

The Evaluation of a Philips Ammonium Ion Selective Electrode

WRc plc

Evaluation Report 200/14/T



NRA

National Rivers Authority

THE EVALUATION OF A PHILIPS AMMONIUM ION SELECTIVE ELECTRODE

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CONTENTS	Page
EXECUTIVE SUMMARY	1
KEY WORDS	1
1. INTRODUCTION	3
2. DETAILS OF EQUIPMENT EVALUATED	5
3. MAJOR FINDINGS AND COMMENTS	7
4. EVALUATION PROCEDURES	9
4.1 Signal Processing	9
4.2 Laboratory	9
4.3 Field Trails	11
5. OBSERVATIONS	13
5.1 Documentation	13
5.2 Design and Construction	13
5.3 Installation	13
5.4 Commissioning	13
5.5 Maintenance and Downtime	14
5.6 Ease of Use	14
6. RESULTS	15
7. INSTRUMENT BEHAVIOUR	23
8. COST OF OWNERSHIP	27
ACKNOWLEDGEMENTS	29
DEFINITIONS AND ABBREVIATIONS	31
REFERENCES	33
APPENDIX A	
LABORATORY ANALYSIS OF WATER QUALITY DATA	35
APPENDIX B	
FIGURES	43

CONTENTS (continued)

Page

APPENDIX C

MANUFACTURER'S SPECIFICATION

51

LIST OF TABLES

		Page
6.1	Flow at sensor surface	15
6.2	Response time	15
6.3	Interference	16
6.4	Electrode separation	16
6.5a	Accuracy tests 1 - 5	17
6.5b	Accuracy tests 6 - 10	17
6.5c	Summary of Accuracy tests 1 -5	18
6.5d	Summary of Accuracy tests 6 - 10	18
6.6	Calibration check dynamic river conditions Class 1A river	19
6.7	Calibration check dynamic river conditions Class 3 river	19
6.8	Calibration check recycled river conditions Class 1A river	20
6.9	Calibration check recycled (Doped) river conditions Class 1A river	20
6.10	Calibration check intermitant river conditions Class 1A river	21
6.11	Calculated random and systematic errors field trials	21
6.12	Calculated random and systematic errors repeat field trials	22

EXECUTIVE SUMMARY

This report describes the results of an evaluation of a Philips 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 clear and well written with instructions for installation, operation and storage. The maintenance requirements of the electrode were low, being a sealed unit, except under certain field conditions, where the water quality was sufficiently poor to necessitate regular cleaning of the electrode to remove foulant.

Laboratory trials to determine sensor accuracy established that the total error (quadrature sum of random and systematic errors) for five test concentrations varied between 0.01 and 0.27 mg l⁻¹ NH₄⁺.

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. It was therefore agreed that the field trials would be repeated. The total error (quadrature sum of random and systematic errors) varied between 0.16 mg l⁻¹ and 1.44 mg l⁻¹.

The Philips Model R9436 094 75253 ammonium electrode cost £396.75, the Philips Model R9436 095 82053 RE15 Double junction reference electrode cost £110.25. The maintenance requirement was replenishing the fill solutions. Replacement of the membrane was necessary on two occasions during the evaluation. This required the electrode to be dismantled. The complete process took about an hour.

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

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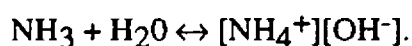
1. INTRODUCTION

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;

- a 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 (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:	Philips Scientific
Supplier:	Philips Scientific York Street Cambridge CB1 2PX
	Tel: 0223 358880 Fax: 0223 374250
Instrument Description:	Ion Selective Electrode - Ammonium (IS 561-NH ₄ ⁺)

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 documentation was clearly written and included diagrams to illustrate the procedure for dismantling and re-assembling the electrode. Information was provided on the intended use of the electrode, recommendations for storage, chemical inertness, trouble-shooting, the operation life span of the electrode

The laboratory trials on accuracy established that the electrode showed good accuracy and precision for the higher concentrations of ammonium tested which were in agreement with manufacturers stated level of reproducibility. However, this level of reproducibility is based on readings taken for concentrations at a higher level than those of interest to this evaluation. At the lower concentrations tested the findings were not in agreement with the manufacturer's specification even though the levels were within the stated range of the electrode.

There was a correlation (95% confidence level) between speed of flow at the sensor surface and the electrode output when low concentrations of ammonium were being tested.

The response time of the electrode varied depending on the direction of the concentration step change. A change from a low to a high concentration required five seconds before stability was achieved, however for the change from a high to a low concentration this time was almost five times longer. This was within the response time of 30 seconds specified by the manufacturer.

The electrode was found to be very susceptible to interference from the chemical species tested. Potassium, sodium, calcium and aluminium all caused some interference with potassium causing the highest level.

The field evaluation of the ammonium electrode identified a problem with the equipment employed in this evaluation. This evaluation was intended to test a component of a monitoring system however 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.

A second problem of a possibly faulty reference electrode required some of the field trials to be repeated. The dynamic flow regimes at both the Class 1A and Class 3 sites were repeated. All the field readings were susceptible to the interference and, therefore, the time spent under field conditions could only be seen as a 'conditioning' period enabling the performance of the electrode to be determined by the calibration data.

The total error (quadrature sum of random and systematic errors) for the dynamic tests were similar for both sites, Class 1A 0.14 and 0.16 mg l⁻¹ at a test level of 0.5 mg l⁻¹ NH₄⁺. Whilst at the higher test level, of 5.0 mg l⁻¹ NH₄⁺ the total errors were 0.65 for Class 1A river and 1.44 mg l⁻¹ for the Class 3A river. Similar total errors were seen for all the water supply test regimes. There was also no significant drift (95% confidence) drift in any of the calibrations over the evaluation period. 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.

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 a Philips Double junction reference 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 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 mg l^{-1} ammonium ions ($2.97 \text{ mg l}^{-1} \text{ NH}_4\text{Cl}$) in 0.1N 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 0.1N 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 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 mg l^{-1} ($0.297 \text{ mg l}^{-1} \text{ NH}_4\text{Cl}$) and 1.0 mg l^{-1} ($2.97 \text{ mg l}^{-1} \text{ NH}_4\text{Cl}$), with all solutions prepared in 0.1N boric acid. Readings were taken for each level of ammonium ion with the addition of the following:

- no interferent,
- 100 mg l^{-1} of potassium chloride,
- 100 mg l^{-1} of sodium chloride,
- 400 mg l^{-1} of calcium chloride,
- 400 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 mg l⁻¹ of (hydrated) aluminium chloride (AlCl₃.6H₂O),

18100 mg l⁻¹ of (hydrated) aluminium chloride (AlCl₃.6H₂O)

no interferent.

4.2.4 Electrode Separation

The electrode was placed in a stirred solution of 0.1 mg l⁻¹ NH₄⁺ (0.297 NH₄Cl) 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⁻¹ NH₄Cl (0.1 mg l⁻¹ NH₄⁺),

1.48 mg l⁻¹ NH₄Cl (0.5 mg l⁻¹ NH₄⁺),

2.97 mg l⁻¹ NH₄Cl (1.0 mg l⁻¹ NH₄⁺),

14.86 mg l⁻¹ NH₄Cl (5.0 mg l⁻¹ NH₄⁺),

29.72 mg l⁻¹ NH₄Cl (10.0 mg l⁻¹ NH₄⁺).

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⁻¹ 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 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 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

The documentation consisted of an instruction booklet for the ammonium electrode and a leaflet for the reference electrode. The ammonium instruction manual was clearly written and included diagrams to illustrate the procedure for dismantling and re-assembling the electrode. Information was provided on the intended use of the electrode, recommendations for storage, chemical inertness, trouble-shooting, the operation life span of the electrode and a general specification including a definition of terms used. In addition, selectivity coefficients for 10 commonly encountered interfering ions were provided.

Although the leaflet provided with the reference electrode did not refer specifically to the RH44/2-SD-1 ground glass sleeve reference electrode recommended in the ammonium electrode manual, adequate information was provided.

5.2 Design and Construction

The electrode has an opaque plastics casing, at one end is the ion selective membrane and at the other is a standard O-size Lemo socket for the signal cable. It uses a liquid fill solution and has a replaceable membrane. Both end pieces can be removed to give access to the membrane and the inner glass cell which contains the fill solution and the electrode. The component parts seem well made and fit together easily; the membrane being held in place by a well fitting packing piece.

The reference electrode provided was a Philips double junction glass reference electrode. It had two fill holes near the top of the electrode and had a ground glass collar to form the active surface.

5.3 Installation

The ammonium electrode requires a stable reference voltage generated by another probe which is unaffected by the presence of ammonium ions. This can be a supplied reference electrode or a pH electrode. The manufacturer provided a double junction reference electrode which was used.

5.4 Commissioning

Before use the electrode needs to be filled and assembled. This requires careful handling of the membrane and glass components, but all necessary tools are provided and the instructions are clear. Once assembled the probe is easy to install and use.

Prior to use the electrode needs to be immersed in 10^{-3} molar NH_4^+ for at least 1 hour.

5.5 Maintenance and Downtime

The membrane was replaced at an early stage in the evaluation. During the field tests it is thought that the replacement membrane also failed. The reference electrode design was found to be unsuitable for field conditions. The glass collar of the electrode could be lifted by a high water flow which meant that the fill solution was lost. In these circumstances it was necessary to constantly replenish the electrode filling solution.

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 fouling was easily removed by washing with de-ionised water and gentle wiping with a tissue. The manufacturer gave no guidance on the removal of foulant. 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 assembling of the electrode required great care and attention to detail to insure that functioned correctly. Once assembled the electrode was easy to use and maintain.

6. RESULTS

Table 6.1 Flow at sensor surface

Stirrer Speed Setting	Electrode	Output	(mV)
	0.1 mg l ⁻¹ NH ₄ ⁺	5.0 mg l ⁻¹ NH ₄ ⁺	0.1 mg l ⁻¹ NH ₄ ⁺ +2.5 g l ⁻¹ Kaolin
0	-83.8	-20.5	-
3	-82.5	-19.6	-65.5
4	-81.9	-19.6	-
5	-81.5	-19.4	-
7	-80.7	-19.0	-
10	-80.2	-19.1	-63.6
0	-80.7	-19.6	-65.0

Table 6.2 Response time

	Step Change	Response Time
Rising Average	0.1 - 5.0 mg l ⁻¹ NH ₄ ⁺	5 ± 1 sec.
Falling Average	5.0 - 0.1 mg l ⁻¹ NH ₄ ⁺	24 ± 2 sec.
Air to 0.1 mg l ⁻¹ NH ₄ ⁺		< 1 sec.

Table 6.3 Interference

Solution	Electrode 0.1 mg l ⁻¹ NH ₄ ⁺	Output	Change 1.0 mg l ⁻¹ NH ₄ ⁺	(mV)
reference + reference + reference + reference + *reference reference + reference + reference	100 mg l ⁻¹ of KCl 100 mg l ⁻¹ of NaCl 400 mg l ⁻¹ of CaCl ₂ 400 mg l ⁻¹ of MgCl ₂ 724 mg l ⁻¹ of AlCl ₃ .6H ₂ O 18100 mg l ⁻¹ of AlCl ₃ .6H ₂ O (after 70 mins settling)	-30.0 -107.1 -119.1 -117.7 -109.1 -111.0 -102.9 -126.8	85.6 8.5 -3.5 -2.1 6.5 7.8 15.9 -8.0	

* New reference solutions

Table 6.4 Electrode separation

Electrode - Reference Separation mm	Electrode Output (mV) 0.1 mg l ⁻¹ NH ₄ ⁺
20	-73.9
90	-74.0

Table 6.5a Accuracy tests 1 - 5

Actual mg l ⁻¹ NH ₄ ⁺	Test 1	Test 2	Test 3	Test 4	Test 5	Mean	Standard Deviation
0.1	-112.0	-104.7	-102.7	-107.9	-103.3	-106.12	3.30
0.5	-69.0	-69.1	-68.3	-69.2	-68.7	-68.86	0.33
1.0	-49.4	-48.4	-48.2	-51.20	-50.70	-49.58	1.2
5.0	-12.0	-10.9	-10.8	-10.7	-10.2	-10.92	0.59
10.0	5.3	6.2	5.8	6.9	6.8	6.2	0.06
mV dec ⁻¹	58.39	55.86	54.77	57.44	55.92	56.48	1.28

Table 6.5b Accuracy tests 6 - 10

Actual mg l ⁻¹ NH ₄ ⁺	Test 6	Test 7	Test 8	Test 9	Test 10	Mean	Standard Deviation
0.1	-104.2	-102.0	-99.7	-106.1	-104.1	-103.2	2.19
0.5	-64.9	-65.0	-65.0	-66.0	-66.1	-65.4	0.53
1.0	-46.7	-47.3	-47.4	-48.8	-48.9	-47.8	0.87
5.0	-7.7	-8.0	-8.1	-8.3	-8.4	-8.1	0.24
10.0	9.7	9.5	8.9	8.9	8.9	9.18	0.35
mV dec ⁻¹	56.95	55.92	54.74	57.55	56.71	56.37	0.97

Table 6.5c Summary of Accuracy tests 1 - 5

	NH ₄ ⁺ mg l ⁻¹				
	0.1	0.5	1	5	10
Mean	0.13	0.52	1.10	5.13	10.07
Systematic Error	-0.03	-0.02	-0.10	-0.13	-0.07
Random Error	0.01	0.01	0.07	0.06	0.21
Total Error	0.03	0.02	0.12	0.15	0.22

Table 6.5d Summary of Accuracy tests 6 - 10

	NH ₄ ⁺ mg l ⁻¹				
	0.1	0.5	1	5	10
Mean	0.11	0.48	0.97	4.86	9.76
Systematic Error	-0.01	0.02	0.03	0.14	0.24
Random Error	0.01	0.01	0.03	0.04	0.12
Total Error	0.01	0.02	0.05	0.15	0.27

Table 6.6 Calibration check dynamic river conditions Class 1A river

Date	Time	Ammonium Chloride + Boric Acid			Ammonium Nitrate + Sodium Sulphate		
		0.5 mg l ⁻¹ NH ₄ ⁺ (mV)	5.0 mg l ⁻¹ NH ₄ ⁺ (mV)	mV dec ⁻¹	0.5 mg l ⁻¹ NH ₄ ⁺ (mV)	5.0 mg l ⁻¹ NH ₄ ⁺ (mV)	mV dec ⁻¹
15/2/93	16:30	-65.9	2.9	69.6	-	-	-
16/2/93	15:24	-53.5	3.9	57.4	-	-	-
17/2/93	16:52	-59.7	4.9	54.8	-	-	-
18/2/93	11:00	-58.0	2.9	60.0	-	-	-
19/2/93	17:00	-57.2	4.5	61.7	-	-	-
22/2/93	16:45	-62.2	7.3	69.5	-	-	-
23/2/93	16:40	-63.9	5.2	69.1	-36.5	12.1	48.6
24/2/93	17:15	-62.50	8.7	71.2	-41.6	12.1	53.7
25/2/93	14:50	-64.7	-3.1	61.6	-52.1	2.2	54.3
26/2/93	10:40	-76.5	2.8	79.3	-41.0	8.8	49.8

Table 6.7 Calibration check dynamic river conditions Class 3 river

Date	0.5 mg l ⁻¹ NH ₄ ⁺ (mV)	5.0 mg l ⁻¹ NH ₄ ⁺ (mV)	mV dec ⁻¹
16/3/93	-61.9	-9.8	52.1
18/3/93	-68.9	-15.7	53.2
19/3/93	-69.4	-16.8	52.6
22/3/93	-74.0	-18.0	56.0
23/3/93	-71.1	-18.2	52.9
26/3/93	-70.9	-18.0	52.9
29/3/93	-70.4	-17.9	52.5

Table 6.8

Calibration check Recycled river conditions Class 1A river

Date	0.5 mg l ⁻¹ NH ₄ ⁺ (mV)	5.0 mg l ⁻¹ NH ₄ ⁺ (mV)	mV dec ⁻¹
03/04/92	-52.6	0.7	53.3
06/04/92	-70.9	0.5	71.4
07/04/92	-108.1	-0.4	70.5
08/04/92	-112.6	-0.1	112.5
10/04/92	-75.0	4.4	79.4

Table 6.9

Calibration check Recycled (Doped) river conditions Class 1A river

DATE	0.5 mg l ⁻¹ NH ₄ ⁺ (mV)	5.0 mg l ⁻¹ NH ₄ ⁺ (mV)	mV dec ⁻¹
27/04/92	-24.6	19	43.6
28/04/92	-7.5	28.4	35.9
29/04/92	3.9	28.4	24.5
30/04/92	23.7	36.6	12.9
01/05/92	27.2	35.2	8.0
05/05/92	18.4	23.0	4.6
06/05/92	12.0	14.2	2.2
08/05/93	19.3	25.3	6.0

Table 6.10 Calibration check Intermittent river conditions Class 1A river

DATE	0.5 mg l ⁻¹	5.0 mg l ⁻¹	mV dec ⁻¹
	NH ₄ ⁺	NH ₄ ⁺	
	(mV)	(mV)	
20/05/92	-44.0	6.1	50.1
21/05/93	-35.5	13.0	48.5
26/05/92	-60.1	-0.7	59.4
27/05/92	-66.4	-1.7	64.7
29/05/92	-80.5	-3.0	77.5

Table 6.11 Random and Systematic Errors

Test	Class 1A		Class 3	
	NH ₄ ⁺ 0.5 mg l ⁻¹	NH ₄ ⁺ 5.0 mg l ⁻¹	NH ₄ ⁺ 0.5 mg l ⁻¹	NH ₄ ⁺ 5.0 mg l ⁻¹
Mean	0.61	5.27	0.34	3.57
Random Error	-0.11	-0.27	0.16	1.43
Systematic Error	0.08	0.59	0.03	0.16
Total Error	0.14	0.65	0.16	1.44
Sample Size	8	8	6	6

Table 6.12 **Calculated random and systematic errors**

Test	Recycled	Undoped	Recycled	Doped	Intermittent	
	NH ₄ ⁺ 0.5 mg l ⁻¹	NH ₄ ⁺ 5.0 mg l ⁻¹	NH ₄ ⁺ 0.5 mg l ⁻¹	NH ₄ ⁺ 5.0 mg l ⁻¹	NH ₄ ⁺ 0.5 mg l ⁻¹	NH ₄ ⁺ 5.0 mg l ⁻¹
Mean	0.20	4.89	3.77	7.98	0.41	4.75
Random Error	0.30	0.11	-3.27	-2.98	0.09	0.25
Systematic Error	0.22	0.11	2.68	3.30	0.26	1.56
Total Error	0.37	0.16	4.23	4.45	0.27	1.58
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.

The manufacturer did not state the recommended separation between the ion selective electrode and the reference electrode. Table 6.5 shows the output of the ion selective electrode when placed at distances of 20 mm and 90 mm from the reference electrode. The data shows that the distance between the electrodes has little effect on the output. The difference recorded (0.1 mV) is less than the overall reproducibility (± 0.5 mV) quoted in the specification.

Table 6.2 shows the effect of varying the sample flow at the electrode surface. A correlation coefficient was calculated to determine the extent of any relationship between flow at the sensor surface and the millivolt output. The strength of the correlation is determined by how close the calculated statistic (r) is to 1 (or -1). For this relationship it was discovered that flow did have a significant (95% confidence limit) effect on sensor output at the lower ammonium concentration tested (0.1 mg/l NH_4^+), whilst at the higher concentration level (5 mg/l NH_4^+) it was not significant. The addition of kaolin appeared to have no effect. A correlation was not calculated for this test due to the small sample size.

The response time of the electrode (table 6.3) varied considerably depending on the direction of the change in ammonium level. With a change from a low concentration (0.1 mg/l NH_4^+) to a higher concentration (0.5 mg/l NH_4^+) the time required to complete 90% of the step change was 5 (± 1) seconds. However, for the reverse case, the response time was nearly four times longer, at 24 (± 2) seconds. A step change from air to 0.1 mg/l NH_4^+ was found to be less than 1 second.

Previous assessments of ammonium ion selective electrodes have shown that they are susceptible to interference from other ionic species, particularly potassium and sodium ions. Table 6.4 shows the change in electrode response following the addition of various ionic species. It can be seen that potassium has 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 the corresponding equivalent ammonium level. This has been achieved by applying the calibration curve calculated from the results in table (6.6). The addition of 100 mg/l of KCl (48 mg/l K^+) would produce a theoretical ammonium level of approximately 3.3 mg/l at 0.1 mg/l NH_4^+ , whilst at 1.0 mg/l NH_4^+ this would be 3.8 mg/l NH_4^+ . This is in agreement with the manufacturer's specification.

Other interferents tested had considerably less effect on the output however they were nearly all outside of the quoted reproducibility of the electrode and would therefore cause an error in any readings. It was also noted that after exposure to aluminium chloride the electrode required a long recovery period before the output returned to the original reference solution level.

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 0.01 and

0.27 mg/l NH₄⁺.

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. The total error (quadrature sum of random and systematic errors) for the dynamic data is similar for all the field trials, except for the doped recycled test this was thought to be due to the failure of the membrane. The membrane was replaced before the next trial. A correlation coefficient calculated for mV against time for the two test concentrations shown that there was no significant (95% confidence) drift in the calibration during the field trials.

During the first field trials it was noted that the reference electrode required frequent refilling. This was thought to be caused by the ground glass sleeve of the reference electrode lifting away from the main body of the electrode due to a changes in water flow rate. This resulted in a loss of the reference solution.

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.

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

Philips Model R9436 094 75253 Ammonium electrode	£396.75
Philips Model R9436 095 82053 RE 15 Double junction reference electrode	£103.25
Set of four membranes	£126.50

The maintenance requirement was replenishing the fill solutions. Replacement of the membrane was necessary on two occasions during the evaluation. This required the electrode to be dismantled. The complete process took about an hour.

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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 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
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 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
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 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
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 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
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 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
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 FIGURES

Table B.1 Class 1 River Data

DATE	Number of Readings	Dissolved Oxygen mg l ⁻¹				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.2 Class 3 River Data

DATE	Number of Readings	Dissolved Oxygen mg l ⁻¹				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
18/03/93	31	58.5	0.5	57.6	59.2	10.6	0.1	10.5	10.8	7.3	0.1	7.2	7.4	884.4	7.0	876.0	894.0	20.5	8.8	17.9	67.6
19/03/93	28	72.5	0.5	71.9	73.5	10.5	0.1	10.4	10.6	7.2	0.0	7.2	7.4	872.9	5.2	865.0	882.3	19.8	0.6	18.6	22.0
22/03/93	31	56.6	1.0	54.5	58.0	10.3	0.2	10.1	10.5	7.2	0.0	7.2	7.3	738.8	7.3	724.9	748.1	92.3	4.1	87.0	99.3
23/03/93	6	55.5	7.1	46.1	60.6	8.7	0.4	8.1	9.0	7.4	0.1	7.2	7.4	811.9	6.9	803.0	816.9	178.8	23.7	147.4	200.0

Table B.3

Class 1 River Data - Intermittent Test

DATE	Number of Readings	Dissolved Oxygen mg l ⁻¹				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
19/05/92	158	11.90	0.33	11.32	12.37	21.02	0.64	19.95	22.01	8.29	0.06	8.18	8.46	465.8	2.6	459.5	471.4	7.16	1.92	1.49	14.22
20/05/92	634	10.44	0.98	8.61	11.64	19.49	0.68	18.51	20.48	8.63	0.07	8.5	8.76	458.5	1.6	455.7	461.4	7.89	1.93	5.52	14.47
21/05/92	624	8.67	0.68	7.53	9.64	20.06	0.74	19	21.64	8.82	0.05	8.75	8.91	455.6	33.9	1.53	470.5	5.00	2.35	1.41	30.35
22/05/92	626	10.74	0.92	9.04	11.82	20.50	0.47	19.7	21.28	8.37	0.05	8.28	8.46	454.5	52.5	1.07	470.5	6.76	1.99	0.00	19.87
23/05/92	640	9.38	0.73	8.05	10.33	18.87	0.17	18.55	19.23	8.71	0.09	8.55	8.86	490.8	1.4	487.6	493.6	4.13	0.57	3.44	6.18
24/05/92	625	11.03	1.01	9.28	12.26	20.4	0.56	19.54	21.18	8.68	0.12	8.48	8.87	481.2	46.9	4	491.5	6.51	1.33	0.00	13.37
25/05/92	643	10.06	0.77	8.56	11.08	20.57	0.73	19.54	21.57	8.74	0.12	8.55	8.97	472.0	38.8	3.53	479.5	6.73	2.50	1.48	26.16
26/05/92	625	8.17	0.61	7.14	9.05	19.5	0.22	18.64	20.15	8.30	0.06	8.2	8.42	483.9	1.6	479.1	486.9	3.85	0.47	3.05	6.11
27/05/92	640	7.88	0.64	6.78	9.27	18.9	0.72	17.89	21.91	8.11	0.03	8.08	8.38	459.0	28.7	6.3	471.4	7.48	2.62	0.00	21.3
28/05/92	478	6.99	0.36	6.46	9.19	20.2	0.55	19.41	21.1	8.52	0.05	8.43	8.65	493.5	27.2	53.7	500.1	4.24	2.35	2.42	18.79
29/05/92	642	8.10	0.74	6.77	9.14	20.2	0.41	19.25	20.87	8.27	0.05	8.2	8.5	487.6	51.7	5.4	498	6.30	2.97	3.27	27.75

Table B.4 Class 1 River Data - Recycled Test

DATE	Number of Readings	Dissolved Oxygen mg l ⁻¹				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				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	Philips																				
Slope	56 ±3 mV																				
Concentration range (as NH ₄ ⁺)	10 ⁻⁶ M to 10 ⁻¹ M 0.02 to 1800 ppm																				
Reproducibility	± 0.5 mV																				
pH range	4 to 10																				
Temperature range	0 to 50 °C																				
Response time	< 30 s																				
24 hour stability	< 1.5 mV																				
Operational life	3 to 12 months																				
Selectivity Coefficients	<table> <tr> <td>Hydrogen H⁺</td> <td>3 x 10⁻²</td> </tr> <tr> <td>Lithium Li⁺</td> <td>2 x 10⁻³</td> </tr> <tr> <td>Sodium Na⁺</td> <td>2 x 10⁻³</td> </tr> <tr> <td>Potassium K⁺</td> <td>2 x 10⁻¹</td> </tr> <tr> <td>Rubidium Rb⁺</td> <td>6 x 10⁻²</td> </tr> <tr> <td>Caesium Cs⁺</td> <td>5 x 10⁻³</td> </tr> <tr> <td>Magnesium Mg²⁺</td> <td>1 x 10⁻⁵</td> </tr> <tr> <td>Calcium Ca²⁺</td> <td>3 x 10⁻⁵</td> </tr> <tr> <td>Strontium Sr²⁺</td> <td>1 x 10⁻⁴</td> </tr> <tr> <td>Barium Ba²⁺</td> <td>3 x 10⁻⁵</td> </tr> </table>	Hydrogen H ⁺	3 x 10 ⁻²	Lithium Li ⁺	2 x 10 ⁻³	Sodium Na ⁺	2 x 10 ⁻³	Potassium K ⁺	2 x 10 ⁻¹	Rubidium Rb ⁺	6 x 10 ⁻²	Caesium Cs ⁺	5 x 10 ⁻³	Magnesium Mg ²⁺	1 x 10 ⁻⁵	Calcium Ca ²⁺	3 x 10 ⁻⁵	Strontium Sr ²⁺	1 x 10 ⁻⁴	Barium Ba ²⁺	3 x 10 ⁻⁵
Hydrogen H ⁺	3 x 10 ⁻²																				
Lithium Li ⁺	2 x 10 ⁻³																				
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