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EVALUATION OF FIELD pH METERS
Summary Report

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EVALUATION OF FIELD pH METERS
Summary Report

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THE EVALUATION OF FIELD pH METERS - Summary Report

A J Chappell

Contents

This report contains technical information on a wide range of different manufacturers' instruments. It is therefore :-

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1 INTRODUCTION AND EXECUTIVE SUMMARY

This report has been prepared to support the proposed migration of pH monitoring into the field. A number meters were obtained for evaluation to assess their suitability for use by field officers, and whether they could provide accurate, quality assured data. The results from each meter have been summarised and are presented here so that they can be readily compared. More detailed information can be found in separate reports for each instrument manufacturer.

The following ten meters were assessed :

> Amarell ad-110, Camlab pH-boy 501, Camlab pH-boy 723, Hanna Agritest, Hanna Checker, Hanna pHep2, Hanna pHep3, Hanna 'new' pHep, WTW P3 and YSI 63.

The Hanna, Camlab and Amarell meters are all 'stick' meters, where the sensor and display are contained in a single unit which is dipped directly into the water. They are all small enough to be carried easily in a pocket.

Of these the Hanna 'new' pHep proved to be the best meter. The Hanna pHep 3 and Camlab pH boy 501 could also be used for field pH measurements however their accuracy was poor at high pH. (Unfortunately the pH boy 501 is being replaced with the 701 and 723 which was not accurate in high pH buffer solutions.) The Hanna checker and Amarell ad-110 both have protruding sensors which are vulnerable to breakage, making them unsuitable for Agency use. The Hanna Agritest also measures conductivity up to 4 mS/cm, but it failed a number of times during the evaluation so proved unsuitable for Agency use .

The Hanna pHep 2 was used in Thames and Welsh regions as part of the 'monitoring for what?' field test. It was easy to use and the readings obtained agreed with laboratory sample analysis, but the calibration screws were difficult to adjust and a number of instruments failed during the test due to calibration drift or because they were left switched on. (see field trial report for more information)

The WTW and YSI have a more traditional structure with a glass pH electrode attached to the display unit via a cable.

The WTW P3 (multi-line) can also measure dissolved oxygen or conductivity using a separate sensor. It has limited logging capability and can store calibration data for AQC purposes. It performed well in the evaluation (although it was not available for all tests) and will be suitable for Agency use where this style of instrument is required.

The YSI 63 measures pH, conductivity and temperature with a single probe. It also has limited logging capability and performed well in the tests. The YSI 60 is a cheaper version which measures pH and temperature only. These meters will also be suitable for Agency use where this style of instrument is required.

The findings of this project are given in section 2 and 3 with an address list of manufacturers' and suppliers' in section 4. Section 2 contains an outline of the range of effects observed for the meters and summarises the results for each instrument. More detail is given in section 3 where the findings are presented for each test. Description of the test methods and more complete results can be found in the individual evaluation reports.

2 OVERVIEW OF RESULTS

In this section the results are summarised to outline the range of errors which can occur during normal use with these meters. The results for each instrument have been presented separately below to give an overall impression. Further detail is given in section 3 and the individual reports on the meters.

The accuracy of all meters was adequate up to pH 9.24 where the errors were within 0.2 pH. However at pH 13 the errors increase up to -1.8 pH (pH boy 723). The repeatability of each meter was good at 0.1pH or better.

Operation in low conductivity water was tested in 10^{-4} molar HCl solution. All the meters tested operated correctly and their readings changed by less than 0.1pH when the conductivity was adjusted from 41 to 1154 µS/cm. (Amarell ad-110, pH boy 723 and pHep3 were not tested)

The temperature test showed that errors caused by a 20°C temperature change varied from <0.1pH to 1.4 pH. This was further complicated as the magnitude and direction of the effect changed with pH for each instrument.

The long term stability of most of the meters was good and they drifted only slightly during the 3 week drift test. The Hanna 'checker' was the least stable with the readings in a pH 7.4 buffer varying from 6.68 to 9.33.

Only two instruments displayed a low battery alarm. The changes caused by reduced battery voltage varied from 0.0 to +3.6pH.

None of the meters tested were effected by the solution flow speed and all the meters responded within 10 seconds to a change of the solution pH.

Amarell ad-110

Accuracy	max error -0.2 at pH 4.0
Low Conductivity	test not done
Temperature (20°C change)	pH 1.7 : -0.3
	pH 13.0 : +0.6
Long term stability	No drift, readings stable
Battery voltage	change by up to +3.6
Automatic shutdown	no
Price (1999)	£32.77

Comments :

The electrode is screwed to the base of the meter and is vulnerable to breakage since it protrudes beyond the meter body. It is protected by a small cap when not in use. The meter is straight forward to operate, with the on/off switch and single point calibration carried by adjusting a trimmer on the back of the meter.

Unfortunately the vulnerability of the probe makes it unsuitable for field use

Camlab pH boy 501

Accuracy	max error -0.4 at pH 13.1
Low Conductivity	change <0.1 pH
Temperature (20°C change)	pH 1.7 : +0.1
	pH 13.0 : +0.3
Long term stability	slight decrease, readings stable
Battery voltage	stable
Automatic shutdown	1 hour
Price (1999)	£99.50

Comments :

The meter looks robust with an integral ISFET based sensor. It is straight forward to operate, with an on/off button located on top of the meter. The single point calibration is straightforward and carried out by applying a few drops of buffer to the sensor and pressing the 'cal' button.

Camlab pH boy 723

Accuracy	max error -1.8 at pH 13.1
Low Conductivity	not tested
Temperature (20°C change)	pH 1.7 : -0.1
	pH 13.0 : +1.4
Long term stability	not tested
Battery voltage	stable
Automatic shutdown	1 hour
Price (1999)	£135.00

Comments :

The '701' and '723' pH boys have been recently developed and will replace the '501'. The meter looks similar to the '501' but has a slightly different reference electrode.

Unfortunately the accuracy test results show large errors at high pH which could make the meter unsuitable for Agency use. This may improve if the manufacturer further develops the meter.

Hanna Checker

Accuracy	max error -0.14 at pH 13.1
Low Conductivity	change <0.1 pH
Temperature (20°C change)	pH 1.7 : -0.58
	pH 13.0 : +0.56
Long term stability	readings unstable
Battery voltage	change by up to +1.19
Automatic shutdown	no
Price (1999)	£23.50

Comments :

The meter is small with a thin detachable pH electrode which is vulnerable to breakage. It is straight forward to operate with the on/off switch located on top of the meter. 2-point calibration is carried out by adjusting two trim-pots using a small screw driver.

Unfortunately the vulnerability of the probe makes it unsuitable for field use

Hanna pHep2

Accuracy	max error -0.3 at pH 13.1
Low Conductivity	change <0.1 pH
Temperature (20°C change)	pH 1.7 : -0.2
	pH 13.0 : +0.6
Long term stability	slight increase, some fluctuations
Battery voltage	change by up to +2.4
Automatic shutdown	no
Price (1999)	£37.60

Comments :

The meter has an integral glass electrode recessed into the base with a separate reference electrode. It is well protected making it robust for field use and is covered by a cap when not in use. It is straight forward to operate, with an on/off button on top of the meter. 2 point calibration is achieved by adjusting two screws located on the back of the meter using a plastic tool provided. The screws are difficult to turn due to the waterproof seals and the tool sometimes flexes.

Hanna pHep3

Accuracy	max error -0.5 at pH 13.1
Low Conductivity	test not done
Temperature (20°C change)	pH 1.7 : -0.2
	pH 13.0 : +0.3
Long term stability	slight increase, readings stable
Battery voltage	stable
Automatic shutdown	15 minutes
Price (1999)	£40.75

Comments :

The pHep 3 is very similar to the pHep 2. The only significant difference is the absence of any calibration screws. It has automatic 2 point calibration activated by holding the on/off button and adjusts to pH 4.0, 7.0 or 10.0 depending upon the pH the reference solution.

Hanna 'new' pHep

Accuracy	max error -0.3 at pH 13.1
Low Conductivity	change <0.1 pH
Temperature (20°C change)	pH 1.7 : -0.3
	pH 13.0 : +0.6
Long term stability	readings stable, slight increase
Battery voltage	stable
Automatic shutdown	no
Price (1999)	£29.00

Comments :

This is slightly larger than the pHep 2. It has a glass electrode which is replaceable and is recessed in the base along with a separate reference electrode. It is guarded during normal use and is covered by a cap when stored. 2 point calibration is carried out by adjusting two trim-pots located on the back of the meter using a small screwdriver.

Hanna Agritest

The Agritest is a dual pH / conductivity meter with a removable head containing both sensors. The probes are close together so could be prone to fouling. The meter is not waterproof and can be easily damaged if immersed too deeply. The pH sensor is calibrated manually at one point by adjusting a small screw. This proved to be inadequate as it could not account for changes in the probe sensitivity.

The Agritest meter obtained for testing failed and was replaced twice when the sensor could not be recalibrated. No tests of the pH sensor could be completed. The conductivity sensor was tested separately however it also failed when the connector between the sensors and the meter head became wet.

Overall this meter is not suitable for Agency field use.

WTW P3

Accuracy	max error -0.38 at pH 13.1
Low Conductivity	change <0.1 pH
Temperature (20°C change)	pH 1.7 : +0.02
	pH 13.0 : +0.05
Long term stability	test not done
Battery voltage	test not done
Automatic shutdown	1 hour
Price (1999)	£660 (includes conductivity meter and memory)

Comments :

This meter is designed for field use and is robust with a separate rugidized double junction electrode. The buttons are clearly labelled making it easy to use. It is calibrated automatically at 2-points in pH 2, 4, 7 or 10 buffers. It can store up to 120 data sets, along with the calibration information. It can also be fitted with a separate sensor to measure either conductivity or dissolved oxygen.

YSI 63

Accuracy	max error +0.09 at pH 1.68
Low Conductivity	change <0.1 pH
Temperature (20°C change)	pH 1.7 : -0.19
	pH 13.0 : +0.60
Long term stability	readings stable, no drift
Battery voltage	stable
Automatic shutdown	no
Price (1999)	£895 (includes conductivity meter and memory)

Comments :

The meter is based on the same design as the YSI single parameter D/O meters (YSI 55, 85, 95) with an ergonomic display unit and a separate probe. The measurement displayed is changed when the 'mode' key is pressed and cycles through the available readings. It is calibrated automatically in 1, 2 or 3 buffers. The instrument also has a pH, conductivity and temperature sensor in a single probe and can store up to 50 readings. The YSI 60 is the same design, but measures pH and temperature only.

3 COMPARATIVE TEST RESULTS

This section summarises and compares the data obtained from the evaluation tests of all 9 meters (Note: no results were obtained for the Hanna Agritest). Descriptions of the test methods and more detailed results are contained in the separate test reports

The tests were carried at out the Environment Agency's instrument evaluation facility at Fobney Mead, using pH buffer standards purchased from Whatman International Ltd. The test program was designed to reflect conditions which could be encountered during normal field use by the Agency.

3.1 Accuracy

Each instrument was calibrated and six measurements were then made in each of 5 different buffer solutions.

Table 1 shows the maximum error and maximum standard deviation found for each meter between pH 1.6 and 9.2. The error and standard deviation at pH 13 is shown separately in table 2.

Table 1 : Accuracy between pH 1.68 and 9.24

Meter	Max error	Max st.dev.
Amarell ad-110	- 0.2 at pH 4.0	0.1
Camlab pH-boy 501	< 0.1	< 0.1
Camlab pH-boy 723 (3 point calibration)	- 0.1	< 0.1
Hanna Checker	+ 0.11 at pH 9.24	0.05
Hanna pHep2	< 0.1	< 0.1
Hanna pHep3	- 0.2 at pH 4.0	0.1
Hanna 'new' pHep	+ 0.1 at pH 1.68	< 0.1
WTW P3	-0.02 at pH 9.24	0.02
YSI 63	+ 0.09 at pH 1.68	0.02

Table 2 : Accuracy at pH 13.06

Meter	Error	St.dev.
Amarell ad-110	< 0.1	0.1
Camlab pH-boy 501	*- 0.4*	*< 0.1*
Camlab pH-boy 723 (3 point calibration)	*- 1.8*	*< 0.1*
Hanna Checker	- 0.14	0.04
Hanna pHep2	- 0.3	< 0.1
Hanna pHep3	- 0.5	< 0.1
Hanna 'new' pHep	- 0.3	< 0.1
WTW P3	-0.38	0.02
YSI 63	-0.02	0.02

3.2 Response time to within 0.2 pH

The response time was measured between pH 4.0 and pH 9.2. All meters responded within 5 seconds, except the Camlab pH-boy 501 and 723, which both responded in 10 seconds for the rising step and less than 5 seconds for the falling step, and the WTW P3 which responded in 10 seconds for each step.

3.3 Warm-up Drift

The instruments were switched off and left over night. When the meter was switched on it was placed in a beaker of pH 7.4 buffer and the reading was then recorded for 30 minutes.

All the meters were within 0.05pH of their final value after 3 minutes. Table 3 below shows the change which occurred for each meter between 10 seconds and 3 minutes after switch-on.

Table 3 : 3 minute Warm up drift

Meter	Drift
Amarell ad-110	< 0.1
Camlab pH-boy 501	+ 0.2
Camlab pH-boy 723	+ 0.1
Hanna Checker	- 0.19
Hanna pHep2	- 0.1
Hanna pHep3	< 0.1
Hanna 'new' pHep	< 0.1
WTW P3	-0.04
YSI 63	-0.04

3.4 Sample temperature

The test was carried out in six different buffer solutions between 5 and 40°C. The temperature was allowed to stabilise for at least 1 hour at each point to ensure that the buffers had reached equilibrium. From the results the change of error with temperature in each buffer was calculated.

Table 4 shows the change in error caused by a 20°C temperature change at pH 1.7 and 13.0.

Table 4 : Effect of a 20°C water temperature change

Meter	change at pH 1.7	change at pH 13.0
Amarell ad-110	- 0.3	+ 0.6
Camlab pH-boy 501	+ 0.1	+ 0.3
Camlab pH-boy 723	- 0.1	+ 1.4
Hanna Checker	- 0.58	+ 0.56
Hanna pHep2	- 0.2	+ 0.6
Hanna pHep3	- 0.2	+ 0.3
Hanna 'new' pHep	- 0.3	+ 0.6
WTW P3	+0.02	+0.05
YSI 63	-0.19	+0.60

3.5 Effect of low conductivity

This test was carried out in 10^{-4} molar HCl. The conductivity of the solution was raised by adding small quantities of a KCl solution.

Table 5 shows the difference between readings in 41µS/cm and 1154µS/cm solutions for each meter.

Table 5 : Reading change at pH 4

Meter	change
Amarell ad-110	n/d
Camlab pH-boy 501	< 0.1
Camlab pH-boy 723	n/d
Hanna Checker	< 0.1
Hanna pHep2	< 0.1
Hanna pHep3	n/d
Hanna 'new' pHep	< 0.1
WTW P3	< 0.1
YSI 63	< 0.1

3.6 Drift test

The meters were calibrated at the start of the test. They were then placed in a test tank which was automatically filled with river water for 5 minutes each hour, for 3 weeks. Meter readings were checked each working day in pH 4.0, 7.4 and 9.2 buffer solutions.

The results in pH 7.4 are summarised in table 6, which shows the standard deviation of the readings over the test period, along with any relevant comments. The results are also shown in figs 1 and 2, where the traces for each meter have been offset for clarity.

Table 6 : Summary of drift test

Meter	St dev at 7.4 pH	Comments
Amarell ad-110	± 0.05	
Camlab pH-boy 501	± 0.07	slight decrease
Camlab pH-boy 501	meter not available	
Hanna Checker	± 0.63	large fluctuations
Hanna pHep2	± 0.14	slight increase
Hanna pHep3	± 0.08	slight increase
Hanna 'new' pHep	± 0.16	
WTW P3	meter not available	
YSI 63	± 0.09	

Fig 1 : Drift test - pH 9.2 buffer readings

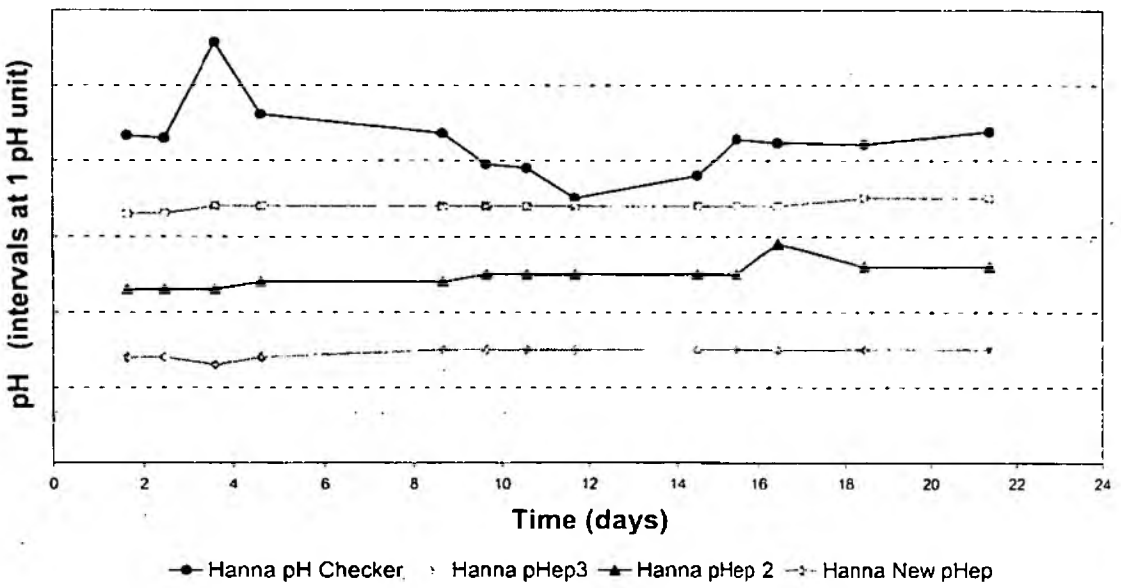
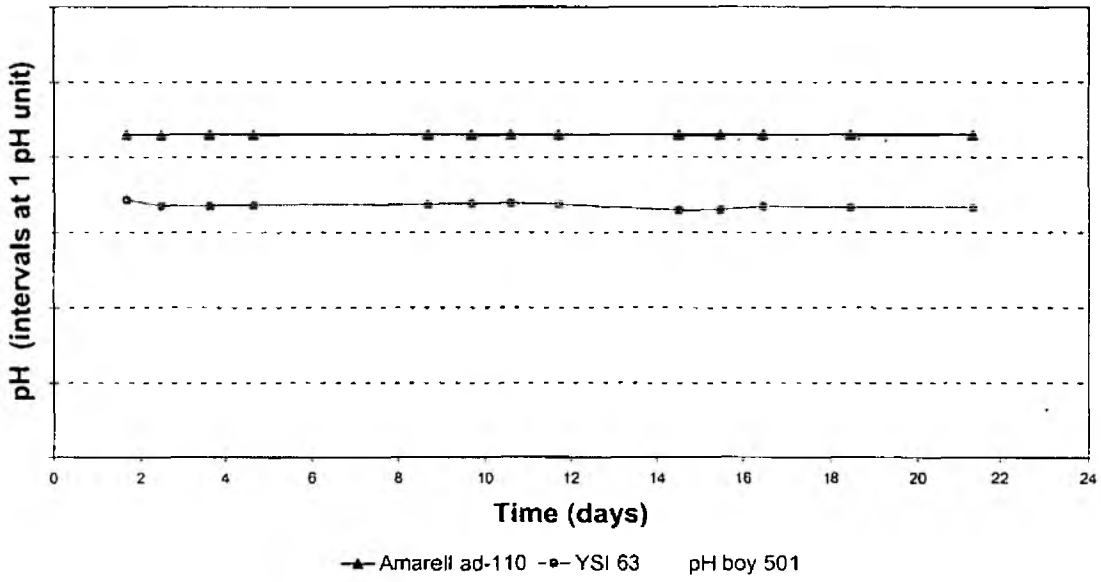


Fig 2 : drift test - 9.2 buffer readings



3.7 Battery voltage

A variable power supply was connected in place of the batteries and the effect of reducing the voltage from the normal operating voltage was recorded.

The results are summarised in table 7 where the normal operating voltage is shown, along with the minimum voltage, the voltage where the low battery alarm switches on and any comments. For details of the reading changes encountered the individual reports should be read.

Table 7 : Effect reduced battery voltage

Meter	Norm. volt	Min. volt	Lo-bat	Max change before Lo-bat	
				pH 7.4	pH 10.0
Amarell ad-110	6.0	2.0	-	-0.4	+3.6
Camlab pH-boy 501	6.0	2.5	4.5	0	0
Camlab pH-boy 723	6.0	3.0	4.75	0	-
Hanna Checker	2.8	1.9	-	+0.19	+1.19
Hanna pHep2	4.2	2.2	-	+0.9	+2.4
Hanna pHep3	5.6	3.5	-	0	0
Hanna 'new' pHep	5.6	3.5	-	0	0
WTW P3	meter not available				
YSI 63	9.0	6.0	6.6	-0.01	-0.02

3.8 Flow effect

A simple flow test was performed and no significant effect was seen on any meter.

3.9 Automatic shutdown time

The meters were switched on for up to 1½ hours and checked regularly to see if they had switched off.

Table 8 : Automatic shutdown time

Meter	approx. shutdown time
Amarell ad-110	n/a
Camlab pH-boy 501	1 hour
Camlab pH-boy 723	1 hour
Hanna Checker	n/a
Hanna pHep2	n/a
Hanna pHep3	15 min
Hanna 'new' pHep	n/a
WTW P3	1 hour
YSI 63	n/a

4 MANUFACTURERS' DETAILS

Amarell ad-110

Dryden Aqua Ltd.
Butlerfield Industrial Estate
Bonnyrigg EH19 3JG
Tel : 01875 822222

pH-boy 501
pH-boy 723

Camlab Limited
Nuffield Road
Cambridge CB4 1TH
Tel : 01223 424222

Checker
pHep 2
pHep 3
'new' pHep
Agritest

Hanna Instruments Ltd
Eden Way
Pages Industrial Park
Leighton Buzzard
Bedfordshire LU7 8TZ
Tel : 01525 850855

WTW P3

Burmarc Limited
Unit 12 Beaver Industrial Estate
Liphook
Hampshire GU30 7EU
Tel : 01428 724777

YSI 63

YSI (UK) Ltd.
Lynchford House, Lynchford Lane
Farnborough, GU14 6LT
Tel: 01252 514711