

PROJECT 220

# The Evaluation of EDT QSE 334 Ammonium Ion Selective Electrode

WRc plc

Evaluation Report 220/17/T



**NRA**

*National Rivers Authority*

# THE EVALUATION OF EDT QSE 334 AMMONIUM ION SELECTIVE ELECTRODE

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Project 220



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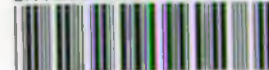
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220/17/T

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## **EXECUTIVE SUMMARY**

This report describes the results of an evaluation of a Qualiprobe QSE334 ammonium ion selective electrode. 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.

Generally the electrode was found to be very easy to operate and maintain.

The documentation received was comprehensive being clear and well written with instructions on the recommended equipment, specifications, setting up, calibration, trouble-shooting, and maintenance.

The maintenance requirements of the electrode were low, except under certain field conditions, where the water quality was sufficiently poor to necessitate regular cleaning of the electrode to remove foulant. It was also necessary to change to membrane of the electrode. This was a very simple procedure requiring the unscrewing of the old module and replacing it.

Laboratory trials to determine sensor accuracy established that the total error (quadrature sum of random and systematic errors) for five test concentrations varied between 0.02 and 0.13 mg/l  $\text{NH}_4^+$ .

During the field evaluation of the ammonium electrode two problems were identified. Initially a faulty reference electrode was found to be causing a problem. This having been resolved it was found that the amplification system employed, which was intended for laboratory usage, was susceptible to interference from other voltage sources present in the field environment. NRA (Thames Region) are currently testing a system that will remove this problem. The total error (quadrature sum of random and systematic errors) varied between 0.27 and -8.28 mg l<sup>-1</sup>  $\text{NH}_4^+$ . This was significant (95% confidence) drift in the calibration at the Class 1 river, before the membrane required replacing during the Class 3A river trials.

Model QSE 334 Ammonium Ion Selective Electrode £220.00 Model E8098 Double Junction Reference Electrode £127.00. The only maintenance required was cleaning of the electrode..

This evaluation has highlighted the difficulties in testing a single component of a monitoring system rather than evaluating a complete instrument.

## **KEY WORDS**

Ammonium Electrode, Evaluation

**NRA Evaluation Report 220/17/T**

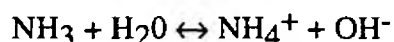
## 1. INTRODUCTION

Ammonium ion selective electrodes are of interest to NRA as a possible low cost, low maintenance, alternative to the existing ammonium measuring devices. They are currently being used as a component in portable, hand-held multi-parameter equipment and have already been assessed (Baldwin, Harman and van Dijk). It is anticipated that they may be of use in other field situations such as;

- transportable multi-parameter monitoring equipment for temporary short or long term installation at remote sites with no provision for power or pumping services;
- small permanent multi-parameter monitoring stations at sites with provision of power and pumping services but severe space limitations.

A detailed discussion on the chemistry of ammonia in water was included in the protocol (Baldwin 1992). However, a resume of the discussion is provided here due to the significance of ammonia chemistry to this evaluation.

Ammonia is very soluble in water in which it forms an equilibrium with the ammonium ion ( $\text{NH}_4^+$ ) thus:



The important equilibrium is the acid-base equilibrium which forms the ammonium ion. This is crucial because it determines the proportion of dissolved ammonia present in the unionised form which is the main toxic species to fish and therefore of the greatest environmental significance. It is important to note that the proportion of unionised ammonia present in any aqueous solution will be a function of other physico-chemical characteristics of the sample, principally pH.

All ion selective electrode potentials are measured relative to a 'reference' electrode. For the purpose of this study the sensing electrode and reference electrode pair were evaluated in combination and are therefore referred to throughout this report as 'the electrode'. Where comments are specific to one of the electrodes this will be made clear in the text.

The definition of tests to be applied under the NRA Instrumentation Assessment and Demonstration project has been previously described (Baldwin 1992). The specific protocol (Baldwin 1992) defines the tests and procedures that have been used in these trials. However, a summary of these tests is included here for information. It must be pointed out that the tests applied to the electrode are, in many instances, outside of the manufacturer's recommended operating conditions and therefore any comments will take this into account.

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.



## 2. DETAILS OF EQUIPMENT EVALUATED

Manufacturer: EDT Instruments Ltd.

Supplier: EDT Instruments Ltd.  
Lorne Rd  
Dover  
Kent CT16 2AA

Tel: 0304 213555  
Fax: 0304 204297

Instrument Description: Ion Selective Electrode - Ammonium  
(QSE334)

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.

Generally the electrode was found to be very easy to operate and maintain. The documentation received was clear and well written with instructions on the recommended equipment, specifications, setting up, calibration, trouble-shooting, and maintenance.

The electrode is made up of two sections, the electrode main body and the sensing module. On to the main body is bonded the signal cable and central electrode. The sensing module is connected to the main body via a screw connection. This allows the membrane to be easily replaced. To ensure a seal between the two parts an 'O'-ring is provided. Care must be taken to ensure that the 'O'-ring is not distorted by over tightening. Overall the unit seemed to be robust and well made.

A significant correlation (95% confidence limits) was found between sensor output and speed of flow at the sensor surface when high concentrations ( $5 \text{ mg l}^{-1}$ ) of ammonium are measured.

The response time of the electrode varied considerably depending on the direction of the concentration step change. A change from a low to a high concentration required  $5 (\pm 1)$  seconds before stability was achieved, however a change from a high to a low concentration required  $20 (\pm 4)$  seconds. This was in agreement with the figure of 3 minutes stated by the manufacturer.

The electrode was found to be very susceptible to interference from some of the chemical species tested. Potassium ions caused the highest levels of interference.

The total error (quadrature sum of random and systematic errors) for five accuracy test concentrations varied between 0.02 and  $0.13 \text{ mg/l NH}_4^+$ . The lowest concentration tested is below the linear detection limit stated by the manufacturer, however the errors obtained at this concentration were similar to those for the other concentrations tested.

During the field evaluation two problems were identified. Initially a faulty reference electrode from another electrode being tested was found to be causing a problem. This having been resolved it was found that the amplification system employed, which was intended for laboratory usage, was susceptible to interference from other voltage sources present in the field environment. NRA (Thames Region) are currently testing a system that will remove this problem. It was therefore agreed that the field trials would be repeated. The total error (quadrature sum of random and systematic errors) is similar for both sites, at test concentration of  $0.5 \text{ mg l}^{-1} \text{ NH}_4^+$  the total error for the Class 1A was  $0.20 \text{ mg l}^{-1}$ , at the Class 3A it was  $0.21 \text{ mg l}^{-1}$ . At the higher test concentration,  $5.0 \text{ mg l}^{-1} \text{ NH}_4^+$ , the total error for the class 1A river was  $1.59 \text{ mg l}^{-1}$  whilst at the Class 3 it was  $1.69 \text{ mg l}^{-1}$ .

The maintenance requirements of the electrode were low, except under certain field conditions, where the water quality was sufficiently poor to necessitate regular cleaning of the electrode to remove foulant. The electrode membrane needed to be replaced, however, this was a very simple and quick procedure.

## 4. EVALUATION PROCEDURES

The Evaluation and Demonstration Facility at Fobney Mead and Lea Marston have been previously described (Baldwin 1991) along with test procedures (Baldwin 1992). A brief description of each test is provided for information.

### 4.1 Signal Processing

The electrode voltage output was connected to an Orion EA940 ion analyser via a Model 607 switch box. The reference electrode provided by the manufacturer was an EDT pH electrode.

The Orion Analyser was interfaced to an IBM PC compatible computer. The direct mV readings, converted concentrations ( $\text{mg l}^{-1} \text{NH}_4^+$ ) and calibration information was stored on the computer. The calibration was performed using a logarithmic conversion followed by a linear least squares regression.

### 4.2 Laboratory

All the laboratory trials were conducted using standard laboratory glassware. The sensor was immersed in the test solutions to a depth of 10 mm, with the reference electrode held at a constant distance of 40 mm. The manufacturer did not specify the separation between the electrodes and so this distance was found by experimentation.

All test solutions were corrected to pH 5.2 by the addition of 0.1 N boric acid. Standard ammonium ion solutions were achieved by calculating the ammonium ion concentration at the pH and temperature following the addition of ammonium chloride.

#### 4.2.1 Flow at Sensor surface

The effect of flow on the sensor was measured by placing the electrode in each of the following solutions:

5.0  $\text{mg l}^{-1} \text{NH}_4^+$  ion (14.86  $\text{mg l}^{-1} \text{NH}_4\text{Cl}$ ) in 0.1N boric acid,

0.1  $\text{mg l}^{-1} \text{NH}_4^+$  ion (2.97  $\text{mg l}^{-1} \text{NH}_4\text{Cl}$ ) in 0.1N boric acid,

0.1  $\text{mg l}^{-1} \text{NH}_4^+$  ion (2.97  $\text{mg l}^{-1} \text{NH}_4\text{Cl}$ ) in 0.1N boric acid with 2.5  $\text{g l}^{-1}$  of kaolin.

For each solution the beaker was placed on a magnetic stirrer and a stable reading was taken with the stirrer switched off. The stirrer was then switched to various speed settings and the reading noted. The solution containing kaolin remained stationary for the minimum period required to obtain the reading in order to reduce settling.

#### 4.2.2 Response Time

The electrode was placed in a stirred solution containing  $0.1 \text{ mg l}^{-1}$  ammonium ions ( $2.97 \text{ mg l}^{-1} \text{ NH}_4\text{Cl}$ ) in  $0.1\text{N}$  boric acid until a stable reading was obtained. The electrode was then quickly transferred to a stirred solution containing  $5.0 \text{ mg l}^{-1} \text{ NH}_4^+$  ions ( $14.86 \text{ mg l}^{-1} \text{ NH}_4\text{Cl}$ ) in  $0.1\text{N}$  boric acid. The electrode response was recorded using a chart recorder attached to the low impedance output of the EA940 amplifier. The sequence was then reversed.

The response time of the electrode was also measured when the electrode was placed into the  $0.1 \text{ mg l}^{-1}$  solution, after being held clear of the liquid for 5 minutes.

The time taken for the electrode response to complete 90% of the step change was then calculated from the chart record.

#### 4.2.3 Interference

The electrode was placed in each of the solutions in turn, and the output was recorded. The solutions were continuously stirred and the electrodes were rinsed with de-ionised water between solutions.

The electrode was tested for interference at two levels of ammonium ion concentration,  $0.1 \text{ mg l}^{-1}$  ( $0.297 \text{ mg l}^{-1} \text{ NH}_4\text{Cl}$ ) and  $1.0 \text{ mg l}^{-1}$  ( $2.97 \text{ mg l}^{-1} \text{ NH}_4\text{Cl}$ ), with all solutions prepared in  $0.1\text{N}$  boric acid. Readings were taken for each level of ammonium ion with the addition of the following:

- no interferent,
- $100 \text{ mg l}^{-1}$  of potassium chloride,
- $100 \text{ mg l}^{-1}$  of sodium chloride,
- $400 \text{ mg l}^{-1}$  of calcium chloride,
- $400 \text{ mg l}^{-1}$  of magnesium chloride,
- no interferent.

Further solutions of ammonium ion were prepared and readings taken for the each ammonium level with the addition of the following:

- no interferent,
- $724 \text{ mg l}^{-1}$  of (hydrated) aluminium chloride ( $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ ),

18100 mg l<sup>-1</sup> of (hydrated) aluminium chloride (AlCl<sub>3</sub>.6H<sub>2</sub>O)

no interferent.

#### 4.2.4 Electrode Separation

The electrode was placed in a stirred solution of 0.1 mg l<sup>-1</sup> NH<sub>4</sub><sup>+</sup> (0.297 NH<sub>4</sub>Cl) ions in 0.1N boric acid. Readings were obtained at an electrode separation of 20 mm and 90 mm.

#### 4.2.5 Calibration accuracy/repeatability

The electrode output was recorded for each of the following solutions:

0.30 mg l<sup>-1</sup> NH<sub>4</sub>Cl (0.1 mg l<sup>-1</sup> NH<sub>4</sub><sup>+</sup>),

1.48 mg l<sup>-1</sup> NH<sub>4</sub>Cl (0.5 mg l<sup>-1</sup> NH<sub>4</sub><sup>+</sup>),

2.97 mg l<sup>-1</sup> NH<sub>4</sub>Cl (1.0 mg l<sup>-1</sup> NH<sub>4</sub><sup>+</sup>),

14.86 mg l<sup>-1</sup> NH<sub>4</sub>Cl (5.0 mg l<sup>-1</sup> NH<sub>4</sub><sup>+</sup>),

29.72 mg l<sup>-1</sup> NH<sub>4</sub>Cl (10.0 mg l<sup>-1</sup> NH<sub>4</sub><sup>+</sup>).

The electrodes were then rinsed and the process repeated four more times. Fresh solutions were then prepared and the process was repeated a further five times.

### 4.3 Field Trials

For the field trials the electrode was installed in a flow cell with a constant flow of 200 l h<sup>-1</sup> of water. The electrode was immersed 10 mm below the water surface with the reference electrode positioned 40 mm away. Details of the flow cell can be found in the ammonium protocol (Baldwin 1992).

To simulate the varied conditions that may be expected under field conditions the electrode was exposed to the following regimes;

- dynamic river conditions in Class 1A river water: water was pumped continuously through the flow cell for two weeks,
- dynamic river conditions in Class 3 river water: water was pumped continuously through

the flow cell for two weeks.

- recycled river conditions in Class 1A river water: water was recycled through the flow cell for two weeks.
- dosed recycled river conditions in Class 1A river water: water was dosed with nominal  $1 \text{ mg l}^{-1}$  ammonium chloride recycled through the flow cell for two weeks.
- periodic river conditions in Class 1A river water: water was pumped periodically through the flow cell for two weeks.

The water passing through the flow cell was monitored continuously for the following parameters: temperature, dissolved oxygen, pH, conductivity, turbidity, ammonium (Class 3 river only).

Daily samples were taken for laboratory analysis.

The calibration of the electrode was checked daily against solutions of  $0.5 \text{ mg l}^{-1} \text{ NH}_4^+$  ( $1.48 \text{ mg l}^{-1} \text{ NH}_4\text{Cl}$ ) and  $5.0 \text{ mg l}^{-1} \text{ NH}_4^+$  ( $14.86 \text{ mg l}^{-1} \text{ NH}_4\text{Cl}$ ). These test solutions were corrected for pH (5.2) and ionic strength ( $500 \text{ mS cm}^{-1}$ ) by the addition of boric acid and calcium chloride respectively.

Before each test the electrode was cleaned and where necessary, the electrolyte replenished.

Whenever the electrode was not under test it was stored according to the manufacturer's recommendations.

## **5. OBSERVATIONS**

### **5.1 Documentation**

A comprehensive manual was received with the ammonium electrode, and a leaflet for the reference electrode. The ammonium Qualiprobe manual included sections on the recommended equipment, specifications, setting up, calibration, trouble-shooting, and maintenance. It was clear and well written.

### **5.2 Design and Construction**

The electrode is made up of two sections, the electrode main body and the sensing module. On to the main body is bonded the signal cable and central electrode. The sensing module is connected to the main body via a screw connection. This allows the membrane to be easily replaced. To ensure a seal between the two parts an 'O'-ring is provided. Care must be taken to ensure that the 'O'-ring is not distorted by over tightening. Overall the unit seemed to be robust and well made.

The reference electrode provided was a double junction glass electrode. This was filled through two holes in its side.

### **5.3 Installation**

The ammonium probe requires assembly; the sensing module is connected to the main body via a screw connection.

### **5.4 Commissioning**

For short term storage the electrode can be stored dry after rinsing with distilled water. For longer periods the manufacturer recommends rinsing and drying the detachable sensing modules before placing them in the Qualiprobe box, away from direct heat. Prior to use the electrode should be immersed for at least two hours in 0.1M  $\text{NH}_4\text{Cl}$ .

### **5.5 Maintenance and Downtime**

The ammonium electrode is a sealed unit and required very little maintenance. The reference electrode however required refilling between and during tests. The inner chamber needed refilling each week; the outer chamber did not need refilling during tests.



It was necessary to replace the membrane on three occasions during the tests. There was slight fouling of the electrode during the field trials on the Class 1a river, with considerably more during the Class 3 river. In both cases the foulant was easily removed by washing with de-ionised water and gentle wiping with a tissue. The manufacturer gave no guidance on the removal of fouling, however, since the electrode is designed for laboratory use it must be assumed that the manufacturer does not expect fouling to occur.

## **5.6 Ease of Use**

The probe was found to be very easy to use and install. The ammonium probe membrane can be easily changed, simply by unscrewing the end piece of the probe and replacing it.

## 6. RESULTS

Table 6.1 Flow at sensor surface

Stirrer Speed Setting	Electrode		Output (mV)
	NH <sub>4</sub> <sup>+</sup> 0.1 mg l <sup>-1</sup>	NH <sub>4</sub> <sup>+</sup> 5.0 mg l <sup>-1</sup>	Addition 2.5g/l Kaolin
0	-89.3	-31.5	-
3	-90.4	-30.1	-73.4
4	-89.8	-29.5	
5	-89.3	-29.5	
7	-87.2	-28.5	
10	-87.3	-28.5	-69.8
0	-90.0	-31.0	-73.8

Table 6.2 Response time

Step Change	Concentration mg l <sup>-1</sup> NH <sub>4</sub> <sup>+</sup>	Response Time (seconds)
Rising Average	0.1 - 5.0	5 ± 1
Falling Average	5.0 - 0.1	20 ± 4
Air to 0.1 mg l <sup>-1</sup> NH <sub>4</sub> <sup>+</sup>		< 1

**Table 6.3 Interference**

Solution	Electrode	Output	
		0.1 mg l <sup>-1</sup> NH <sub>4</sub> <sup>+</sup>	1.0 mg l <sup>-1</sup> NH <sub>4</sub> <sup>+</sup>
reference solution + 100 mg l <sup>-1</sup> of KCL		83.6	39.3
reference solution + 100 mg l <sup>-1</sup> of NaCl		4.8	-1.5
reference solution + 400 mg l <sup>-1</sup> of CaCl <sub>2</sub>		-5.0	-0.6
reference solution + 400 mg l <sup>-1</sup> of Mgcl <sub>2</sub>		-5.1	-3.0
reference solution *		5.6	0.7
reference solution + 724 mg l <sup>-1</sup> of AlCl <sub>3</sub> 6H <sub>2</sub> O		3.2	-3.1
reference solution + 18100 mg l <sup>-1</sup> of AlCl <sub>3</sub> 6H <sub>2</sub> O		5.4	-1.9
reference solution		0.7	-1.7

\* New reference solutions

**Table 6.4 Electrode separation**

Electrode to Reference Separation (mm)	Electrode Output (mV)
20	-78.3
90	-78.4

Table 6.5a Accuracy tests 1 - 5

Actual mg l <sup>-1</sup> NH <sub>4</sub> <sup>+</sup>	Test 1 mV	Test 2 mV	Test 3 mV	Test 4 mV	Test 5 mV	Mean mV	Standard Deviation mV
0.1	-125.2	-119.6	-118.6	-123.0	-120.6	-121.4	2.4
0.5	-87.9	-87.1	-87.6	-88.4	-88.1	-87.8	0.4
1.0	-67.2	-66.4	-66.5	-71.0	-70.0	-68.2	1.9
5.0	-30.9	-30.2	-30.6	-31.0	-30.5	-30.6	-0.3
10.0	-13.5	-13.9	-13.8	-13.8	-13.7	-13.7	0.1
mV/dec	55.96	53.52	53.16	55.10	54.22	54.29	1.03

Table 6.5b Accuracy tests 6 - 10

Actual mg l <sup>-1</sup> NH <sub>4</sub> <sup>+</sup>	Test 6 mV	Test 7 mV	Test 8 mV	Test 9 mV	Test 10 mV	Mean mV	Standard Deviation mV
0.1	-131.1	-126.9	-123.5	-130.5	-128.7	-126.6	2.8
0.5	-93.5	-91.8	-93.7	-92.0	-92.5	-92.7	0.8
1.0	-74.6	-73.9	-74.2	-74.7	-74.9	-74.5	0.4
5.0	-35.7	-35.1	-35.1	-34.8	-35.1	-35.2	0.3
10.0	-18.2	-18.0	-18.3	-18.0	-17.7	-18.0	0.2
mV/dec	54.92	53.46	53.76	56.46	55.81	54.88	1.15

**Table 6.5c Summary of Accuracy tests 1 - 5**

	NH <sub>4</sub> <sup>+</sup> mg l <sup>-1</sup>				
	0.1	0.5	1	5	10
Mean	0.12	0.47	1.04	4.95	9.87
Systematic Error	-0.02	0.03	-0.04	0.05	0.13
Random Error	0.01	0.01	0.10	0.07	0.03
Total Error	0.02	0.03	0.11	0.09	0.13

**Table 6.5d Summary of accuracy tests 6 - 10**

	NH <sub>4</sub> <sup>+</sup> mg l <sup>-1</sup>				
	0.1	0.5	1	5	10
Mean	0.11	0.47	0.95	5.04	10.36
Systematic Error	-0.01	0.03	0.05	-0.04	-0.36
Random Error	0.00	0.00	0.01	0.03	0.07
Total Error	0.01	0.03	0.05	0.05	0.37

Table 6.6 Calibration check dynamic river conditions Class 1A river

Date	Time	0.5 mg l <sup>-1</sup>	5.0 mg l <sup>-1</sup>	mV/de	0.5 mg l <sup>-1</sup>	5.0 mg l <sup>-1</sup>	mV/de
		NH <sub>4</sub> <sup>+</sup> mV	NH <sub>4</sub> <sup>+</sup> mV	c	NH <sub>4</sub> <sup>+</sup> mV	NH <sub>4</sub> <sup>+</sup> mV	c
15/02/93	16:30	-105.5	-38.3	67.2	-	-	-
16/02/93	15:24	-93.3	-37.5	55.8	-	-	-
18/02/93	11:00	-91.3	-34.1	57.2	-	-	-
19/02/93	17:00	-96.6	-40.6	56.0	-	-	-
22/02/93	16:45	-104.4	-42.2	62.2	-	-	-
23/02/93	16:40	-118.2	-45.8	72.4	-80.5	-34.5	46.0
24/02/93	17:15	-122.5	-39.3	83.2	-89.5	-35.1	54.4
25/02/93	14:50	-114.2	-52.3	61.9	-102.5	-45.5	57.0
26/02/93	10:40	-142.4	-55.3	87.1	-92.9	-38.8	54.1
01/03/93	11:40	-	-	-	-98.9	-30.9	68.0
02/03/93	09:10	-	-	-	-110.7	-40.7	70.0

Table 6.7 Calibration check dynamic river conditions Class 3 river

Date	0.5 mg l <sup>-1</sup>	5.0 mg l <sup>-1</sup>	mV/de
	NH <sub>4</sub> <sup>+</sup> (mV)	NH <sub>4</sub> <sup>+</sup> (mV)	c
16/03/93	-39.1	3.7	42.8
18/03/93	13.7	8.1	5.6
19/03/93	8.9	17.8	8.9
22/03/93	9.1	19.8	10.7
23/03/93	-71.2	-25.0	46.2
26/03/93	-76.5	-27.6	48.9
29/03/93	37.4	41.4	-4.0

**Table 6.8 Calibration check recycle river conditions Class IA river**

DATE	0.5 mg l <sup>-1</sup>	5.0 mg l <sup>-1</sup>	mV/dec
	NH <sub>4</sub> <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	
	(mV)	(mV)	
03/04/92	-64.1	-26.5	37.6
06/04/92	-116.9	-39.8	77.1
07/04/92	141.3	-43.3	98.0
08/04/92	-130.2	-39.0	91.2
10/04/92	-113.2	-40.9	72.3

**Table 6.9 Calibration check recycle (Doped) river conditions Class IA river**

DATE	0.5 mg l <sup>-1</sup>	5.0 mg l <sup>-1</sup>	mV/dec
	NH <sub>4</sub> <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	
	(mV)	(mV)	
27/04/92	-121.4	-58.4	63.0
28/04/92	-140.0	-52.0	88.8
29/04/92	-129.0	-53.0	76
30/04/92	-114.8	-48.9	65.9
01/05/92	-107.9	-56.0	51.9
05/05/92	-118.0	-56.0	62.0
06/05/92	-114.9	-65.8	49.1
08/05/93	-109.5	57.0	52.5

Table 6.10 Calibration check Intermittant river conditions Class 1A river

DATE	0.5 mg l <sup>-1</sup>	5.0 mg l <sup>-1</sup>	mV/dec
	NH <sub>4</sub> <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	
	(mV)	(mV)	
20/05/92	-103.1	-42.2	60.9
21/05/93	-107.5	-46.7	60.8
26/05/92	15.0	21.7	6.7
27/05/92	24.8	27.7	2.9
29/05/92	18.9	31.6	12.7

Table 6.11 Calculated random and systematic errors

Test	Class	1A	Class	3
	NH <sub>4</sub> <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>
	0.5 mg l <sup>-1</sup>	5.0 mg l <sup>-1</sup>	0.5 mg l <sup>-1</sup>	5.0 mg l <sup>-1</sup>
Mean	0.24	4.44	8.78	11.48
Random Error	0.07	1.31	11.30	13.79
Systematic Error	0.26	0.56	-8.28	-6.48
Total Error	0.27	1.43	14.01	15.24
Sample Size	4	4	6	6



**Table 6.12**      **Calculated random and systematic errors**

Test	Recycled	Undoped	Recycled	Doped	Intermittent	
	NH <sub>4</sub> <sup>+</sup> 0.5 mg l <sup>-1</sup>	NH <sub>4</sub> <sup>+</sup> 5.0 mg l <sup>-1</sup>	NH <sub>4</sub> <sup>+</sup> 0.5 mg l <sup>-1</sup>	NH <sub>4</sub> <sup>+</sup> 5.0 mg l <sup>-1</sup>	NH <sub>4</sub> <sup>+</sup> 0.5 mg l <sup>-1</sup>	NH <sub>4</sub> <sup>+</sup> 5.0 mg l <sup>-1</sup>
Mean	0.09	1.06	0.54	5.60	26.84	33.70
Random Error	0.41	3.94	-0.04	-0.60	-26.34	-28.70
Systematic Error	0.15	0.38	0.19	1.04	31.48	34.49
Total Error	0.43	3.96	0.19	1.20	41.05	44.87
Sample Size	4	4	7	7	4	4

## 7. INSTRUMENT BEHAVIOUR

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

Table 6.1 shows the results from varying the flow at the sensor surface. It was found that flow did have a significant effect (90% confidence limits) on sensor output at the higher ammonia concentration levels. The flow rate was not significant at the lower concentration. The addition of kaolin similarly appeared to have no effect.

The response time of the electrode (Table 6.2) varied considerably depending on the direction of the ammonium change. With a change from a low concentration (0.1 mg/l  $\text{NH}_4^+$ ) to a higher concentration (0.5 mg/l  $\text{NH}_4^+$ ) the electrode responded within 5 seconds. However, for the reverse case, the response time was four times longer at 20 seconds. This is within the manufacturer's specification of less than three minutes.

Previous assessments of ammonium ion selective electrodes have shown that they are susceptible to interference by other ionic species, particularly potassium and sodium. Table 6.3 shows the electrode change after the addition of various ionic species. It can be seen that potassium had a marked effect on the electrode output. The effect this would have on the electrode output can be demonstrated by converting the millivolt change into a corresponding equivalent ammonium level. This is achieved by applying the calibration curve calculated from the results in table 6.5. The addition of 100 mg/l of KCl (48 mg/l  $\text{K}^+$ ) would produce a theoretical ammonium level of approx. 3 mg/l at 0.1 mg/l  $\text{NH}_4^+$  whilst at 4 mg/l  $\text{NH}_4^+$  this would be 1 mg/l  $\text{NH}_4^+$ . This is in agreement with the manufacturer's specification.

The manufacturer did not state a recommended distance between the electrode and the reference electrode. Table 6.4 shows the recorded output for the electrode when placed at different distances from the reference electrode. It can be seen that increasing the distance between the electrodes had little effect on the voltage output.

The instrument accuracy results are presented in tables 6.5a - 6.5d. The total error (quadrature sum of random and systematic errors) for five test concentrations varied between 0.02 and 0.13 mg/l  $\text{NH}_4^+$ . The lowest concentration tested is below the linear detection limit stated by the manufacturer, however the mean and standard deviation achieved is still within acceptable limits.

The manufacturer states that the mV/decade value should be  $56 \pm 2$  before it should be used. It can be seen that the values obtained are generally slightly below the lower limit, although the mean value for the ten tests is within the stated range.

The ammonium electrode was then evaluated under a series of five different field conditions. However, during the evaluation at Class 1A river water some erroneous readings were observed. There were differences between readings taken in the flow cell and the same water sample measured in a beaker. Investigation of this phenomenon identified a possible problem with a reference electrode. In the initial configuration of the apparatus several electrode pairs were tested in parallel. Unfortunately this meant that the faulty reference electrode interfered with all the readings. It was therefore decided to employ a single reference electrode. The dynamic flow regime tests would be repeated for the Class 1A and Class 3 rivers

The single reference electrode appeared to have considerably reduced the difference in readings between flow cell and beaker. However when the electrode was transferred to the Class 3A site erroneous readings were again seen. On checking the amplifier box it was found that there was a voltage source present in the water supply which was contributing to the electrode readings. This voltage source was not consistent and therefore changes seen in the electrode readings could not be contributed to changes in the ammonium levels or the characteristics of the electrode alone. To be able to take readings that were not effected by this 'earthing' effect a new amplification system would be required. The NRA (Thames Region) have designed and are testing a system that will enable such measurements to be made. However this evaluation was designed to test a component of a measuring system and not develop a new amplification system. All field readings would therefore be susceptible to the variations seen previously, however, the calibration check data would be valid due to the readings being taken in a separate vessel. The time spent under field conditions, therefore, could only be seen as a 'conditioning' period.

The daily calibration check data is shown in Tables 6.6 to 6.10. The tables show the calibration check data for the three field trials not repeated as well as those repeated. The electrode output was recorded for standard ammonium solutions corrected for pH, temperature and ionic strength. The solutions were corrected for pH and ionic strength with boric acid. During the test concern was expressed that the boric acid may form complexes with the ammonium and therefore would not be detected by the electrode. The solutions were changed to ammonium nitrate (corrected for ionic strength with sodium sulphate). Table 6.11 is the calculated random and systematic errors for the electrode for the ammonium nitrate solutions for the dynamic tests. Table 6.12 is the calculated random and systematic errors for the electrode for the earlier tests. There was a significant drift (95% confidence) in the calibration over time for the Class 1A site before the membrane was replaced during the Class 3 trials. It can be seen that low  $\text{mV dec}^{-1}$  readings were still recorded. The calculated random and systematic errors (Table 6.8) reflect this situation. The total error (quadrature sum of random and systematic errors) varies considerably for the two sites. Although even the lower values for the Class 1A trial are much higher than those achieved under laboratory conditions. Due to the nature of a Class 1A river there was only slight soiling of the electrode and therefore only limited cleaning was required. Conversely, during the evaluation at the Class 3 river, there was a large build up of foulant in the flow cell and on the electrode. A considerable amount of foulant was removed on each occasion. A difference of up to 20 mV in the reading before and after cleaning was observed. Even though no statistically significant drift in the electrode was identified, the presence of the foulant on the electrode membrane could be expected to affect the performance of the membrane.

For the other field tests there was no drift (95% confidence) in the millivolt per decade although it can be seen that for all the tests the value fluctuates during the test period. During the evaluation some problems were experienced with the reference electrode becoming contaminated with river water.

Data from automatic water quality instrumentation for the field tests shown in Tables B1 to B5. Other water quality parameters were monitored by daily sampling and laboratory analysis these results are provided in tables A1 to A5.

## 8. COST OF OWNERSHIP

Model QSE 334 Ammonium Electrode	£220.00
Model E8098 Double Junction Reference Electrode	£127.00
Set of three replacement membranes for Ammonium Electrode	£145.00

The maintain requirements were low; commissioning and installation took less than an hour, whilst maintenance required daily cleaning were the water quality was poor, the replacement of the membranes simply required the old one to be unscrewed and replaced by the new.

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## **DEFINITIONS AND ABBREVIATIONS**

**Error (of indication) of a measuring instrument (BS 5233):** The indication of a measuring instrument minus the true value of the measurement.

**Response time (WSA/FWR 7-00-02):** The time interval from the instant a step change occurs in the value of the property to be measured to the instant when the change in the indicated value passes (and remains beyond) 90% of its steady state amplitude difference.

**Random Error:** describes the way in which repeated measurements are scattered around a central value. It therefore defines the precision of the instrument.

**Systematic Error (Bias):** is present when results are consistently greater or smaller than the true value. The magnitude and direction of systematic error will depend on the properties of the sample (pH, temperature, turbidity, interfering species).

**Drift:** Change of the indicators of an instrument, for a given level of concentration over a stated period of time under reference conditions which remain constant.

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## **APPENDIX A LABORATORY ANALYSIS OF WATER QUALITY PARAMETERS**

**Table A1 Water Quality Laboratory Analysis Class 1A River**

Date	Time	pH	Sulphate as SO <sub>4</sub> mg l <sup>-1</sup>	Conductivity µS cm <sup>-1</sup>	Copper as Cu µg l <sup>-1</sup>	Ammoniacal N as N mg l <sup>-1</sup>	Nitrite as N mg l <sup>-1</sup>	Chloride as Cl mg l <sup>-1</sup>	Calcium as Ca mg l <sup>-1</sup>	Magnesium as Mg mg l <sup>-1</sup>	Sodium as Na mg l <sup>-1</sup>	Potassium as K mg l <sup>-1</sup>	Nitrate as N mg l <sup>-1</sup>
16/02/93	15:15	8.0	35	543	<5	0.09	<0.05	22	121	3	11	2	5.6
17/02/93	16:50	8.1	32	533	15.3	<0.05	<0.05	21	138	3	11	2	5.4
18/02/93	11:00	8.0	33	532	<5	<0.05	<0.05	22	122	3	11	2	5.4
19/02/93	11:00	8.0	31	532	<5	<0.05	0.05	24	115	3	11	2	5.5
22/02/93	17:00	8.2	29	532	<5	<0.05	<0.05	24	118	3	12	2	5.4
23/02/93	17:15	8.1	146	533	5.6	<0.05	<0.05	24	122	2	11	2	5.4
24/02/93	16:55	8.1	31	540	5.3	<0.05	<0.05	21	117	2	11	2	5.7
25/02/93	10:00	8.0	30	537		<0.05	<0.05	20					5.4
26/02/93	11:00	7.9	31	536		<0.05	<0.05	21					5.4

**Table A2 Water Quality Laboratory Analysis - Class 3 River**

Date	Time	pH	Sulphate as SO <sub>4</sub> mg l <sup>-1</sup>	Conductivity µS cm <sup>-1</sup>	Copper as Cu µg l <sup>-1</sup>	Ammoniacal N as N mg l <sup>-1</sup>	Nitrite as N mg l <sup>-1</sup>	Chloride as Cl mg l <sup>-1</sup>	Calcium as Ca mg l <sup>-1</sup>	Magnesium as Mg mg l <sup>-1</sup>	Sodium as Na mg l <sup>-1</sup>	Potassium as K mg l <sup>-1</sup>	Nitrate as N mg/l mg l <sup>-1</sup>
09/03/93	12:00	7.3	130	928	50.9	4.8	0.47	129	76	18	101	17	14.1
12/03/93	12:00	7.3	131	962		2.8	0.33	148	87	20	112	18	12.7
16/03/93	16:30	7.3	133	925	53	1.9	0.36	127	80	18	103	17	17.5
18/03/93	16:00	7.5	140	987	51	1.7	0.38	148	81	18	110	17	15.5
19/03/93	16:40	7.2	151	960	51	2.0	0.38	142	85	18	105	17	15.8
22/03/93	18:00	7.0	127	800	58	1.7	0.29	130	65	14	86	13	11.4
23/03/93	12:25	7.1	126	894	49	2.0	0.34	135	76	17	92	14	12.1
26/03/93	13:00	7.1	145	989	42	2.0	0.32	153	87	19	109	16	13.4
29/03/93	12:50	7.4	148	927	47	2.4	0.26	134	87	20	93	16	13.4

**Table A3 Water Quality Laboratory Analysis Class 1A River - Recycled Test**

Date	Time	pH	Sulphate as SO <sub>4</sub> mg l <sup>-1</sup>	Conductivity µS cm <sup>-1</sup>	Copper as Cu µg l <sup>-1</sup>	Ammoniacal N as N mg l <sup>-1</sup>	Nitrite as N mg l <sup>-1</sup>	Chloride as Cl mg l <sup>-1</sup>	Calcium as Ca mg l <sup>-1</sup>	Magnesium as Mg mg l <sup>-1</sup>	Sodium as Na mg l <sup>-1</sup>	Potassium as K mg l <sup>-1</sup>	Nitrate as N mg l <sup>-1</sup>
03/04/92	16:30	7.6	42.0	521		0.15	0.021	36.0	105.0	4.0	17.0	4.0	3.99
06/04/92	09:50	7.7	39.0	540		<0.05	0.018	33.0	104.0	4.0	17.0	7.0	5.15
07/04/92	09:30	8.2	-	519		<0.05	0.008	34.0	103.0	4.0	17.0	8.0	5.98
08/04/92	09:32	8.1	-	557		<0.05	0.003	34.0	106.0	4.0	17.0	9.0	5.90
10/04/92	10:23	8.6	41.0	545		<0.05	0.001	33.0	107.0	4.0	17.0	8.0	6.20

Table A4

## Water Quality Laboratory Analysis Class 1A River - Recycled (Doped) Test

Date	Time	pH	Sulphate as SO <sub>4</sub> mg l <sup>-1</sup>	Conductivity µS cm <sup>-1</sup>	Copper as Cu µg l <sup>-1</sup>	Ammoniacal N as N mg l <sup>-1</sup>	Nitrite as N mg l <sup>-1</sup>	Chloride as Cl mg l <sup>-1</sup>	Calcium as Ca mg l <sup>-1</sup>	Magnesium as Mg mg l <sup>-1</sup>	Sodium as Na mg l <sup>-1</sup>	Potassium as K mg l <sup>-1</sup>	Nitrate as N mg l <sup>-1</sup>
27/04/92	09:40	8.7	37.0	562	0.015	<0.05	<0.001	42.0	112.0	4.0	17.0	8.0	6.0
28/04/92	15:40	8.6	37.0	560	0.1	<0.05	0.002	42.0	111.0	4.0	17.0	7.0	6.0
29/04/92	09:35	8.6	35.0	564	0.069	<0.05	0.006	42.0	114.0	4.0	17.0	9.0	7.0
30/04/92	09:30	8.6	36.0	575	0.057	0.57	0.029	47.0	112.0	4.0	17.0	9.0	7.0
01/05/92	09:30	8.7	35.0	574	0.052	0.28	0.125	46.0	113.0	4.0	17.0	9.0	7.1
05/05/92	09:30	8.6	36.0	583	0.043	<0.05	0.001	49.0	113.0	4.0	17.0	9.0	7.3
06/05/92	11:30	8.6	33.6	578	0.049	<0.05	0.005	49.0	120.0	4.0	19.0	10.0	5.4
08/05/92	09:50	8.6	36.0	590	0.048	<0.05	0.001	51.0	121.0	4.0	19.0	10.0	7.3

**Table A5 Water Quality Laboratory Analysis Class 1A River - Intermittent Test**

Date	Time	pH	Sulphate as SO <sub>4</sub> mg l <sup>-1</sup>	Conductivity µS cm <sup>-1</sup>	Copper as Cu µg l <sup>-1</sup>	Ammoniacal N as N mg l <sup>-1</sup>	Nitrite as N mg l <sup>-1</sup>	Chloride as Cl mg l <sup>-1</sup>	Calcium as Ca mg l <sup>-1</sup>	Magnesium as Mg mg l <sup>-1</sup>	Sodium as Na mg l <sup>-1</sup>	Potassium as K mg l <sup>-1</sup>	Nitrate as N mg l <sup>-1</sup>
20/05/92	11:10	8.8	49	442	<7	<0.05	0.020	25	97	3	15	2	1.8
21/05/92	09:30	8.6	34	459	<0.1	<0.06	0.026	25	106	3	17	3	1.8
22/05/92	10:00	8.3	27		<1	<0.05	0.028	25	98	3	16	3	2
26/05/92	11:10	8.2	24	468	<7	<0.05	0.032	24	99	2	15	3	2
27/05/92	09:40	8.2	25	470	<1	<0.05	0.038	23	104	3	15	1	2.10
28/05/92	09:20	8.1	276	474	<7	<0.05	0.018	23	102	3	15	2	2.0
29/05/92	11:00	8.0	20.6	476	<8	0.10	0.066	23	99	3	15	3	2.2

## APPENDIX B WATER QUALITY DATA





Table B.1 Class I River Data

DATE	Number of Readings	Dissolved Oxygen mg l <sup>-1</sup>				Temperature °C				pH				Conductivity µS				Turbidity FTU			
		Mean	Sd	Min	Max	Mean	Sd	Min	Max	Mean	Sd	Max	Min	Mean	Sd	Min	Max	Mean	Sd	Min	Max
10/02/93	395	12.03	0.03	11.96	12.07	7.55	0.08	7.43	7.68	8.33	0.01	8.32	8.34	503.9	0.6	502.6	504.9	7.67	0.32	7.11	10.51
11/02/93	1412	12.17	0.48	7.01	12.71	7.20	0.24	6.97	9.80	8.31	0.03	8.19	8.40	490.4	76.8	6.3	520.6	8.22	2.48	0	67.00
12/02/93	1440	12.41	0.05	12.31	12.92	6.95	0.08	6.87	8.17	8.28	0.01	8.15	8.40	498.6	40.3	7.0	503.4	8.03	4.11	0	96.32
13/02/93	1440	12.40	0.04	12.25	12.84	7.18	0.16	6.99	8.47	8.27	0.01	8.18	8.43	499.0	40.5	7.0	505.0	6.20	0.96	0	13.16
14/02/93	1440	12.39	0.06	12.29	12.85	7.15	0.08	7.04	8.18	8.27	0.01	8.17	8.43	499.8	40.4	7.0	505.0	6.05	1.02	0	13.54
15/02/93	1440	12.47	0.07	12.25	12.85	7.15	0.21	6.82	8.69	8.27	0.02	8.19	8.44	498.4	40.3	6.9	507.5	6.49	3.57	0	100.89
16/02/93	1440	12.31	0.08	12.11	12.43	7.76	0.27	7.40	8.15	8.26	0.01	8.24	8.29	501.6	0.9	499.1	503.7	7.95	3.94	1.03	100.66
17/02/93	1243	12.08	0.06	11.93	12.59	8.44	0.24	8.15	9.63	8.26	0.01	8.18	8.40	497.9	43.4	6.7	503.7	7.50	1.88	0	35.23
18/02/93	846	11.90	0.36	7.80	12.03	8.88	0.55	8.58	18.06	8.27	0.01	8.05	8.36	497.7	50.6	7.7	522.7	7.96	3.26	0	54.28
19/02/93	1440	12.09	0.12	11.88	12.25	8.15	0.22	7.69	8.58	8.27	0.01	8.22	8.29	500.9	1.8	497.7	503.3	7.48	2.67	0	40.38
20/02/93	1440	12.34	0.27	8.08	12.55	7.40	0.17	7.14	9.59	8.28	0.01	8.24	8.35	497.4	15.6	276.1	509.0	7.09	3.63	0	48.61
21/02/93	1440	12.35	0.25	8.27	12.51	7.16	0.20	6.87	9.06	8.26	0.01	8.22	8.30	497.2	2.2	484.5	522.9	8.06	5.78	1.98	64.74
22/02/93	1440	12.48	0.26	8.43	12.66	6.81	0.18	6.48	8.27	8.27	0.01	8.24	8.29	496.2	2.0	487.7	522.3	6.05	3.18	0	100.87
23/02/93	1440	12.47	0.24	8.43	12.61	6.98	0.26	6.55	8.29	8.27	0.01	8.22	8.29	495.0	1.8	483.7	519.6	6.73	5.37	4.74	70.98
24/02/93	1440	12.40	0.09	12.26	13.07	7.42	0.28	7.07	9.98	8.26	0.02	8.17	8.38	493.3	40.0	7.3	498.6	5.52	1.86	0	65.24
25/02/93	1440	12.24	0.07	12.12	12.86	7.70	0.15	7.50	10.53	8.27	0.01	8.18	8.40	493.4	40.1	7.4	499.4	5.69	2.54	1.01	84.82
26/02/93	1440	12.16	0.07	12.05	12.80	7.48	0.22	7.03	10.29	8.27	0.01	8.17	8.38	494.0	40.0	7.5	499.7	5.97	3.93	2.14	64.43
27/02/93	1440	12.48	0.18	12.20	13.27	6.62	0.25	6.10	9.02	8.27	0.02	8.14	8.36	489.1	40.0	7.5	495.1	6.46	5.01	2.69	71.77
28/02/93	1440	12.87	0.16	12.62	13.62	5.49	0.26	5.03	7.65	8.29	0.02	8.13	8.38	487.6	39.5	8.0	493.0	5.69	4.71	3.28	60.18
01/03/93	1440	13.01	0.08	12.79	13.55	5.01	0.19	4.71	6.13	8.29	0.02	8.12	8.34	486.6	39.3	8.0	492.6	4.73	1.34	3.49	43.12
02/03/93	665	12.80	0.12	10.47	12.88	5.10	1.02	4.99	5.25	8.28	0.01	8.23	8.31	491.8	1.1	487.1	506.4	4.09	4.14	3.42	86.25

**Table B.4 Class 1 River Data - Recycled Test**

DATE	Number of Readings	Dissolved Oxygen mg l <sup>-1</sup>		Oxygen		Temperature °C				pH				Conductivity µS				Turbidity FTU			
		Mean	Sd	Min	Max	Mean	Sd	Min	Max	Mean	Sd	Max	Min	Mean	Sd	Min	Max	Mean	Sd	Min	Max
04/04/92	1428	10.22	0.04	10.03	10.32	19.22	0.47	18.56	19.96	8.66	0.03	8.59	8.72	569.9	0.77	559.8	570.6	2.56	1.24	0.71	13.58
05/04/92	1428	9.11	0.07	9.00	9.26	19.23	0.41	18.48	19.82	8.71	0.02	8.68	8.75	570.8	1.36	567.4	574.4	0.22	0.36	0.00	1.00
06/04/92	1428	8.87	0.09	8.69	9.03	19.66	0.39	19.00	20.2	8.59	0.15	7.00	9.29	567.2	1.52	563.4	570.5	0.16	0.37	0.00	4.90
07/04/92	549	9.18	0.04	9.03	9.24	20.13	0.64	18.89	20.93	8.68	0.03	8.61	8.73	561.2	1.50	557.9	564.0	0.17	0.39	0.00	3.74
08/04/92	1428	9.06	0.05	8.99	9.22	19.97	0.16	19.45	20.24	8.69	0.02	8.65	8.73	554.9	1.49	550.7	558.3	0.18	0.44	0.00	7.54
09/04/92	1428	8.74	0.21	6.03	8.84	19.74	0.47	18.68	20.66	8.70	0.05	8.61	8.77	499.4	45.81	3.7	517.0	3.94	0.87	2.23	14.08
10/04/92	1427	9.16	0.09	9.01	9.29	17.65	0.31	17.29	18.67	8.68	0.04	8.58	8.76	575.2	0.43	573.8	575.7	0.27	0.47	0.00	5.24
11/04/92	711	9.23	0.01	9.18	9.25	17.23	0.05	17.16	17.4	8.78	0.01	8.76	8.83	534.5	0.56	532.8	535.8	0.15	0.37	0.00	5.53
12/04/92	1205	9.09	0.08	8.99	9.24	18.96	0.24	18.58	19.52	8.70	0.03	8.62	8.77	548.9	3.38	544.1	554.4	0.32	0.42	0.00	4.48
13/04/92	578	9.46	0.14	9.22	9.65	18.35	0.62	17.59	19.45	8.77	0.00	8.77	8.79	542.1	4.04	534.3	549.1	0.02	0.25	0.00	0.37

**Table B.5 Class 1 River Data - Recycled (Doped) Test**

DATE	Number of Readings	Dissolved Oxygen mg l <sup>-1</sup>				Temperature °C				pH				Conductivity µS				Turbidity FTU			
		Mean	Sd	Min	Max	Mean	Sd	Min	Max	Mean	Sd	Max	Min	Mean	Sd	Min	Max	Mean	Sd	Min	Max
22/04/92	549	10.22	0.04	10.03	10.32	20.13	0.64	18.89	20.93	8.81	0.00	8.81	8.84	602.4	2.0	597.2	606.61	0.08	0.29	0.00	2.35
23/04/92	874	10.22	0.24	3	10.36	20.62	0.21	20.26	20.97	8.66	0.03	8.59	8.72	586.5	0.4	585.3	587.95	0.42	0.39	0.00	5.27
24/04/92	1423	10.09	0.05	9.98	10.16	19.76	0.16	19.58	20.12	8.71	0.01	8.68	8.75	569.9	0.7	559.8	570.6	0.12	0.34	0.00	1.34
25/04/92	1054	10.52	0.09	10.32	10.64	19.55	0.03	19.5	19.63	8.75	0.05	8.67	8.82	602.0	20.3	1.0	606.06	2.56	1.24	0.71	13.58
26/04/92	1440	10.49	0.08	10.18	10.65	19.76	0.06	19.64	19.86	8.71	0.05	8.61	8.79	584.7	3.7	567.7	589.48	0.46	0.61	0.00	3.84
27/04/92	1424	10.16	0.16	9.86	10.39	21.58	0.20	21.36	22.05	8.79	0.01	8.77	8.81	572.5	1.0	570.5	574.73	0.08	0.29	0.00	1.44
28/04/92	1232	10.32	0.06	10.16	10.4	20.32	0.71	0.00	20.77	8.80	0.00	8.80	8.81	603.6	1.5	600.8	606.18	0.93	0.45	0.22	4.37
29/04/92	1310	10.36	0.03	10.29	10.42	19.58	0.29	18.8	20.00	8.69	0.13	6.06	8.76	586.4	3.7	581.8	592.53	1.01	1.15	0.00	10.01
30/04/92	701	10.48	0.03	10.42	10.53	21.34	0.67	20.49	22.58	8.72	0.03	8.67	8.78	583.0	1.6	570.4	584.44	0.19	0.22	0.00	1.32
01/05/92	15	10.14	0.00	10.14	10.15	20.21	0.22	19.92	20.79	8.73	0.26	1.00	8.79	606.9	0.1	606.7	607.23	0.09	0.31	0.00	1.36
02/05/92	1418	9.826	0.12	9.56	9.98	19.91	0.23	19.62	20.3	8.72	0.04	8.64	8.8	595.3	33.3	6.3	606.18	0.72	0.39	0.19	1.88
03/05/92	908	10.56	0.01	10.53	10.59	22.64	0.43	22.03	23.39	8.70	0.02	8.63	8.76	583.4	0.5	581.9	584.53	1.63	1.14	0.00	14.1
04/05/92	1313	10.11	0.16	7.03	10.35	21.43	0.00	21.43	21.44	8.77	0.02	8.71	8.8	608.7	1.3	606.3	612.03	0.10	0.23	0.00	0.36
05/05/92	825	9.73	0.08	9.58	9.92	21.15	0.46	20.17	21.68	8.78	0.00	8.78	8.79	613.9	2.5	609.4	617.43	0.16	0.19	0.00	0.94
06/05/92	1428	10.14	0.11	9.98	10.31	22.79	0.37	21.95	23.38	8.79	0.01	8.76	8.84	616.0	1.1	613.1	617.61	0.47	0.30	0.00	0.98
07/05/92	1169	10.30	0.04	10.15	10.45	21.38	0.42	20.73	22.06	8.81	0.01	8.76	8.83	614.8	1.3	611.7	616.72	0.69	0.35	0.20	2.81
08/05/92	339	10.46	0.03	10.39	10.5	20.27	0.25	20.05	21.06	8.76	0.02	8.71	8.8	616.9	0.5	615.6	618.87	0.30	0.50	0.00	2.96

## APPENDIX C

## MANUFACTURER'S SPECIFICATION

Manufacturer	EDT instruments Ltd. Lorne Rd Dover Kent CT16 2AA
Concentration range (as $\text{NH}_4^+$ )	$10^{-6}\text{M}$ to $10^{-1}\text{M}$ 0.02 mg/l to 1.8g/l
Linear detection limit	$10^{-5}\text{M}$ 0.18 mg/l
mV/decade	$56 \pm 2$ mV
pH range	5 - 8
Potential drift	1 - 2 mV/day
Selectivity Coefficients Ratio (maximum level)	Potassium $1.2 \times 10^{-1}$ Sodium $2.0 \times 10^{-3}$ Rubidium $4.3 \times 10^{-2}$ Cesium $4.8 \times 10^{-3}$ Lithium $4.2 \times 10^{-3}$ Magnesium $2.0 \times 10^{-4}$
Response time	up to 3 min.
Temperature range	0-50 deg °C