

Specification for

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

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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.

A British Standard does not purport to include all the necessary provisions of a contract. Users of British Standards are responsible for their correct application.

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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 $pX = pa_X = -\log a_X$, where a_X is the single ion activity of the species X, or alternatively as $pX = pc_X = -\log c_X$, 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:

$$I = \frac{1}{2} \sum c_i z_i^2 \quad (1)$$

where

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

z_i is the charge 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

- 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 $\text{AgI} + \text{Ag}_2\text{S}$).
- 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

- Positively charged, e.g. those of quaternary ammonium salts or salts of transition metal complexes such as derivatives of 1, 10-phenanthroline.
- Negatively charged, e.g. bulky anions such as dialkyl phosphate $[(\text{RO})_2\text{PO}_2^-]$ and tetrakis (p-chlorophenyl) borate anions.
- 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:

$$k = RT(\ln 10)/z_X F = 59.159/z_X \text{ mV per decade of } p a_X = pX \text{ at } 25^\circ \text{C (see 1.2.1.6).} \quad (2)$$

where

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

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. $9.648456 \times 10^4 \text{ C mol}^{-1}$.

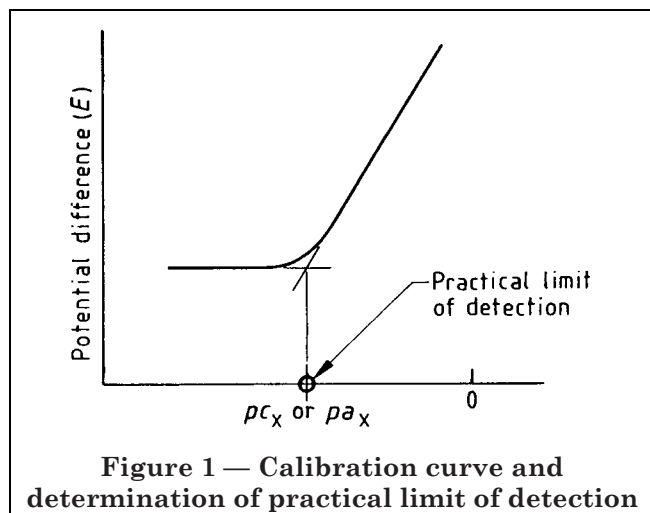


Figure 1 — Calibration curve and determination of practical limit of detection

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:

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

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. $8.31441 \text{ J K}^{-1} \text{ mol}^{-1}$;

T is the thermodynamic temperature (in K);

F is the Faraday constant and is equal to $9.648456 \times 10^4 \text{ C mol}^{-1}$;

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