



## Standard Terminology Used with Ion-Selective Electrodes<sup>1</sup>

This standard is issued under the fixed designation D 4127; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last approval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

*This standard has been approved for use by agencies of the Department of Defense.*

### 1. Scope

1.1 This terminology includes those terms recommended by the International Union of Pure and Applied Chemistry,<sup>2</sup> 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:

D 1129 Terminology Relating to Water<sup>3</sup>

### 3. Terminology

3.1 *Definitions*—For other definitions used in this terminology, refer to Terminology D 1129.

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

**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,  $\gamma$ , 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.

**activity limit**—the lowest activity that can be measured in a solution that is well buffered with respect to the ion being measured. The activity limit will vary as a function of solution pH.

**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**<sup>2</sup>—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  $p_{A_A}$  ( $-\log$  activity of the species measured,  $A$ ) or  $p_{C_A}$  ( $-\log$  concentration of species measured,  $A$ ) be plotted on the abscissa (horizontal axis) with increasing activity to the right.

**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. 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**<sup>2</sup>—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.

**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:

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<sup>2</sup> *Recommendations for Nomenclature of Ion-Selective Electrodes*, IUPAC Commission on Analytical Nomenclature, Pergamon Press, Oxford, 1976.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 11.01.

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

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**<sup>2</sup>—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.

**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. For low liquid junction potentials, the ionic strength of the filling solution must be high compared to the sample solution.

**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  $\text{Cl}^-$  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.

**Gran's plot paper**—a type of graph paper designed to eliminate calculations when measurements are made by the Gran's plot technique. Electrode potentials in millivolts are plotted on the vertical antilogarithmic axis and either volume of reagent added or sample concentration on the horizontal linear axis. Special Gran's plot papers can be constructed that automatically correct for volume changes occurring during titrations.

**hysteresis (electrode memory)**<sup>2</sup>—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.

**interfering substance**<sup>2</sup>—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,  $\text{Na}^+$  for the  $\text{Ca}^{++}$  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,  $\text{CN}^-$  present in the measurement of  $\text{Ag}^+$ ).

**internal reference electrode**<sup>2</sup>—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.

**ion-selective electrode**<sup>2</sup>—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.

(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 (that is, Ag<sub>2</sub>S, AgI/Ag<sub>2</sub>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 that is heterogeneous in nature.

(2) *noncrystalline 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 (for example, filter, glass frit, etc.) or nonporous (for example, 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*—Glass electrodes are ion-selective electrodes in which the sensing membrane is a thin piece of glass whose chemical composition determines the selectivity of the electrode. In this group are: hydrogen ion-selective electrodes and monovalent cation-selective electrodes.

(b) *electrodes with a mobile carrier*:

(1) *positively charged*—bulky cations (for example, 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 (for example, filter or PVC), provide membranes that are sensitive to changes in the activities of anions.

(2) *negatively charged*—complexing agents (for example, of type (RO)<sub>2</sub>PO<sub>2</sub><sup>−</sup>) or bulky anions (for example, tetra-*p*-chlorophenylborate anions) that when dissolved in a suitable organic solvent and held in an inert support (for example, filter or PVC), provide membranes that are sensitive to changes in the activities of cations.

(3) *uncharged (neutral) carrier*—electrodes based on solutions of molecular carriers of cations (for example, antibiotics, macrocyclic compounds or other sequestering agents) that can be used in membrane preparations which show sensitivity and selectivity to certain cations.

(B) Sensitized Ion-selective Electrodes

(1) *gas-sensing electrodes*:

(a) *secondary reaction type*—sensors composed of an indicating and a reference electrode that uses a gas-permeable membrane or an air gap to separate the sample solution from a thin film of an intermediate solution, which is 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

(for example, air-gap electrode). This intermediate solution interacts with the gaseous species in such a way to produce a change in a measure value (for example, pH) of the intermediate solution. This change is sensed by the ion-selective electrode and is proportional to the partial pressure of the gaseous species in the sample.

(b) *redox reaction type*—a gas sensing electrode using a platinum redox electrode, typified by the hydrogen gas electrode. This responds to the redox equilibrium between hydrogen gas and hydrogen ion in solution.

(c) *amperometric detector*—this is a type that uses an amperometric detector, generally behind a gas permeable membrane. Such devices have been used for oxygen and for free chlorine.

(2) *enzyme substrate electrodes*—sensors in which an ion-selective electrode is covered with a coating containing an enzyme that 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.

NOTE 1—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.

**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 = (1/2)Σ*Z*<sup>2</sup>*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**<sup>2</sup>—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.

**isopotential point**<sup>2</sup>—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.

**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**<sup>2</sup>—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  $I$ .

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.

**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.

**liquid ion-exchange electrode membrane**—a porous plastic disk, permeable to the ion exchanger, and impermeable to water, which allows the ion exchanger to contact the sample solution and separates the internal filling solution from the sample.

**gas electrode membrane**—a plastic film, permeable to gases but impermeable to water, separating the electrode from the simple solution.

**crystal membrane or solid-state electrode membrane**—a thin single or mixed crystal that is an ionic conductor and that separates the internal reference element or internal reference solution from the sample solution.

**Nernst equation**—a mathematical description of electrode behavior:

$$E = E_x + 2.3 RT/zF \log A$$

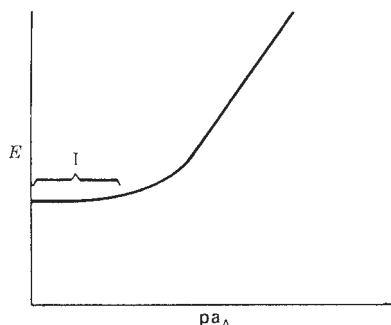


FIG. 1 Limit of Detection

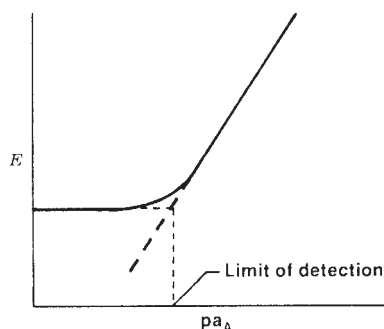


FIG. 2 Practical Limit of Detection

where:

- $E$  = total potential developed between the sensing and reference electrodes, mV,
- $E_x$  = potential dependent on the choice of reference electrodes,
- $RT/zF$  = Nernst factor,
- $R$  and  $F$  = constants,
- $z$  = charge on the ion, including sign,
- $T$  = temperature, and,
- $A$  = activity of the ion to which the electrode is responding.

**Nernst factor**—the term  $2.3RT/nF$  in the Nernst equation, which is equal (at  $T = 25^\circ\text{C}$ ) to 59.16 mV when  $n = 1$  and 29.58 mV when  $n = 2$ , and which includes the sign of the charge on the ion in the term  $n$ . The Nernst factor varies with temperature. This factor is often referred to as the *electrode slope*.

**Nernstian response**<sup>2</sup>—the response of an ion-selective electrode is over a given range of activity (or concentration) in which a plot of the potential of such an electrode in conjunction with a reference electrode versus 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  $pa_A$  at  $25^\circ\text{C}$ ).

**pH electrode**—an ion-selective electrode, made of glass, that responds to hydrogen ion activity. Wide-range pH electrodes function over the activity range  $1 M \text{H}^+$  (pH 0) to  $10^{-14} M \text{H}^+$  (pH 14). pH electrodes may be subject to “acid error” in strongly acidic solutions and are also subject to “alkaline error” caused by response to sodium or other cations in basic solutions.

**pH/mV meter**—an instrument that measures and displays the voltage developed between a sensing electrode and a reference electrode placed in a solution, and can convert the voltage developed by a pH electrode to a corresponding pH value.

**analog pH/mV meter**—an instrument that displays voltages, pH units, or other concentration units by means of a needle pointer and scale.

**digital pH/mV meter**—an instrument with digital display of millivolts or pH units. Less operator error is associated with digital instruments since there is no need for interpolation and no risk of confusing scales.

**pH unit**—a tenfold change in hydrogen ion activity, expressed as the negative logarithm of the hydrogen ion activity. Thus a solution of pH 7 is  $10^{-7} M$  in hydrogen ion activity, and a



pH 8 solution is  $10^{-8}M$ . The lower the solution pH, the more acid the solution. Occasionally, ion levels are expressed in  $pX$  units. Thus  $pNa = 3.5$  is equivalent to  $10^{-3.5}M Na^+$ , or  $3.0 \times 10^{-4}M$ .

**practical response time**<sup>2</sup>—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 at which the potential of the cell becomes equal to its steady-state value within 1 mV. The experimental conditions used should be stated, that is, 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.

**redox (ORP) electrode**—a metallic electrode, usually platinum, used to follow reversible oxidation-reduction reactions. The potential developed between the redox electrode and reference electrode is a Nernstian function of the ratio of a species in two different oxidation states. Redox (ORP) electrodes are primarily used to determine a species in one oxidation state by titration with a reagent that oxidizes or reduces the species being determined.

**redox (ORP) potential**—the potential developed by a metallic electrode when placed in a solution containing a species in two different oxidation states. Some sensing electrodes, notably the early silver billet electrodes, act as redox (ORP) electrodes as well as sensing electrodes in certain types of solutions, leading to measurement errors.

**reference electrode**—that half of the electrode pair which provides a constant potential regardless of solution composition. The potential developed by the sensing electrode is measured against this reference potential to give an overall system potential which can be converted to the level of the species sensed.

**single-junction reference electrode**—a reference electrode containing a single electrolyte. The electrolyte (1) provides a constant level of the ion sensed by the reversible reference element and (2) forms a low-junction potential liquid junction with the sample solution.

**double-junction reference electrode**—a reference electrode that utilizes two separate filling solutions: an inner solution to provide a constant level of the ion sensed by the reference element and an outer filling solution that provides a low-junction potential liquid junction with the sample solution. The liquid junction potential between the inner and outer solutions is constant but not necessarily zero.

**calomel reference electrode**—a reference electrode with an internal reference element of mercury/mercurous chloride. The filling solution is usually saturated KCl, saturated with mercurous chloride.

**silver/silver chloride reference electrode**—a reference electrode with an internal reference element of silver and silver chloride. The filling solution must contain chloride and be saturated with respect to silver chloride. Saturated KCl, 1 M KCl, and equitransferent filling solutions are all commonly

used. Ag/AgCl electrodes have better thermal characteristics than calomel electrodes and are therefore preferable for specific ion measurements and precision pH measurements.

**ceramic junction reference electrode**—a reference electrode in which the filling solution contacts the sample solution by means of a small porous ceramic junction.

**fiber or frit-type reference electrode**—a reference electrode in which the filling solution contacts the sample solution by means of asbestos fibers or a small sintered piece of porous glass.

**sleeve-type reference electrode**—a reference electrode in which the filling solution contacts the sample solution by means of a narrow ring-shaped opening between a removable outer sleeve and the inner body of the electrode. The space between the body and sleeve widens above the tip to form a reservoir for the filling solution. Sleeve-type electrodes provide exceptionally stable junction potentials, making them especially suitable for specific ion and precision pH measurements. The junction area, due to its size and the high-leak rate of the internal filling solution, does not easily become clogged.

**response time**—the length of time necessary to obtain a stable electrode potential when the electrode is removed from one solution and placed in another of different concentration. Response time depends on the electrode type, the magnitude and direction of the concentration change, temperature, and the presence of electrode interferences, if any. After exposure to a change in concentration, values of apparent concentration asymptotically approach the true concentration. Under most conditions, an electrode will exhibit a value within 1 mV of the final value within 1 min.

**selectivity constant**—a measure of a liquid ion exchange or glass electrode's response to an interfering ion compared to its response to the ion being measured. The smaller the selectivity constant, the greater the electrode's preference for the ion being measured. The principal use of selectivity constants is in determining whether an electrode can be used in a particular application. Since selectivity constants vary somewhat with the ratio of the two ions, they should not be used to correct for errors caused by interferences. The term *selectivity constant* is sometimes mistakenly applied to solid-state electrodes (that are based on solubility product) to indicate the maximum allowable ratio of interference to ion being measured. Unlike liquid and glass electrodes, solid-state electrodes exhibit an *all-or-nothing* response to an interference, with no interference as long as the critical ratio is not exceeded.

**slope**—the angle between the horizontal axis and the line formed by plotting electrode potentials against ion level on semilogarithmic graph paper. By analogy, slope has also come to be a measure of electrode response to the ion being detected. Theoretical Nernstian slope, which is temperature-dependent, is 59.16 mV at 25°C for a ten-fold change in the activity of a monovalent ion and 29.58 mV for a divalent ion. Less than theoretical slopes (that is, smaller millivolt changes per decade) are observed if potentials are plotted against concentration, if interferences are present, or if liquid electrodes need renewal. Greater than theoretical slopes are

relatively rare and usually indicate that more than one electrode process is occurring.

**selective ion meter**—an instrument that measures the potential of pH and ion-selective electrodes and displays it directly in concentration or activity units, such as pH, moles per litre, or milligrams per litre, on a logarithmic scale. Millivolt scales are provided for titrations and to verify proper electrode operation.

**streaming potential**—a potential that is generated in dilute solutions moving at high velocity through small channels. [Liquid junction potential problems are often wrongly confused with streaming potentials.]

**time response paper**—a special graph paper on which electrode potentials are plotted on the vertical antilogarithmic axis and time is plotted on the horizontal axis as the reciprocal of time. The plot is extrapolated to time-equals-infinity to determine the final electrode potential that would be observed at complete system equilibrium. Time response paper is useful for evaluating electrode performance and for rapidly estimating solution concentration in cases where electrode response is slow, such as close to the lower limit of detection.

### 3.3 Definitions of Terms Relevant to the Measurement Techniques:

**analate addition**—a variation of the known addition measurement technique in which the sample (analate) is added to a reagent containing the ion being measured. The electrode is placed in the reagent, and the sample concentration is calculated from the change in electrode potential after the addition of the sample.

**analate subtraction**—a variation of the known subtraction measurement technique in which the sample (analate) is added to a reagent containing an ion that reacts with the species being determined. The electrode is placed in the reagent, the change in electrode potential is observed when the sample is added, and the sample concentration calculated.

**direct measurement**—determination of sample concentration or activity by directly relating the electrode potential to the level of the species being measured. The level can be read from a calibration curve or the log scale of a selective ion meter.

**standard addition or known addition**<sup>2</sup>—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 versus a suitable reference electrode.

**standard subtraction or known subtraction**<sup>2</sup>—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 (for example, a complexing agent) that reacts stoichiometrically with the ion of interest are employed to determine the original activity or concentration of the ion.

**titration**—a quantitative analytical technique for measuring the concentration of a species by incremental addition of a reagent (titrant) containing a species that reacts with the sample species. Sensing electrodes can be used to follow titrations if they respond to either the species being deter-

mined or the titrant ion. Electrode potentials are plotted against millilitres of titrant added, either on standard coordinate graph paper or on Gran's plot paper, and the equivalence point (when equivalent amounts of the two species are present) is determined from the curve.

**back titration**—a titration in which an excess of reagent is added to the sample to complex or precipitate the species being determined. The excess reagent is then determined by second titration, usually with the species that was originally in the sample. Back titrations are useful for increasing accuracy in the analysis of very dilute solutions.

**complexometric titration**—a titration in which the titrant and sample ion form a complex. Many classic complexometric titrations can conveniently be followed by electrode. The success of the titration depends on the lower limit of detection of the electrode, the strength of the complex, and the possible presence of ions that compete for the complexing agent or which interfere with the electrode. Examples of complexometric titrations are the determination of calcium with EDTA, and acid-base titrations.

**differential titration**—determination of the concentration of two or more species in one sample by titration with a reagent containing a species that reacts with both sample species. In order to obtain distinct end-point breaks, the formation constants or solubility products of the two species formed must differ by several orders of magnitude.

**indicator titration**—in ion-selective electrode work, a type of differential complexometric titration in which a metal ion complex is added to the sample as an electrode indicator, and a different metal ion in the sample is determined by titration with the complexing agent contained in the indicator. An electrode that responds to the indicator metal ion is used to detect the point at which the titrant has complexed all of the ion being determined. An abrupt change in the indicator ion concentration occurs when excess complexing agent is added.

**precipitation titration**—a titration in which the titrant and the sample species form a precipitate. An electrode can be used to follow the titration if it senses either of the ions involved in the reaction. The success of the titration depends on the lower limit of detection of the electrode, the solubility of the precipitate, the reaction rate, and the possible presence of other species which are also precipitated by the titrant. Examples of precipitation titrations are the determination of halides with silver nitrate and sulfate with lead ion.

**redox (ORP) titration**—a titration in which the ratio of two different oxidation states of a species is changed by the incremental addition of an oxidizing or reducing agent. A redox (ORP) electrode, which responds to the logarithm of the ratio of the activities of the two oxidation states, is used to follow the titration. Among the many substances that can be determined in this manner are H<sub>2</sub>O<sub>2</sub>, I<sub>2</sub>, Fe<sup>+3</sup>, MnO<sub>4</sub><sup>-</sup>, and Sn<sup>++</sup>. Differential titrations are possible in some cases.

**R titration**—a titration in which the sensing electrode responds to an ion introduced by a reagent prior to titration. A synonym for *indicator titration*.

**S titration**—a titration in which the sensing electrode responds to the ion being removed from the sample by the titrant.

**T titration**—a titration in which the sensing electrode responds to the titrant ion, not to the sample species being determined.

### 3.4 Definitions of Terms Relevant to Conditions Affecting Measurement:

**polarizability**—the inability of an electrode to reproduce a reading after a minute electrical current has been passed through the membrane. Glass pH electrodes are especially prone to polarization errors caused by small currents flowing from the pH meter input circuit and from static electrical charges built up as the electrodes are removed from the sample solution, or when the electrodes are wiped.

**suspension effect**—the change in junction potential when a reference electrode is immersed to different depths in a solution containing resins or charged colloids, such as certain clays and soils. The suspension effect, which can be as large as 100 mV, does not occur with sensing electrodes.

**temperature effects**—changes in potential developed between a sensing and reference electrode due to changes in temperature. The slope of a sensing electrode varies with temperature, as does the potential developed by the internal reference element in the reference electrode. In addition, the solubility of salts such as AgCl or Hg<sub>2</sub>Cl<sub>2</sub> changes with temperature. It is therefore advisable to measure all samples and standardizing solutions at the same temperature.

**temperature range**—those temperatures at which electrode measurements can be made. The lower temperature limit is set by the freezing point of the solution that has the highest freezing point (including the sample as well as all filling solutions). The upper temperature limit is set by the boiling point of the solutions, except for liquid ion exchange electrodes, whose upper temperature limit is determined by the solubility of the ion exchange solution. Electrode life decreases with exposure to high temperatures. In many cases, the limit of detection also rises with increasing temperature. For these reasons, it is preferable to cool hot solutions before measurement.

## 4. Significance and Use

4.1 The need to identify and understand the relationships of species found in water systems increases with the continuing demand for improved water quality and pollution control. Among instruments available for this purpose, ion-selective electrodes have been found suitable in many applications, especially where color or turbidity limits the usefulness of colorimetry.

## 5. Summary

5.1 This terminology is common to ion-selective electrodes, but independent of the source of manufacture. Conditions that affect certain of these parameters are discussed.

## 6. Keywords

brines; electrodes; terminology; waste water; water

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