

INTERNATIONAL UNION OF
PURE AND APPLIED CHEMISTRY

ANALYTICAL CHEMISTRY DIVISION

COMMISSION ON ANALYTICAL NOMENCLATURE

RECOMMENDATIONS FOR
NOMENCLATURE OF ION-SELECTIVE
ELECTRODES

(RECOMMENDATIONS 1975)

PERGAMON PRESS
OXFORD · NEW YORK · PARIS · FRANKFURT

ANALYTICAL CHEMISTRY DIVISION
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INTRODUCTION

The rapid expansion of activity in the field of ion-selective electrodes makes it highly desirable to achieve some standardization of nomenclature in this area.

The report has been widely circulated by the Commission to other Commissions of the Analytical Chemistry Division and to experts in many countries in first, second, and third draft forms. It has been modified many times in the light of comments received over a period of two years. This final report incorporates most of the suggestions made on previous drafts, and was prepared by a subcommittee consisting of G. G. Guilbault (*Chairman*), R. A. Durst, M. S. Frant, H. Freiser, E. H. Hansen, T. S. Light, E. Pungor, G. Rechnitz, N. M. Rice, T. J. Rohm, W. Simon, and J. D. R. Thomas.

I. GENERAL RECOMMENDATIONS

(a) *Definition of terms*

1. *Activity, activity coefficient and concentration.* Refer to the *Manual of Symbols and Terminology for Physicochemical Quantities and Units* (Butterworths, London, 1973 edition).

2. *Calibration curve.* This is a plot of the potential (emf) of a given ion-selective electrode cell assembly (ion-selective electrode combined with an identified reference electrode) vs the logarithm of the ionic activity (concentration) of a given species. For uniformity, it is recommended that the potential be plotted on the ordinate (vertical axis) with the more positive potentials at the top of the graph and that pa_A (-log activity of the species measured, A) or pC_A be plotted on the abscissa (horizontal axis) with increasing activity to the right.

3. *Limit of detection.* A calibration curve ordinarily has the shape shown in Fig. 1.

By analogy with definitions adopted in other fields, the limit of detection should be defined as the concentration for which, under the specified conditions, the potential E deviates from the average potential in region I by some arbitrary multiple of the standard error of a single measurement of the potential in region I.

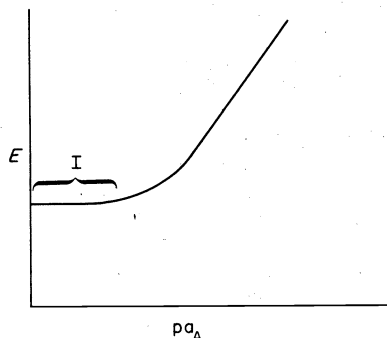


Fig. 1.

In the present state of the art, and for the sake of practical convenience, a simpler (and more convenient) definition is recommended at this time. The practical limit of detection may be taken as the activity (or concentration) of A at the point of intersection of the extrapolated linear segments of the calibration curve, as shown by the following illustration:

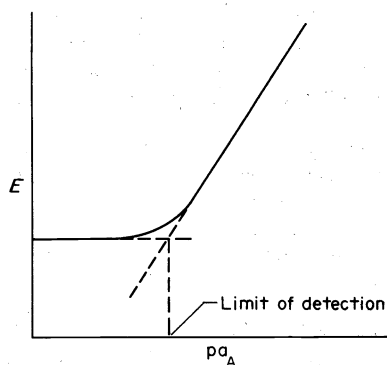


Fig. 2.

Since many factors affect the detection limit, the experimental conditions used should be reported, i.e. composition of the solution, the history and preconditioning of the electrode, stirring rate, etc.

4. *Drift.* This is the slow non-random change with time in the potential (emf) of an ion-selective electrode cell assembly maintained in a solution of constant composition and temperature.

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5. *Hysteresis* (electrode memory). Hysteresis is said to have occurred if, after the concentration has been changed and restored to its original value, there is a different potential observed. The reproducibility of the electrode will consequently be poor. The systematic error is generally in the direction of the concentration of the solution in which the electrode was previously immersed.

6. *Membrane*. This refers to 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 (see II for listing of membranes).

7. *Ion-selective electrodes*. These are electrochemical sensors, the potentials of which are linearly dependent on the logarithm of the activity of a given ion in solution. Such devices are distinct from systems which involve redox reactions (Class I and II electrodes).

Comment: The term "ion-specific electrode" is not recommended. The term "specific" implies that the electrode does not respond to additional ions. Since no electrode is truly specific for one ion, the term "ion-selective" is recommended as more appropriate. "Selective ion-sensitive electrode" is a little used term to describe an ion-selective electrode.

The potential response has as its principal component the free-energy change associated with mass transfer (by ion-exchange, adsorption, solvent extraction or some other mechanism) across a phase boundary.

8. *Interfering substance*. This is any species, other than the ion being measured, whose presence in the sample solution affects the measured potential of a cell.

Interfering substances fall into two classes: "electrode" interferences and "method" interferences. Examples of the first class would be those substances which give a similar response to the ion being measured and whose presence generally results in an apparent increase in the activity (or concentration) of the ion to be determined (e.g. Na^+ for the Ca^{2+} electrode), those species which interact with the membrane so as to change its chemical composition (i.e. organic solvents for the liquid or polyvinylchloride (PVC) membrane electrodes) or electrolytes present at a high concentration giving rise to appreciable liquid-junction potentials. The second class of interfering substance is that which interacts with the ion being measured so as to decrease its activity or apparent concentration, but where the electrode continues to report the true activity (i.e. CN^- present in the measurement of Ag^+).

9. *Reference electrode*. An electrode which maintains a virtually invariant potential under the conditions prevailing in an electrochemical measurement, and which serves to permit the observation, measurement or control of the potential of the indicator (or test) or working electrode. (*Comment*: Practical reference electrodes are generally constructed so that their electrolyte solutions serve as salt bridges to the solutions under investigation).

10. *Internal reference electrode*. This is a reference electrode which is contained inside an ion-selective electrode assembly. *Comment*: The system frequently consists of a silver-silver chloride electrode in contact with an appropriate solution containing chloride and a fixed concentration of the ion for which the membrane is selective.

11. *Ionic-strength adjustment buffer*. A pH buffered solution of high ionic strength added to samples and calibration solutions before measurement in order to achieve identical ionic strength and hydrogen ion activity. In addition, complexing agents and other components are

often added to minimize the effects of certain interferences.

12. *Nernstian response*. An ion-selective electrode is said to have a Nernstian response over a given range of activity (or concentration) in which a plot of the potential of such electrode in conjunction with a reference electrode vs the logarithm of the ionic activity of a given species (a_A) is linear with a slope of $2.303 \times 10^3 RT/z_A F$ mV/decade ($59.16/z_A$ mV per unit of $\text{p}a_A$ at 25°C).

13. *Practical response time*. The length of time which elapses between the instant at which an ion-selective electrode and a reference electrode are brought into contact with a sample solution (or at which the concentration of the ion of interest in a solution in contact with an ion-selective electrode and a reference electrode is changed) and the first instant at which the potential of the cell becomes equal to its steady-state value within 1 mV. The experimental conditions used should be stated, i.e. the stirring rate, the composition of solution of which the response time is measured, the composition of the solution to which the electrode was exposed prior to this measurement, the history and preconditioning of the electrode, and the temperature.

14. *Combination electrode*. An electrochemical apparatus which incorporates an ion-selective electrode and a reference electrode in a single assembly, thereby avoiding the need for a separate reference electrode.

15. *Potentiometric selectivity coefficient*. $k_{A,B}^{\text{pot}}$ defines the ability of an ion-selective electrode to distinguish between different ions in the same solution. It is not identical to the similar term used in separation processes. The selectivity coefficient is evaluated by means of the ion-selective electrode emf response, in mixed solutions of the primary ion, A, and interfering ion, B, (or less desirably, in separate solutions). The activities of the primary ion, A, and the interfering ion, B, at which $k_{A,B}^{\text{pot}}$ is determined should always be specified, as the value of $k_{A,B}^{\text{pot}}$ is defined by the modified Nernst equation. The smaller the value of $k_{A,B}^{\text{pot}}$, the greater the electrode's preference for the principal ion, A, as described later.

Comment: The terms *selectivity constant* and *selectivity factor* are frequently used instead of selectivity coefficient. However, in order to standardize the terminology associated with ion-selective electrodes, use of the term selectivity coefficient is recommended, as is the fixed interference method for its evaluation (see III. D. 2).

16. *Standard addition or known addition method*. This is a procedure for the determination of the 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 of an ion-selective electrode vs a suitable reference electrode.

17. *Standard subtraction or known subtraction*. This is a variation of the standard addition method. 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.

18. *Isopotential point*. For a cell containing an ion-selective electrode and a reference electrode there is often a particular activity of the ion concerned for which the potential of the cell is independent of temperature. That activity, and the corresponding potential, define the isopotential point. The identity of the reference electrode, and the composition of the filling solution of the measuring electrode, must be specified.

II. CLASSIFICATION OF ION-SELECTIVE ELECTRODES

A. Primary electrodes

1. *Crystalline electrodes.* May be homogeneous or heterogeneous.

a. *Homogeneous Membrane Electrodes* are ion-selective electrodes in which the membrane is a crystalline material prepared from either a single compound or a homogeneous mixture of compounds (i.e., Ag_2S , $\text{AgI}/\text{Ag}_2\text{S}$).

b. *Heterogeneous Membrane Electrodes* are formed when 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 which is heterogeneous in nature.

2. *Non-crystalline electrodes.* In these electrodes a support, containing an ionic (either cationic or anionic) species or an uncharged species, forms the ion-selective membrane which is usually interposed between two aqueous solutions. The support used can be either porous (e.g. Millipore filter, glass frit, etc.) or non-porous (e.g. glass or inert polymeric material such as PVC, yielding with the ion-exchanger and the solvent a "solidified" homogeneous mixture). These electrodes exhibit a response due to the presence of the ion-exchange material in the membrane.

a. *Rigid matrix electrodes (e.g. glass electrodes)* are ion-selective electrodes in which the sensing membrane is a thin piece of glass. The chemical composition of the glass determines the selectivity of the membrane. In this group are:

hydrogen ion-selective electrodes
monovalent cation-selective electrodes

b. *Electrodes with a mobile carrier:*

(1) *Positively charged*—bulky cations (e.g. those of quaternary ammonium salts or salts of transition metal complexes such as derivatives of 1, 10-phenanthroline) which, when dissolved in a suitable organic solvent and held on an inert support (e.g. Millipore filter or PVC), provide membranes which are sensitive to changes in the activities of anions.

(2) *Negatively charged*—Complexing agents (e.g. of type $(\text{RO})_2\text{PO}_2^-$) or bulky anions (e.g. tetra-*p*-chlorophenylborate anions) which, when dissolved in a suitable organic solvent and held in an inert support (e.g. Millipore filter or PVC), provide membranes which are sensitive to changes in the activities of cations.

(3) *Uncharged Carrier*—Electrodes based on solutions of molecular carriers of cations (e.g. antibiotics, macrocyclic compounds or other sequestering agents) which can be used in membrane preparations which show sensitivity and selectivity to certain cations.

B. Sensitized ion-selective electrodes

1. *Gas sensing electrodes* are sensors composed of an indicating and a reference electrode which use a *gas-permeable membrane* or an *air-gap* to separate the sample solution from a thin film of an intermediate solution, which 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 measure 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: An exception to this

classification is the hydrogen gas electrode which responds both to the partial pressure of hydrogen and to pH. The oxygen electrode fits under this classification although, in contrast to all other sensors, it is an amperometric and *not* a potentiometric device).

2. *Enzyme substrate electrodes* are sensors in which 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 which reacts with the enzyme to be assayed.

III. CONSTANTS AND SYMBOLS

A. *The modified Nernst equation for ion-selective electrodes and definition of $k_{A,B}^{\text{pot}}$*

$$E = \text{constant} + \frac{2,303RT}{z_A F} \log [a_A + k_{A,B}^{\text{pot}}(a_B)^{z_A/z_B} + k_{A,C}^{\text{pot}}(a_C)^{z_A/z_C} \dots]$$

E is the experimentally observed potential of a cell (in millivolts)

R is the gas constant and is equal to $8.31441 \text{ JK}^{-1} \text{ mol}^{-1}$

T is the thermodynamic temperature (in $^\circ\text{K}$)

F is the Faraday constant and is equal to $(9.648670 \pm 0.000054) \times 10^4 \text{ C mol}^{-1}$

a_A is the activity of the ion, A

a_B and a_C are the activities of the interfering ions, B and C, respectively

$k_{A,B}^{\text{pot}}$ is the potentiometric selectivity coefficient

z_A is an integer with sign and magnitude corresponding to the charge of the principal ion, A

z_B and z_C are integers with sign and magnitude corresponding to the charge of interfering ions, B and C, respectively

The "constant" term includes the standard or zero potential of the indicator electrode, E_{ISE}^0 , the reference electrode potential, E_{Ref} , and the junction potential, E_J (all in millivolts).

B. *Ionic strength of a solution is defined by $I = 1/2 \sum c_i z_i^2$*

I is the ionic strength; c_i is the concentration in mole per liter of an ion, i ; z_i is the charge of the ion, i .

C. *Other symbols*

Sign conventions should be in accord with IUPAC recommendations (*Manual of Symbols and Terminology for Physicochemical Quantities and Units*, Butterworths, London, 1973 edition, p. 27).

D. *Methods for determining $k_{A,B}^{\text{pot}}$*

1. *Fixed interference method.* The potential of a cell comprising an ion-selective electrode and a reference electrode is measured with solutions of constant level of interference, a_B , and varying activity of the primary ion, a_A . The potential values obtained are plotted vs the activity of the primary ion. The intersection of the extrapolation of the linear portions of this curve will indicate the values of a_A which are to be used to calculate $k_{A,B}^{\text{pot}}$ from the equation:

$$k_{A,B}^{\text{pot}} = a_A / (a_B)^{z_A/z_B}$$

2. *Separate solution method.* The potential of a cell

comprising an ion-selective electrode and a reference electrode is measured with each of two separate solutions, one containing the ion A at the activity a_A (but no B), the other containing the ion B at the same activity $a_B = a_A$ (but no A). If the measured values are E_1 and E_2 , respectively, the value of $k_{A,B}^{\text{pot}}$ may be calculated from the equation:

$$\log k_{A,B}^{\text{pot}} = \frac{E_2 - E_1}{2,303RT/z_A F} + \left(1 - \frac{z_A}{z_B}\right) \log a_A$$

This method is recommended only if the electrode exhibits a Nernstian response. It is less desirable because it does not represent as well the actual conditions under which the electrodes are used.