PROJECT 220

The Evaluation of a Nico Elit 051 Ammonium Ion Selective Electrode

WRc plc

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NRA
National Rivers Authority

THE EVALUATION OF A NICO ELIT 051 AMMONIUM ION SELECTIVE ELECTRODE

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EXECUTIVE SUMMARY

This report describes the results of an evaluation of a Nico Research ammonium ion selective electrode marketed by BPS International plc. 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.

Installation of the electrode was simple, although some difficulty was experienced in mounting the electrode in a standard laboratory electrode holder, due to its small diameter.

Laboratory trials to determine sensor accuracy established that the electrode performed better than the manufacturer's specification of 2% reproducibility at levels of ammonium as low as 1 mg l^{-1}. This was well below the manufacturer's stated lower limit of 9 mg l^{-1}. Below this there was loss of precision. The total error (quadrature sum of random and systematic errors) for five test concentrations varied between 0.08 and 0.48 mg l^{-1} 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. 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 varying between 0.20 and 1.69 mg l^{-1} NH_4^+.

The electrode cost £275 including a Corning reference electrode. 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 220/16/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 (NH_4^+) thus:

$$NH_3 + H_20 \leftrightarrow NH_4^+ + OH^-$$

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 physio-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:	Nico Research and Engineering Moscow C.I.S
Supplier:	BPS International Plc Units 8 & 9 Ironbridge Close Off Great Central Way London NW10 0UF Tel: 081 451 6556 Fax: 081 451 2053
Instrument Description:	Solid State Ion Selective Electrode - Ammonium (Elit 51)

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 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 cleaning of the electrode to remove foulant.

Laboratory trials to determine sensor accuracy established that the electrode performed better than the manufacturer's specification of 2% reproducibility at levels of ammonium as low as 1 mg l^{-1}. This was well below the manufacturer's stated lower limit of 9 mg l^{-1}. The total error (quadrature sum of random and systematic errors) for five test concentrations varied between 0.08 and 0.48 mg l^{-1} NH_4^+.

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 35 (± 5) seconds before stability was achieved, however, a change from high to low concentration required 160 (± 20) seconds.

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 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 0.20 and 0.21 mg l^{-1} at a test level of 0.5 mg l^{-1} NH_4^+. Whilst at the higher test level, of 5.0 mg l^{-1} NH_4^+ the total errors were 1.59 for Class 1A river and 1.69 mg l^{-1} for the Class 3A river. Similar total errors we 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 an Corning double junction electrode.

The Orion Analyser was interfaced to an IBM PC compatible computer. The direct mV readings, converted concentrations (mg l^{-1} 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 20 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 mg l^{-1}l NH_4^+ ion (14.86 mg l^{-1} NH_4Cl) in 0.1N boric acid,

0.1 mg l^{-1} NH_4^+ ion (2.97 mg l^{-1} NH_4Cl) in 0.1N boric acid,

0.1 mg l^{-1} NH_4^+ ion (2.97 mg l^{-1} NH_4Cl) 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 mg l^{-1} NH_4Cl) in 0.1N boric acid until a stable reading was obtained. The electrode was then quickly transferred to a stirred solution containing 5.0 mg l^{-1} NH_4^+ ions (14.86 mg l^{-1} NH_4Cl) 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 mg l^{-1} NH_4Cl) and 1.0 mg l^{-1} (2.97 mg l^{-1} NH_4Cl), 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 ($AlCl_3.6H_2O$),

18100 mg l^{-1} of (hydrated) aluminium chloride ($AlCl_3.6H_2O$)

no interferent.

4.2.4 Electrode Separation

The electrode was placed in a stirred solution of 0.1 mg l^{-1} NH_4^+ (0.297 NH_4Cl) 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} NH_4Cl (0.1 mg l^{-1} NH_4^+),

1.48 mg l^{-1} NH_4Cl (0.5 mg l^{-1} NH_4^+),

2.97 mg l^{-1} NH_4Cl (1.0 mg l^{-1} NH_4^+),

14.86 mg l^{-1} NH_4Cl (5.0 mg l^{-1} NH_4^+),

29.72 mg l^{-1} NH_4Cl (10.0 mg l^{-1} NH_4^+).

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 Trails

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} ammoinum 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 mg l^{-1} NH_4^+ (1.48 mg l^{-1} NH_4Cl) and 5.0 mg l^{-1} NH_4^+ (14.86 mg l^{-1} NH_4Cl). 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, double sided, A4 sheet with instructions on installation, operation, storage and specifications. It was clearly written and contained all necessary information about the ammonium electrode. The documentation for the reference electrode was a plastic coated card with operating instructions, precautions, and maintenance information. It was also well written but did not include the formulation of the external filling solution. (This information was subsequently obtained by contacting the manufacturer).

5.2 Design and Construction

The ammonium electrode is a sealed unit, 130 mm long and 10 mm diameter. The PVC ion selective membrane is positioned at one end; at the other end is a larger diameter section through which the cable is connected. It appeared to be well constructed, with the cable securely connected.

5.3 Installation

Installation of the electrode was simple, although some difficulty was experienced in mounting the electrode in a standard laboratory electrode holder, due to its small diameter.

5.4 Commissioning

The electrode was stored either dry or in 10^{-4} molar NH_4Cl. Before use the electrode required to be soaked in 10^{-2} molar NH_4Cl for at least 15 minutes.

5.5 Maintenance and Downtime

The ammonium electrode is a sealed unit and required very little maintenance. The reference electrode required refilling between and during tests.

There was slight fouling of the electrode during the field trails 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 reasonable to assume that the manufacturer does not expect fouling to occur.

5.6 Ease of Use

As previously mentioned the electrode is a sealed unit and therefore was very simple to use. The only difficulty with the electrode was the small diameter meant that it would not fit into a standard laboratory electrode

6. RESULTS

Table 6.1 Flow at sensor surface

Stirrer Speed Setting	Electrode 0.1 mg l^{-1} NH_4^+	Output 5.0 mg l^{-1} NH_4^+	(mV) 0.1 mg l^{-1} NH_4^+ +2.5 g l^{-1} Kaolin
0	158.2	211.2	-
3	162.2	211.3	175.4
4	162.9	212.6	-
5	163.5	212.6	-
7	164.3	212.5	-
8	163.3	212.8	177.2
0	161.2	212.9	174.0

Table 6.2 Response time

	Step Change	Response Time Seconds
Rising Average	0.1 - 5.0 mg l^{-1} NH_4^+	35 ±5
Falling Average	5.0 - 0.1 mg l^{-1} NH_4^+	160 ±20
Air to 0.1 mg l^{-1} NH_4^+		< 6

Table 6.3 Interference

Solution		Electrode Output Change (mV) 0.1 mg l^{-1} NH_4^+	1.0 mg l^{-1} NH_4^+
reference +	100 mg l^{-1} of KCl	100.9	37.8
reference +	100 mg l^{-1} of NaCl	23.7	-0.8
reference +	400 mg l^{-1} of $CaCl_2$	-12.7	-6.8
reference +	400 mg l^{-1} of $MgCl_2$	-8.7	-8.9
*reference		15.6	2.5
reference +	724 mg l^{-1} of $AlCl_3.6H_2O$	-3.4	-11.6
reference +	18100 mg l^{-1} of $AlCl_3.6H_20$	0.3	-11.8
reference +		6.6	-3.6

* New reference solutions

Table 6.4 Electrode separation

Electrode - Reference Separation (mm)	Electrode Output (mV) 0.1 mg l^{-1} NH_4^+
20	166.6
90	167.0

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	111.30	136.50	139.00	122.40	128.48	128.48	10.29
0.5	145.90	159.00	161.00	156.00	156.36	156.36	5.49
1.0	180.10	186.20	187.00	179.50	182.82	182.82	3.15
5.0	220.00	222.70	222.90	223.10	222.54	222.54	1.35
10	241.80	242.40	241.50	242.40	242.04	242.04	0.35
mV dec^{-1}	66.95	55.30	53.58	61.33	56.57	58.75	4.84

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	120.20	135.60	140.30	126.80	130.80	130.74	6.95
0.5	160.40	164.40	164.70	163.90	163.80	163.44	1.56
1.0	182.00	184.00	184.80	182.00	182.30	183.02	1.16
5.0	222.80	223.00	223.20	223.10	223.60	223.14	0.27
10.0	240.60	241.30	240.30	240.80	239.00	240.40	0.77
mV dec^{-1}	60.55	53.96	51.83	57.37	55.26	55.79	2.98

Table 6.5c Summary of Accuracy tests 1 - 5

	Electrode Output (mV) NH$_4^+$ mg l^{-1}				
	0.1	0.5	1	5	10
Mean	0.2	0.6	1.4	5.4	10.5
Systematic Error	-0.14	-0.08	-0.37	-0.42	-0.46
Random Error	0.06	0.04	0.17	0.11	0.15
Total Error	0.15	0.17	0.41	0.43	0.48

Table 6.5d Summary of Accuracy tests 6 - 10

	Electrode Output (mV) NH$_4^+$ mg l^{-1}				
	0.1	0.5	1	5	10
Mean	0.17	0.54	1.12	5.11	9.87
Systematic Error	-0.07	-0.04	-0.11	-0.11	0.13
Random Error	0.04	0.01	0.06	0.05	0.24
Total Error	0.08	0.04	0.13	0.12	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}
15/02/93	16:30	212.4	281.2	67.2	-	-	-
16/02/93	15:24	211.2	275.7	64.5	-	-	-
18/02/93	11:00	211.3	277.9	66.6	-	-	-
19/02/93	17:00	196.2	272.1	75.9	-	-	-
22/02/93	16:45	202.9	271.4	68.5	-	-	-
23/02/93	16:40	187.9	269.7	81.8	-	-	-
24/02/93	17:15	179.7	272.0	92.3	219.0	273.1	54.0
25/02/93	14:50	195.3	264.4	69.1	215.9	273.9	58.0
26/02/93	10:40	177.7	266.6	88.9	227.8	279.0	51.2
01/03/93	11:40	-	-	-	211.8	282.9	71.1
02/03/93	09:10	-	-	-	205.9	273.7	67.8

Table 6.7 Calibration check dynamic river conditions Class 3 river

Date	Ammonium Sodium	Nitrate + Sulphate	mV dec^{-1}
	0.5 mg l^{-1} NH_4^+ (mV)	5.0 mg l^{-1} NH_4^+ (mV)	
16/03/93	253.9	301.9	48.0
18/03/93	247.3	299.6	52.3
19/03/93	249.3	299.9	50.6
22/03/93	236.9	288.5	51.6
23/03/93	245.3	295.8	50.5
26/03/93	237.1	293.8	56.7
29/03/93	242.4	287.6	45.2

Table 6.8 Calibration check Recycle 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	159.9	210.8	50.9
06/04/92	158.7	224.5	65.8
07/04/92	147.3	220.8	73.5
08/04/92	141.9	219.7	77.8
10/04/92	207.6	218.9	11.3

Table 6.9 Calibration check Recycle (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	128.7	216.5	87.8
28/04/92	140.2	216.4	76.2
29/04/92	138.4	210.2	71.8
30/04/92	144.4	216.6	72.2
01/05/92	143.8	213.3	69.5
05/05/92	153.5	217.5	64.0
06/05/92	147.4	215.4	68.0
08/05/93	147.8	214.7	66.9

Table 6.10 Calibration check Intermittent river conditions Class 1A river

DATE	0.5 mg l^{-1} (mV)	5.0 mg l^{-1} (mV)	mV dec^{-1}
20/5/92	139.8	208.6	68.8
21/5/93	133.0	208.3	75.3
26/5/92	100.00	200.2	100.2
27/5/92	109.8	205.2	95.4
29/5/92	109.9	197.9	88.0

Table 6.11 Calculated 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	0.45	6.08	0.30	3.55
Random Error	0.20	1.17	0.07	0.87
Systematic Error	0.05	-1.08	0.20	1.45
Total Error	0.20	1.59	0.21	1.69
Sample Size	4	4	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	0.37	7.41	0.73	4.83	0.30	4.55
Random Error	0.13	-2.41	-0.23	0.17	0.20	0.45
Systematic Error	0.14	1.79	0.14	0.31	0.17	0.57
Total Error	0.19	3.00	0.27	0.35	0.26	0.72
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.

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. Increasing the distance between the electrodes had little effect on the voltage output. The difference recorded, 0.4 mV, is less than the 2% reproducibility (3.3 mV) stated by the manufacturer.

Table 6.1 shows the results from varying the flow at the sensor surface. To determine if there was any relationship between flow at the sensor surface and millivolt output a correlation coefficient was calculated. The strength of correlation is determined by how close the calculated statistic (r) is to 1 (or -1). For this relationship it was found that flow did not have a significant effect on sensor output at either of the ammonium concentration levels (for 0.1 mg/l NH_4^+ $r = 0.78$, 5.0 mg/l $r = 0.82$). The addition of kaolin similarly appeared to have no effect. A correlation coefficient was not calculated for this test due to the small sample size.

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 NH_4^+) to a higher concentration (0.5 mg/l NH_4^+) the electrode responded within 35 (±5) seconds. However, for the reverse case, the response time was over four times longer at 160 (±20) 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 and sodium both have 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 concentration. 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 K^+) would produce a theoretical ammonium level of approximately 4.5 mg/l at 0.1 mg/l NH_4^+ whilst at 1.0 mg/l NH_4^+ this would be 3 mg/l NH_4^+. This is in agreement with the manufacturer's specification.

Similarly the addition of 100 mg/l of NaCl (40 mg/l Na^+) was found to produce a change of 0.15 mg/l NH_4^+ at 0.1 mg/l NH_4^+. Again this is in agreement with the manufacturer's specification.

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 0.08 and 0.48 mg/l NH_4^+. This variation is larger than the 2% reproducibility stated by the manufacturer however it should be remembered that this is only stated for a range 9.0 - 9000 mg l^{-1}.

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 both sites. The variability seen in millivolt per decade seen at the end of the tests would suggest that there was some drift in the calibration of the electrode. Although a correlation coefficient calculated for mV against time for the two test concentrations did not confirm this (95% confidence). 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 the 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. The total errors for all these different flow regimes are comparable with those results seen in the dynamic tests. The fact that the total errors for the intermittent water supply are similar to those achieved in the dynamic tests would suggest that this mode of operation would enable the life of the electrode to be extended and reduce the maintenance of the electrode whilst still achieving good results.

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

The electrode cost £275 including a Corning reference electrode.

The electrode is a sealed unit and therefore the only maintenance required was to clean the membrane of the electrode. In the Class 1A river the amount of cleaning was very small whereas at the Class 3 the electrode required cleaning on each visit.

The reference electrode required daily refilling of the fill solutions.

The lifetime of the electrode was stated as several years although damage to the membrane surface and hydrolysis of the adhesive used to mount the membrane in position will reduce this considerably. During the six months of the evaluation the electrode continued to function properly even after immersion for two weeks in the very aggressive waters of a Class 3A river.

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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 and interfering species).

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

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APPENDIX A LABORATORY 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	Conductivity	Copper as Cu	Ammoniacal N as N	Nitrite as N	Chloride as Cl	Calcium as Ca	Magnesium as Mg	Sodium as Na	Potassium as K	Nitrate as N
			$mg\ l^{-1}$	$\mu S\ cm^{-1}$	$\mu g\ l^{-1}$	$mg\ l^{-1}$	$mg\ l^{-1}$	$mg\ l^{-1}$	$mg\ l^{-1}$	$mg\ l^{-1}$	$mg\ l^{-1}$	$mg\ l^{-1}$	$mg\ l^{-1}$
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 - Recycle (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
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 Mean	Sd	Min	Max	Temperature °C Mean	Sd	Min	Max	pH Mean	Sd	Max	Min	Conductivity µS Mean	Sd	Min	Max	Turbidity FTU 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^{-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
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 MANUFACTURERS SPECIFICATION

Supplier:	BPS International Plc Units 8 & 9 Ironbridge Close Off Great Central Way London NW10 OUF	
Slope	56 mV/decade	
Concentration range (as NH_4^+)	9.0 - 9000 mg/l (0.5 - 5 10^{-4} mole/l)	
pH range	1 - 8.5	
Electrode Resistance (maximum)	100 Mohm	
Reproducibility	2%	
Potential Drift	1 mV/8 hr	
Selectivity Coefficients (maximum level, mole/l, for 10% error at 10^{-3}M NH_4^+)	Potassium Sodium	9.0×10^{-4} 2.2×10^{-2}
Dimensions	130 x 10 mm	
Immersion Depth	10 mm (May be immersed further to obtain more rapid temperature equilibrium)	