) a stable results is still not achieved. The manufacturer specifies a minimum recommended flow rate of 0.30 m s⁻¹. It should be noted that at the nominal zero flow rate the percentage saturation readings were unstable (\pm 3 % dissolved oxygen).

The different depth at which the readings were taken does not have an affect on the readings (Table 6.5). The low percentage saturation values are due to 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 (at standard pressure) 100% air-saturation would be achieved at a dissolved oxygen level of 11.11 mg 1⁻¹, whilst at 30°C there would be 7.44 mg 1⁻¹ present. It can be seen that at both levels the meter reading is correct and the percentage saturation is also within the manufactures 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.

Calibrating in dechlorinated tap water gave more accurate results than calibrating in air (Table 6.7).

The instrument accuracy was tested on 5 separate occasions and compared with a range of oxygen nitrogen gas mixtures. These results are presented in tables 6.8a - 6.8e. The random and systematic errors for the instrument and the Winkler determinations are provided in Table 6.8f. The total error (quadrature sum of random and systematic errors) for five test concentrations varied between 3.0 and 5.1%. 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 times for the oxygen sensor (Tables 6.9) are in agreement with the that stated by the manufacturer. However the temperature sensor response (Table 6.10) is over twice the twenty seconds stated by the manufacturer.

This instrument does not provide any salinity correction facility, although tables are provided in the documentation.

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

Table 6.14 shows the systematic and random errors for the calibration check data for the Class 1A and 3 river. This test shows the accuracy of the instrument calibration. The total error was 2.3% in the Class 3 river but rose to nearly 3.5% in the Class 1A river. If this is compared to the Winkler determinations for the accuracy 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 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 determinations. The total error was 0.4 mg l⁻¹ for both sites. It can be seen that the variations are small, particularly if the variability in the Winkler measurements are assumed to be similar to those seen in the accuracy tests.

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

8. COST OF OWNERSHIP

Instrument £870.00

Spares sensor £ 44.00

Battery Pack £ 31.50

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9. MANUFACTURER'S COMMENTS

- 1. It is stated that the sensor capsule shelf life "appears to be only about 2 months", but there is no indication of how this estimate was made. It is certainly contrary to our experience, which indicates a shelf life of 6 months or more.
- 2. It is claimed that table 6.4 shows that "even at the highest flow rate tested (0.33 ms⁻¹) a stable result is still not achieved". Inspection of the table, including it's footnote, suggests that stable, but different, readings were obtained for the two measurements made at 0.33 ms⁻¹. Nevertheless, if the Table 6.4 results are used to plot a graph of %sat. readings against flow this has the expected characteristic shape, with a "plateau" region appearing at flow rates in excess of about 0.2 ms⁻¹.
- 3. The instrument does not incorporate salinity correction facilities, but salinity correction information is provided in the Operating Instructions to enable users to calculate dissolved oxygen concentrations from %sat. readings obtained in waters of known salinity.
- 4. The instrument was not designed to be calibrated in air, which produces a slightly higher sensor output current than calibration in water in equilibrium with the same air.
- 5. We were surprised to read that the working shield did not fit securely on to the sensor, and could actually fall off in use. This item has been produced for many years and the only complaints have been occasional suggestions that, even after many fitting and removal operations, it still fits too tightly.

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
- ABB Kent-Taylor 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	рН	Sulphate as SO ₄	Conductivity	Copper as Cu	Ammoniacal N as N	Nitrite as N	Chloride as Cl	Calcium as Ca	Magnesium as Mg	Sodium as Na	Potassium as K	Nitrate as N
				mg I ^{-l}	μS cm ⁻¹	μg I ⁻¹	mg l ^{- l}	mg 1-1	mg I ⁻¹	mg I ⁻¹	mg i-1	mg l ⁻¹	mg I ⁻¹	mg I ⁻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	П	2	5.7
	08/02/93	10:50	8.1	45	535	<5	<0.05	0.05	23	115	3	11.5	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	II .				5.5
	11/02/93	14:05	8. t	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	рН	Sulphate as SO ₄	Conductivity	Copper as Cu	Ammoniacal N as N	Nitrite as N	Chloride as Cl	Calcium as Ca	Magnesium as Mg	Sodium as Na	Potassium as K	Nitrate as
			mg 1 ⁻¹	μS cm ⁻¹	μg I ⁻¹	mg I ^{-]}	mg (* l	mg 1 ⁻¹	mg l ⁻¹	mg l ⁻¹	mg I ^{- [}	mg l ⁻¹	mg l ⁻¹
15/02/93	16:00	7.1	128	835	30.4	1.45	0.27	100	74	18	72	15	15.5
16/02/93	15:00	7.0	135	911	45.7	1.51	0.39	123	85	21	90	16	15.0
17/02/93	14:45	7.2	148	908	40.5	1.63	0.36	124	81	20	89	15	12,4
18/02/93	14:10	7.3	148	936	40.6	1.40	0.37	130	81	19	87 .	14	12.7
23/02/93	10:30	7.6	154	936	40.3	1.90	0.33	114	84 .	19	95	16	14.1
24/02/93	15:50	7.0	140	956	42.3	1.70	0.29	127	74	17	98	16	13.6
25/02/93	10:00	7.1	148	979	43.0	2.60	0.34	129	85	19	93	15	11.7
26/02/93	11:57	7.2	144	993	66.0	3.70	0.27	142	89	20	96	14	10.5
01/03/93	14:20	7.2	135	971	47.0	3.90	0.25	141 .	80	18	102	15	14.3

APPENDIX B - FIGURES

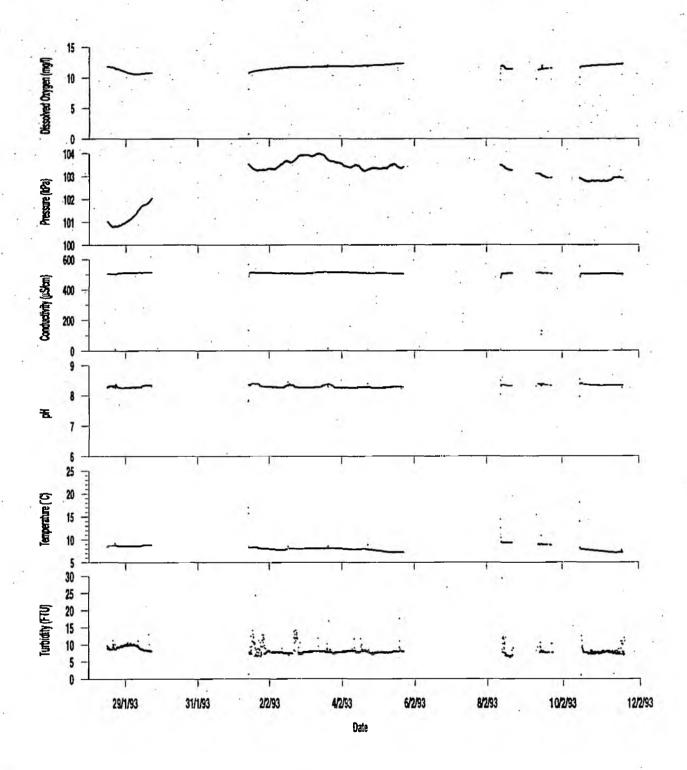


Figure B1 Water Quality Parameters Class 1A River

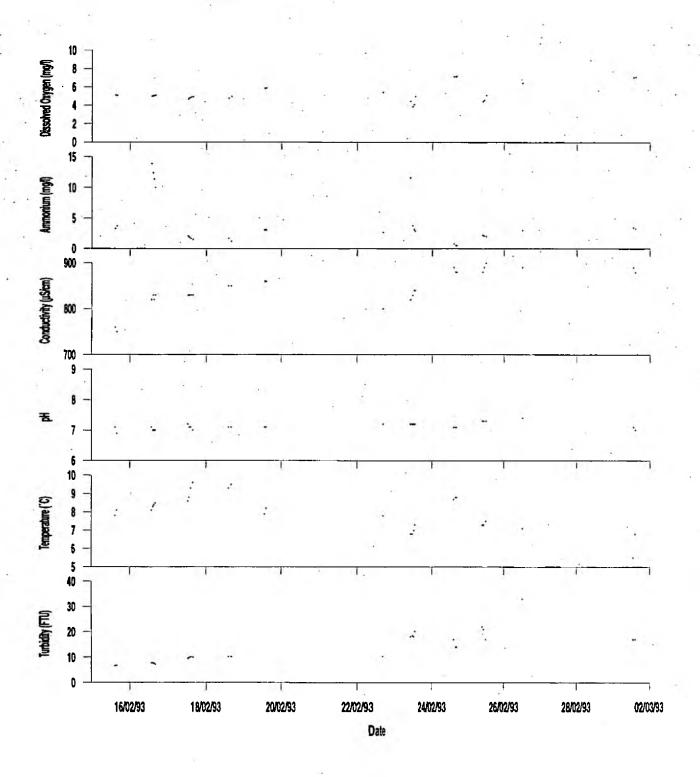


Figure B2 Water Quality Parameters Class 3 River

APPENDIX C - MANUFACTURER'S SPECIFICATIONS

Oxygen Measurement

RANGES: 0 to 19.9 mg l⁻¹ dissolved oxygen

0 to 199.9 % air saturation

ACCURACY ± 0.2 mg l-1

±2% air saturation

Temperature Measurement

RANGE: 0 to +40°C

ACCURACY ± 1.0°C

Instrument Environment

Temperature range -5 to +50°C

Power Supply Internal Battery - 9V PP3

External power e.g. car battery 11 to 17V d.c.Circuit protected

against wrong polarity

Supply Voltage - via adaptor (to B.S. 3861 Part III) 220-240V 50-60Hz (200 to 260V extreme limits or 110-120V 60Hz (100

to 130V extreme limits)

Response Time

(90% change) Oxygen - 20 seconds at a constant 20°C

Temperature - 20 seconds

Probe Model 7136 oxygen sensor housing a thermistor