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Standard Terminology Used with Ion-Selective Electrodes[1]

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1. Scope

1.1 This terminology covers those terms recommended by the International Union of Pure and Applied Chemistry (IUPAC),[2] and is intended to provide guidance in the use of ion-selective electrodes for analytical measurement of species in water, wastewater, and brines.

2. Referenced Documents

2.1 *ASTM Standards:*[3]
D1129 Terminology Relating to Water

3. Terminology

3.1 *Definitions*—For other definitions used in this terminology, refer to Terminology D1129.

3.2 *Definitions of Terms Relevant to Ion-Selective Electrode Technology:*

acid error, *n*—in very acid solutions, the activity of water is reduced (less than unity) causing a non-Nernstian response in glass electrodes.

DISCUSSION—A positive error in the pH reading results.

activity, *n*—the thermodynamically effective concentration of a free ion in solution.

DISCUSSION—In dilute solutions, ionic activity, and concentration are practically identical, but in solutions of high ionic strength, or in the presence of complexing agents, activity may differ significantly from concentration. Ionic activity, not concentration, determines both the rate and the extent of chemical reactions.

activity coefficient, *n*—a factor, γ, that relates activity, *A*, to the concentration, *C* of a species in solution:

$$A = \gamma C$$

DISCUSSION—The activity coefficient is dependent on the ionic strength of the solution. Ions of similar size and charge have similar activity coefficients.

alkaline error, *n*—in alkaline solutions, where hydrogen ion activity becomes very small, some glass electrodes respond to other cations, such as sodium.

DISCUSSION—A negative error in the pH reading results. By changing the composition of the glass, the affinity of the glass for sodium ion can be reduced. Such electrodes are known as lithium glass, high-pH, or full-range electrodes.

analate, *n*—the sample being analyzed; used in the terms "analate addition" and "analate subtraction".

DISCUSSION—This term differs from the term "analyte," which describes the chemical species of interest in an analytical test.

asymmetry potential, *n*—the potential across a glass pH electrode membrane when the inside and outside of the membrane are in contact with solutions of identical pH.

DISCUSSION—This term has also been used to define the observed potential differences between identical electrode pairs placed in identical solutions.

calibration curve, *n*—a plot of the potential (emf or E) 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.

DISCUSSION—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 (–log concentration of species measured, *A*) be plotted on the abscissa (horizontal axis) with increasing activity to the right. See Fig. 1 and Fig. 2. Region I of Fig. 1 represents the segment of the curve where the potential no longer changes in response to changes of the measured species activity and the electrode no longer demonstrates Nernstian response.

IUPAC

activity standard, *n*—a standardizing solution whose value is reported in terms of ionic activity.

DISCUSSION— If the electrode is calibrated using activity standards, the activity of the free, unbound ion in the sample is determined.

concentration standard, *n*—a standardizing solution whose value is reported in terms of total concentration of the ion of interest.

DISCUSSION—If the electrode is calibrated using pure-concentration standards and measurements made on untreated samples, results must be corrected for the sample ionic strength and the presence of complexing agents. More commonly, a reagent is added to all standards and samples before measurement in order to fix the ionic strength, thus avoiding the need for correction.

[1] This terminology is under the jurisdiction of ASTM Committee D19 on Water and is the direct responsibility of Subcommittee D19.05 on Inorganic Constituents in Water.

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[2] *Recommendations for Nomenclature of Ion-Selective Electrodes*, IUPAC Commission on Analytical Nomenclature, Pergamon Press, Oxford, 1976.

[3] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

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