INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

ANALYTICAL CHEMISTRY DIVISION

COMMISSION ON ANALYTICAL NOMENCLATURE*

RECOMMENDATIONS FOR PUBLISHING MANUSCRIPTS ON ION-SELECTIVE ELECTRODES

(Recommendations 1981)

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Introduction

Papers on ion-selective electrodes are concerned with fundamental aspects, developments, appraisal and applications. While it may be difficult to lay down guidelines for publishing manuscripts on fundamental aspects, prospective readers of papers on ion-selective electrode developments, appraisal and applications can more easily reach intelligent decisions on advantages and limitations if attention is given to a set specification. Of prime importance is the objective that all papers should aim at consistency in preferred usages. In this respect special attention is directed to the report of The Analytical Nomenclature Commission of the International Union of Pure and Applied Chemistry on 'Recommendation for Terms and Symbols in the Field of Ion-Selective Electrodes." The definitions of most frequently used terms taken from this report are given below, and are followed by summaries of the essential points to be included in papers on new electrode developments and applications respectively. This present report was prepared by a committee consisting of G. G. Guilbault (Chairman), J. D. R. Thomas, R. A. Durst, M. S. Frant, H. Freiser, E. H. Hansen, T. S. Light, G. J. Moody, E. Pungor, G. Rechnitz, N. M. Rice, T. J. Rohm, W. Simon.
It has been circulated in first, second and third draft forms and was discussed in a joint meeting of IDCNS, Commission I.3, V.3, and V.5 in Warsaw. This provisional report was circulated for 12 months, revised in light of all comments, and the final copy was approved at Davos (1979).

ION-SELECTIVE ELECTRODE NOMENCLATURE AND DEFINITIONS

A. DEFINITIONS OF MOST FREQUENTLY USED TERMS

1. Calibration Curve is a plot of the potential (emf) of a given ion-selective electrode cell assembly (ion-selective electrode combined with an identified reference electrode) versus the logarithm of the ionic activity (or 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 pa_A be plotted on the abscissa (horizontal axis) with highest activity (lowest pa_A) to the left.

2. Limit of Detection. A calibration curve ordinarily has the following shape.
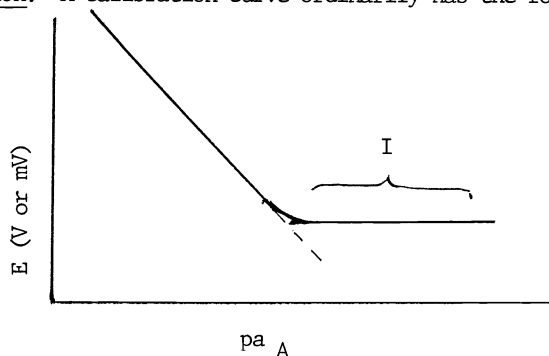
By analogy with definitions adopted in other fields, the limit of detection should be defined as that concentration for which, under the specified conditions, the potential E deviates from the average potential in region I by some stated arbitrary multiple of the standard error of a single measurement of the potential in region I. (i.e. point of extrapolated intersection shown in the illustration).

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) at the point of intersection of the extrapolated lines as illustrated.

E

— Limit of Detection

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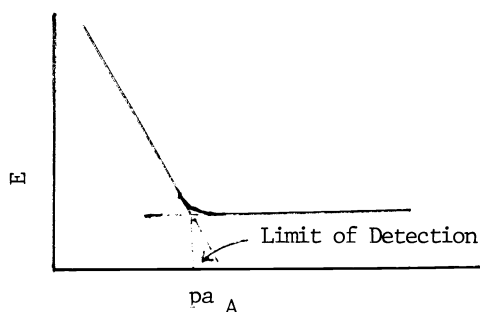
Since many factors affect the detection limit, the experimental conditions used should be reported, i.e., composition of the solution, the history and preconditioning of the electrode, stirring rate, etc.

3. Drift 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.

4. Interfering Substance is any species, other than the ion being measured, whose presence in the sample solution affects the measured emf of a cell.

Interfering Substances fall into two classes. (a) Electrode interferences and (b) Method interferences. Examples of the first class would be those substances which give a response similar 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^{++} electrode), those species which interact with the membrane so as to change the chemical composition (e.g. organic solvents for the liquid or poly(vinylchloride (PVC) membrane electrodes). The second class of interfering substances are those which interact with the ion being measured so as to decrease its activity or apparent concentration, but where the electrode continues to report the true activity (e.g., CN^- present in the measurement of Ag^+).

5. The modified Nernst (Nikolsky) Equation for Ion-Selective Electrodes and Definition of $k_{A,B}^{pot}$.

$$E = \text{constant} + \frac{2303\ R\ T}{z_A\ F}\ \text{Log}\ [a_A + k_{A,B}^{pot}\ (a_B)^{z_A/z_B}]$$

E is the experimentally observed potential of an I.S.E.

R is the gas constant (and is equal to 8.3144 J K^{-1} mol^{-1}).

T is the thermodynamic temperature (in K).

F is the Faraday constant (and is equal to 9.64846×10^4 C mol^{-1}).

a_A is the activity of the ion, A (for concentrations measured in mol l^{-1} or molality in mol kg^{-1}).

a_B is the activity of the interfering ion, B (for concentrations measured in mol l^{-1} or molality in mol kg^{-1}).

$k_{A,B}^{pot}$ 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 is an integer with sign and magnitude corresponding to the charge of an interfering ion, B.

The "constant" term includes the standard potential of the indicator electrode, E_{ISE}^0, the reference electrode potential, E_{Ref}, and the junction potential, E_j (all in millivolts). This equation can only be rigorously derived when $z_A = z_B$.

6. Nernstian Response. An ion-selective electrode is said to have Nerstian response

over a given range of activity (or concentration) for which a plot of the potential of such an electrode in conjunction with a reference electrode vs. the logarithm of the ionic activity of a given species ($\underline{a}_A$) is linear with a slope of (approximately) $2,303RT/z_A \underline{F}$ ($59.16/\underline{z}_A$ mV at 25°C).

7. <u>Practical Response Time</u>. 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 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 when the potential of the cell becomes equal to its steady-state value within 1mV. 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.

   The main definition takes in "static response time" while the alternative (within the parentheses) takes in "dynamic response times".

8. <u>Assessment of Selectivity of Electrode</u>

a. Potentiometric Selectivity Coefficient, $k_{A,B}^{pot}$ 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 should preferably be evaluated by measuring the response of an ion selective electrode in solutions containing both the primary ion, A, and interfering ion, B (fixed interference method). Alternatively, the separate solution method could be used to calculate the selectivity coefficient. The method is less desirable because it does not approximate as well the conditions under which the electrodes are used.

   The activity of the primary ion A and the interferant B at which $k_{A,B}^{pot}$ is determined should always be specified since the value of $k_{A,B}^{pot}$ is not strictly constant but defined by the modified Nernst equation. The smaller the value of $k_{A,B}^{pot}$, the greater the electrode's preference for the primary ion, A.

b. <u>Fixed Interference Method.</u> The emf of a cell comprising an ion-selective electrode and a reference electrode is measured with solutions of constant level of interferant, $\underline{a}_B$, and varying activity of the primary ion, $\underline{a}_A$. The potential values obtained are plotted versus the logarithm of the activity of the primary ion. The intersection of the extrapolations of the linear portions of this curve (i.e., where the two terms under the log sign in the expanded Nernst equation have an equal contribution) will indicate the values of $\underline{a}_A$ which are to be used to calculate $k_{A,B}^{pot}$ from:

$$\underline{k}_{A,B}^{pot} = (\underline{a}_A / \underline{a}_B)^{\underline{z}_A / \underline{z}_B}$$

9. <u>Separate Solution Method</u>. The emf 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 $\underline{a}_A$ (but no B), the other containing the ion B, at the same activity $\underline{a}_B = \underline{a}_A$ (but no A). If the measured values are E_1 and E_2, respectively, the value of $k_{A,B}^{pot}$ may be calculated from the following equation if the Nernstian equation holds for the indicator ion:

$$\log \underline{k}_{A,B}^{pot} = \frac{\underline{E}_2 - \underline{E}_1}{2303 \underline{RT/z}_A \underline{F}} + (1 - \frac{\underline{z}_A}{\underline{z}_B}) \log \underline{a}_A$$

This method is not recommended except in those cases where the mixed solution method is not feasible, e.g., non-alignment of emf plots for primary and interferent primary solutions, respectively.

B. CLASSIFICATION OF ION-SELECTIVE ELECTRODES

Electrodes should be classified using the system described in Pure and Applied Chem. <u>48</u>, 127 (1976). (see also the compendium, pp. 168-175)

C. PAPERS ON NEW OR MODIFIED ELECTRODES

Such papers should include the following essential information:

(a) Constructional details, including the membrane and conditions of its preparation, inner filling solution, internal reference electrode and contacts. Pretreatment should be specified as should the cell assembly - including the reference electrode employed. For commercial electrodes it is adequate to quote the manufacturer's name and model designation.

(b) Calibration range, including slope, detection limit and influence of pH, the latter expressed as a potential/pH diagram for at least two levels of activity of the measured ion, the substance used to effect a pH change and the nature of the acid added.

(c) Stability, including details of storage conditions an drift and information on its susceptibility to attack by chemical agents such as acids, bases, or complexing agents.

(d) Static or dynamic response times with specific information on how these are obtained with respect to solution conditions, stirring rate, pretreatment, etc. Any change in response time with electrode age should be noted.

(e) Interfering substances ought to be classified according to type with selectivity for the primary ion over other counter-ions being computed by the Fixed Interference Method at specified interference levels. The selectivity coefficients should be measured on a newly made electrode and indication given how the coefficients change during electrode lifetime.

(f) Any limitations of the electrode should be clearly stated along with details of operational lifetimes and rejuvenating treatment (which should be evaluated in terms (b) and (e)).

D. PAPERS ON APPLICATIONS FOR DIRECT CONCENTRATION/ACTIVITY MEASUREMENTS

These papers can with advantage refer to papers describing characteristics of the electrode employed and which would fall into category C above. Attention ought also to be given to:

(a) Details of the cell assembly employed and especially of the reference electrode.

(b) Interferences and their possible elimination.

(c) Details of experimental procedure including ionic-strength adjustment and calibrating standards.

(d) A comparison of activity/concentration values obtained with those obtained by traditional or alternative established procedures (if they exist) using appropriate statistical tests.

(e) Recovery tests.

(f) The electrometer or potentiometer used in the emf measurements, as well as its sensitivity, should be specified by manufacturer and model designation.

E. PAPERS ON TITRATION APPLICATIONS

In addition to a mention of papers describing electrode characteristics and attention to items listed in D. special attention must be given to:

(a) Method used for correct end-point location.

(b) Possible interferences.

(c) The possibility of electrode damage during usage.

F. PAPERS ON ON-LINE PROCESS APPLICATIONS AND AUTOMATIC METHODS

Reports on applications to on-line continuous monitoring systems ought to include reference to associatedwork on electrode characteristics and preliminary experimentation on direct concentration/activity measurement. This, and especially measurements on intermittent samples, will help to characterize possible errors due to the additional parameters of the flowing system. Specific mention should be made of:

(a) Dynamic response-time behavior of the cell.

(b) Full details of cell design including the reference electrode and the supplementary addition of reagents.

(c) Definition of calibration procedure (e.g., on-line, continuous flow or batch, etc.) and frequency of calibration requirements.