Specification for

Ion-selective electrodes, reference electrodes, combination electrodes and ion-selective electrode meters for determination of ions in solution

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Committees responsible for this British Standard

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British Kinematograph, Sound and Television Society
British Pharmacopoeia Commission
Chemical Industries Association
Electricity Supply Industry in England and Wales
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Contents

Foreword

This British Standard has been prepared under the direction of the Laboratory Apparatus Standards Policy Committee.

The most practised method of potentiometry is the determination of hydrogen ions, i.e. pH measurement, but because of its importance this is dealt with separately in BS 1647, BS 2586 and BS 3145.

Potentiometric determination of ion concentrations/activities received a fillip in the early 1970s with the commercial availability of a new range of ion-selective membrane electrodes [1, 2, 3] related to the familiar pH glass electrode, but responsive to a variety of other cations, for example K^+ and Ca^{2+}, and anions, for example F^- and NO_3^-, some of which could not previously be determined potentiometrically.

This British Standard covers this new range of ion-selective (membrane) electrodes and reference electrodes and an outline of procedures for using ion-selective electrodes is given in Appendix A.

Summary of pages

This document comprises a front cover, an inside front cover, pages i and ii, pages 1 to 18, 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.

Section 1. General

1.1 Scope

This British Standard specifies performance requirements and other requirements for ion-selective electrodes, reference electrodes and combination (dual) ion-selective electrodes in general laboratory use, and for ion-selective electrode meters for laboratory use.

NOTE 1 An outline of procedures used for determining ionic species (except hydrogen ion), and neutral species indirectly, using ion-selective electrodes, is given in Appendix A.

NOTE 2 Recommended tests of performance of electrodes are described in Appendix B.

NOTE 3 Instrument check tests are described in Appendix C.

NOTE 4 Appendix D covers standard reference solutions for direct potentiometry.

NOTE 5 The titles of the publications referred to in this standard are listed on the inside back cover. The numbers in square brackets represent the bibliographical references given in Appendix E.

1.2 Definitions

For the purposes of this British Standard the following definitions apply.

1.2.1 General

1.2.1.1
pX

the quantity defined by analogy with pH as $\text{pX} = \text{p}a_\text{X} = -\log a_\text{X}$, where a_X is the single ion activity of the species X, or alternatively as $\text{pX} = \text{p}c_\text{X} = -\log c_\text{X}$, where c_X is the species concentration of X in mol/L

1.2.1.2
reference standards

aqueous solutions which are the basis for standardizing the ISE cell (see **1.2.1.12**)

NOTE Values may be assigned as described in Appendix D.

1.2.1.3
practical response time

the length of time that elapses between the instant at which an ion-selective electrode and a reference electrode are brought into contact with a sample solution (or instant at which the concentration of the ion of interest is changed) and the first instant when the potential change of the cell has reached 90 % of the final value

NOTE The experimental conditions used should be stated, i.e. the stirring rate, the ionic concentration and composition of solution of which the response time is measured, the ionic concentration and composition of the solution to which the electrode was exposed prior to this measurement, the history and preconditioning of the electrode, and the temperature.

1.2.1.4
liquid junction

any junction between two electrolyte solutions of different composition. Across such a junction there arises a potential difference, called the liquid junction potential

NOTE In the ISE cell, the junction is between the test, or standard, solution and the filling solutions, or the bridge solution (see **1.2.3.3**), of the reference electrode.

1.2.1.5
residual liquid junction (potential) error

an error arising from breakdown in the assumption that the liquid junction potential remains constant on change of solution

1.2.1.6
slope factor, k

the temperature-dependent proportionality factor between potential difference and pX for monovalent ions

NOTE Values of k are given in Table 1.

1.2.1.7
test solution

the solution of which the ionic activity, or ionic concentration, is required

1.2.1.8
drift

this is the slow, non-random change with time in the potential difference of an ion-selective reference electrode cell maintained in a solution of constant composition and temperature

1.2.1.9
hysteresis (electrode memory)

the occurrence of a different value in the potential difference after the concentration has been changed and then restored to its original value. The reproducibility of the electrode is consequently poor. The systematic error is generally in the direction of the concentration of the solution in which the electrode was previously immersed. Hysteresis may occur as a result of temperature change

1.2.1.10
membrane

a continuous layer covering a structure or separating two electrolytic solutions. The membrane of an ion-selective electrode is responsible for the potential response and selectivity of the electrode

1.2.1.11
interfering substance

any species, other than the ion being measured, whose presence in the sample solution affects the measured potential difference of a cell

1.2.1.12
ISE cell

electrochemical cell, which is the basis of practical measurements, consisting of an ion-selective electrode (ISE) (see **1.2.2.1**) responding to the species X and a reference electrode (see **1.2.3.1**) dipping in the test solution

1.2.1.13
ionic-strength adjustment buffer

a pH-buffered solution of high ionic strength added to both sample and calibration solutions before measurement in order to achieve identical strength and hydrogen ion activity. Complexing agents and other components are often added to minimize the effects of certain interferences

1.2.1.14
standard addition method (or known addition method)

a procedure for the determination of the activity or concentration of a particular species in a sample by adding known amounts of that species to the sample solution and recording the change in potential difference of the ion-selective cell

1.2.1.15
standard subtraction method (or known subtraction method)

a variation of the standard addition method (see **1.2.1.14**). In this procedure changes in the potential resulting from the addition of a known amount of a species which reacts stoichiometrically with the ion of interest (e.g. a complexing agent) are employed to determine the original activity or concentration of the ion

1.2.1.16
ionic strength of a solution

the ionic strength of a solution I (in mol/L) is defined by the following equation:

$$I = ½\Sigma c_i z_i^2 \qquad (1)$$

where

c_i is the concentration of the ion, i (in mol/L);

z_i is the change of the ion, i.

1.2.1.17
gran plot

a means of evaluating titration, or standard addition, results in which a suitable function of the potential difference of the measuring cell is plotted on the vertical axis against volume increments on the horizontal axis, giving a linear plot allowing the concentration of the sensed species to be obtained from the intercept on the horizontal axis [4]

1.2.2 Ion-selective electrodes

1.2.2.1 ion-selective electrode (ISE)

1.2.2.1.1
general

electrode responding to ions of species X, usually consisting of a membrane in the form of a disc, or other suitable shape, of special material attached to a stem of plastics or glass complete with internal reference electrode (see **1.2.2.2**) and, optionally, an internal filling solution system (see **1.2.2.3**). Other geometrical forms may be appropriate for special applications, e.g. flow electrodes for measurement of ionic species in body fluids

ion-selective electrodes may be classified as crystalline, non-crystalline and sensitized (see **1.2.2.1.2** to **1.2.2.1.4**)

1.2.2.1.2
crystalline electrodes

these are categorized as follows

a) Homogeneous, in which the membrane is a crystalline material prepared from either a single compound or a homogeneous mixture of compounds (e.g. Ag_2S and $AgI + Ag_2S$).

b) Heterogeneous, in which an active substance, or mixture of active substances, is mixed with an inert matrix, such as silicone rubber or PVC, or placed on hydrophobized graphite, to form the sensing membrane.

1.2.2.1.3
non-crystalline electrodes

these consist of a matrix containing an ion-exchanger which is usually interposed between two aqueous solutions. The matrix may be porous (e.g. cellulose ester) or non-porous [e.g. glass or inert polymeric material such as polyvinyl chloride (PVC)]

typical of this class are glass electrodes in which the sensing membrane is a thin piece of glass. The chemical composition of the glass determines the selectivity of the membrane, e.g. hydrogen ion-selective electrodes (see BS 2586) and monovalent cation-selective electrodes

electrodes with a mobile carrier are categorized as follows

a) Positively charged, e.g. those of quaternary ammonium salts or salts of transition metal complexes such as derivatives of 1, 10-phenanthroline.

b) Negatively charged, e.g. bulky anions such as dialkyl phosphate $[(RO)_2PO_2^-]$ and tetrakis (p-chlorophenyl) borate anions.

c) Uncharged or neutral carrier, e.g. antibiotics, macrocyclic compounds or other sequestering agents.

1.2.2.1.4
sensitized ion-selective electrodes

these are categorized as follows

a) *Gas sensing electrodes.* These are sensors composed of an indicator and a reference electrode and use a gas-permeable membrane or an air-gap to separate the sample solution from a thin film of an intermediate solution that is either held between the gas membrane and the ion-sensing membrane of the electrode or placed on the surface of the electrode using a wetting agent (e.g. air-gap electrode). This intermediate solution interacts with the gaseous species in such a way as to produce a change in a measured value (e.g. pH) of the intermediate solution. This change is then sensed by the ion-selective electrode and is proportional to the partial pressure of the gaseous species in the sample.

NOTE Gas-sensing electrodes are in fact whole electrochemical cells.

b) *Enzyme substrate electrodes* In these an ion-selective electrode is covered with a coating containing an enzyme which causes the reaction of an organic or inorganic substance (substrate) to produce a species to which the electrode responds. Alternatively, the sensor could be covered with a layer of substrate that reacts with the enzyme to be assayed. An example is an ammonium ion-selective electrode coated with urease for urea determination.

1.2.2.2
internal reference electrode (of an ion-selective electrode)

electrode, e.g. silver-silver chloride, electrically connected to the screened input cable to the meter, and in contact with the internal filling solution

NOTE In all-solid-state electrodes the material of the reference electrode is deposited directly on to the membrane and the internal filling solution is unnecessary.

1.2.2.3
internal filling solution (of an ion-selective electrode)

aqueous electrolyte solution, which may be gelled, containing a fixed concentration of ion X and a fixed concentration of the ion to which the inner reference electrode is reversible, e.g. chloride ion in the case of silver-silver chloride or calomel electrodes

1.2.2.4
screened cable

coaxial shielded cable connecting the ion-selective electrode internal reference electrode system to a plug for input to the measuring instrument (ISE meter)

NOTE Some electrodes may be provided with detachable screened cables.

1.2.2.5
screened ion-selective electrode

ion-selective electrode in which the screening is continued down almost the whole length of the stem of the electrode

NOTE Combination electrodes are screened by the external reference electrode filling solution (see **1.2.3.1** and **1.2.3.2**).

1.2.2.6
zero point (of an ion-selective electrode)

value of the pX of a solution, which in combination with a stated outer reference electrode, gives zero potential difference from the cell

1.2.2.7
electrode error

deviation of an ion-selective electrode from the X ion response function

1.2.2.8
calibration curve of an ion-selective electrode

a plot of the potential difference of a given ion-selective electrode cell against the logarithm of the ionic activity (or concentration) of species X

NOTE A calibration curve usually has the shape shown in Figure 1. An ionic-strength adjustment buffer (see **1.2.1.13**) may be used.

1.2.2.9
practical limit of detection

the concentration (or activity) of X at the point of intersection of the extrapolated linear segments of the calibration curve, as shown in Figure 1

NOTE Since many factors affect the detection limit, it is important that the experimental conditions be reported, i.e. composition of the solution, the history and preconditioning of the electrode, stirring rate, etc.

1.2.2.10
Nernstian response

an ion-selective electrode is said to have a Nernstian response over a given range of activity (or concentration) when a plot of the potential of such an electrode, in conjunction with a reference electrode, against the logarithm of the ionic activity of a given species (a_X) is linear with a slope factor k given by the following equation:

$$k = RT(\ln 10)/z_XF = 59.159/z_X \text{ mV per decade of } pa_X = \text{pX at } 25\ ^\circ\text{C (see \textbf{1.2.1.6})}. \qquad (2)$$

where

R is the gas constant, i.e. 8.31441 J $\cdot$ K^{-1} mol^{-1};

T is the thermodynamic temperature (in K;

ln 10 = 2.302585;

z_X is an integer with sign and magnitude corresponding to the charge of the primary ion, X;

F is the Faraday constant,
i.e. 9.648456×10^4 C·mol^{-1}.

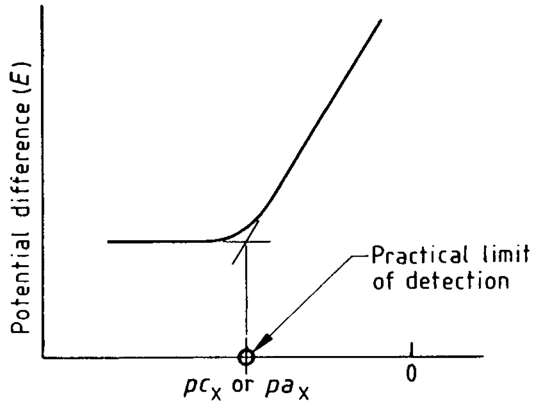

Figure 1 — Calibration curve and determination of practical limit of detection

1.2.2.11
selectivity coefficient, $k_{X,Y}$

the ability of an ion-selective electrode to distinguish between different ions in the same solution. The selectivity coefficient is evaluated by means of the ion-selective electrode potential response in mixed solutions of the primary ion, X, and interfering ion, Y, (or, less desirably, in separate solutions). The concentrations of the primary ion, X, and the interfering ion, Y, at which $k_{X,Y}$ is determined should always be specified. The value of $k_{X,Y}$ is defined by the Eisenman-Nikolsky equation (see **1.2.2.12**). The smaller the value of $k_{X,Y}$, the greater the electrode's preference for the primary ion, X

NOTE The terms "selectivity constant" and "selectivity factor" have been used instead of selectivity coefficient. "Selectivity coefficient" is preferable and the fixed interference method is preferable for its evaluation.

1.2.2.12
modified Nernst equation, Eisenman-Nikolsky equation, for ion-selective electrodes, and $k_{X,Y}$

if the potential difference between an ion-selective electrode (predominantly response to species X) and a suitable reference electrode is measured in mixed solutions containing ions Y and Z, for example, the following equation often applies:

$$E = \text{constant} + \frac{RT\,(\ln 10)}{z_X F} \times \log[a_X + k_{X,Y}(a_Y)^{z_X/z_Y} + k_{X,Z}(a_Z)^{z_X/z_Z}] \tag{3}$$

where:

E is the experimentally observed potential difference;

the "constant" includes the standard potential of the ion-selective electrode, the reference electrode potential and the junction potential;

R is the gas constant, i.e. 8.31441 J·K^{-1} mol^{-1};

T is the thermodynamic temperature (in K);

F is the Faraday constant and is equal to 9.648456×10^4 C·mol^{-1};

a_X is the activity of the ion, X;

a_Y and a_Z are the activities of the interfering ions, Y and Z, respectively;

$k_{X,Y}$ is the temperature dependent, potentiometric selectivity coefficient;

z_X is an integer with sign and magnitude corresponding to the charge of the primary ion, X;

z_Y, z_Z are integers with the same sign as z_X and magnitude corresponding to the charges on the interfering ions, Y and Z, respectively.

1.2.3 Reference electrodes

1.2.3.1
reference electrode

external electrode system that comprises an inner element, usually calomel or silver-silver chloride, a chamber containing the appropriate filling solution and a device for forming the liquid junction, e.g. ceramic plug, fritted disc or ground glass sleeve

1.2.3.2
filling solution (of a reference electrode)

solution containing the anion to which the reference electrode of the ISE cell is reversible, e.g. chloride for silver-silver chloride electrode. In the absence of a bridge solution (see **1.2.3.3**) a high concentration of filling solution, comprising cations and anions of almost equal mobility, is employed as a means of keeping the liquid junction potential small and approximately constant on substitution of test solution for standard solution(s)

1.2.3.3
bridge solution (of a double junction reference electrode)

solution of high concentration of inert salt, preferably comprising cations and anions of equal mobility, optionally interposed between the reference electrode filling (see **1.2.3.2**) and both the test and standard solution, when the test solution and filling solution are chemically incompatible. This procedure introduces into the ISE cell a second liquid junction

1.2.4 Combination electrodes

1.2.4.1
combination (or dual) electrode

ion-selective electrode in which an external reference electrode system, with a means of forming the liquid junction, is incorporated

1.2.5 ISE meters

1.2.5.1
laboratory ISE meter

high impedance input instrument designed for general laboratory use in conjunction with ion-selective electrodes and reference electrodes (see **1.2.3.1**) enabling the potential difference between the electrodes immersed in a solution to be measured

NOTE Many ISE meters are also pH meters and vice versa.

1.2.5.2
moving index instrument

indicating ISE instrument in which the index is a pointer moving over a fixed scale

1.2.5.3
range (of an ISE meter)

interval or intervals in millivolts (or pX, see **1.2.1**) over which the instrument is usable

1.2.5.4
scale interval (of an ISE meter)

value of the measured quantity corresponding to a scale division

1.2.5.5
scale division (of an ISE meter)

interval between two consecutive minor scale marks

1.2.5.6
scale spacing (of an ISE meter)

linear or curvilinear length, measured along the scale base, between the axes of two consecutive minor scale marks

1.2.5.7
digital ISE meter

meter in which the value of the measured quantity is displayed as a group of digits

1.2.5.8
representation unit (of an ISE meter)

minimum increment between two successive output states of a digital ISE meter

1.2.5.9
slope factor adjustment (of an ISE meter)

control, with the same design as that on a pH meter, used in conjunction with two-point standardization procedures to correct for non-Nernstian but linear response of the ISE cell

1.2.5.10
error (of indication)

difference ($v_i - v_c$) between the value indicated by the ISE meter (v_i) and the true value of the measured quantity (v_c), which is taken as equivalent to the d.c. potential difference applied from a potentiometer

1.2.5.11
calibration

operation of determining the errors (of indication) of an ISE meter

1.2.5.12
intrinsic error

error of an ISE meter under reference conditions

1.2.5.13
input current (of an ISE meter)

current flowing through the ISE cell under specified conditions of input voltage

1.2.5.14
(overall) instrument error

whole error of an ISE meter under specified conditions of use

1.2.5.15
influence quantity

any quantity, generally external to the ISE meter which may affect the performance of the meter

1.2.5.16
common mode input voltage

a voltage applied to both input terminals together

1.2.5.17
common mode rejection ratio (CMRR)

ratio of input voltage range to maximum change in input offset voltage over this range

1.2.5.18
usable range

the region of linear response (see **1.2.1.6**) but not extending down to the practical limit of detection (see **1.2.2.9**)

Section 2. Ion-selection electrodes

NOTE Definitions specific to ion-selective electrodes are given in **1.2.2**.

2.1 Performance

2.1.1 Electrical resistance

The d.c. resistance of an ion-selective electrode (membrane resistance) measured at 25 °C shall not exceed 1 GΩ.

NOTE The membrane resistance is normally less than 1 MΩ except for glass electrodes (see **B.4.4**).

2.1.2 Screening, insulation and connector

The screened cable to the electrode, or to the internal reference electrode of an ion-selective electrode, shall be of the low noise, flexible type and terminate in a screened plug appropriate to the meter being used. The insulation resistance, measured using a suitable meter for high d.c. resistance between the internal conductor to the internal reference electrode and the screen on the plug, shall be at least 1 000 times greater than the membrane resistance at the same temperature.

NOTE A number of suitable screened plug connectors are currently in use. However, BNC connectors are strongly preferred and recommended.

2.2 Information to be supplied by the manufacturer

2.2.1 Type of ion-selective electrode

The manufacturer shall state the type of ion-selective electrode.

NOTE 1 Suitable forms of description are, for example; “crystalline fluoride ion-selective electrode” or “PVC membrane neutral carrier calcium ion-selective electrode”.

NOTE 2 Ion-selective electrodes of a variety of dimensions are appropriate depending on the application. The manufacturer should give the following information.

a) The following dimensions (with tolerance):
   1) overall length of stem and sensing region below the cap;
   2) length of the cap into which the connecting cable is secured;
   3) diameter of the cap;
   4) diameter of the stem;
   5) diameter of the sensitive region;
   6) the length of cable provided.
b) The type of plug termination fitted.
c) The d.c. resistance of the electrode at 25 °C.
d) The minimum feasible sample volume.
e) The internal reference electrode and the composition of the inner filling solution.

2.2.2 Conditioning

The manufacturer shall state how the ion-selective electrode shall be treated before bringing it into use.

2.2.3 Usable range and practical lower limit of detection

The manufacturer shall state the usable range and the practical lower limit of detection of the ion-selective electrode derived from the calibration curve, determined in accordance with **B.1**, in a stated medium with stated type of reference electrode under stated conditions.

NOTE The performance of an electrode changes with age and depends on the media to which it has been exposed. In particular, its response time (see **B.3**) may increase.

2.2.4 Interferences and selectivity

The manufacturer shall state all likely interfering species.

NOTE It is recognized that selectivity coefficients are only a guide to performance in the presence of interfering species. The manufacturer should provide selectivity data in the form of selectivity coefficients preferably determined by the mixed solution method as described in **B.2**. The concentrations of the mixed primary and interfering ions and the use of ionic-strength adjustment buffer should be reported.

2.2.5 Zero point

The pX value at which the e.m.f. of an ion-selective electrode, with a stated reference electrode, is zero at 25 °C shall be stated together with an estimate of its tolerance.

Section 3. Reference electrodes

NOTE Definitions specific to reference electrodes are given in **1.2.3**.

3.1 Performance

3.1.1 Electrode potential

The measured value of any new sample shall not exceed the manufacturer's stated value by more than ± 5 mV.

NOTE 1 With use, the potential of the electrode may change. With the common type of electrode this can arise from the following two sources.

a) Change in filling or bridge solution concentration due to ingress of water, or egress of ions (these may not occur at equivalent rates).

b) Ingress of ions that poison the electrode from test solutions. An electrode, depending on its design, may tolerate the effects of these for a considerable time before its electrode potential is affected through a change in species concentration at the insoluble salt-metal interface, although there may also be changes in liquid junction potential.

Tests for ascertaining whether or not a reference electrode is prone to these effects are described in **B.4.1**.

The effect in a) can be minimized by storing electrodes, when out of use, in the filling solution and not in distilled water.

NOTE 2 In use, any hole for refilling the electrode should be uncovered.

3.1.2 Electrical resistance

The electrical resistance for any new electrode shall not exceed 100 kΩ (see **B.4.2**).

3.2 Information to be supplied by the manufacturer

3.2.1 Temperature range

The manufacturer shall state the usable temperature range of the reference electrode.

3.2.2 Connections

The manufacturer shall state whether the connection from the reference electrode has been taken to the screen of the meter plug or to a separate plug.

3.2.3 Leak rate

For the free-flow type of electrode, the manufacturer shall state the leak rate of a typical electrode under a specified head of filling solution as micromoles of stated ion constituent per day (24 h), determined for chloride-filled electrodes as described in **B.4.2.3**.

NOTE For electrodes with other types of filling or bridge solution an appropriate analytical method should be chosen.

3.2.4 Electrode system

The manufacturer shall state which electrode is used for the inner element, the composition and concentration of the filling solution, and the type of device used for forming the liquid junction. The composition and concentration of the bridge solution shall be stated for double junction reference electrodes.

NOTE The bridge solution is commonly used to overcome leakage of chloride from the filling solution contaminating the test solution. The variation of the second liquid junction potential, between the bridge solution and the test solution, with the composition of the test and standard solutions may be greater than for the usual type of reference electrode.

3.2.5 Electrode potential

The manufacturer shall state the potential difference of a new electrode at 25.0 ± 0.5 °C in concentrated potassium chloride solution measured with respect to an electrode immersed in concentrated potassium chloride solution saturated with silver chloride (see **B.4**).

3.2.6 Electrical resistance

The manufacturer shall state the electrical resistance of a typical new electrode, measured by the d.c. or a.c. method described in **B.4.3**.

NOTE 1 The manufacturer should state the diameter of the straight shaft plug (2 mm, 3 mm or 4 mm) normally fitted for the reference electrode cable termination. The preferred size is 3 mm.

NOTE 2 The manufacturer should state the dimensions of the stem and cap and the length of cable fitted.

Section 4. Combination electrodes

NOTE A definition specific to combination electrodes is given in **1.2.4**.

4.1 Performance

4.1.1 Reference electrode component

The reference electrode component shall comply with **3.1.1** and **3.1.2**.

4.1.2 Screening, insulation and connectors

The screened cable to the internal reference electrode of the ISE shall be of the low-noise flexible type and terminate in a screened plug appropriate to the meter being used.

NOTE The connection to the reference electrode may be taken to the screen of the plug or a separate plug.

The insulation resistance measured, using a suitable meter for high d.c. resistance, between the internal conductor to the internal reference electrode and the reference electrode plug or, if this is not provided, the screen on the plug, shall be at least 1 000 times greater than the membrane resistance measured at the same temperature. This measurement shall be carried out with the electrode dry.

4.2 Information to be supplied by the manufacturer

4.2.1 The manufacturer shall state the usable temperature range of a combination electrode.

4.2.2 The manufacturer shall give the following information regarding the ion-selective electrode component of a combination electrode.

a) The following dimensions (with tolerance):
  1) overall length of stem and sensing region below the cap;
  2) length of the cap into which the connecting cable is secured;
  3) diameter of the cap;
  4) diameter of the stem;
  5) diameter of the sensitive region;
  6) the length of cable provided.
b) The type of plug termination fitted.
c) The d.c. resistance of the electrode at 25 °C.
d) The minimum feasible sample volume.
e) The internal reference electrode and the composition of the inner filling solution.

Section 5. ISE meters

NOTE Definitions specific to ISE meters are given in **1.2.5**.

5.1 Performance and design

5.1.1 Presentation of measured quantity

The value of the measured quantity shall be presented in one of the following forms:

a) a moving index instrument;

b) a digital instrument;

c) a recording instrument;

d) a computer-readable output.

NOTE The principal form of presentation is usually a) or b) with c) and/or d) as optional accessories.

5.1.2 Scale range(s)

5.1.2.1 mV *range*

The principal millivolt range of the instrument shall be not less than ± 1999.9 mV.

5.1.2.2 pX *range*

If scaled in pX in addition to millivolts, the principal scale of the instrument shall cover the pX range 0 to 19.

5.1.3 Scales and marking

5.1.3.1 *General*

All types of instrument shall be scaled in millivolts and optionally in concentration and/or pX.

5.1.3.2 *Moving index instruments*

The scales should be divided and marked in order to facilitate interpolation by eye into fifths. The index (knife edge) and minor scale mark thickness shall be not greater than one-tenth of a scale division.

5.1.3.3 *Digital instruments*

The representation unit on both the millivolt and pX scales and on any expanded scale shall be indicated.

5.1.3.4 *Multi-range instruments*

The range in use shall be clearly indicated and marked on the front panel.

5.1.4 Input from ion-selective electrode

The input socket shall be so designed as to make good electrical contact with the screened plug (see **2.1.2**) that connects to the ion-selective electrode.

5.1.5 Input from reference electrode

The reference electrode input socket shall be designed so as to make good electrical contact with the reference electrode plug.

5.1.6 Reference electrode input

Instruments shall tolerate the reference electrode input being earthed, floating or ± 2 V from earth, and reference electrode resistance up to 100 kΩ. Under all these conditions, additional errors of indication shall be less than 20 % of the scale interval or one representation unit on the most sensitive scale.

5.1.7 Input current

5.1.7.1 *Input current at zero voltage*

When tested as described in Appendix C, the input current at zero voltage shall not cause an error of indication of more than 10 scale intervals or 50 representation units on the most sensitive scale of the instrument when a 10 GΩ source resistor is used (equivalent to one scale interval or five representation units if a 1 GΩ resistance glass electrode is used).

NOTE 1 For a moving index meter with 0.05 scale interval, this corresponds to an input current of 3 pA when a 1 GΩ resistance, glass ion-selective electrode is used.

NOTE 2 A glass electrode with 1 GΩ resistance at 25 °C might have a resistance of about 10 GΩ at 0 °C, and this would result in an error of indication due to input of 10 scale intervals if the electrode is calibrated at 25 °C and used at 0 °C. However, a glass electrode with a resistance lower than 1 GΩ at 25 °C would normally be selected for use at lower temperatures.

5.1.7.2 *Input current change per volt*

When tested in accordance with Appendix C, the change in input current over the pX range 0 to 19 shall not lead to an indication error greater than two scale intervals or 10 representation units on the most sensitive scale when a 10 GΩ resistor is used (equivalent to 20 % of a scale interval or one representation unit if a 1 GΩ resistance electrode is used).

NOTE For a moving index ISE meter with 0.05 pX scale interval, this corresponds to a change in input current per volt of 0.5 pA if a 1 GΩ resistance ion-selective electrode is used.

5.1.8 Set standard control

The instrument shall be provided with a control for setting the zero point of the ion-selective electrode or, in the case of a microprocessor-based instrument, facilities for the user to key in zero points.

NOTE 1 The range of the control should be sufficient to allow for the use of a variety of zero points specified by the manufacturer.

NOTE 2 In microprocessor-based instruments, the set standard control is not provided and the user is required to key-in the values of the reference standard solution(s) used, or, in some cases, the instrument itself provides the values from microprocessor memory. The former option should always be available and the user's choice of standard reference solutions should not be restricted.

5.1.9 Temperature-compensating devices

5.1.9.1 *General*

Instruments with a pX scale shall be provided with a device by means of which readings on the pX scale can be corrected for changes in solution temperature from the reference temperature of 25 °C.

NOTE The device may be either manually operated (see **5.1.9.2**) or automatic (see **5.1.9.3**) (slope factor compensation).

5.1.9.2 *Manually operated slope factor compensation*

A manually operated, slope factor compensating device shall be designed and scaled in order to permit interpolation by eye into fifths. There shall be a scale mark at 25 °C and the scale interval of the device in degrees Celsius shall be 200 times the numerical value of the scale interval (or five representation units) in pX on the most sensitive scale of the instrument.

NOTE 1 For a test solution differing by 3 in pX from a standard solution when both solutions are at 25 °C, an error of 1 °C in setting the manual slope factor at 25 °C leads to an error of 0.01 pX.

NOTE 2 If measurements are required to 0.01 pX, the compensating device should be scaled every 2 °C to permit interpolation to 0.4 °C. However, the tolerance in linearity of the variable resistors used for compensating devices is usually not better than ± 1 %, which corresponds to ± 1 °C for a 0 °C to 100 °C range.

NOTE 3 When tested in accordance with Appendix C, a manual temperature-compensating device should not lead to an error of indication of more than 40 % of the scale interval or two representation units at 25 °C (or at the reference temperature stated by the manufacturer), or more than two scale intervals or 10 representation units at any other temperature.

5.1.9.3 *Automatic temperature compensation*

The device shall consist of either a separate platinum (or other metal) resistance thermometer or a thermistor incorporated in the electrode stem.

When tested in accordance with Appendix C, an automatic temperature compensating device shall not lead to an indication error of more than 40 % of a scale interval or two representation units on the most sensitive scale at pX 7.

5.1.10 Slope factor adjustment

Slope factor adjustment control (if fitted) shall be scaled in percentage of the theoretical slope factor. It shall be possible to set this control to the value (100 %) corresponding to the theoretical slope factor without incurring an error of indication of more than 20 % of the scale interval or one representation unit at the extremes of the principal pX scale of the instrument.

5.1.11 Stability

5.1.11.1 *General*

When tested with the input short-circuited and a 1 GΩ resistance connected across the input terminals, the instrument shall comply with **5.1.11.2** and **5.1.11.3**.

5.1.11.2 *Temperature stability*

When the instrument is submitted to the maximum temperature change declared by the manufacturer, the error of indication for any change of 3 in pX shall be not greater than 20 % of the scale interval or one representation unit on the most sensitive range.

5.1.11.3 *Stability to mains supply variation*

When the instrument is submitted to the maximum supply voltage variation specified by the manufacturer, the error of indication shall be not greater than 20 % of the scale interval at either end of the millivolt scale or of the pX scale.

5.1.11.4 *Stability to electrical noise*

When the set standard control is adjusted to give an on-scale reading, the uncertainty of measurement due to short-term (5 min) noise shall not exceed 20 % of the scale interval or one representation unit.

5.1.11.5 *Low voltage warning for battery powered instruments*

Means shall be provided for monitoring battery voltage and generating an audible or visual signal if the voltage drop is such as to result in an indication error of 20 % or more of a scale interval or one representation unit on the most sensitive scale.

5.1.12 Indication errors

When determined in accordance with **C.1**, the intrinsic error of indication arising from graduation and non-linearity at any point shall not exceed, on any range, 20 % of the scale interval for instruments with scales or one representation unit for digital instruments.

If switching between scales without restandardizing is intended, the error of indication arising from scale incompatibility shall not exceed 20 % of the principal scale interval or one representation unit when switching between the principal scale and an expanded scale, or 50 % of the expanded scale interval or two representation units when switching between expanded scales of the same scale interval but different scale range.

5.1.13 CMRR test

For instruments with dual high impedance input, the value of the common mode rejection ratio tested in accordance with Appendix C shall be greater than 80 dB (corresponding to a rejection ratio of one in 10 000).

5.1.14 Overall instrument error

The overall instrument error shall not exceed, at any point on any range, 50 % of the scale interval or two representation units on that range.

5.1.15 Electrical safety and earthing

The instrument shall comply with BS 4743 regarding electrical safety and earthing and with IEC[1] 173 regarding colour coding of the mains supply lead (mains instruments only).

5.2 Information to be supplied by the manufacturer

The following information shall be supplied by the manufacturer.

a) The principal method of presentation adopted and which optional methods are available together with a description of them, e.g. RS 232 and isolated potentiometric recorder output.

b) Whether a positive millivolt scale refers to a positive polarity of the ion-selective electrode or of the reference electrode input.

c) For instruments with scales and charts, the scale spacing in millimetres and the scale interval on both the millivolt and pX scales. For a multirange instrument this shall be given for all scale ranges.

d) For instruments with digital presentation, the representation unit on both the millivolt and pX scales and on any expanded scale and the height of the numerical display.

e) Whether the diameter of the shaft of the reference electrode plug is 3 mm (preferred) or 2 mm or 4 mm.

f) The zero point values of ion-selective electrodes to which the set standard control can be set.

g) The recommended values of influence quantities and their ranges. These shall be stated in accordance with BS 4889 with the exception of permitted temperature range and mains supply voltage variation.

h) The maximum temperature change to be applied for testing temperature stability. This shall be not less than 1 °C for meters with 0.001 pX scale intervals and not less than 5 °C for meters with 0.01 pX scale intervals.

i) The maximum mains supply voltage variation to be applied when testing for tolerance to voltage variation. This shall be not less than + 6 % or – 10 % of the nominal mains supply voltage.

j) The range of any temperature-compensating device (in °C).

k) For multi-range instruments, whether or not the meter should be separately standardized on each pX scale.

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[1] International Electrotechnical Commission

Appendix A Outline of procedures for using ion-selective electrodes

A.1 Direct measurement (direct potentiometry)

Measurement is made against a suitable, nominally potential-invariant reference electrode in the ISE cell which is as follows.

Reference electrode | X | X-responsive electrode

The potential difference of the X-responsive electrode with regard to the reference electrode varies with the activity of the ionic species X according to the Nernst equation:

$$E = \text{constant} + \frac{(\ln 10)\,\mathrm{R}T}{z_X \mathrm{F}} \log a_X \qquad (4)$$

(see **1.2.2.12**)

By analogy with pH measurements, if the cell is calibrated with a standard reference solution, S, of pX = – log c_X or – log a_X, then:

$$\mathrm{pX} - \mathrm{pX(S)} = \frac{E(\mathrm{S}) - E}{k/z_X} \qquad (5)$$

where

E and E(S) are the potential differences measured when the unknown and standard solution respectively are used (in mV);

k is the slope factor;

z_X (with sign) is the valence (charge) on X.

NOTE Numerical values of k are given in Table 1.

As the slope of E plotted against – log c_X or – log a_X for several standard solutions (the calibration curve; see **B.1**) may experimentally fall below the theoretical value of k/z_X for a variety of reasons, it may be advisable to perform the standardization with two standard reference solutions, S_1 and S_2, that have pX values that lie on either side of that of the test solution. Accordingly,

$$\mathrm{pX} - \mathrm{pX(S_1)} = \frac{E(\mathrm{S_1}) - E}{E(\mathrm{S_1}) - E(\mathrm{S_2})}\,[\mathrm{pX(S_2)} - \mathrm{pX(S_1)}] \qquad (6)$$

The performance of the electrode system can then be described in terms of the percentage theoretical slope *PTS* by the following equation:

$$PTS = 100\,\frac{[E(\mathrm{S_1}) - E(\mathrm{S_2})](/k/Z_X)}{[\mathrm{pX(S_2)} - \mathrm{pX(S_1)}]} \qquad (7)$$

NOTE 1 The behaviour of the whole cell, in particular variations in liquid junction potential, contributes to the measured value of *PTS*, which therefore depends markedly on the choice of S_1 and S_2. The error in the determined value of *PTS* also depends on the value of pX(S_2) – pX(S_1) and is large if this is small.

NOTE 2 An error of ± 1 mV in potential measurement leads to an error of ± 3.9 % in the concentration measurement of a singly charged ion and a 7.8 % error in that of a doubly charged ion at 25 °C.

NOTE 3 The assignment of pX(S) values is described in Appendix D. pX values may be based on the concentration of X instead of on activity.

Table 1 — Values of the slope factor *k* at temperatures from 0 °C to 95 °C

Temperature, *t*	Slope factor	Temperature, *t*	Slope factor
°C	mV	°C	mV
0	54.199	50	64.120
5	54.191	55	65.112
10	56.183	60	66.104
15	57.175	65	67.096
20	58.167	70	68.088
25	59.159	75	69.081
30	60.152	80	70.073
35	61.144	85	71.065
37	61.540	90	72.057
40	62.136	95	73.049
45	63.128		

NOTE $k = 2.302585\ \mathrm{R}T/\mathrm{F}$
where
R = 8.31441 J·K^{-1} mol^{-1};
F = 9.648456 × 10^{4} C·mol^{-1};
T (in K) = 273.15 + t.

A.2 Standard addition and subtraction methods

NOTE See [6].

A.2.1 *Standard addition method*

In a variant of direct potentiometry a known increment, or increments, of S is added to the sample containing X and, from the change in potential difference (ΔE) brought about by the addition, the concentration of X in test solution can be calculated from the following equation:

$$c_X = c_S\left(\frac{V_S}{V_X + V_S}\right)\left[10^{z_X \Delta E/k} - \frac{V_X}{V_X + V_S}\right]^{-1} \qquad (8)$$

where

$\Delta E = (E_1 - E)$ and E and E_1 are the potential differences before and after addition (in mV);

c_X is the unknown concentration of X present in volume V_X (in mol/L);

c_S is the concentration of standard solution of S added in volume V_S (in mol/L).

NOTE 1 Graphical treatment, e.g. Gran plots of multiple standard addition data, is preferable.

NOTE 2 If the ISE cell is calibrated, the practical rather than the theoretical slope, k/z_X, should be used.

A.2.2 *Standard subtraction method*

A known increment of a reagent that reacts stoichiometrically with the ion X is added to a known volume of the sample. From the change in potential difference brought about by the addition, the concentration of X in the unknown sample can be obtained. If *n* moles of reagent react with 1 mole of X, then:

$$c_X = \left(\frac{(V_S c_S}{V_X}\right) [1 - 10^{z_X \Delta E/k}]^{-1} \qquad (9)$$

NOTE 1 Use of multiple standard subtraction and graphical treatment, e.g. Gran plots, improves accuracy.

NOTE 2 If the ISE cell is calibrated, the practical rather than the theoretical slope, k/z_X, should be used.

A.2.3 *Analyte addition method*

This method is particularly applicable if the volume of the sample is too small to be measured directly. Measurements are made with the standard solution (S), then the small, known volume (V_X) of the sample is added. From the change in potential difference brought about by the addition, the concentration of X in the sample can be determined from the following equation:

$$c_X = c_S \left[\left(\frac{V_S + V_X}{V_X}\right) 10^{z_X \Delta E/k} - \left(\frac{V_S}{V_X}\right) \right] \qquad (10)$$

where

$\Delta E = (E_1 – E)$ and E and E_1 are the potential differences before and after addition (in mV).

A.3 Titration methods

Titration methods offer an increase in accuracy over direct potentiometry in that the potential change in the vicinity of the end point is much greater. Titrations may be of the acid-base, precipitation, complex formation or redox types. The ion-selective electrode may respond to the analyte ion, the titrant species or an indicator ion, selected so that it only responds to the titrant when the analyte concentration is low. The Gran plot is a method of evaluating the data.

A.4 Zero point potentiometry

NOTE See [7].

This is a titration method performed with a symmetrical cell as follows.

$$\text{Ion-selective electrode 1} \mid \text{Standard solution 1} \parallel \text{Test solution 2} \mid \text{Ion-selective electrode 2}$$

Electrodes 1 and 2 are identical in type and have negligible bias potential (intercomparison potential difference in a common electrolyte). The potential difference is adjusted to $E = 0$ by adding known quantities of primary ion to the more dilute solution or by diluting the more concentrated solution with distilled water or by complexing the primary ion in the more concentrated solution.

A.5 Flow methods

The measurement of potential difference of the ISE electrode in flowing solutions has the following advantages:

a) the ion-selective electrode is continously in contact with fresh reagent so that there is no influence of the ISE on the sample solution;

b) faster response is usually obtained;

c) the reference electrode can be placed downstream so that leakage of ion from the liquid junction can not disturb the sample;

d) serial analysis of a great number of samples can be achieved quickly.

NOTE Simple modifications to end caps of ion-selective electrodes can be made to accommodate flowing solutions, but more complex flowing cells have been designed offering stirring and thermostating of solutions.

Appendix B Check tests on electrodes

B.1 Calibration curve

Measure the potential difference between the ion-selective electrode and a suitable reference electrode in at least six stirred solutions of varying concentration of species X over the typical useful range of $10^{–6}$ to 10^0 mol/L. Plot the calibration curve as shown in Figure 1 (see **1.2.2.9**), and determine graphically the practical slope and the practical lower limit of detection.

It is recommended that the potential difference be plotted as the ordinate (vertical axis) with the more positive values at the top of the graph and that $\text{pX} = \text{p}c_X$ or $\text{p}a_X$ (– log activity of the species measured, X) be plotted on the abscissa (horizontal axis) with increasing activity to the right.

Select the points, which by eye approximately lie in the linear portion of the curve, and perform a linear regression analysis. Report the practical slope, its estimated error and the useful range of the ISE cell. Repeat the calibration in the reverse order 10^0 to 10^{-6} mol/L and determine any hysteresis.

NOTE 1 *Gas electrode calibration.* The treatment of both standard and test solution should be identical, i.e. the total dilution of all samples, pH, temperature, osmotic strength and complexation state should be the same. For some gases, e.g. sulphur dioxide, it may be necessary to standardize a stock solution by an independent chemical method immediately before preparation of the standard solutions because the reagents available are relatively impure, e.g. sodium sulphite or potassium metabisulphite for sulphur dioxide, and the resulting solutions are unstable. Hysteresis may be pronounced.

NOTE 2 *Enzyme electrode calibration*. Enzyme electrodes may require frequent calibration because of loss of enzyme activity and the effect of interfering substances (enzyme inhibitors). Furthermore the speed of response is slower (1 min to 2 min) than with other ion-selective electrodes. Standard solutions should match test solutions closely. Hysteresis may be pronounced.

B.2 Methods for determining selectivity coefficient

B.2.1 *Fixed interference method*

Measure the potential difference of a cell comprising an ion-selective electrode and a suitable reference electrode with solutions of constant level of interference, a_Y, and varying activity of primary ion, a_X. Plot the potential difference values obtained against log activity of the primary ion, X. The intersection of the extrapolation of the linear portions of the curve indicates the value of a_X that is to be used to calculate k_{XY} from the following equation:

$$k_{XY} = a_X/(a_Y)^{z_X/z_Y} \qquad (11)$$

where

k_{XY} is the selectivity coefficient;

a_X, a_Y z_X and z_Y are as defined in **1.2.2.12**.

B.2.2 *Separate solution method*

Measure the potential difference of a cell comprising an ion-selective electrode and a suitable reference electrode with each of two separate solutions, one containing the ion, X, at the same activity a_X (but no Y), the other containing the ion Y at activity $a_Y = a_X$ (but no X). If the measured values are E_X and E_Y respectively, k_{XY} is calculated from the following equation:

$$\log k_{XY} = \frac{E_Y - E_Z}{RT(\ln 10)/z_X\mathrm{F}} + \left[1 - \frac{z_X}{z_Y}\right] \log a_X \qquad (12)$$

where

E, R, T, z_X, z_Y, a_X and F are as defined in **1.2.2.12**.

NOTE This method is recommended only if the electrode exhibits a Nernstian response separately in both solutions X and Y. It is less satisfactory than the fixed interference method because it does not also represent the actual conditions under which electrodes are used.

B.3 Response time

Unlike pH glass electrodes, the response time of ion-selective electrodes approximately follows an exponential law:

$$E_t = E_0 + (E_\infty - E_0)(1 - \exp(-bt))$$

where

E_0, E_t and E_∞ are potential difference values (measured at times 0, t and infinity) (in mV) and b is a fitting parameter.

This equation may be used with caution to obtain infinity readings if $(E_\infty - E_0) \leq 30$ mV. However, the practical response time or 90 % time is generally a more useful concept. For detailed discussion see the IUPAC document "Definition and determination of response time of ion-selective electrodes" [8].

B.4 Methods for assessing reference electrodes

B.4.1 *Measurement of the electrode potential of a reference electrode*

Measure the potential difference at 25.0 ± 0.5 °C between the reference electrode and a silver-silver chloride electrode immersed in concentrated potassium chloride solution saturated with silver chloride, according to the following cell scheme.

Ag | AgCl	potassium chloride, c(KCl) $\geq$ 3.5 mol/L Saturated with AgCl	potassium chloride, c(KCl) $\geq$ 3.5 mol/L	Reference electrode

Here the double bars indicate liquid junctions at ceramic plugs, frits or otherwise, and "Reference electrode" refers to the electrode under test complete with its filling solution and, in the case of double junction electrodes, with its bridge solution changed to potassium chloride, c(KCl) $\geq$ 3.5 mol/L. The stability of the potential of a reference electrode is more important than its actual value. A new calomel reference electrode with liquid junction should show a potential difference, as determined in paragraph 1 of this subclause, of + 45 ± 10 mV. Deviations after usage indicate one of the effects described in Note 1 to **3.1.1**.

NOTE 1 Silver-silver chloride reference electrodes with potentials that should not vary by more than ± 1 mV between unused electrodes are available commercially. Variation between mercury-calomel KCl (concentrated) electrodes is expected to be greater than this.

NOTE 2 The inner element of a silver-silver chloride KCl (concentrated) reference electrode can be constructed by one of the methods described in **A.3.4** of BS 2586:1979. Ceramic plugs and frits are available commercially. Adequate coating with silver chloride and, additionally, saturation of potassium chloride with silver chloride is essential because of the increased solubility of the latter in concentrated chloride solutions.

B.4.2 *Methods for assessing design and performance of reference electrodes*

B.4.2.1 *Ingress of water*. Repeat the measurement described in **B.4.1** after immersing the reference electrode in at least 100 cm^3 of water at ambient temperature for several days with the liquid junction formed 1 cm below the water surface. Deviation from the first measured value should not exceed ± 2 m V after 2 weeks for an electrode of good design.

B.4.2.2 *Egress of electrolyte (from chloride-filled electrodes)*. Mount a reference electrode so that it dips 1 cm below its junction in 10 cm^3 of distilled water. After 3 days estimate the chloride lost from the electrode by either of the following methods:

a) potentiometric titration with 0.1 mol/L silver nitrate and a silver-indicating electrode;

b) by conductance measurement by comparison with diluted potassium chloride solutions.

Measure the hydrostatic head of the filling solution. Similar tests can be devised for electrodes with different filling solutions and double junction electrodes with non-chloride-containing bridge solutions by choosing an appropriate analytical method.

NOTE For a cylindrical electrode with transparent stem, a rough indication of the filling solution leak rate can be found by measuring the drop in height of the surface of the filling solution over a period of days or weeks. This is a measure of the volume loss, which is not necessarily equivalent to the salt loss. Any hole for refilling the electrode should be uncovered during these tests.

B.4.2.3 *Ingress of ions from test solutions*

B.4.2.3.1 *Non-destructive test (non-sealed electrodes only)*. Immerse the electrode in a solution of sodium fluoride, $c(\mathrm{NaF}) = 0.1$ mol/L. After 48 h to 60 h remove the filling solution (or the bridge solution for double liquid junction electrodes) with a syringe attached to catheter tubing. Estimate the fluoride concentration using the following cell.

Fluoride ISE	Sample	Potassium chloride, $c(\mathrm{KCl}) \geq 3.5$ mol/L	AgCl | Ag

The cell can be calibrated with standards made by adding small amounts of sodium fluoride, $c(\mathrm{NaF}) = 0.1$ mol/L to portions of the filling or bridge solution. Calculate the ingress rate as micromoles of fluoride per 24 h.

B.4.2.3.2 *Destructive test (sealed and unsealed electrodes)*. Mount the reference electrode in a closed vessel containing 10 % ammonium sulphide solution. After 2 weeks, remove and rinse the electrode with distilled water. Repeat the measurement described in **B.4.1**.

A change in potential difference of more than ± 6 mV is indicative of a reference electrode that would be prone to poisoning if exposed continuously in certain flow analysis applications.

B.4.3 *Electrical resistance*

Measurement may be made by either of the following methods.

a) *d.c. method.* place the reference electrode in a solution of potassium chloride, $c(\mathrm{KCl}) = 0.1$ mol/L with silver-silver chloride electrode according to cell.

Reference electrode	potassium chloride, $c(\mathrm{KCl}) = 0.1$ mol/L	AgCl | Ag

Measure the potential difference as follows:

1) directly;

2) after 10 s while passing a current of 0.1 μA through the cell;

3) after 10 s while passing a current of 0.1 μA in the reverse direction through the cell.

A change in potential of ± 10 mV, corresponding to a resistance of less than 100 kΩ, is acceptable for an electrode usable with most ISE meters.

NOTE A suitable source would be a 1.5 V dry battery in series with a 15 MΩ resistor.

b) *a.c. method.* Place the reference electrode in a solution of potassium chloride, $c(\mathrm{KCl}) = 4.0$ mol/L saturated with silver chloride and introduce a silver-silver chloride electrode. Apply an a.c. voltage ($\leq$ 5 V, 50 Hz) and measure the a.c. current. Calculate the resistance of the electrode from the ratio of the r.m.s. voltage to the r.m.s. current.

NOTE 1 A commercially available conductivity or resistance meter can be used provided it applies the specified voltage.

NOTE 2 Method b) is more appropriate than method a) for reference electrodes having very small surface areas where polarization may result if method a) is used.

B.4.4 *Membrane resistance*

The following method, which uses the ISE meter itself as the measuring instrument and a known value, screened resistor (e.g. for glass electrodes $R_S = 100$ MΩ or 500 MΩ), is preferred.

Method. Immerse the electrode and reference electrode in a suitable solution at 25 °C. Record the reading (V_1) and then shunt the input with the resistor and record the new value (V_2). The electrode resistance is then given by $R_S(V_1 - V_2)/V_2$.

Alternatively, the membrane resistance, particularly of glass electrodes, may be determined with a meter for measuring high d.c. resistance which applies a voltage of less than 500 V. Highly reproducible values are not usually obtainable by this method because of the effect of the polarizing voltage on the electrode and it may not then be usable for some hours after the test.

Appendix C Instrument check tests

C.1 Errors of indication

C.1.1 *Millivolt scales*

The compliance tests described should be performed with the apparatus ready for use after warm-up time and within the ranges of influence quantities (temperature, humidity, etc.) specified by the manufacturer.

Calibrate the scale using a potentiometer to apply a voltage directly across the input terminals of the instrument. In all tests carry out measurements with applied voltage differences of increasing and decreasing increments to test for hysteresis.

Before checking the millivolt scale, set the temperature-compensating device (if any) in accordance with the manufacturer's instructions.

NOTE 1 This is only necessary on certain ISE meters where the temperature-compensating device remains in circuit on switching to the millivolt scales. Such instruments should not be used as millivoltmeters without ascertaining that the temperature-compensating device can be set accurately to the value stated by the manufacturer.

Test the principal millivolt scale at 100 mV intervals and expanded scales at 25 mV or 50 mV intervals, using a potentiometer that has a scale interval at least one-fifth of that of the scale being tested.

NOTE 2 This means for a 500 mV scale with a scale interval of 10 mV a potentiometer with settings of 2 mV is required.

If the set standard control is effective on the millivolt scale, use the control to set the zero scale initially. Check both positive and negative regions of the millivolt scale by reversing the input connections, with a double check of the scale zero.

C.1.2 *pX scales*

Before checking the pX scales, set the temperature-compensating device to 25 °C (or to the calibration temperature stated by the manufacturer).

With the input terminals shorted, adjust the set standard control so that the indicator reads 7.000. Vary the manual temperature-compensating device between its extreme settings, readjusting the set standard control if necessary, until such variation produces no discernible change in indicator reading. Calibrate the principal scale at nine points between 0 and 19 by applying voltages (appropriate to 25 °C) from the potentiometer as shown in Table 2.

For checking expanded pX scales, calculate the appropriate values for the applied potential differences from the slope factor, i.e. $k = 59.159$ mV at 25 °C.

For ISE meters graduated for temperatures other than 25 °C, calculate applied potential differences using the slope factor values given in Table 1.

C.2 Input current

C.2.1 *Input current at zero voltage*

Adjust the set standard control with the input terminals shorted so that the indicator reads mid-scale. Connect a screened 10 GΩ (± 10 %) resistor across the terminals. Observe the change in reading.

C.2.2 *Input current change per volt*

Apply a voltage of 0.5 V between the ISE and reference electrode inputs.

NOTE This can be done with a potentiometer but high accuracy is not required and a suitable source is the voltage drop across one of three 100 kΩ resistors connected in series across a 1.5 V dry battery.

Adjust the set standard control so that the indication is mid-scale. Connect a 10 GΩ (± 10 %) screened resistor in series with the voltage source and observe the change in reading. Reverse the polarity of the input voltage and repeat the observation. Record the difference between the greater of these two changes in reading and the value obtained from **C.2.1**.

C.3 Temperature-compensating device

Adjust the set standard control with input shorted so that no discernible change in indicator reading is observed on adjusting the manual temperature-compensating device between its extreme settings.

NOTE The indicated value is then the pX reading at which the temperature-compensating device is inoperative.

Apply voltage to the input terminals with either different setting of the manual temperature control or the temperature-sensing device immersed for 30 min in baths at different temperatures (± 0.1 °C) as given in Table 3. Observe the change in reading from the set value (the indication error).

NOTE With some microprocessor-based instruments, the user is required to key-in the value of the temperature of the solution. If a scaled temperature-compensating device is not provided, the procedure can not be applied.

Table 2 — Applied voltages for calibrating pX scales ($z_X = \pm 1$)

ΔpX scale reading	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
± applied Voltage (m*V*)	59.16	118.32	177.48	236.64	295.80	354.95	414.11	473.27	532.43	591.59

NOTE The values given are applicable to meters with a 0.001 pX scale interval and may be approximated appropriately for less than accurate instruments.

Table 3 — Applied voltages for calibrating temperature-compensating devices

Temperature setting or bath temperature (°C)	0	40	60	80	100
± **applied voltage** (mV)	379.38	434.93	462.71	490.49	518.27

C.4 Reference electrode input load

Connect a 2 V battery between instrument and earth, and then reverse the connection, using a 100 kΩ resistor in series with the reference electrode.

C.5 Overall instrument error

Determine the overall instrumental error in accordance with **C.1.1** but apply the voltages from the potentiometer through a 1 GΩ (± 10 %) screened resistor to the ion-selective, electrode input terminal.

NOTE Under these conditions the test approximates closely to normal usage.

C.6 CMRR test

NOTE Some instruments have dual high impedance input so that the reference electrode input is electrically similar to the ISE electrode input.

Apply the maximum common mode input voltage, V_c, and record the output reading. Apply an input voltage, V_i, to the instrument using a simulator and adjust it such that the resulting output reading equals the value previously recorded. Calculate the value using the following equation:

CMRR (in dB) = $-20 \log (V_c/V_i)$.

NOTE With dual high impedance input instruments, the manufacturer's recommendations with regard to earthing should be observed.

Appendix D Standard reference solutions for direct potentiometry

D.1 Concentration-based pX standards

Although it can not be disputed that electrodes provide a measure of ion-activity rather than of ion-concentration, it may be more appropriate to prepare concentration standards than activity standards for measurements with ion-selective electrodes. When conditions in the ISE cell are arranged such that the residual liquid junction potential is negligible (i.e. the standard and test solution are closely matched in concentration of X and overall ionic composition), the use of concentration standards furnishes the concentration of the test solution. Concentration standards may be prepared in solvent only, or preferably in an ionic medium, e.g. a high concentration of electrolyte containing no interfering substances (ionic-strength adjustment buffer).

NOTE 1 It is necessary to ensure that under the prevailing conditions of concentration, pH, temperature etc. the ion X remains in the same form (not hydrolyzed) over the concentration calibration range if a linear calibration is required.

NOTE 2 Activity effects for concentration standards prepared in solvent only affect the linearity of calibration curves at and above approximately 0.1 mol/L for monovalent ions and 0.05 mol/L for divalent ions.

D.2 Activity pX standards

Since the measurement of pX with an ion-selective electrode in the ISE cell is analogous to the measurement of pH with a hydrogen ion-responsive glass electrode, it can be considered that pX standards are required in the same way that pH standards are required for pH measurement. However, for several reasons the approach can not be entirely the same. Although the Bates-Guggenheim equation [9] for single ion activity coefficients may be used for singly charged ions, its applicability is restricted to ionic strengths not greater than 0.1 mol/L. The equation is as follows:

$$\log \gamma_i = -AI^{1/2}/(1 + 1.5\ I^{1/2}) \qquad (14)$$

A different approach based on the thermodynamics of electrolyte solutions and the hydration of ions is advocated [10, 11].

To use pX values based on this approach [12], the test solution should be bracketed by two standards to allow for possible non-theoretical response if a full calibration curve is not determined. These pX values are only appropriate to the standard reference solution chosen. Note that pCl is different for sodium chloride, $c(\mathrm{NaCl}) = 0.1\ \mathrm{mol \cdot kg^{-1}}$ from that for potassium chloride, $c(\mathrm{KCl}) = 0.1\ \mathrm{mol \cdot kg^{-1}}$. These pX values are totally inapplicable to mixed electrolyte solutions.

D.3 Metal-ion buffers: pX values

A different problem arises for pX standards above 5 or 6 when adsorption on the walls of the container becomes important. Metal ion buffers with added complexing agent have been proposed [12] to overcome this problem. The principle is the same for anions if complexing ligands are available.

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