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**EVALUATION OF AN
ANALYTICAL SENSORS
AMMONIUM PROBE FOR
THE GRANT\YSI 3800**

National Rivers Authority

National Evaluation Centre Manager
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EVALUATION OF AN ANALYTICAL SENSORS
AMMONIUM PROBE FOR THE GRANT\YSI 3800

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Contents

Executive Summary

1. Introduction
2. Results Summary and Comments
 - 2.1 Implications for use
 - 2.2 Instrument performance
 - 2.3 Comments from field use
3. Test Results
4. Test procedures
5. References

Acknowledgements

Appendix A : Estimates of uncertainty and the practical limit of detection

Appendix B : Ammonium \ ammonia chemistry

Appendix C : Calibration Solutions

EXECUTIVE SUMMARY

This report describes the results of tests carried out on an Analytical Sensors ammonium ISE (ion selective electrode), picked at random from a batch delivered to Thames Region and fitted into a Grant\YSI 3800 water quality monitor.

The results show that the sensor is significantly more reliable than the one which it replaces and that field staff have increasing confidence in the readings produced by it.

It is affected by water flow ($\pm 3\%$) and also responds to potassium (8%) and sodium (0.1%), as do all ammonium ISE's.

The accuracy in laboratory calibration standard solutions is -3% bias with $\pm 0.3\%$ precision, however the accuracy in normal field use will be between $\pm 10\%$ and $\pm 15\%$ due to other factors (interference, drift, etc).

The limit of detection was found to be less than 0.01 mg/l, but the presence of potassium and other interferences in the field needs to be considered as a 0.1 mg/l change in the potassium level would change the instrument reading by approximately 0.01 mg/l.

The lifetime of the probe tested is greater than 10 months, and the estimated minimum lifetime of probes used in the field is approximately 4 months.

1. INTRODUCTION

Ammoniacal-N is a common pollutant generated mainly by sewage and occasional agricultural discharges. It exists in water as both ammonium and ammonia and the relative proportions are determined by pH and temperature. Ammonia is the more toxic species but in most natural water ammonium is dominant. Most on-line monitoring stations adjust the river water with sodium hydroxide to convert all the ammonium to ammonia and use the ammonia ISE to measure the total ammoniacal-N. This is not practical for hand held instruments so an ammonium ISE is used (which is less reliable) and the pH is measured enabling the ammonia and total ammoniacal-N to be calculated.

The Grant\YSI 3800 was originally supplied with an Ingold ammonium ISE, but this proved to be unreliable. Grant now supply ISE's produced by Analytical Sensors, and one of these was selected for testing at random from a number supplied for use in Thames region.

The tests were carried out between June 1994 and April 1995 at the NRA evaluation laboratories at Reading and Lea Marston. The test findings are presented in sections 2 and 3. In section 2 the results are summarised along with comments from field use and the implications for use. Section 3 contains the detailed test results after some initial data analysis. The test methods are outlined in section 4.

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2. RESULTS SUMMARY AND COMMENTS

This section provides a summary of the test results and includes subjective comments about the instrument arising from the tests and from field use.

2.1 Implications for use

From the tests carried out we can estimate the uncertainty of field results produced by this probe. To do this we need to take account of the effects of flow and temperature along with the laboratory accuracy. The accuracy of the calibration solutions is also significant since they directly affect the probe. For a properly maintained and calibrated instrument the uncertainty will be better than :

$\pm 15\%$ of reading or $\pm 0.3\text{mg/l}$ whichever is greater

This estimate does not include any errors caused by the presence of potassium and sodium

All ammonium ISE's also respond to potassium and sodium. The response to potassium was 8% (ie 100 mg/l of potassium produces a false reading of 8 mg/l ammoniacal-N) and the response to sodium was 0.1%. This will add an offset to all readings which would normally be between +0.2 to +2.0 mg/l (or greater) in fresh water due to potassium. (The Kennet has approximately 2mg/l of potassium and the Tame has approximately 17mg/l) In some rivers or streams this may be higher especially if they carry landfill run-off.

In sea water there is up to 380 mg/l potassium plus up to 10 500 mg/l of sodium, which would create an offset of approximately 40 mg/l. This error would swamp any normal ammonium reading. The instrument has an optional salinity correction but this does not work well enough to make the instrument useable in estuarine and saline conditions.

The bulk of the difference found in the flow test (approximately 0.3 mg/l) was between flow and no-flow conditions, so this effect will normally be substantially reduced by ensuring that the probe is in flowing or stirred water.

The temperature test showed that the sensor reading changed with temperature. This will be significant if difference between the water temperature and the calibration temperature is large, eg in a cold river at 3°C (20°C cooler than a laboratory) the error could be up to +4 mg/l or +40% of reading. The error was reduced by leaving the sonde in the water so that the temperature of the probe has time to settle.

The effectiveness of the 3 point calibration for temperature compensation was not tested. This would probably reduce the temperature effect but the random variations between measurements, even during calibration, mean that it is unlikely to accurately eliminate the effect. It is also possible that the size of this effect may vary between probes.

The probe has a fast response time of less than 9 seconds, but there is a settling/warm-up time of up to 3 hours during which the reading changes by up to 10%. This will have very little effect on single shot readings, but will be significant for survey work due to drift after deployment.

The limit of detection in laboratory conditions was less than 0.01 mg/l however the practical LOD in the field will be higher than this because of the other influences e.g changes in temperature or potassium. If the instrument is being used for logging or survey work at a single site then the limit of detection may approach the laboratory value, but if the instrument is switched off and transported some distance then the limit of detection will be closer to the overall instrument uncertainty estimated above.

2.2 Instrument performance

Accuracy

The probe was calibrated at 1 and 100 mg/l ammoniacal-N, and the reading was checked in a number of known solutions made up using ammonium chloride in de-ionised water buffered to pH 6.2 with HCl and to 2000 μ S/cm with Lithium Acetate (adds approximately 178 mg/l of lithium to the solution).

The results showed a bias of -3% of reading and a precision of $\pm 3\%$ of reading compared to the laboratory analysis. The largest difference between the instrument reading and the laboratory analysis of the solutions was +4.2 mg/l at 100 mg/l, this is equal to 4.2% of reading. The largest error expressed as % of reading was -6.7% at 3.0 mg/l, ie -0.2 mg/l.

Further accuracy checks carried out during the evaluation produced a wider spread of results. The uncertainty from these results is estimated as $\pm 10\%$ reading with a minimum of ± 0.4 mg/l and a maximum of ± 3 mg/l.

Response time

The response time of the instrument when transferred between solutions of 1 mg/l and 100 mg/l was less than 9 seconds. However there is also a long slow warm-up drift of up to 10% over approximately 3 hours - see below.

Temperature test

The test was carried out in dosed river water. The difference between the laboratory analysis and the instrument reading at different temperatures varied between +5.1 and -4.3 mg/l.

There appears to be a linear correlation between the difference (error) and the temperature. The correlation varies between -0.2 mg/l/ $^{\circ}$ C (-2% reading/ $^{\circ}$ C) for initial readings and -0.1 mg/l/ $^{\circ}$ C (-1% reading/ $^{\circ}$ C) for readings after 1 hour at 10 mg/l.

The uncertainty in laboratory readings for this measurement is $\pm 25\%$ reading, which probably accounts for most of the scatter in the readings since the measurements were carried out over a number of days.

Flow test

The instrument reading changed by approximately +0.3 mg/l (equivalent to 3 % of reading at 10 mg/l) when the flow speed changed from 0 m/s to 0.37 m/s. The effect is not linear with the steepest change at low flow.

Chemical Interference

Standard ammoniacal-N solutions were made up and different levels of potassium, sodium, and lithium salts were added. The following cross sensitivities of the probe to each of these metals were calculated from the instrument readings :

Potassium	8%
Sodium	0.1%
Lithium	<0.1%

(ie 10 mg/l of potassium produces a reading of 0.8 mg/l ammoniacal-N, etc)

Salinity Compensation

The Grant\YSI 3800 has an optional salinity correction to reduce the errors produced by potassium and sodium in sea water. This was tested in saline solutions of ammoniacal-N made up using a sea salt mixture obtained from Sigma chemicals. The salinity correction reduced the error but did not eliminate it.

The interference due to sodium and potassium without the salinity correction was between +1.6 to +1.8 mg/l ammoniacal-N per lppt increase in salinity. With salinity correction the interference was between +0.5 and +0.9 mg/l ammoniacal-N per lppt increase in salinity.

Limit of detection test

A limit of detection test in de-ionised water gave a limit of detection of less than 0.01 mg/l.

For the mV measurements of the instrument the LOD was 9.3mV at -103mV which is equivalent to 0.008mg/l in de-ionised water.

NOTE : these values cannot be applied directly to a river measurement because of various chemical and physical interferences which could cause similar changes to the reading.

Spiked recovery

The electrode recovery was 96%.

The instrument reading was 4.76 mg/l in a 50:50 mix of river water (with no ammoniacal-N) and a 10 mg/l standard solution. The mixture should have caused a reading of 4.96 mg/l.

Fouling and Drift at Lea Marston - Continuous immersion

The sonde was placed in a tank filled with water pumped continuously from the river Tame at Lea Marston. The results recorded by the instrument corresponded well with the ammoniacal-N and potassium levels in samples taken for analysis. They also mirrored the permanent ammonia monitor except for an offset of +1 mg/l due to interference from potassium.

After the drift test the probe calibration was checked and the readings were high by approximately 10% (of reading).

Drift test at Fobney Mead - intermittent immersion

The instrument was calibrated at the start of the test then dipped up to 20 times each day for 1 month in a tank of water drawn each day from the river Kennet at Fobney Mead and dosed with ammonium chloride. There was a reasonable correlation between the results recorded with the grant meter and regular laboratory analysis. There is no significant drift of the instrument results compared to the laboratory analysis of total ammoniacal-N, however there does seem to be a calibration offset which may have occurred in the initial calibration. The results are significantly better than those for the ammonium probe originally fitted to the instrument (see evaluation report 1993 : NRA\eval.03:1\93).

Short term \ warm-up drift

A warm-up drift of approximately 10% reading varying between 2 and 5 hours was found during the tests. This may not be significant in most cases, but if the instrument is to be used for logging or is allowed to settle during a day then, as the probe is usually calibrated within a few minutes of switch on, the readings may approximately 10% high.

Calibration Solutions

A number of different calibration solutions have been used for operational instruments and a check was made to ensure their interchangeability. The solutions tested were

1. NH_4Cl , $\text{LiC}_2\text{H}_3\text{O}_2 \cdot 2\text{H}_2\text{O}$, HCl , NaN_3
2. NH_4Cl , $\text{LiC}_2\text{H}_3\text{O}_2 \cdot 2\text{H}_2\text{O}$, HCl
3. NH_4NO_3 , EDTA

NaN_3 act as a biocide. $\text{LiC}_2\text{H}_3\text{O}_2 \cdot 2\text{H}_2\text{O}$ with HCl , and EDTA are used to adjust the pH and the conductivity.

When the probe was calibrated in solution 2 the highest readings were obtained in spiked river water (5.11 mg/l), and the lowest readings were obtained after calibration in solution 1 (4.81 mg/l). The difference was 0.3 mg/l (6% reading).

Each solution gives good results but solution 3 is the preferred in Thames region because it is easier to make than the others and the turnover of solution is high enough not to require a separate biocide. Where turnover is lower a biocide may be required, but the choice of solution will be dictated by the resources and time available.

Electrode Lifespan

An electrode which had been used regularly for approximately 10 months was calibrated at 1 and 100 mg/l (solution made up using NH_4Cl , $\text{LiC}_2\text{H}_3\text{O}_2 \cdot 2\text{H}_2\text{O}$, and NaN_3), and readings were made in the same solution at 1, 10 and 100 mg/l, and in dosed Kennet water. The test was then repeated using an electrode which had only been used occasionally and had been stored dry for approximately 10 months. Both electrodes produced readings within the uncertainties calculated above in the reference solutions and both had a span of > 50mV per decade. However the older electrode was less accurate in the dosed river water than the new electrode.

2.3 Comments from field use

A number of Analytical Sensors ammonium electrodes are already in use in Thames region instruments, and the following comments were provided by M.Loewenthal.

The probes are easy to maintain and replace, and seem to have a minimum operational lifetime of approximately 4 months (with a slope of 50 mV/decade). The 3 point calibration (for temperature) has never been carried out and is not regarded as necessary.

The calibration solution used was made with ammonium chloride and was buffered with HCl and Lithium acetate. The recommended solution also includes Sodium Azide as a biocide but this was omitted because of the rapid turnover of solutions. This was subsequently changed after results showed a zero error in known clean rivers of approximately 1 mg/l, the cause of this is not know but may be due to unforeseen bacterial action in the calibration solution. The solution now used does not show this effect and is made with ammonium nitrate and is buffered with EDTA.

The probe is regarded by field officers as good for sampling measurements and good for survey use. The worst drift observed after a 1 week survey was from 1.0 to 1.5 mg/l.

There is a significant increase in the confidence of field officers in the results provided by Grant meters fitted with this probe.

2.4 Manufacturer's comments (from Grant YSI).

We feel that the quality of the test protocol and the report are of a very high standard.

The results correlate well with our laboratory and field test results.

We thought the inclusion of comments from field use was a very valuable addition to the laboratory evaluation.

We were surprised that the 3 point calibration protocol, which was installed to minimise temperature variation errors, is not utilised when there is a significant difference between calibration and sampling temperatures.

3. TEST RESULTS

Accuracy

The sonde was calibrated in 1 and 100 mg/l ammoniacal-N then placed in buffered standard solutions made to known concentrations of ammonium (the recipes are given in section 4). The results of table 1 can be summarised as -3% bias with $\pm 0.3\%$ precision compared to laboratory readings.

Table 1 : Readings in known solutions

Solution Ammoniacal-N mg/l	Laboratory Ammoniacal-N mg/l	Mean Grant Readings Ammoniacal N	
		mg/l $\pm \sigma_{n-1}$	mV
0.0	0.0	0.0 \pm 0.0	-77.2
1.0	0.95	0.96 \pm 0.02	-0.9
3.0	3.0	2.79 \pm 0.02	28
(10)	8.8	8.76 \pm 0.04	54
30.0	30.4	29.7 \pm 0.2	86
100.0	104.0	99.8 \pm 0.3	114.4

Throughout the evaluation a number of other accuracy checks were carried out in carefully prepared solutions. The results are not included in table 1 because the solutions were not sent for analysis, but the average and standard deviations of the results obtained are given below in table 2.

The solutions used were made up using de-ionised water, ammonium chloride, acid (to adjust the pH), and a salt - normally Lithium Acetate - (to adjust the conductivity). The instrument was normally calibrated at 1 and 100 mg/l.

Table 2 : Combined uncertainties in reference solutions

Solution Ammoniacal-N mg/l	Average Grant reading mg/l amm-N	Standard deviation		sample size
		σ_{n-1}	mg/l	
0.0	0.0	0.0		9
0.1	0.135	0.091		4
1.0	0.996	0.152		24
3.0	2.60	0.46		12
10	9.12	1.07		26
30	28.98	1.87		12
100	99.4	1.2		14

Response Times

The response of the probe was checked a number of times during the evaluation by transferring the sonde quickly between two known solutions with 1 and 100 mg/l ammoniacal-N (the recipes given in section 4). The values given are the time to complete 90% of the step change. Towards the end of the tests a much slower drift of up to 3 hours was detected, this may have implications for calibration accuracy but further investigation is needed to quantify this effect.

Table 3 : Response times during the evaluation

Step Change 1 to 100 mg/l	Response time (seconds)	
	rising	falling
Initial test	6.7	4
After LM drift test	6.2	6.5
After 458 dips	8.7	8.3
after overnight soak in 100ppm NH ₄ ⁺ solution	6.3	6

Flow Test

The sonde was calibrated and placed in the flow tank at Fobney Mead. Ammonium Chloride was added to the water to generate a signal and the flow speed was changed as shown. Table 4 shows the instrument readings obtained and the variation compared to the initial zero flow condition. There appears to be a change of approximately 0.3 mg/l between zero and maximum flow, equivalent to 3 % of reading.

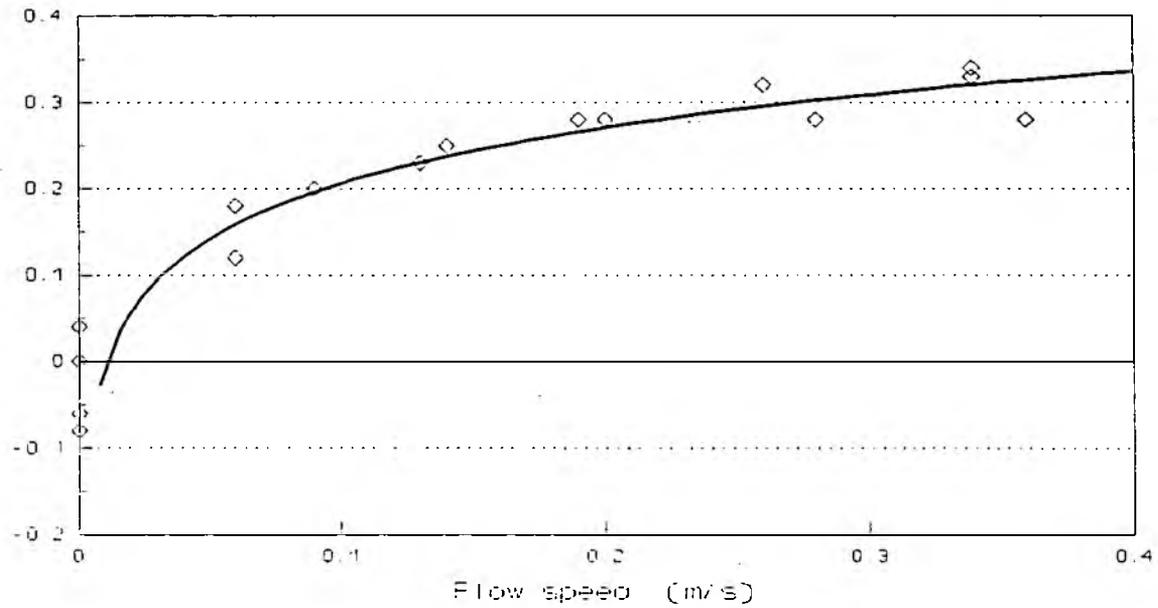
Laboratory analysis of the water showed that the ammonium levels remained stable throughout the test.

Table 4 : Reading at different flow rates

Flow Speed m/s	Grant Total Ammoniacal N	Variation mg/l
0	10.21	reference
0.06	10.39	+0.18
0.14	10.46	+0.25
0.2	10.49	+0.28
0.26	10.53	+0.32
0.34	10.55	+0.34
0	10.25	+0.04
0.34	10.54	+0.33
0.28	10.49	+0.28
0.19	10.49	+0.28
0.13	10.44	+0.23
0.09	10.41	+0.20
0.06	10.33	+0.12
0	10.13	-0.08
0.36	10.49	+0.28
0	10.15	-0.06

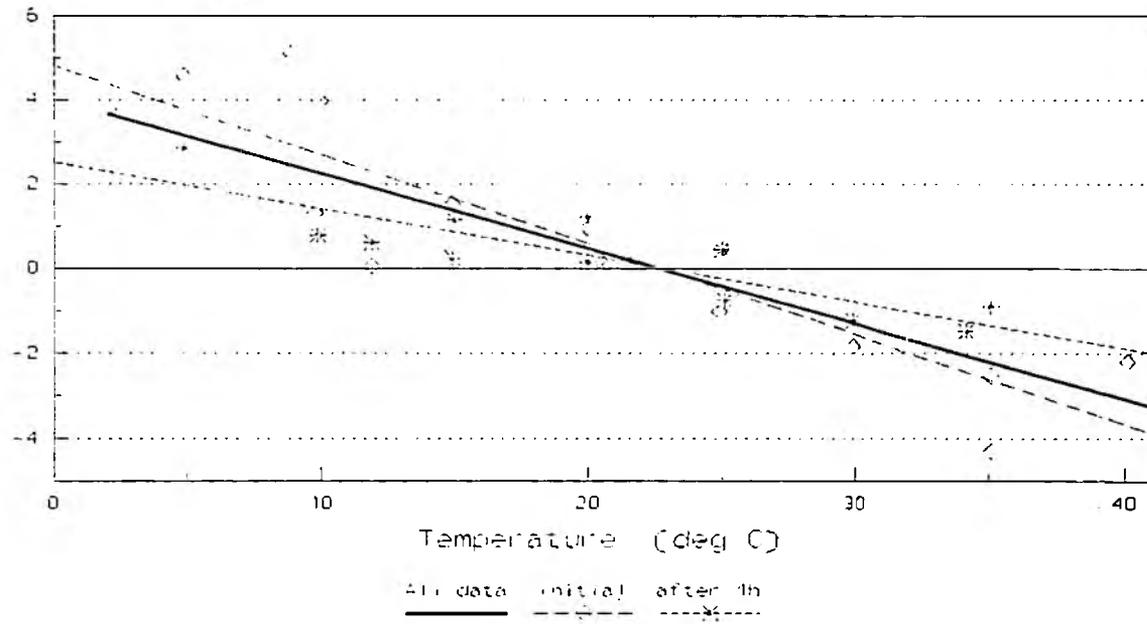
Flow Test

Variation (mg/l)



Temperature Test

Difference (mg/l)



Temperature Test

The sonde was placed in a tank of river water dosed with ammonium chloride to provide a signal and the water temperature was changed as shown. The readings and the laboratory analysis are given below, along with the differences.

The tank was allowed to stabilise at each temperature, the sonde was then placed in the water and the initial stable reading was recorded (i). The sonde then remained in the water and a reading was taken after approximately 1 hour, it was then removed and the temperature was changed (h).

The temperature was taken up to 40°C to amplify any effect and to provide a large enough data set for curve fitting. The thick lines separate readings taken on different days.

Table 5 : Effect of water temperature

Temperature °C	Grant Total Ammoniacal N i \ h (*)	Laboratory Ammoniacal N i \ h (*)	Difference mg/l i \ h (*)
8.9	13.32 \ -	8.2 \ -	+5.1 \ -
2.1	12.39 \ 13.83	8.6 \ -	+3.8 \ -
9.8	9.51 \ 9.19	8.2 \ 8.4	+1.3 \ +0.8
15.0	7.82 \ 8.44	- \ 8.2	- \ +0.2
20.0	7.35 \ 7.62	6.4 \ 6.4	+1.0 \ +1.2
25.0	6.67 \ 6.74	6.2 \ 6.3	+0.5 \ +0.4
29.9	5.28 \ 5.78	7.1 \ 7.0	-1.8 \ -1.2
35.1	4.18 \ 5.71	6.7 \ 6.6	-2.5 \ -0.9
40.1	3.41 \ -	5.6 \ -	-2.2 \ -
20.2	5.61 \ 6.05	5.4 \ 5.9	+0.2 \ +0.2
11.9	10.16 \ 10.61	10.1 \ 10.0	+0.1 \ +0.6
35.1	5.81 \ -	10.1 \ -	-4.3 \ -
34.2	- \ 7.83	- \ 9.3	- \ -1.5
25.0	7.19 \ 7.25	8.2 \ 8.0	-1.0 \ -0.8
15.0	9.33 \ 8.94	7.8 \ 7.8	+1.5 \ +1.1
4.9	11.88 \ 10.04	7.3 \ 7.2	+4.6 \ +2.8
10	9.37 \ -	5.4 \ -	+4.0 \ -

- * i. initial stabilised reading after placing sonde in tank ;
- h. reading after approximately 1 hour in the tank

Chemical Interferents : Potassium

The sonde was placed in different solutions with known levels of ammonium and potassium. The mg/l and the mV readings are shown in table 6. The pH during the test was 6.3

Table 6 : Grant readings (mg/l : mV) at different potassium levels

		Potassium concentration mg/l as K ⁺ : (mV)		
		0	10	100
NH ₄ ⁺ concentration mg/l as N	0	0 : (-62)	0.93 : (9)	6.57 : (58)
	1	0.93 : (9)	1.76 : (25)	7.63 : (62)
	100	103.0 : (128)	105.5 : (128)	113.6 : (129)

Chemical interferents : Sodium

The sonde was placed in different solutions with known levels of ammonium and sodium. The mg/l and the mV readings are shown in table 7. The pH during the test was 6.6

Table 7 : Grant readings (mg/l : mV) at different Sodium levels

		Sodium concentration mg/l as Na ⁺ : (Mv)		
		0	1 000	10 000
NH ₄ ⁺ concentration mg/l as N	0	0.20 : (-28)	1.05 : (13)	11.94 : (70)
	1	0.88 : (10)	2.06 : (30)	12.96 : (72)
	100	91.84 : (128)	96.54 : (128)	125.1 : (129)

Chemical interferents : Lithium

The sonde was placed in different solutions with known levels of ammonium and lithium. The mg/l and the mV readings are shown in table 8. The pH during the test was 6.7 ± 1.0

Table 8 : Grant readings (mg/l : mV) at different Lithium levels

		Lithium concentration mg/l as Li ⁺ : (mV)		
		0	100	1 000
NH ₄ ⁺ concentration mg/l as N	0	0 : (-121)	0 : (-77)	0.17 : (-35)
	1	0.72 : (5)	0.81 : (8)	0.99 : (9)
	100	101.5 : (131)	100.3 : (130)	98.6 : (126)

Salinity Test

The sonde was placed in different solutions with known levels of ammonium to which known amounts of 'Sea Salts' were added (obtained from Sigma chemicals - see section 4 for assay). The mg/l and the mV readings with and without the salinity correction are shown below in tables 9 and 10. The pH during the test was 6.0 ± 2.3

**Table 9 : Grant readings (mg/l) at different salinity levels
salinity correction OFF**

		Salinity ppt : (mV)		
		0.4	9.0	26.5
NH ₄ ⁺ concentration mg/l as N	0	0.0 : (-47)	14.0 : (79)	41.8 : (104)
	1	1.0 : (20)	14.6 : (80)	43.2 : (104)
	100	98.9 : (134)	111.2 : (132)	143.5 : (120)

**Table 10 : Grant readings (mg/l) at different salinity levels
salinity correction ON**

		Salinity ppt : (mV)		
		0.4	9.0	26.5
NH ₄ ⁺ concentration mg/l as N	0	- : (-47)	4.5 : (79)	18.5 : (104)
	1	- : (20)	5.6 : (80)	19.4 : (104)
	100	- : (134)	102.9 : (132)	134.5 : (120)

Limit of Detection

The electrode was calibrated before the test, then placed in duplicate solutions of de-ionised water to provide a blank sample. The water was changed regularly during the test to reduce contamination from the sonde. The mg/l and mV readings obtained are given below in table 11.

From these results the limit of detection can be calculated as :

$$\text{LOD (by experiment)} = < 0.01 \text{ mg/l or } 9.3 \text{ mV (at } -103.5\text{mV)}$$

[Note : This LOD would not normally be achieved on a river because of calibration, temperature, flow and chemical variations which could create a similar change in reading, eg changes of approximately 0.1 mg/l of K⁺ or 10 mg/l of Na⁺]

Table 11 : Readings in de-ionised water

First Grant Reading		Second Grant Reading		Difference	
mg/l	mV	mg/l	mV	mg/l	mV
0.00	-110	0.00	-111	0.00	1
0.00	- 93	0.00	- 96	0.00	3
0.00	- 98	0.00	- 99	0.00	1
0.00	- 92	0.00	- 95	0.00	3
0.00	-101	0.00	-104	0.00	3
0.00	-102	0.00	-102	0.00	0
0.00	-102	0.00	-103	0.00	1
0.00	- 93	0.00	- 93	0.00	0
0.00	-116	0.00	-121	0.00	5
0.00	-117	0.00	-122	0.00	5

Spiking Recovery Test

Readings were taken in fresh river water and in a 10 mg/l standard solution. 1 litre of river water and 1 litre of solution were then mixed and a further reading was made. The results are given in table 12. The recipe for the standard solution is given in section 4.

The recovery calculated from these results is 96%

Table 12 : Spiking recovery results

Solution	Grant $\text{NH}_4^+\text{-N}$ mg/l
10mg/l $\text{NH}_4^+\text{-N}$ Standard	9.62
River Water	0.30
50:50 River water and Standard mix	4.76

Fouling and Drift at Lea Marston - continuous immersion

The instrument was placed in a tank of flowing water drawn from the river Tame at Lea Marston at set to run in the interval logging mode. Regular samples were taken for laboratory analysis. The results are shown in the graph below, the higher line is data obtained from the Grant\YSI 3800, the lower line is data from the Severn Trent monitoring station ammonia monitor. The large rise in the Grant signal from 25 to 27 June corresponds to a period when the water supply to the test tank was interrupted.

At the end of the test the sonde was rinsed in de-ionised water and the reading was checked in calibration solutions.

Total Ammoniacal N

Logging test in tank at Lea Marston

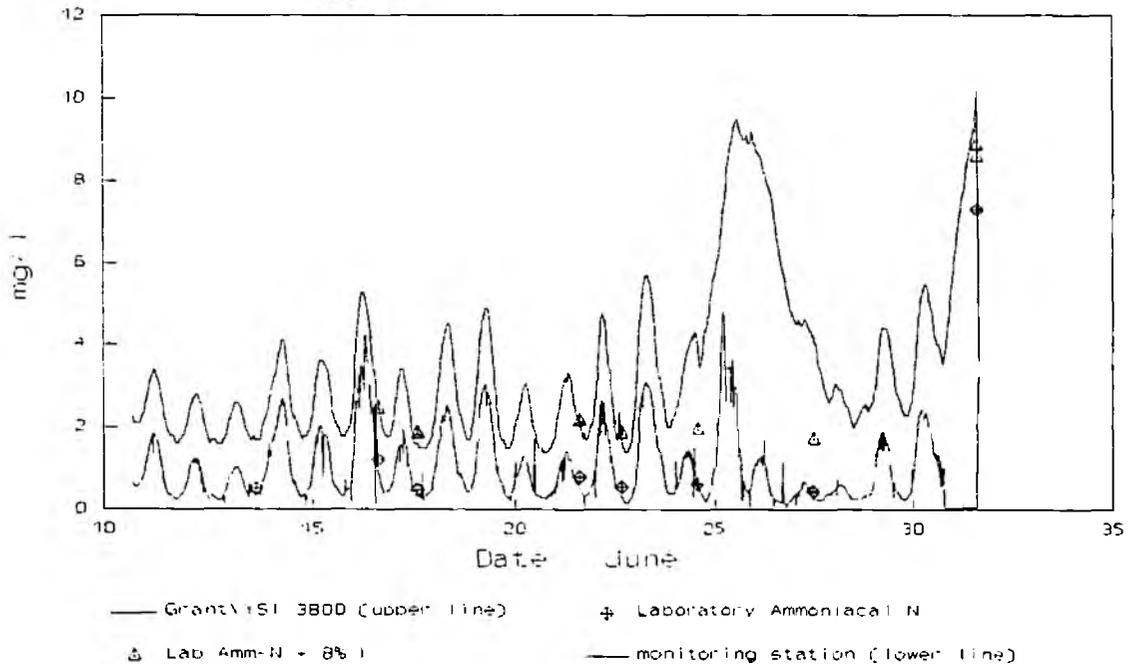


Table 13 : Calibration check after drift test

Solution Ammoniacal-N mg/l	Mean Grant Readings Ammoniacal N	
	mg/l	mV
1.0	1.31	5
10.0	11.80	64
100.0	110.2	124

Drift test at Fobney Mead - intermittent immersion

The instrument was calibrated at the start of the test then dipped up to 20 times each day for 1 month in a tank of water drawn each day from the river Kennet at Fobney Mead and dosed with ammonium chloride. A number of results were recorded with the grant meter and regular samples were taken for laboratory analysis. The results shown in the graph below are the differences between the laboratory analysis of total ammoniacal-N and the value calculated from the grant results ($\text{NH}_4^+\text{-N} + \text{NH}_3\text{-N}$). The results are significantly better than those for the ammonium probe originally fitted to the instrument.

At the end of the test the sonde was rinsed in de-ionised water and the reading was checked in calibration solutions.

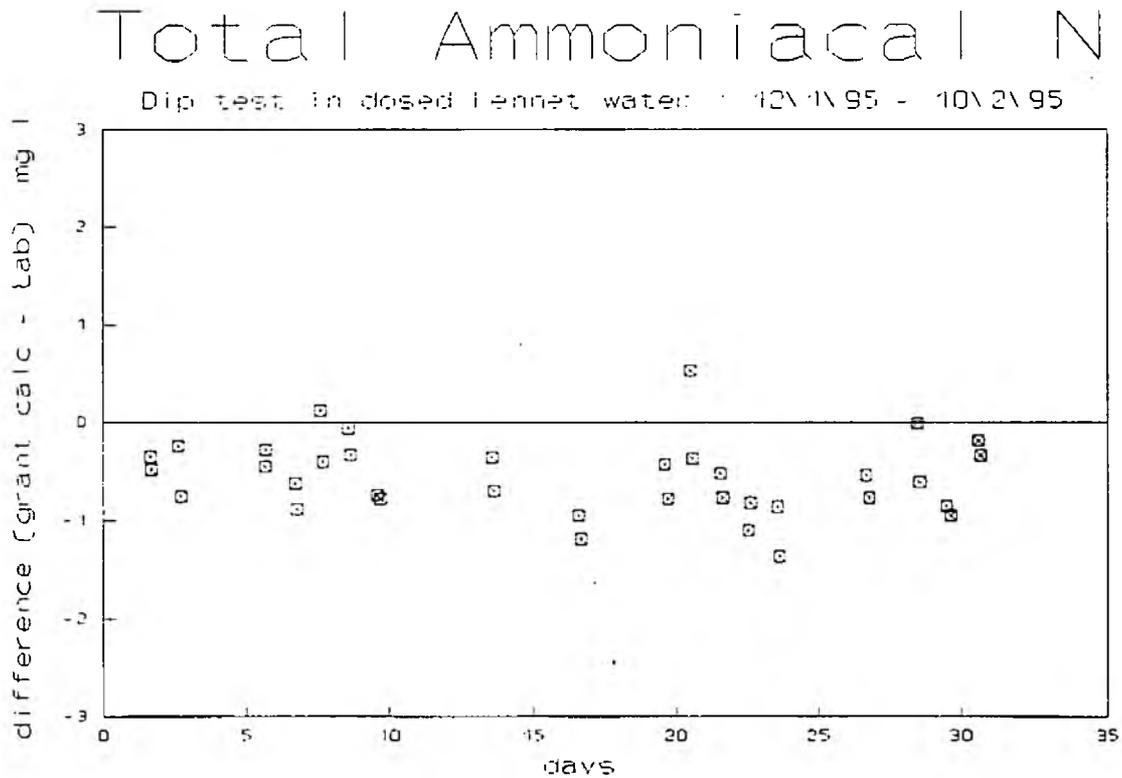


Table 14 : Calibration check after drift test

Solution Ammoniacal-N mg/l	Mean Grant Readings Ammoniacal N	
	mg/l	mV
1.0	0.64	22
10.0	7.18	76
100.0	77.18	128

Short Term \ warm-up drift

A simple short term drift was carried out a number of times on the probe during the evaluation. Each time the instrument was switched off over night and stored dry with a small amount of water in the sonde cup to keep the membranes moist. It was then set to log data every 2 minutes and placed in stable ammonium solutions for some time.

The graphs produced below show the settling of the probe immediately after switch on.

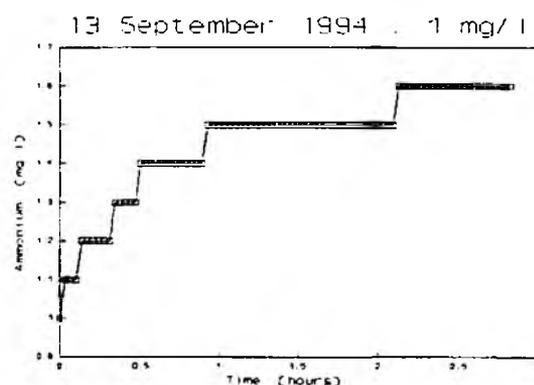
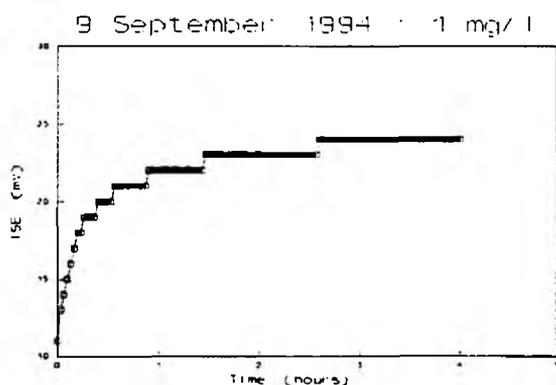
In each case the probe quickly get within 10% of the final reading and seems stable, but then drifts for up to 4 hours.

Table 15 : Short term drift times

Date : Solution	Initial "stable" reading	Final reading	Drift time hh:mm
9/9/94 : 1 mg/l	19 mV	24 mV	2:16
12/9/94 : 1 mg/l	1.7 mg/l	1.7 mg/l	-
13/9/94 : 1 mg/l	1.2 mg/l	1.6 mg/l	1:54
8/12/94 : [dr]	5.1 mg/l	4.8 mg/l	3:02
16/2/95 : 10mg/l	78 mV	79 mV	3:34
19/4/95 : 1 mg/l	20 mV	24 mV	2:58
20/4/95 : 1 mg/l	0.9 mg/l	1.0 mg/l	2:36
24/4/95 : 100mg/l	95.3 mg/l	100.0 mg/l	5:46

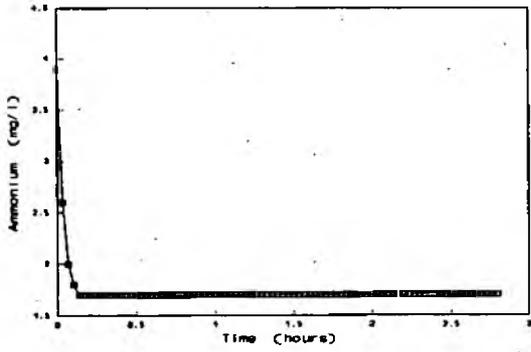
[dr] : dosed river

Short term \ Warm-up drift graphs

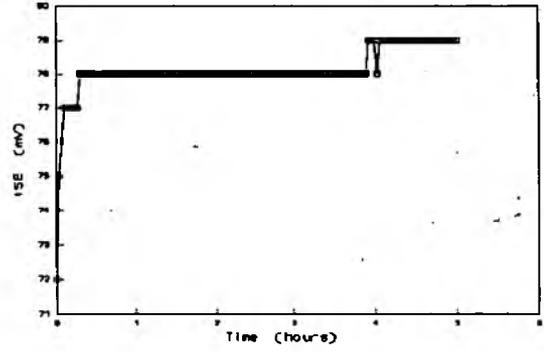


Short term \ Warm-up drift graphs - continued

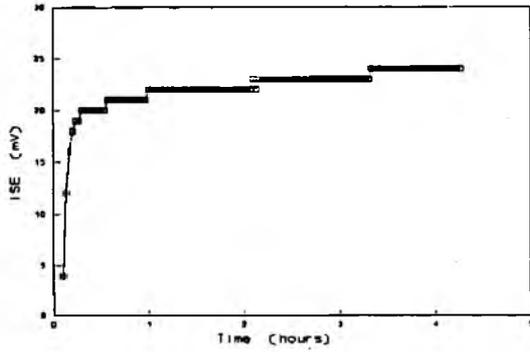
12 September 1994 : 1 mg/l



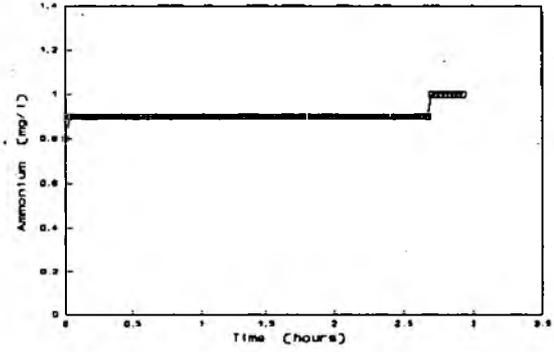
16 February 1995 : 10 mg/l



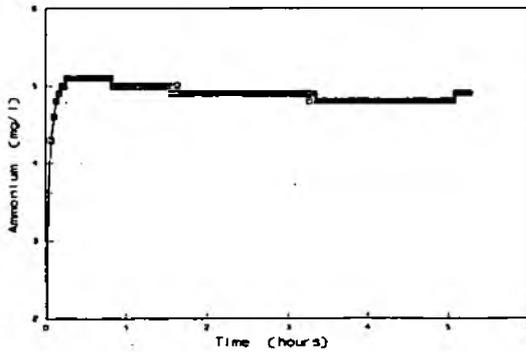
19 April 1995 : 1 mg/l



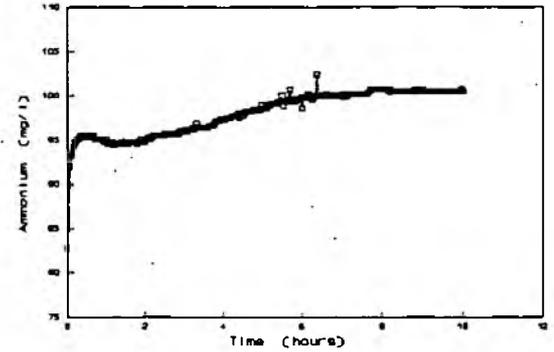
20 April 1995 : 1 mg/l



8 December 1994 : Dosed River



24 April 1995 : 100 mg/l



Calibration Solutions

A number of different calibration solutions were checked to see if there was any significant difference in the readings produced.

The solutions tested consisted of :

1. NH_4Cl , $\text{LiC}_2\text{H}_3\text{O}_2 \cdot 2\text{H}_2\text{O}$, HCl , NaN_3 ,
2. NH_4Cl , $\text{LiC}_2\text{H}_3\text{O}_2 \cdot 2\text{H}_2\text{O}$, HCl
3. NH_4NO_3 , EDTA

The probe was calibrated in each solution and measurements were made in fresh, and dosed Kennet water.

Table 16 : Readings in fresh Kennet water

Calibration Solution	Readings		
	NH_4^+ mg/l	NH_3 mg/l	ISE mV
1	0.22	0.01	-43
2	0.26	0.01	-44
3	0.20	0.01	-44

Table 17 : Readings in Kennet water dosed with NH_4Cl

Calibration Solution	Readings		
	NH_4^+ mg/l	NH_3 mg/l	ISE mV
1	4.81	0.27	25
2	5.11	0.34	25
3	4.94	0.38	25

Laboratory analysis of the dosed water gave a value of 5.4 mg/l (\pm approx 1.5 mg/l) ammoniacal-N

Electrode lifespan

This test was carried out when the electrode used for most of these tests was approximately 10 months old. It was calibrated at 1 and 100 mg/l, and readings were taken in the same solution at 1, 10 and 100 mg/l, and in dosed Kennet water. The test was then repeated using an electrode which had only been used occasionally and had been stored dry for approximately 10 months. The solution was made up using NH_4Cl , $\text{LiC}_2\text{H}_3\text{O}_2 \cdot 2\text{H}_2\text{O}$, and NaN_3 .

Table 18 : Old (used) electrode

Solution Concentration mg/l	Readings	
	Tot. Am-N	ISE mV
1.0	1.06	22
10.0	10.50	77
100.0	103.6	132
River \ 5.2 ± 1.5	6.28	64

Table 19 : New electrode

Solution Concentration mg/l	Readings	
	Tot. Am-N	ISE mV
1.0	1.20	-11
10.0	9.93	38
100.0	104.5	93
River \ 5.4 ± 1.5	5.08	25

4. TEST PROCEDURES

Accuracy

The probe was calibrated at 1 and 100 mg/l ammoniacal-N and the sonde was then placed in five solutions carefully made up to known levels of ammonium. The test was carried out 10 times, and samples of the solutions were sent to the Fobney laboratory for analysis. (The 10 mg/l solution produced questionable results and was checked using an ISE based ammonia analyzer, the lab analysis, and a spectro-photometric kit. All the analysis confirmed the Grant reading and therefore it was decided that the analysis was probably more accurate than the solution although the cause of the error has not yet been found.)

The test solutions and the calibration solutions were made using dried ammonium chloride weighed into volumetric glassware, and dissolved in a buffered solution containing 2.602 g/l of lithium acetate dihydrate (which adds 178 mg/l of Lithium to the solution), and a few drops of HCl to adjust the pH to 6. This recipe was used since it is recommended by Grant and was normally used in Thames region.

Response time

A number of times throughout the evaluation a response time test was carried out. Each time the probe was calibrated only if necessary. The test was carried out by transferring the sonde from a 1 mg/l ammoniacal-N solution to a 100 mg/l ammoniacal-N solution, and vice versa. The readings were recorded every 5, 10, 30, 60 seconds, or 5 minutes - the interval increased as the reading stabilised - and were plotted against time. From the curve the response time, 90% of the step change, was calculated.

Temperature test

The sonde was placed in a large insulated tank filled with Kennet water dosed with ammonium chloride. The test was carried out with a number of other instruments and the temperature was changed as shown in the result.

At each temperature the sonde was placed in the tank and all the Grant parameters were allowed to stabilise and were recorded. The sonde then remained in the water for approximately 1 hour and a further set of readings were taken. The sonde was then removed and the water temperature was changed.

At each measurement a sample was collected and sent to the Fobney lab for analysis of pH, conductivity, total ammoniacal-N, and turbidity. The water temperature was measured with a calibrated mercury in glass thermometer.

Flow test

The sonde was placed in the large flow tank at Fobney filled with Kennet water dosed with ammonium chloride. The sonde was suspended by its cable from a bar above the water surface and was allowed to swing freely with the water flow on approximately 70 cm of cable. The flow speed was varied as shown in the results and was measured using an electromagnetic flowmeter.

At each flow speed all the Grant parameters were noted and samples were collected at regular intervals for analysis of pH, conductivity, total ammoniacal-N, and turbidity.

Chemical interference

The chemical interferences of Potassium, Sodium, and Lithium were each tested by generating solutions of 0, 1, and 100 mg/l ammoniacal-N as shown in the accuracy test, with zero and two different levels of the interferent.

a) Potassium interference

Potassium was added as KCl to give solutions of 0, 10 and 100mg/l K⁺ at each ammonium concentration. The instrument was calibrated and thoroughly cleaned prior to the test and 6 to 8 measurements were made in each solution.

b) Sodium interference

Sodium was added as NaCl to give solutions of 0, 1000 and 10 000 mg/l Na⁺ at each ammonium concentration. The instrument was calibrated and thoroughly cleaned prior to the test and 1 to 2 measurements were made in each solution.

c) Lithium interference

The ammoniacal-N solutions were made up using MgSO₄ (added until the conductivity reached ≈1500μS/cm) in place of lithium acetate. Lithium was added as Lithium acetate to give solutions of 0, 100 and 1000 mg/l Li⁺ at each ammonium concentration.

Salinity compensation

The salinity compensation was checked in a similar manner to the interference tests. Ammoniacal-N solutions of 0, 1, and 100 mg/l were made and commercial sea salts were added to produce salinities of 0, 8.5, and 24.8 ppt. Several ammoniacal-N readings were made in each solution with the salinity correction switched on and off, and the results are given as total ammoniacal-N to remove the effects of pH variation.

The sea salt was purchased from Sigma Chemical and had the following assay as % by weight:

Cl⁻ 55.26 %, Na⁺ 30.66 %, SO₄²⁻ 7.58% %, Mg²⁺ 3.72 %, Ca²⁺ 1.17 %,
K⁺ 1.09 %, HCO₃⁻ 0.426 %, others 0.094 %.

Limit of detection

On ten separate occasions the ammoniacal-N reading in a blank sample (de-ionised water) was measured in duplicate. Because of the digital limitations of the signal processing all the readings were 0.00 mg/l so the test was then repeated with the mV signal selected on the instrument. The results were analyzed statistically to give the limit of detection.

Spiked recovery

Readings were made in a 10mg/l ammoniacal-N standard solution prepared as shown in the accuracy test. A further reading was made in river water taken from the Kennet at Fobney Mead. 1 litre of 10 mg/l solution and 1 litre of river water were then mixed (using volumetric glassware) and measurements were made of the mixed solution.

Fouling and Drift - continuous immersion

The instrument was calibrated according to manufacturer's instructions and was then immersed in water from the river Tame for 3 weeks at Lea Marston. The trend in levels of D/O, temperature, pH, conductivity, NH₃ and turbidity of the water were monitored using standard Severn-Trent region monitoring station. The instrument was checked at least three times each week and a number of samples were taken for laboratory determination of a number of species including total ammoniacal-N, pH, potassium, and others at each visit. The level of fouling was assessed after the test.

Fouling and drift - intermittent use

The probe was calibrated according to manufacturer's instructions and was then immersed up to 5 times in class 1 river water and returned to its normal storage condition for 3 weeks. The sonde was also placed in the intermittent immersion tank at Fobney to be immersed automatically more than 15 times.

A quarter of the measurements were made in fresh river water but in order to generate a measurable level of ammonium it was necessary to trap a sample of water and add a known amount of ammonium chloride. Samples were taken during the test for analysis by the laboratory at Fobney Mead of pH, conductivity, total ammoniacal-N, potassium, etc.

Short term \ warm-up drift

Before the test the instrument was switched off over night. The following morning logging was started at 2 minute intervals. The sonde was held in air for a few minutes and was then placed in a known solution for up to 4 hours. The logged data was then retrieved and plotted against time to show any drift. The test was carried out a number of times so that the drift in both the ammonium concentration and the mV values could be tested.

Calibration Solutions

Three different sets of solutions of 1, 10, and 100 mg/l ammoniacal-N were made up and in each solution the pH was adjusted to below 6 and the conductivity was adjusted to approximately 1000 $\mu\text{S}/\text{cm}$ using :

1. NH_4Cl , $\text{LiC}_2\text{H}_3\text{O}_2 \cdot 2\text{H}_2\text{O}$, HCl , NaN_3
2. NH_4Cl , $\text{LiC}_2\text{H}_3\text{O}_2 \cdot 2\text{H}_2\text{O}$, HCl
3. NH_4NO_3 , EDTA

The probe was then calibrated in each solution in turn and readings were recorded in river water and in river water dosed with ammonium chloride.

Electrode lifespan

An electrode which had been used for approximately 10 months was calibrated and its readings in 1, 10, and 100 mg/l calibration solutions, and in dosed river water were checked. The test was repeated with an electrode which had been only occasionally used and the results were compared.

5. REFERENCES

NRA evaluation report 1\93 : A Chappell; The Evaluation of Grant\YSI 3800 Water Quality Monitor

NRA project record 220/7/T : I.Baldwin; Protocol for the investigation of ion selective ammonium electrodes and their applications in field measurement

NRA R&D note 288 : S.Clegg; Establishment of Practical pH scales and ammonium ionisation in estuaries

NRA Guildford office : B.Penny; Interim report on the field evaluation of effluents by the Grant\YSI 3800 multilogger

BSI : BS 5233 : (1986) Terms used in metrology

Handbook of Chemistry and Physics - 67th edition

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APPENDIX A : Ammonium\ammonia chemistry

An equilibrium is set up between ammonium and ammonia gas in an aqueous solution by a reversible reaction involving hydrogen ions.



The relationship between ratios of dissolved ammonium and ammonia in water, and pH are known, and is described by the following equations :

$$\frac{|NH_3|}{|NH_4^+|} = \frac{10^{pH}}{10^c}$$

where

$$c = \frac{2729.69}{T} + 0.1105 - 0.000071T$$

T : absolute temperature (K)

There is also be an additional affect caused by the ionic strength of the water which can be estimated from the conductivity. This has been corrected for in the instrument.

As a rule of thumb there is approximately a 50:50 ratio of ammonium to ammonia at pH 9.2, this becomes 95:5 ammonium to ammonia at pH 8.2, and 99.5:0.5 at pH 7.2, etc.

Further information may be found in publications such as 'Standard Methods for the examination of Water and Wastewater', NRA-R&D note 288 (Establishment of practical pH scales and ammonia ionisation in estuaries - part 1), or the various 'blue books'.

Appendix B : Calibration Solutions

The function of a calibration solution is to provide a known ammonium concentration which the instrument measurement scale can be set up against. Since the probe responds to ammonium, and because of the ammonium/ammonia chemistry the solution pH needs to be less than 6, also the response of an ISE is unstable at low conductivity so a salt (which does not affect the probe) is added. If a solution is to be stored for a long time then some form of biocide is needed to prevent bacteria changing the solution composition.

The Thames region staff initially used the solution recommended by Grant\YSI:

Ammonium generator	:	3.819 g/l NH_4Cl stock solution (\approx 1000 mg/l $\text{NH}_4\text{-N}$ diluted as required)
pH adjustment	:	HCl
Ionic strength adjustment	:	2.602 g/l Lithium Acetate
Biocide	:	10 mg/l Sodium Azide

Because of the high turnover of solution the biocide was omitted. After approximately 1 year of use a discrepancy was noticed with the instrument reading being significantly higher than the laboratory analysis, even allowing for potassium interference. As a result of this, and for consistency and ease of production the solution has now been changed to that used for the fixed stations :

Ammonium generator	:	5.717 g/l NH_4NO_3 stock solution (\approx 1000 mg/l $\text{NH}_4\text{-N}$ diluted as required)
Ionic strength & pH	:	750 mg/l EDTA (Ethylenediamine tetra- acetic acid disodium salt)

This solution is used in the permanent monitoring stations as a dual calibrant for ammonia and nitrate monitors so the storage time of any batch is short. The EDTA adds enough sodium to generate a false ammonium reading of approximately 0.1 mg/l, this is advantageous since the minimum levels of potassium encountered in various rivers is approximately 2 mg/l equivalent to an ammonium signal of approximately 0.2 mg/l

**EVALUATION OF AN
ANALYTICAL SENSORS
AMMONIUM PROBE FOR
THE GRANT\YSI 3800**

