Control Samples for pH Determination in Low Ionic Strength Waters

Suitability for Analytical Quality Control

WRc plc

R&D P-10

CONTROL SAMPLES FOR pH DETERMINATION IN LOW IONIC STRENGTH WATERS.

RESTRICTION: This report is restricted to the National Rivers Authority
and equivalent bodies in Scotland and Northern Ireland

The work described in this report was carried out under contract to
the Department of the Environment, whose permission to publish has
been given. This report has been produced as part of
the Technical Services Contract for the National Rivers Authority
(NRA).

Any enquiries relating to this report should be referred to the author
at the following address:

WRc Medmenham, Henley Road, Medmenham, PO Box 16, Marlow,
Buckinghamshire SL7 2HD. Telephone: Henley (0491) 571531

CONTROL SAMPLES FOR pH DETERMINATION IN LOW IONIC STRENGTH WATERS

M J Gardner, R Gill and J E Ravenscroft

SUMMARY

Natural waters of relatively low ionic strength are especially sensitive to contamination. There is particular interest in changes in the acid status of such waters. Studies of acidification and any consequent changes in the chemistry of low ionic strength waters rely heavily on the accurate determination of pH value. This measurement poses problems which might be difficult to detect and overcome unless appropriate Analytical Quality Control (AQC) procedures are implemented.

The aim of this work was to test the suitability of several samples for use in routine AQC for pH determination in low ionic strength waters. Four solutions, two dilute mineral acids and two low ionic strength buffer solutions, were tested. All were found suitable for AQC work. The long term standard deviation of results for all solutions was less than 0.04 pH units.

Use of dilute mineral acids as control samples is recommended because these are likely to be representative of real samples in terms of ionic strength, and hence in their susceptibility to errors.

Report No PRS 2293-M; November 1989
11 pages
Project Ref: 8.3a

CONTENTS

SECTION 1 - INTRODUCTION

It is recognised that pH measurements in solutions of low ionic strength can be subject to important errors. Investigations carried out on commercially available electrodes (Davison and Woof 1985, Midgely and Torrance 1979, Koch and Marinenko 1983) and interlaboratory studies (Tyree 1983, Davison and Gardner 1986) suggest that errors of around 0.1 units are common and those up to 1 pH unit and larger cannot be ruled out.

One of the principal causes of error in pH determinations in low ionic strength samples is the variation of liquid junction potential with ionic strength for many types of commercial reference electrodes (Covington et al 1983, 1985). This is known to be responsible for errors in measurements for natural samples which have been calibrated against standard buffer solutions of comparatively high ionic strength. In many cases, however, error cannot be easily attributed to a particular cause and problems such as poor calibration practice (eg use of incorrect buffer solutions or contamination of samples with buffer), damaged electrodes, meter malfunction etc may each play a part in the production of erroneous results.

The rational approach to controlling errors in pH determination (as in other sorts of analysis) is to adopt a reliable and well-defined experimental procedure and to maintain quality control checks on the analytical system as part of routine practice (Cheeseman and Wilson 1978). This idea is incorporated in the method for pH determination in low ionic strength water recently published by the Standing Committee of Analysts (HMSO 1988). In addition to a detailed description of the experimental procedure, the method prescribes a number of checks on electrode performance to be carried out routinely. Measurements of slope factor and stirring shift (the difference between stirred and quiescent readings) to check electrode suitability are followed by a determination on a control solution in each batch of analysis.

The detection of error and the demonstration of adequate accuracy for routine analysis thus rests on checks using control samples. The aim of this paper is to report tests carried out to assess the suitability of different solutions for use in routine quality control and to present data on long-term precision, achieved under conditions typical of routine analysis, for pH determination on low ionic strength waters.

SECTION 2 - IDEAL CONTROL SAMPLE CHARACTERISTICS

An ideal solution to be used as a quality control sample in the determination of pH in low ionic strength waters should possess the following properties:

(a) It should be of known pH value. This provides a means of identifying *systematic* errors.

(b) It should behave in the same way as real samples with respect to likely sources of error. The susceptibility to error of the control solution should be at least as large as that of real samples. This ensures that the control analysis is an effective indicator of errors which are likely to apply to the analysis of real samples.

(c) It should be stable over several batches of analysis - or it should be possible to prepare identical aliquots of it, freshly for each batch of analysis. If stability is in question, then the maximum time over which storage is acceptable should be established.

2.1 NATURAL WATER SAMPLES FOR QUALITY CONTROL

A natural water sample might be considered to be a suitable control sample since it could be chosen to be similar to real samples in its composition and hence its susceptibility to error. Such a sample would suffer from the drawback of being of unknown pH, and probably of being less stable (and hence less comparable from one batch of analysis to the next) than artificial control samples.

2

2.2 ARTIFICIAL CONTROL SAMPLES

Artificial or prepared control solutions are of known pH value (for the purposes of AQC) but may not be subject to the same sources of error as real samples. An independently prepared buffer sample will be adequate to detect many of the sources of error which may be present during measurement, but the specific problem of the ionic strength dependence of liquid junction potential is only addressed by control solutions of ionic strength similar to the water samples of interest (10^{-3} M to 10^{-4} M). Low ionic strength is therefore an important characteristic of suitable artificial control samples.

A diagnostic test for possible errors caused by junction potential changes is the so-called "stirring shift" - the difference in measured pH between stirred and unstirred samples. Large stirring shift is at least indicative of a sensitivity in measured pH to turbulence in the solution under examination and therefore of an additional source of error. It has been recommended that, ideally, only electrode systems showing no important stirring shift should be used (Davison and Woof 1985, Galloway et al 1979). Suitable control solutions should therefore produce low stirring shifts for electrode systems which are operating well but should provide an indication of poor performance by giving a stirring shift of a similar size as that for a real sample.

SECTION 3 - SOLUTIONS TESTED

Preliminary tests using stored natural samples as controls showed sample stability to be inadequate. The work reported here was carried out on the following artificial samples:

- NBS (high ionic strength) buffer solutions of pH value 4.00 and 6.88
- a dilute solution of hydrochloric acid in deionised water (pH 5)
- a dilute solution of hydrochloric acid in deionised water (pH 4)
- a low ionic strength buffer solution (pH 4)
- 0.01M potassium hydrogen phthalate

3

- a low ionic strength buffer solution (pH 7)
- 0.0025M disodium hydrogen phosphate, 0.0025M potassium hydrogen phosphate

SECTION 4 - EXPERIMENTAL

Tests were carried out using two electrode systems: (a) a dual electrode system consisting of separate pH (Corning 09723) and reference (Corning 004341) electrodes (both from Fisons, Loughborough) and (b) a combination pH/reference electrode (Amagruss 19051, Plovgem, Maidstone). The reference component of the dual electrode system had a raised (1 m) reservoir of saturated KCl filling solution to increase the flow through the ceramic frit. The plug used to top up the reference element on the combination electrode was removed before use - in accordance with the manufacturer's instructions.

The two systems were chosen to represent typical commercial pH systems operating satisfactorily under conditions of routine analysis. The same pH meter (Micro II, Oxford Laboratory Supplies, High Wycombe) was used for measurements with both electrode systems. All reagents used were of Analar grade.

Tests were conducted in 14 batches over a period of 7 weeks with the aim of evaluating the precision likely to be achieved for the test samples under conditions of routine analysis. Each measurement used 50 ml of sample and involved stirring for 2 min with a magnetic stirrer in an open glass beaker, recording the "stirred" reading, switching off the stirrer and allowing 2 min for the sample to become quiescent before taking a final "quiescent" reading. All measurements were made in a water bath at 20 + 1 °C. For each batch of analysis the electrodes were calibrated using solutions prepared freshly from commercially available sachets of buffer powder (BDH Chemicals, Poole). Determinations were made in duplicate, in random order with the proviso that measurements on the high ionic strength NBS buffers were made at the end of each batch to avoid possible contamination or carry over to the lower ionic strength samples.

4

In order to make the batch of measurements more representative of routine analysis and to include variation in the ionic strength of the solutions presented to the electrodes, a tapwater sample (conductivity approx 25 mg $CaCO_3$/L, alkalinity approx 25 mg $CaCO_3$/L) was measured, using the test procedure, in between each measurement on the control solutions under examination.

The control samples were refrigerated when not in use. Each was prepared, from Volucon standardised hydrochloric acid (BDH Chemicals, Poole) or from Analar reagents, at the start of batches 1, 3, 9 and 12 of the 14 batches in the tests. No systematic changes were observed during the approximate 10-day lifetime of any control solution or between an old aliquot of each solution and its freshly-prepared successor. When not in use, the glass and combination electrodes were stored in a pH 4 buffer. The separate reference electrode was stored in a saturated KCl solution.

Further tests to assess the response of the control solutions (measured as the stirring shift) to an electrode system which responded poorly to samples of low ionic strength were also carried out. This involved taking the combination electrode and reducing the level of filling solution in the reference element to the minimum required to make contact. This, it was hoped, would reduce flow at the liquid junction and increase susceptibility to anomalous ionic strength effects.

SECTION 5 - RESULTS

5.1 LONG-TERM PRECISION TESTS

The results of the test of precision are shown in Table 1. The mean pH and the total standard deviation of results is given for the six solutions examined. The total standard deviation is derived from an analysis of variance as described by Wilson (Wilson 1970). It represents the overall standard deviation of any result in any batch of analysis and incorporates random error arising both within a batch and

Table 1. Mean pH and Precision for Long-term Tests

	Accepted pH Value		Measured pH Value – Mean and Total Standard Deviation over 14 batches of analysis					
			DUAL ELECTRODE SYSTEM			COMBINATION ELECTRODE		
			stirred	quiescent	stirring shift	stirred	quiescent	stirring shift
pH 4.00	4.00	Mean	4.010	4.010	0.000	4.001	4.003	0.002
NBS Buffer		Sw	0.013	0.013		0.008	0.009	
		St	0.013	0.013		0.009	0.009	
pH 6.88	6.88	Mean	6.880	6.889	0.009	6.878	6.882	0.004
NBS Buffer		Sw	0.018	0.018		0.011	0.011	
		St	0.019	0.035		0.012	0.012	
10^{-5} M	5.001	Mean	5.010	5.028	0.014	4.994	5.018	0.024
HCl		Sw	0.018	0.014		0.012	0.012	
		St	0.025	0.023		0.025	0.025	
10^{-4} M	4.005	Mean	4.029	4.034	0.005	4.003	4.017	0.015
HCl		Sw	0.011	0.010		0.003	0.003	
		St	0.017	0.017		0.015	0.015	
0.0025M	7.082	Mean	7.071	7.077	0.006	7.043	7.069	0.016
Buffer a		Sw	0.016	0.010		0.004	0.004	
		St	0.027	0.030		0.022	0.022	
0.01M	4.112	Mean	4.105	4.110	0.005	4.082	4.091	0.009
Buffer b		Sw	0.013	0.009		0.003	0.004	
		St	0.018	0.017		0.014	0.014	

Notes.

Sw: Within batch standard deviation (14 degrees of freedom)
St: Total standard deviation (between 13 and 27 degrees of freedom (Cheeseman and Wilson 1978)

Dilute buffer solutions a – 0.025M Na_2HPO_4, 0.025M KH_2PO_4 – and b 0.01M potassium hydrogen phthalate are described in Covington et al (1983). The accepted pH values for these solutions are taken from this paper. The pH values for the dilute acids are calculated as the negative logarithm of hydrogen ion activity calculated using the Davies equation (Mattock 1961).

between one batch and another. The difference between the quiescent and stirred readings is given as the stirring shift.

The results of tests on a deliberately "impaired" electrode system are shown in Table 2.

SECTION 6 - DISCUSSION

The differences between the accepted values for the pH of the control solutions and mean observed values shown in Table 1 are small in relation to the needs of most pH determinations. The largest mean bias for an individual solution was - 0.039 pH units. Taking all the control solutions together, the overall mean bias was less than 0.002 units. Both the electrode systems exhibited an overall precision, as indicated by the total standard deviation, of less than 0.03 pH units, for all the test solutions. The total standard deviation for the combination electrode was in all cases lower for the combination electrode than for the glass/reference pair.

Caution is necessary in making any comparison of the performance of the two electrode systems as they are not necessarily representative of any corresponding "type" of electrode. It has been noted (Covington et al 1985, Galloway et al 1979) that, owing to their smaller, less free flowing liquid junctions, many combination pH electrodes are more prone to error in low ionic strength samples than systems having a separate reference electrode. The consistently larger stirring shift for the combination electrode supports this view for the two electrodes tested. On the other hand, it was noticeable that the combination electrode was quicker to come to a stable reading than the dual electrode system. Slow response and stirring shift are two potential sources of error which appeared to affect the two electrode systems to different extents. On the whole, however, both systems performed well and would meet the precision and bias targets defined for river quality monitoring (Analytical Quality Control (Harmonised Monitoring) Committee 1984).

7

Table 2.   Response of an "Impaired" Electrode

Sample	Mean Measured pH		Bias		Stirring Shift	Nos of Results
	Stirred	Quiescent	Stirred	Quiescent		
Natural Water A	7.169	7.265			0.096	10
Natural Water B	7.332	7.405			0.073	8
10^{-5} M HCl	4.948	5.024	-0.053	+0.025	0.076	4
10^{-4} M HCl	3.960	4.028	-0.045	+0.023	0.068	4
0.0025M Buffer a	7.002	7.006	-0.080	-0.016	0.064	4
0.01M Buffer b	4.069	4.102	-0.043	-0.010	0.036	4

Notes
Natural water A: conductivity 50 μS/cm, hardness 25 mg $CaCO_3$/L
Natural water B: conductivity 78 μS/cm, hardness 27 mg $CaCO_3$/L

All measurements were carried out in a single batch.
Bias is with respect to the accepted pH values given in Table 1.

The performance of the electrode system with a reduced flow through the
liquid junction was degraded only to a small extent. Nevertheless, as
expected, the results for stirred samples were all lower than those for
quiescent samples. The magnitude of the negative bias for stirred
control samples increased by a factor of two to three. Two points
concerning the stirring shift are worth noting. Firstly, the increase
in stirring shift corresponded to the increase in bias and secondly, the
size of the stirring shift for the control solutions was similar to that
for the two natural waters tested. This supports the use of the
stirring shift as a guide to potential errors relating to ionic
strength.

SECTION 7 - CONCLUSIONS

It is concluded that all of the four solutions tested might be suitable
for use as quality control samples for the determination of pH in low
ionic strength samples. The use of the dilute acid samples is
recommended since these are of an ionic strength nearer to that of
natural waters of interest. They are stable (under refrigerated
storage) over at least one week. The results support the use of the
stirring shift as a means of identifying problems connected with low
ionic strength.

It is worth emphasising the fact that many types of electrode may
perform adequately and that ultimately, no recommendations on the choice
of equipment can guarantee acceptable accuracy; reliance must be placed
on the use of a well-defined analytical procedure supported by practical
checks on performance.

REFERENCES

ANALYTICAL QUALITY CONTROL (HARMONISED MONITORING) COMMITTEE (1984) Accuracy of the determination of pH and electrical conductivity in river water. Analyst 109, 431-437.

CHEESEMAN R V and WILSON A L (1978) A Manual of Analytical Quality Control for the Water Industry, Water Research Centre Technical Report TR66, 170p.

COVINGTON A K, WHALLEY P D and DAVISON W (1983) Procedures for the measurement of pH in low ionic strength solutions, including freshwaters. Analyst 108, 1528-1532.

COVINGTON A K, WHALLEY P D and DAVISON W (1985) Improvements in the precision of pH measurements. Anal Chim Acta 165, 221- 230.

DAVISON W and WOOF C (1985) Performance tests for the measurement of pH with glass electrodes in low ionic strength solutions. Anal Chem 57, 2567-2570.

DAVISON W and GARDNER M J (1986) Inter-laboratory comparisons of the determination of pH in poorly buffered freshwater. Anal Chim Acta 182 17-31.

GALLOWAY J N, COSBY B J and LIKENS G E (1979) Precipitation: Measurement of pH and alkalinity. Limnol Oceanogr 24, 1161-1165.

HMSO (1988) The Determination of pH in Low Ionic Strength Waters, 1988, Methods for the Examination of Waters and Associated Materials, Her Majesty's Stationery Office, London, 17p.

KOCH W F and MARINENKO G (1983) In Sampling and Analysis of Rain edited by S A Campbell. ASTM STP 823, 10-17.

MATTOCK G (1961) pH Measurement and Titration. Heywood and Co, London, 406p.

MIDGELY D and TORRANCE K (1979) Assessment of glass electrodes for determining pH in boiler feed water. Analyst 104, 63-72.

TYREE S Y (1983) In Sampling and Analysis of Rain edited by S A Campbell. ASTM STP 823, 18-28.

WILSON A L (1970) The performance characteristics of analytical methods III. Talanta 17, 31-44.