Designation: D4127 – 06

Standard Terminology Used with Ion-Selective Electrodes[1]

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—in very acid solutions, the activity of water is reduced (less than unity) causing a non-Nernstian response in glass electrodes. A positive error in the pH reading results.

activity—the thermodynamically effective concentration of a free ion in solution. 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—a factor, γ, that relates activity, *A*, to the concentration, *C* of a species in solution:

$$A = \gamma C$$

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

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

asymmetry potential—the potential across a glass pH electrode membrane when the inside and outside of the membrane are in contact with solutions of identical pH. This term has also been used to define the observed potential differences between identical electrode pairs placed in identical solutions.

calibration curve—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 (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 (−log concentration of species measured, *A*) be plotted on the abscissa (horizontal axis) with increasing activity to the right.

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activity standard—a standardizing solution whose value is reported in terms of ionic activity. If the electrode is calibrated using activity standards, the activity of the free, unbound ion in the sample is determined.

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

combination electrode—an electrochemical apparatus that incorporates an ion-selective electrode and a reference electrode in a single assembly thereby avoiding the need for a separate reference electrode. **IUPAC**

concentration—the actual amount of a substance in a given volume of solution. When measuring ionic concentrations by electrode, a distinction is made between the concentration of the free, unbound ion, and total concentration that includes ions bound to complexing agents.

dissociation constant—a number indicating the extent to which a substance dissociates in solution. [For a simple two-species complex *AB*, the constant is given by the product of the molar concentrations of *A* and of *B* divided by the molar concentrations of the undissociated species *AB*. For example, with hydrofluoric acid:

$$([H^+][F^-])/([HF]) = K = 6.7 \times 10^{-4} \text{ at } 25°C$$

The smaller the value of *K*, the less the complex is dissociated. *K* varies with temperature, ionic strength, and the nature of the solvent.]

drift—this is the slow nonrandom change with time in the potential (emf) of an ion-selective electrode cell assembly maintained in a solution of constant composition and temperature. **IUPAC**

electrode life—the length of time that an electrode functions usefully. Life-time of solid-state and glass electrodes is limited by mechanical failure of the electrode body or chemical attack on the sensing membrane, and can range from a few days, if the electrode is used continuously in hot or abrasive flowing streams, to several years under normal laboratory conditions. The life-time of liquid membrane electrodes is limited by loss of ion exchanger with use, and is generally 1 to 6 months.

electrode pair—a sensing electrode and a reference electrode; the reference electrode may be separate or combined in one body with the sensing electrode.

electrolyte—a substance that ionizes in aqueous solution; also, a solution containing ions. Weak electrolytes are only slightly dissociated into ions in solution (acetic acid), and strong electrolytes are highly dissociated (HCl, NaCl).

equitransference—equal diffusion rates of the positively and negatively charged ions of an electrolyte across a liquid junction.

equitransferent filling solution—a reference electrode filling solution in which the diffusion rates of negatively and positively charged ions are equal.

filling solution—the solution inside a sensing or reference electrode that is replenished periodically. Solutions that are permanently sealed within the electrode (like the buffer inside a pH electrode) are usually called internal reference solutions to differentiate them from filling solutions.

internal filling solution of sensing electrode—in liquid membrane electrodes, an aqueous internal filling solution contacts the internal reference element and the membrane, which is saturated with ion exchanger. The filling solution normally contains a fixed level of chloride and of the ion for which the electrode was designed; the concentration of this ion determines the zero potential point of the electrode. In addition, the filling solution is saturated with silver chloride to prevent the silver chloride of the internal reference element from dissolving.

reference electrode filling solution— a concentrated salt solution contacting the internal reference element and the sample solution. The composition of the filling solution is chosen to maximize stability of the potentials developed at the internal reference element/filling solution interface and the filling solution/sample junction. In general, filling solutions for AgCl internal construction reference electrodes should: (*1*) contain Cl⁻ and be saturated with AgCl to prevent the reference element from dissolving; (*2*) be at least ten times higher in total ionic strength than the sample; (*3*) be equitransferent; (*4*) not contain the ion being measured or an ion that interferes with the measurement.

flowthrough electrodes—ion-selective and reference electrodes designed for anaerobic measurements. The two electrodes are connected by plastic tubing to a syringe or peristaltic pump, and the sample is pumped through the electrodes at a constant rate. Ion-selective electrodes can be made in a flow through configuration for the measurement of very small samples (0.2 to 0.3 mL) or samples that must be measured anaerobically.

Gran's plots—a method of plotting apparent concentration (as derived from the electrode potential) versus the volume of reagent added to the sample. Gran's plots are especially useful for plotting titrations that would give poor end-point breaks if plotted conventionally. They can also be used to determine concentration by known addition with greater precision than can be obtained by a single addition measurement.

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. **IUPAC**

interfering substance—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 (for example, Na⁺ for the Ca⁺⁺ electrode), those species which interact with the membrane so as to change its chemical composition (that is, organic solvents for the liquid or poly(vinyl chloride) (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 (that is, CN^- present in the measurement of Ag^+). **IUPAC**

internal reference electrode—a reference electrode that 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. **IUPAC**

ion-selective electrode—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 that involve redox reactions.

Discussion—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. **IUPAC**

ionic strength—the weighted concentration of ions in solution, computed by multiplying the concentration (c) of each and every ion in solution by the corresponding square of the charge (Z) on the ion, summing and dividing by 2: ionic strength = $(\frac{1}{2})\sum Z^2 C$. Conductivity measurements give a rough estimate of ionic strength. The ionic strength (and to a lesser extent, the concentration of nonionic dissolved species) largely determines the activity coefficient of each ion in the solution.

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. **IUPAC**

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. **IUPAC**

junction potential—the portion of the total observed potential developed between the sensing and reference electrodes that is formed at the liquid/liquid junction between the reference electrode filling solution and the sample solution. For accuracy, the junction potential should be as low and as constant as possible despite variations in the composition of the sample solution. Reference electrode filling solutions should be judiciously chosen to minimize liquid junction potential.

limit of detection—a calibration curve ordinarily has the shape shown in Fig. 1.
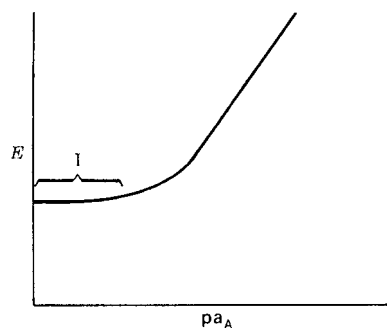

FIG. 1 Limit of Detection

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.

In the present state of the art, and for the sake of practical convenience, a simple (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 in Fig. 2. Since many factors affect the detection limit, the experimental conditions used should be reported, that is composition of the solution, the history and preconditioning of the electrode, stirring rate, etc. **IUPAC**

mean ionic activity coefficient— *for a salt that is composed of two monovalent ions,* the geometric mean of the individual ionic activity coefficients. (The geometric mean is obtained, in this case, by multiplying the two individual ionic activity coefficients and then taking the square root.) It is important because, unlike individual ionic activity coefficients, it can be measured by a variety of techniques, such as freezing point depression and vapor pressure, as well as by paired sensing electrodes.

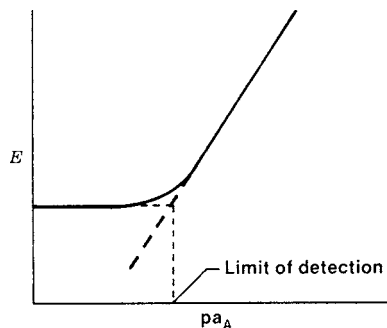**membrane**—a thin space of material covering a structure of separating solutions and permitting selection transport of a chemical species between the two solutions.

FIG. 2 Practical Limit of Detection