

Electrochemical analyzers —

Part 2: Method for specifying performance of pH value analyzers

[IEC title: Expression of performance of electrochemical
analyzers — Part 2: pH value]

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- British Industrial Measuring and Control Apparatus Manufacturers' Association (BEAMA)
- British Telecommunications
- Department of Industry (British Calibration Service)
- Department of Industry (National Physical Laboratory)
- Electricity Supply Industry in England and Wales
- Electronic Engineering Association
- Institution of Electronic and Radio Engineers
- Scientific Instrument Manufacturers' Association (BEAMA)

The following bodies were also represented in the drafting of the standard, through subcommittees and panels:

- Engineering Equipment and Materials Users' Association
- Water Research Centre

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Contents

	Page
Committees responsible	Inside front cover
National foreword	ii
1 Scope	1
2 Object	1
3 Definitions and symbols	1
4 Procedure for statement	3
5 Recommended standard values and ranges of influence quantities affecting the performance of electronic units	3
6 Verification of values	4
Appendix A Values of the slope factor $k = 2.3026 RT/F$	9
Appendix B Reference buffer solutions: pH as a function of temperature	9
Appendix C Test solutions	10
Appendix D Alternative procedures for measuring delay time (T_{10}), rise (fall) time (T_r , T_f) and 90 % time (T_{90})	11
Bibliography	8
Index of definitions	8
Figure D.1 — Relation between T_{10} , T_r (T_f) and T_{90}	11
Publications referred to	Inside back cover

National foreword

This Part of BS 6438 has been prepared under the direction of the Electronic Equipment Standards Committee. It is identical with IEC Publication 746-2:1982 “*Expression of performance of electrochemical analyzers — Part 2: pH value*”, published by the International Electrotechnical Commission (IEC).

This Part of BS 6438 should be read in conjunction with Part 1. Other Parts in preparation include electrical conductivity and dissolved oxygen content.

Terminology and conventions. The text of the International Standard has been approved as suitable for publication as a British Standard without deviation. Some terminology and certain conventions are not identical with those used in British Standards.

Cross-reference

International Standard	Corresponding British Standard
IEC 746-1:1982	BS 6438 <i>Electrochemical analyzers</i> Part 1:1984 <i>Method for specifying performance common to all analyzers</i> (Identical)

Additional information. The pH values as a function of temperature for the reference buffer solutions given in Appendix B may differ by as much as 0.03 from the values given in BS 1647 “*pH scale*” depending upon the particular reference buffer solution and the temperature. This should not normally be a problem within the precision of the instrument likely to be used. If higher precision is sought it is advisable to consult BS 1647 for values and procedures.

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Summary of pages

This document comprises a front cover, an inside front cover, pages i and ii, pages 1 to 12, an inside back cover and a back cover.

This standard has been updated (see copyright date) and may have had amendments incorporated. This will be indicated in the amendment table on the inside front cover.

1 Scope

This standard is applicable to analyzers, sensor units and electronic units used for the determination of pH values of aqueous solutions using glass-electrodes. IEC Publication 746-1: Expression of Performance of Electrochemical Analyzers, Part 1: General, includes further definition of the scope and provides for the general aspects of all electrochemical analyzers, including pH.

It also contains specifications for simulators used for testing pH electronic units.

2 Object

This standard is intended to specify the terminology, definitions, requirements for statements by manufacturers and performance tests for analyzers, sensor units and electronic units used for the determination of pH value of aqueous solutions.

3 Definitions and symbols

See Clause 3 of IEC Publication 746-1, plus the following.

3.1 Symbols

a_{H^+}	=	hydrogen ion activity
pH	=	pH of the solution measured at temperature t
pH(S_1)	=	pH of the first reference buffer solution, at temperature t
pH(S_2)	=	pH of the second reference buffer solution, at temperature t
pH _i	=	pH at isopotential point
E	=	electromotive force in the measured sample at temperature t
$E(S_1)$	=	electromotive force in the first reference buffer solution, at temperature t
$E(S_2)$	=	electromotive force in the second reference buffer solution, at temperature t
E_i	=	electromotive force at the isopotential point
F	=	the Faraday constant
R	=	the molar gas constant
t	=	temperature in degrees Celsius
T	=	the thermodynamic temperature in degrees Kelvin of sample, buffer solutions and sensors ($T = t + 273.15$)

3.2 pH value

A measure of the conventional hydrogen ion activity a_{H^+} in an aqueous solution given by the expression:

$$\text{pH} = -\log a_{\text{H}^+}$$

Although this expression can be used to give an interpretation to pH values under certain limiting conditions, a_{H^+} cannot be rigorously obtained from electromotive force measurements, and an operational definition is adopted in terms of pH values assigned to certain reference buffers. The measurement is performed by determining the e.m.f. E between a pair of electrodes immersed in the sample to be measured, according to the cell scheme:

Reference electrode | Sample | Glass electrode E

and a measurement with the same electrode pair at the same temperature in a reference buffer solution of pH (S_1) according to

Reference electrode | Reference (S_1) | Glass electrode $E(S_1)$

The e.m.f.'s E , $E(S_1)$, etc. are defined as the difference of the potential of the right-hand (glass electrode) minus the potential of the left-hand (reference electrode).

The pH of the sample is then given by:

$$\text{pH} = \text{pH}(S_1) - \frac{[E - E(S_1)]}{k} \quad (1)$$

where $k = 2.3026 RT/E$.

Numerical values for k , which is known as the theoretical slope factor, at temperatures from 0 to 95 °C, are given in Appendix A.

3.3 Percentage of theoretical slope (PTS)

Under some conditions, the performance of the electrode pair may fall below the theoretical expectation, that is, below the value of k at the appropriate temperature. Such a deviation is expressed as a percentage of the theoretical slope (PTS) and may be determined by replacing the sample by a second reference buffer of pH value $\text{pH}(S_2)$ which yields an indicated e.m.f. of $E(S_2)$, then:

$$\text{PTS} = \frac{100 [E(S_2) - E(S_1)]}{k [\text{pH}(S_1) - \text{pH}(S_2)]} \quad (2)$$

NOTE For the best accuracy, the difference in pH value between the two reference buffer solutions should be as large as possible. However, neither solutions A nor I in Appendix B should be used.

Equations (1) and (2) can be combined by substituting the practical slope k' for factor k in equation (1), where $k' = \frac{k(\text{PTS})}{100}$:

$$\text{pH} = \text{pH}(S_1) + \frac{[E - E(S_1)] [\text{pH}(S_1) - \text{pH}(S_2)]}{[E(S_1) - E(S_2)]}$$

and the two reference buffers are usually chosen to bracket the pH of the sample.

3.4 Zero point (pH)

The pH value at which the pH measuring cell (sensor unit) reads 0 V at a given temperature. If not otherwise specified it is understood to be 25 °C.

3.5 Isopotential point of the sensor unit

The point of intersection on an e.m.f. versus pH plot of pH calibration curves taken at different temperatures. The isopotential point is dependent on the temperature coefficients of both pH and reference electrodes. The co-ordinates are pH_i and E_i . Using these co-ordinates, the pH value of the sample can be calculated by:

$$\text{pH} = \text{pH}_i - \frac{[E - E_i]}{k'}$$

3.6 Sodium error

The error in the e.m.f. caused by sensitivity of the pH electrode for sodium ions.

3.7 Reference buffer solution

An aqueous solution prepared according to a specific formula, using recognized analytical grade chemicals and water having a conductivity of no more than $2 \mu\text{S} \cdot \text{cm}^{-1}$. The pH value of reference buffer solutions may, because of the variations in the purity of available commercial chemicals, differ by as much as ± 0.01 from accepted values. For higher accuracy, solutions may be prepared with chemicals that have been characterized and certified by a national standards laboratory.

3.8 Input offset voltage

That voltage that is applied between the input terminals to obtain zero output voltage.

3.9 Common mode input voltage

A voltage that is applied to both input terminals at the same time.