

The Evaluation of Ingold Ion Selective Ammonium Electrode

WRc plc

Evaluation Report 220/23/T



NRA

National Rivers Authority

THE EVALUATION OF INGOLD ION SELECTIVE AMMONIUM ELECTRODE

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Project 220

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EXECUTIVE SUMMARY

This report describes the results of the evaluation of an Ingold ammonium ion selective electrode supplied by Grant Instruments. 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 amount of documentation received was limited but well written.

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.

Laboratory trials to determine sensor accuracy established that the total error (quadrature sum of random and systematic errors) for five test concentrations varied between 0.00 and 0.37 mg l⁻¹ NH₄⁺.

During the field evaluation of the ammonium electrode two problems were identified. Initially the reference electrode was found to be faulty, 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 0.24 mg l⁻¹ and 1.42 mg l⁻¹ NH₄⁺. This was significant (90% confidence) drift in the calibration at the Class 1A site.

The Model WQL3831 Ammonium Ion Selective Electrode currently costs £460.00. The Model WQL5731 Double Junction Reference Electrode costs £147.00. The membrane was replaced during the laboratory evaluation and the electrode was replaced during the field tests. The reference electrode failed during the field evaluation.

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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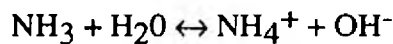
1. INTRODUCTION

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;

- 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

Ingold

Supplier

Grant Instruments Ltd
Barrington
Cambridge
CB2 5QZ

Tel: 0763 260811

Fax: 0763 262410

Instrument Description

Ion Selective Electrode - Ammonium

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 easy to operate and maintain.

The limited documentation supplied with the electrodes was clear and well written and included instructions for installation and operation.

The maintenance requirements of the electrode were low, except under certain field conditions, where the water quality was sufficiently poor to necessitate cleaning of the electrode to remove foulant. Unfortunately, for field applications the electrode performance was adversely affected by the reference electrode which required a high level of maintenance.

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

Laboratory trials on accuracy established that the electrode performed very good for all levels of ammonium tested. The total error (quadrature sum of random and systematic errors) varied between 0.00 mg l^{-1} and 0.37 mg l^{-1} for the range of test solutions ($0.1 - 5.0 \text{ mg l}^{-1} \text{ NH}_4^+$).

The response time of the electrode varied considerably depending on the direction of the concentration step change.

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

The field evaluation of the ammonium electrode identified a problem with the signal processing instrumentation. 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, that of a faulty reference electrode, required that some of the field trials be repeated. Since all of the field readings were possibly subject to interference, the time spent under field conditions could only be seen as a 'conditioning' period enabling the performance of the electrode to be determined only by the calibration data.

The total error (quadrature sum of random and systematic errors) at the lower test concentration ($0.5 \text{ mg l}^{-1} \text{ NH}_4^+$) is similar for all the tests. Whilst at the higher test concentration ($5.0 \text{ mg l}^{-1} \text{ NH}_4^+$) there was a decrease in the error for the intermittent flow regime test. 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.

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 Grant double junction pH/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 least squares linear 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 0.1N boric acid. Standard ammonium ion solutions were achieved by calculating the ammonium ion concentration at the pH and temperature of the sample 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 and

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 ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$),

18100 mg l⁻¹ of (hydrated) aluminium chloride (AlCl₃.6H₂O) and
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⁺) and
- 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 and 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 received was a single A4 sheet with instructions on the connections and fill solutions for the ammonium and reference electrodes.

5.2 Design and Construction

The ammonium electrode is made up of two sections, the electrode main body and the membrane module. At one end there is a co-axial connector for connection of the signal cable. At the other end the membrane module is connected to the main body via a screw connection. It appeared to be well constructed; the co-axial connector affording a secure connection.

5.3 Installation

The red end cap is unscrewed from the ammonium electrode to allow the connection of a co-axial connector.

5.4 Commissioning

The ammonium electrode was stored either dry or in the test tube provided. Before use the electrode required to be soaked in 0.05M NH_4Cl .

5.5 Maintenance and Downtime

During the field trials the membrane was replaced. This was simply achieved by unscrewing the old membrane module and replacing it with the new module. The electrode worked for a short period before subsequent failure. On this occasion the electrode was replaced.

There were differences between readings taken in the flow cell and the same water sample measured in a beaker. Investigation of this effect identified that some of the differences could be attributed to a faulty reference electrode. A different reference electrode was therefore employed. However, the effect was again seen during the field trials on the Class 3 river. 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.

There was slight fouling of the electrode during the field trials on the Class 1A river, and considerably more during the trials on 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 is reasonable to assume that the manufacturer does not expect fouling to occur.

5.6 Ease of Use

The electrode was very simple to use. As the membrane module is connected to the main body via a screw connection changing the membrane was very simple. Care was required to ensure that the module was not over tightened, which could damage the membrane.

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 ⁺	0.1mg l ⁻¹ NH ₄ ⁺ +2.5 g l ⁻¹ Kaolin
0	-86.3	7.6	
3	-69.6	24.6	-67.8
4	-69.3	27.4	
5	-68.8	28.4	
7	-67.7	29.9	
8	-68.3	30.5	-60.8
0	-84.5	19.0	-77.8

Table 6.2 Response time

	Step Change mg l ⁻¹ NH ₄ ⁺	Response Time Seconds
Rising Average	0.1 - 5.0	5 ± 1
Falling Average	5.0 - 0.1	96 ± 30
Air to 0.1 mg l ⁻¹ NH ₄ ⁺		< 2

Table 6.3 Interference

Solution		Electrode 0.1 mg l ⁻¹ NH ₄ ⁺	Output	Change 1.0 mg l ⁻¹ NH ₄ ⁺	(mV)
reference +	100 mg l ⁻¹ of KCl	56.6		14.4	
reference +	100 mg l ⁻¹ of NaCl	-20.8		-21.5	
reference +	400 mg l ⁻¹ of CaCl ₂	-23.6		-28.7	
reference +	400 mg l ⁻¹ of MgCl ₂	-47.8		-35.4	
*reference		0.1		-0.9	
reference +	724 mg l ⁻¹ of AlCl ₃ .6H ₂ O	-23.6		-28.7	
reference +	18100 mg l ⁻¹ of AlCl ₃ .6H ₂ O	-12.3		-10.1	
reference	(after 70 mins settling)	-10.9		-15.0	

* New reference solutions

Table 6.4 Electrode separation

Electrode - Reference Separation mm	Electrode 0.1	Output mg l ⁻¹	(mV) NH ₄ ⁺
23		-67.8	
90		-68.0	

Table 6.5a Accuracy tests 1 - 5

Actual mg l ⁻¹ NH ₄ ⁺	Test 1 (mV)	Test 2 (mV)	Test 3 (mV)	Test 4 (mV)	Test 5 (mV)	Mean	Standard Deviation
0.1	-108.1	-110.3	-110.1	-109.9	-109.9	-109.7	0.8
0.5	-73.0	-74.3	-74.3	-74.2	-74.3	-74.0	0.5
1.0	-56.1	-57.0	-56.9	-57.2	-57.0	-56.8	0.4
5.0	-16.5	-17.2	-17.2	-17.3	-17.1	-17.1	0.3
10.0	0.4	0.2	0.2	0.4	0.1	0.1	0.3
mV dec ⁻¹	54.6	55.5	55.4	55.1	55.3	55.2	0.3

Table 6.5b Accuracy tests 6 - 10

Actual mg l ⁻¹ NH ₄ ⁺	Test 6 (mV)	Test 7 (mV)	Test 8 (mV)	Test 9 (mV)	Test 10 (mV)	Mean	Standard Deviation
0.1	-108.8	-108.4	-108.2	-108.4	-108.7	-108.5	0.2
0.5	-73.7	-73.6	-73.5	-73.7	-73.7	-73.6	0.1
1.0	-57.3	-57.1	-56.9	-57.2	-57.1	-57.1	0.1
5.0	-17.5	-17.6	-17.3	-17.6	-17.5	-17.5	0.1
10.0	-0.2	-0.5	-0.2	-0.6	-0.4	-0.4	0.2
mV dec ⁻¹	54.4	54.3	54.3	54.3	54.2	54.4	0.1

Table 6.5c Summary of Accuracy tests 1 - 5

	NH ₄ ⁺ mg l ⁻¹				
	0.1	0.5	1	5	10
Mean	0.10	0.44	0.92	4.94	10.16
Systematic Error	0.00	0.06	0.08	0.06	-0.16
Random Error	0.00	0.00	0.00	0.03	0.12
Total Error	0.00	0.06	0.08	0.07	0.20

Table 6.5d Summary of Accuracy tests 6 - 10

	NH ₄ ⁺ mg l ⁻¹				
	0.1	0.5	1	5	10
Mean	0.11	0.47	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	Ammonium Chloride + Boric Acid			Ammonium Nitrate + Sodium Sulphate		
		0.5 mg l ⁻¹ (mV)	5.0 mg l ⁻¹ (mV)	slope	0.5 mg l ⁻¹ (mV)	5.0 mg l ⁻¹ (mV)	slope
15/02/93	16:30	-101.7	-31.5	70.2	-	-	-
16/02/93	15:24	-89.6	-30.0	59.6	-	-	-
18/02/93	11:00	-88.7	-24.7	64.0	-	-	-
19/02/93	17:00	-104.3	-31.2	73.1	-	-	-
22/02/93	16:45	-114.9	-36.0	78.9	-	-	-
23/02/93	16:40	-112.2	-35.7	76.5	-69.0	-29.7	39.3
24/02/93	17:15	-114.4	-32.7	81.7	-81.7	-28.6	53.1
25/02/93	14:50	-102.5	-52.2	50.3	-88.8	-37.7	51.1
26/02/93	10:40	-122.7	-39.7	83.0	-79.5	-29.6	49.9
01/03/93	11:40	-	-	-	-94.3	-28.8	65.5
02/03/93	09:10	-	-	-	-105.7	-45.1	60.6

Table 6.7 Calibration check Intermittant river conditions Class 1A river

Date	Ammonium Sodium 0.5 mg l ⁻¹ (mV)	Nitrate + Sulphate 5.0 mg l ⁻¹ (mV)	mV dec ⁻¹
20/05/93	-70.2	-11.2	59.0
21/05/93	-73.5	-11.8	61.7
26/05/93	-108.7	-9.7	99.0
27/05/93	-110.3	-11.3	99.0
29/05/93	-88.8	-13.4	75.4

Table 6.8 Calibration check dynamic river conditions Class 3A river

Date	Ammonium Sodium 0.5 mg l ⁻¹ (mV)	Nitrate + Sulphate 5.0 mg l ⁻¹ (mV)	mV dec ⁻¹
16/03/93	-64.3	-19.6	44.7
18/03/93	-71.9	-18.5	53.2
19/03/93	-74.0	-22.1	51.9
22/03/93	-77.2	-23.6	53.6
23/03/93	-77.6	-26.2	51.4
26/03/93	-81.5	-29.5	52.0
29/03/93	-81.2	-29.5	51.7

Table 6.9 Calculated random and systematic errors

Test	Class 1A		Class 3		Intermittant	
	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	0.19	4.69	0.26	3.89	0.29	5.04
Random Error	0.07	1.05	0.05	0.89	0.21	-0.04
Systematic Error	0.31	0.31	0.24	1.11	0.21	0.18
Total Error	0.31	1.09	0.24	1.42	0.30	0.19
Sample Size	4	4	7	7	4	4

7. INSTRUMENT BEHAVIOUR

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

Table 6.1 shows the results of varying the flow at the sensor surface. It was found that flow had a significant effect (90% confidence limits) on sensor output. The addition of kaolin 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 ($0.1 \text{ mg l}^{-1} \text{ NH}_4^+$) to a higher concentration ($0.5 \text{ mg l}^{-1} \text{ NH}_4^+$) the electrode responded within 5 seconds. However, for the reverse case, the response time was 96 seconds.

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 400 mg l^{-1} of MgCl_2 ($102 \text{ mg l}^{-1} \text{ Mg}^{2+}$) was found to produce a change of -47.8 mV at $0.1 \text{ mg l}^{-1} \text{ NH}_4^+$ ($0.09 \text{ mg l}^{-1} \text{ NH}_4^+$), and a change of -35.4 mV at $1.0 \text{ mg l}^{-1} \text{ NH}_4^+$ ($0.8 \text{ mg l}^{-1} \text{ NH}_4^+$).

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 0.20 and $1.42 \text{ mg l}^{-1} \text{ NH}_4^+$.

The ammonium electrode was then evaluated under a series of five different field conditions. However, during the evaluation on the 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 that the reference electrode was faulty. A different reference electrode was therefore employed. This 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 new amplification systems. It was therefore agreed that the field trials would be repeated. The field readings taken at the Class 3 site would still be susceptible to the variations seen previously, however they would not be effected by the faulty reference electrode. The calibration check data would be valid however the time spent under field conditions could only be seen as a 'conditioning' period.

The daily calibration check data for the two test sites is shown in Tables 6.6 to 6.8. 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 which would not be detected by the electrode. The solutions were changed to ammonium nitrate (corrected for ionic strength with sodium sulphate).

There was no significant (90% confidence) drift in any of the calibrations during the field trials.

Table 6.9 is the calculated random and systematic errors for the electrode for the ammonium nitrate solutions for both sites. The total error (quadrature sum of random and systematic errors) at the lower test concentration ($0.5 \text{ mg l}^{-1} \text{ NH}_4^+$) is similar for all the tests. Whilst at the higher test concentration ($5.0 \text{ mg l}^{-1} \text{ NH}_4^+$) there was a decrease in the error for the intermittent flow regime test.

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 Class 1A and Class 3 river are shown in Tables B1 to B3 respectively. Other water quality parameters were monitored by daily sampling and laboratory analysis these results are provided in Tables A1 to A3.

8. COST OF OWNERSHIP

Model WQL3831 Ammonium Electrode	£460.00
Grant Model WQL3874 pH/reference electrode	£147.00
Membrane Caps (set of six)	£ 26.00

The membrane was replaced during the laboratory evaluation and the electrode was replaced during the field tests. Exchange of membranes is a very simple task and only requires a few minutes.

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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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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 ⁻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 - 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 1A 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
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 1A 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

APPENDIX C MANUFACTURER'S SPECIFICATION

No specification was supplied with this electrode.