This book has been prepared by the United States Department of Commerce and National Burea of Standards in 1969 for public distribution and consumption. The purpose is to provide a basic introduction to pH and Ion Selective measurement theory and practice. As this book is now somewhat antiquated it is best suited as a historical overview for this field and a basic theoretical treatment of analytical aqueous electrochemistry.

Table of Contents for Selective Ion Electrode Paper (1969)

FORWARD

Ion Selective Electrodes represent a major advance in analytical technique. For the first time in analytical chemistry the activities of many ions can be determined quickly and conveniently in a non-destructive manner. Unfortunately, misconceptions concerning the simplicity of the method have in the past, led to some disappointments. This could have been entirely avoided if the user had been aware of what was involved in this method of analysis. This booklet has been designed to introduce the fundamental aspects of electrochemical measurement by ion-selective electrodes. Accordingly, detailed accounts of individual electrodes are not given — references to certain electrodes are only made to illustrate general principles. Further information on ion-selective electrodes can be obtained from electrode manufacturers and from publications such as "Ion-Selective Electrodes" — this book was prepared by the United States Department of Commerce, National Bureau of Standards (1969), edited by R. Durst and is recommended to anyone intending to use ion-selective electrodes.

ELECTRODE CHARACTERISTICS

(a) DRIFT

The drift of most solid-state and glass Ion Selective Electrodes compares well to the drift of a good quality pH Electrode (typically 1-4mV/day). However, higher accuracy is frequently required for specific ion measurements than with pH, so the more frequent the recalibration with standards, the better. The exact frequency of calibration depends on the accuracy required. Liquid membrane electrodes can drift up to 8mV/day. The above comments apply of course to measurements at a constant temperature and under conditions where the membrane (or sample) is not undergoing a change.

(b) REPRODUCIBILITY

A reproducibility of 1mV/decade is a typical figure for careful measurements under ideal conditions. If special precautions are taken w.r.t. liquid junction potentials, washing techniques, shielding from external charges and if conditions of measurements are matched very closely, reproducibilities of 0.1mV can be obtained. Considerable experience in electrochemical measurements on the operator's part is a prerequisite in this case.

(c) RESPONSE TIME

When an electrode is used around the middle of its measuring range, electrochemical equilibrium is usually attained in less than 15 seconds. At the lower limit of detection, longer response times (up to 3 mins) are more usual. If an electrode has a very slow response time ()5 mins) or never gives a stable indication (with due consideration to the inherent drift — see notes on drift) it can mean:—

(i) A liquid junction potential problem

(ii) The membrane surface (or sample ?) is changing in some manner, e.g. is being poisoned by interfering ions or is being coated with — say, a protein, oil or fat.

(iii) The electrode is approaching the end of its useful life.

(d) LIMIT OF DETECTION

The lower limit of detection in the case of the solid-state electrodes is governed by the solubility product of the membrane material. If an electrode is left in distilled water for sufficiently long, the membrane will equilibrate to form a saturated solution of the membrane material, so naturally, the electrode cannot sense solutions of lower activity than the activity of the membrane — saturated solution. As this process is fairly

slow (sometimes days) and as only an extremely small amount of the membrane dissolves anyway, it is quite safe to wash electrodes in distilled water and also to leave electrodes immersed in distilled water. If the membrane material is appreciably soluble in solutions of high activity of the ion of interest, an upper limit of detection is placed on its use also. This does not mean that such an electrode cannot be used in solutions of high activity, but simply that repeated use will reduce the life time of the electrode (See notes on Life Time). Examples are the Cl^- and CN^- electrodes. The solubility product of

$$Ag_2S \quad (K_{sp} \, Ag_2S = 1 \times 10^{-51})$$
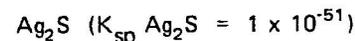
would indicate that a silver ion activity of $< 10^{-20}M$ could be detectable. In practice, it is very difficult to prepare very dilute solutions $< 10^{-8}M$ without ionic absorption onto and desorption from the surfaces of the containing vessels and the electrodes. This problem is analogous to the difficulty faced by an analyst in attempting to obtain accurate pH readings in very dilute unbuffered solutions.

In the case of the liquid membrane electrodes, the lower limit of detection is defined by the solubility of the organic ion exchanger in the sample solution.

(e) ACCURACY

The logarithmic relationship between sample activity and millivolts means that electrodes give constant accuracy throughout their measuring range — measurements in solutions of very low activity are just as accurate as measurements of high activity. Divalent ion measurements are not as accurate as monovalent because the $\frac{1}{2}$ term in the Nerst equation halves the slope, but does not change the magnitude of drifts, etc.

(f) LIFE OF AN ELECTRODE

Most solid-state and glass electrodes when used in ideal solutions, under normal laboratory conditions, have a life time of 1-2 years. This time will be considerably reduced if the electrode:—

(i) Is subjected to extremes of temperature regularly.

(ii) Is placed in solutions which irreversibly damage the membrane (see interferences — selectivity).

(iii) Is placed in a sample which is agitated and contains materials which can cause abrasive action. (Particularly important in single crystal and glass membranes).

A contracted slope and/or a sluggish response is/are the first symptoms of an electrode losing its sensing ability. Liquid type membrane electrodes

which have replaceable membranes can be used for as long as supplies of the membrane supports and ion exchanger exist.

(g) SELECTIVITY

An electrode which responds to other species of ions besides the one it is intended to measure (the primary ion) exhibits interference by these ions. **ALL** electrodes produced so far, (including the pH electrode) have this problem to some degree, electrodes are best termed "ion selective" rather than "ion specific". Some electrodes are more responsive to interferring ions than to primary ion; therefore, it is necessary to consider which ions are likely to be in a sample **BEFORE** measurements are made so that the measurements are meaningful and the membrane is not damaged.

All that is necessary in order to understand the qualitative and quantitive aspects of interference is a familiarity with the chemical properties of the membrane.

(i) Glass Membranes

Selectivity in glass membranes is determined by the relative magnitude of mobility ratios and ion exchange equilibrium constants. The only highly selective glass membrane is the H^+ responsive glass.

(ii) Solid State Membranes

As far as ionic migration is concerned, solid state membranes are very selective. The most common cause of interference in these types is simply a chemical reaction taking place on the surface of the membrane.

Two types of chemical reactions can occur:—

(a) The deposition of a layer of (relatively) insoluble material on the membrane surface which prevents membrane—solution contact.

(b) Dissolution of the membrane as a soluble reaction product.

Consider the solid state silver chloride membrane. AgCl (whether an electrode membrane or a reagent chemical) reacts with bromide ion (if in sufficient concentration)

$$AgCl + Br^- \rightarrow AgBr + Cl^-$$
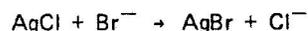
because the resultant product, silver bromide, is more insoluble ($K_{sp} = 8 \times 10^{-13}$) than silver chloride ($K_{sp} = 1 \times 10^{-10}$). The layer of silver bromide built up on the membrane surface prevents the equilibration of chloride ion in solution with the silver chloride of the membrane, consequently the electrode will no longer respond to chloride ion. Restoration of the chloride response necessitates removal of the AgBr

layer, either by abrasion or soaking in a very strong chloride solution, which favours the reverse reaction. Similarly, it would be expected that iodide ($K_{sp}AgI = 1 \times 10^{-16}$) and sulphide ($K_{sp}Ag_2S = 1 \times 10^{-51}$) would interfere. The allowable limits of Br^- I^- or $S^=$ activities (w.r.t. to a particular Cl^- activity) will depend on the ratio of the solubility product of Ag Br, AgI or Ag_2S to that of AgCl. This ratio (calculated or experimental) is known as a "selectivity constant". Silver chloride also reacts with aqueous NH_3 and CN^- to form comparatively stable soluble silver complexes, i.e., $Ag(NH_3)_2^+$ and $Ag(CN)_2^-$. Placing a chloride electrode in an ammonia or cyanide solution results in the dissolution of the membrane:

$$K_{stab\ const} = \frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2} \tag{11}$$

The allowable levels of CN^- and NH_3 are governed by the ratio of the stability constant for the respective complex to the solubility product of AgCl. On the other hand, common cations (except Hg^{++}) would not be expected to interfere to any significant extent; neither would F^- NO_3^- and $SO_4^=$ etc. AgCl is stable in acid solutions, indicating a pH independance.

In strong Cl^- solutions (> 1.0 MCl^-) AgCl is appreciably soluble, and use of a chloride electrode in such solutions for long periods of time reduces the lifetime of the electrode:

NaCl (M)	Ag^+ (M x 10^5)
0.933	8.6
1.43	18.4
2.27	57.0
3.00	119.4
4.17	333.5
5.04	603.9

TABLE (3)

Effect of NaCl on the Solubility of AgCl

Essentially similar arguments can be used to predict the selectivity of all other solid-state electrodes.

(iii) Liquid Membranes

Selectivity is a function of the values of the various complex ion stability constants (primary ion: other ions) and the properties of the solvent. Selectivity constants are difficult to predict and are best determined experimentally.

Substance	K_{sp}	Substance	K_{sp}
AgBr	7×10^{-13}	CuSCN	1×10^{-11}
AgBrO$_3$	5×10^{-5}	FeS	4×10^{-19}
AgCNS	1×10^{-12}	Hg$_2$Br$_2$	5×10^{-23}
AgCl	1×10^{-10}	Hg$_2$Cl$_2$	3×10^{-18}
Ag$_2$C$_2$O$_4$	5×10^{-12}	Hg$_2$I$_2$	1×10^{-28}
AgCrO$_4$	2×10^{-12}	HgS	4×10^{-54}
AgI	1×10^{-16}	LaF$_3$	1×10^{-24}
AgIO$_3$	2×10^{-8}	MgF$_2$	7×10^{-9}
Ag$_3$PO$_4$	2×10^{-18}	NiS	1×10^{-24}
Ag$_2$S	1×10^{-51}	PbBr$_2$	8×10^{-5}
Ag$_2$SO$_4$	8×10^{-5}	PbCl$_2$	2×10^{-4}
BaSO$_4$	9×10^{-11}	PbCrO$_4$	2×10^{-14}
CaCO$_3$	5×10^{-9}	PbF$_2$	4×10^{-8}
CaF$_2$	3×10^{-11}	PbI$_2$	9×10^{-9}
CaSO$_4$	2×10^{-4}	PbS	5×10^{-29}
CdS	1×10^{-28}	PbSO$_4$	2×10^{-8}
CoS	3×10^{-26}	ZnS	1×10^{-23}
CuS	1×10^{-44}		

TABLE (4)
Table of Solubility Products at the Laboratory Temperature.

USE OF ELECTRODES

(a) METHODS OF USE

Ion Selective Electrodes can be used to measure activity by direct potentiometry (and also concentration if activity coefficients are known), or concentration by titration methods. In some applications activity is the more meaningful, particularly in biological systems. In industrial analysis, concentration is usually the parameter required. Important points of both applications will be discussed below.

(i) Direct Potentiometry.

In this, the activity of the sample is compared to measured activities of standard solutions (cf. buffer calibration in pH measurements). If the reading is in mV or pX, then an antilog conversion is required to produce a linear relationship between mV (pX) and activity. Logarithmic graph paper can be used or alternatively, a calibration curve can be constructed. A direct reading of activity is possible if the output is in the M or ppm antilog form provided the slope is corrected.

"Standard" solutions are essentially "standard" (i.e., of accurately known composition) w.r.t. **CONCENTRATION** rather than activity. This is because a standard solution is prepared by weighing out a certain quantity of compound (containing a specific amoung of the desired ion) and dissolving it in a known volume of solvent. If the solution is not dilute, it will depart from ideal and the concentration will not be the same as the activity, as shown in Section 1. Fortunately, activity coefficients or related data (see table (1)) can be obtained for many simple electrolytes and, hence, measurement of either activity **OR** concentration of a sample containing a **SINGLE** electrolyte is possible. A sample containing many electrolytes or a non-aqueous solvent presents a different problem. The **ACTIVITY** can be measured directly by comparing to standards of known activity. The **CONCENTRATION** can be obtained by making standards with identical composition to the sample w.r.t. the other electrolytes or solvent composition, and constructing a calibration curve.

Some ions, for which there are no electrodes, can be measured by adding a relatively insoluble salt (in powder form) of the ion and measuring the activity of the complementary cation or anion of the salt, the level of which will be determined by the activity of the ion via the solubility product.

La^{3+} can be measured by adding solid LaF_3 to the sample and measuring the F^- activity.