

A Beginners Guide to Ion-Selective Electrode Measurements

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Please Email chris.rundle@nico2000.net with any comments or suggestions for improvement.



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ADDITIONAL INFORMATION - Available at www.nico2000.net.

GLOSSARY OF TERMS AND CALCULATIONS

INTERNET LINKS & BIBLIOGRAPHY

Including over 100 links to Research Papers and Articles about Ion-Selective Electrode theory and practice available on the WWW.

OPERATING INSTRUCTIONS FOR ELIT ION-SELECTIVE ELECTRODES

CATALOGUE OF NICO2000 ELECTROCHEMICAL PRODUCTS (pdf) .

MS "POWER POINT" PRESENTATION

DEMONSTRATION SOFTWARE FOR ELIT ION ANALYSERS

FOREWORD AND RATIONALE.

Ion-Selective Electrodes (ISEs) have been widely used for more than thirty years, yet it is still remarkably difficult for the beginner to find an adequate explanation of the basic principles and applications of this technology. Manufacturer's advertising pamphlets tend to oversimplify the principles of operation and gloss over the difficulties and limitations, whereas numerous scientific research papers and specialist text books tend to overwhelm the non-specialist with endless equations for complex electrochemical reactions, masses of mathematical formulae, and many unnecessary details. Moreover, most of these works are now more than twenty years old and do not contain any reference to modern computer-based techniques.

It is hoped that this guide will fill the gap between these two extremes. Its aim is to give sufficient information, in relatively simple language and with the minimum of technical detail and mathematics, to enable the non-specialist to gain an appreciation of the advantages and disadvantages of ISE measurements and to assist the new analyst in achieving the best possible results when using this technology. It also gives details of the latest developments in data acquisition and processing using meterless computer interfaces and sophisticated software.

ACKNOWLEDGEMENTS

I would like to express my deep gratitude to Heinz Kreuzberg for introducing me to ISEs, for encouraging me to write this guide and, most importantly, for masterminding much of the development of the computer interfaces discussed in the last part of the work. I am also indebted to Dr. Alexander Kapustin for giving me basic training in the theory and practice of ISE measurements and for patiently answering my interminable questions, and to Dr. Jonathan Slater for providing additional background information by allowing me to see his course notes on Principles of Electroanalysis and Potentiometry.

The latter part of this guide would not have been possible without the inspired and dedicated work of Yiyang Cui and Feng Xiao in developing and writing the computer programmes which were essential to permit any further advances in the techniques and data processing of ISE measurements. Their patience and understanding in the face of many months of bombardment with interminable requests for changing and re-writing the software cannot be praised too highly.

Much of the information provided here has also been confirmed by reference to the British Standards Specification for Ion-Selective Electrodes, BS7310:1990, and gleaned from several ISE manufacturer's catalogues and advertising material.

Chris C Rundle. 5 May 2000.

INTRODUCTION TO ION SELECTIVE ELECTRODES

a) Applications

Ion-selective electrodes are used in a wide variety of applications for determining the concentrations of various ions in aqueous solutions. The following is a list of some of the main areas in which ISEs have been used.

Pollution Monitoring: CN, F, S, Cl, NO₃ etc., in effluents, and natural waters.

Agriculture: NO₃, Cl, NH₄, K, Ca, I, CN in soils, plant material, fertilisers and feedstuffs.

Food Processing: NO₃, NO₂ in meat preservatives.

Salt content of meat, fish, dairy products, fruit juices, brewing solutions.

F in drinking water and other drinks.

Ca in dairy products and beer.

K in fruit juices and wine making.

Corrosive effect of NO₃ in canned foods.

Detergent Manufacture: Ca, Ba, F for studying effects on water quality.

Paper Manufacture: S and Cl in pulping and recovery-cycle liquors.

Explosives: F, Cl, NO₃ in explosive materials and combustion products.

Electroplating: F and Cl in etching baths; S in anodising baths.

Biomedical Laboratories: Ca, K, Cl in body fluids (blood, plasma, serum, sweat).

F in skeletal and dental studies.

Education and Research: Wide range of applications.

b) Advantages.

1) When compared to many other analytical techniques, Ion-Selective Electrodes are relatively inexpensive and simple to use and have an extremely wide range of applications and wide concentration range.

2) The most recent plastic-bodied all-solid-state or gel-filled models are very robust and durable and ideal for use in either field or laboratory environments.

3) Under the most favourable conditions, when measuring ions in relatively dilute aqueous solutions and where interfering ions are not a problem, they can be used very rapidly and easily

(e.g. simply dipping in lakes or rivers, dangling from a bridge or dragging behind a boat).

4) They are particularly useful in applications where only an order of magnitude concentration is required, or it is only necessary to know that a particular ion is below a certain concentration level.

- 5) They are invaluable for the continuous monitoring of changes in concentration: e.g. in potentiometric titrations or monitoring the uptake of nutrients, or the consumption of reagents.
- 6) They are particularly useful in biological/medical applications because they measure the activity of the ion directly, rather than the concentration.
- 7) In applications where interfering ions, pH levels, or high concentrations are a problem, then many manufacturers can supply a library of specialised experimental methods and special reagents to overcome many of these difficulties.
- 8) With careful use, frequent calibration, and an awareness of the limitations, they can achieve accuracy and precision levels of ± 2 or 3% for some ions and thus compare favourably with analytical techniques which require far more complex and expensive instrumentation.
- 9) ISEs are one of the few techniques which can measure both positive and negative ions.
- 10) They are unaffected by sample colour or turbidity.
- 11) ISEs can be used in aqueous solutions over a wide temperature range. Crystal membranes can operate in the range 0°C to 80°C and plastic membranes from 0°C to 50°C .

Beginners Guide to ISE Measurement. Chapter 3.

BASIC THEORY OF ISE MEASUREMENTS.

Ion-Selective Electrodes are part of a group of relatively simple and inexpensive analytical tools which are commonly referred to as Sensors. The pH electrode is the most well known and simplest member of this group and can be used to illustrate the basic principles of ISEs.

a) The pH Electrode

This is a device for measuring the concentration of hydrogen ions and hence the degree of acidity of a solution - since pH is defined as the negative logarithm of the hydrogen ion concentration;

i.e. pH=7 means a concentration of 1×10^{-7} moles per litre. (To be more precise, the term 'concentration' should really be replaced by 'activity' or 'effective concentration'. This is an important factor in ISE measurements. The difference between activity and concentration is explained in more detail later (Chapter 6), but it may be noted here that in dilute solutions they are essentially the same. Nevertheless, in order to avoid confusion, the more familiar term (concentration) will be used in this section.)

The most essential component of a pH electrode is a special, sensitive glass membrane which permits the passage of hydrogen ions, but no other ionic species. When the electrode is immersed in a test solution containing hydrogen ions the external ions diffuse through the membrane until an equilibrium is reached between the external and internal concentrations. Thus there is a build up of charge on the inside of the membrane which is proportional to the number of hydrogen ions in the external solution.

Because of the need for equilibrium conditions there is very little current flow and so this potential difference can only be measured relative to a separate and stable reference system which is also in contact with the test solution, but is unaffected by it (see later for a discussion of reference electrodes). A sensitive, high impedance millivolt meter or digital measuring system must be used to measure this potential difference accurately.

The potential difference developed across the membrane is in fact directly proportional to the Logarithm of the ionic concentration in the external solution. Thus, in order to determine the pH of an unknown solution, it is only necessary to measure the potential difference in two standard solutions of known pH, construct a straight line calibration graph by plotting millivolts versus pH ($= -\text{Log} [\text{H}^+]$) then read off the unknown pH from the measured voltage.

In order to measure the electrode potential developed at the ion-selective membrane the ISE/pH electrode must be immersed in the test solution together with a separate reference system and the two must be connected via a millivolt measuring system. At equilibrium, the electrons added or removed from the solution by the ISE membrane (depending on whether it is cation or anion sensitive) are balanced by an equal and opposite charge at the reference interface. This causes a positive or negative deviation from the original stable reference voltage which is registered on the external measuring system.

The relationship between the ionic concentration (activity) and the electrode potential is given by the Nernst equation:

$$E = E^0 + (2.303RT/nF) \times \text{Log}(A)$$

Where E = the total potential (in mV) developed between the sensing and reference electrodes.

E^0 = is a constant which is characteristic of the particular ISE/reference pair.

(It is the sum of all the liquid junction potentials in the electrochemical cell, see later)

2.303 = the conversion factor from natural to base10 logarithm.

R = the Gas Constant (8.314 joules/degree/mole).

T = the Absolute Temperature.

n = the charge on the ion (with sign).

F = the Faraday Constant (96,500 coulombs).

$\text{Log}(A)$ = the logarithm of the activity of the measured ion.

Note that $2.303RT/nF$ is the **Slope** of the line (from the straight line plot of E versus $\text{log}(A)$ which is the basis of ISE calibration graphs) and this is an important diagnostic characteristic of the electrode - generally the slope gets lower as the electrode gets old or contaminated, and the lower the slope the higher the errors on the sample measurements.

For practical use in measuring pH, it is not normally necessary for the operator to construct a calibration graph and interpolate the results for unknown samples. Most pH electrodes are connected directly to a special pH meter which performs the calibration automatically. This determines the slope mathematically and calculates the unknown pH value for immediate display on the meter.

These basic principles are exactly the same for all ISEs. Thus it would appear that all can be used as easily and rapidly as the pH electrode: i.e. simply by calibrating the equipment by measuring two known solutions, then immersing the electrodes in any test solution and reading the answer directly from a meter. Whilst it is certainly true that some other ions can be measured in this simple fashion, it is not the case for most. Unfortunately, some ISE advertising material tends to gloss over this fact and gives the reader a rather rosy view of the capabilities of this technique. There are several factors which can cause difficulties when ISE technology is applied to the measurement of other ions. These are listed below and discussed in more detail in later sections. Nevertheless, it must be stressed here that as long as these difficulties are recognised and steps are taken to overcome them, then ISEs can still be a very useful and cost-effective analytical tool.

b) Differences Between pH and Other Ion-Selective Electrodes

i) In contrast to the pH membrane, other ion-selective membranes are not entirely ion-specific and can permit the passage of some of the other ions which may be present in the test solution, thus causing the problem of ionic interference.

ii) Most ISEs have a much lower linear range and higher detection limit than the pH electrode. Many show a curved calibration line in the region 10^{-5} to 10^{-7} moles/l and very few can be used to determine concentrations below 1×10^{-7} moles/l. Thus, for low concentration samples, it may be necessary to construct a calibration graph with several points in order to define the slope more precisely in the non-linear range.

iii) The calculation of ionic concentration is far more dependent on a precise measurement of the potential difference than is the pH, because the pH depends on the order of magnitude of the concentration rather than the precise value. For example it would take an error of more than 5 millivolts to cause a change of 0.1 pH units, but only a 1 millivolt error will cause at least a 4% error in the calculated concentration of a mono-valent ion and more than 8% for a di-valent ion. This is because the theoretical value for the slope at 25°C is 59.2 for mono-valent ions and 29.6 for di-valent ions. In practical application, however these slopes can vary considerably because of variations in temperature, deviations from "ideal" behaviour, and minor impurities or contamination of the ion-selective membrane, or if samples are measured near the detection limit of the electrode, in the non-linear range. The critical factor is not so much the actual value of the slope but that this should be as high as possible and remain constant over the range of concentrations and the time period required for the analyses. Thus, when measuring other ion concentrations, it is essential to take extra precautions to minimise any errors in the measurement of the electrode potential.

iv) For ion concentration measurements, steps must be taken to minimise the effect of the Ionic Strength of the sample. This is because pH is defined as the log of the **Activity** of the ion (which is measured directly by any ISE) but most measurements of other ions require the actual concentration, which can differ significantly from activity in samples with complex matrices and high Ionic Strength.

v) It is more usual to plot a calibration graph using the ionic concentration with a logarithmic scale on the X-axis rather than the pX factor (analogous to pH) on a linear axis.

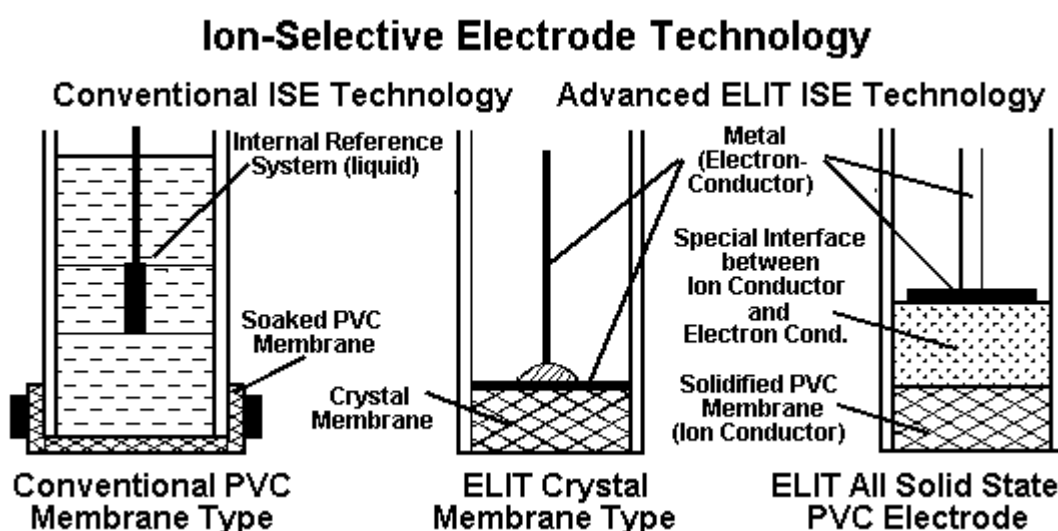
vi) Some ISEs will only work effectively over a narrow pH range.

Beginners Guide to ISE Measurement. Chapter 4.

TYPES OF ION SELECTIVE ELECTRODES

a) General Discussion

Ion selective electrodes come in various shapes and sizes. Each manufacturer has its own distinctive features, but very few give details of the internal construction of the electrode or composition of the ion-selective membranes. These are the most important factors which control the performance of the electrode, and are often kept as closely guarded trade secrets. Nevertheless, there are certain features that are common to all. All consist of a cylindrical tube, generally made of a plastic material, between 5 and 15 mm in diameter and 5 to 10 cm long. An ion-selective membrane is fixed at one end so that the external solution can only come into contact with the outer surface, and the other end is fitted with a low noise cable or gold plated pin for connection to the millivolt measuring device. In some cases the internal connections are completed by a liquid or gel electrolyte, in others by an all-solid-state system.



Ion-selective membranes are currently only available for a limited number of commonly occurring ionic species. Examination of manufacturer's catalogues reveals that the most common are:

CATIONS: Ammonium (NH_4^+), Barium (Ba^{++}), Calcium (Ca^{++}), Cadmium (Cd^{++}), Copper (Cu^{++}), Lead (Pb^{++}), Mercury (Hg^{++}), Potassium (K^+), Sodium (Na^+), Silver (Ag^+).

ANIONS: Bromide (Br^-), Chloride (Cl^-), Cyanide (CN^-), Fluoride (F^-), Iodide (I^-), Nitrate (NO_3^-), Nitrite (NO_2^-), Perchlorate (ClO_4^-), Sulphide (S^-), Thiocyanate (SCN^-).

The manner in which these different membranes select and transport the particular ions is highly variable and in many cases highly complex. It is far beyond the scope of this work to explain in detail the exact mechanism for each ion. Moreover, it is not necessary for the analyst to understand these mechanisms in order to use the electrodes satisfactorily. Nevertheless, it may be of interest to the general reader to give some indication of these processes. There are two main types of membrane material, one based on a solid crystal matrix, either a single crystal or a polycrystalline compressed pellet, and one based on a plastic or rubber film impregnated with a complex organic molecule which acts as an ion-carrier. The development of these organic membranes was based on biological research which revealed that some antibiotics and vitamins can induce cationic permeation through cell membranes.

One example of each membrane type is described below as an illustration of the range of technologies employed.

b) Crystal-Membrane Electrodes e.g. Fluoride.

The Fluoride electrode is a typical example of the first type. Here the membrane consists of a single lanthanum fluoride crystal which has been doped with europium fluoride to reduce the bulk resistivity of the crystal. It is

100% selective for F^- ions and is only interfered with by OH^- which reacts with the lanthanum to form lanthanum hydroxide, with the consequent release of extra F^- ions. This interference can be eliminated by adding a pH buffer to the samples to keep the pH in the range 4 to 8 and hence ensure a low OH^- concentration in the solutions.

c) Impregnated-PVC-Membrane Electrodes e.g. Potassium.

The Potassium electrode was one of the earliest developed and simplest examples of the second type. The membrane is usually in the form of a thin disc of PVC impregnated with the macrocyclic antibiotic valinomycin. This compound has a hexagonal ring structure with an internal cavity which is almost exactly the same size as the diameter of the K^+ ion. Thus it can form complexes with this ion and preferentially conducts it across the membrane. Unfortunately it is not 100% selective and can also conduct small numbers of sodium and ammonium ions. Thus these can cause errors in the potassium determination if they are present in high concentrations. The majority of other ISEs suffer from similar limitations (see later section on 'interference').

Several other complex processes are employed in ion-selective membranes and details of these can be found in specialist electrochemistry textbooks and in catalogues from manufacturers of "ionophores".

d) Care and Maintenance of ISEs.

When handling ISEs, care should be taken to avoid damaging the membrane surface. If the electrodes are in frequent use then they can simply be left hanging in the electrode holder with the membrane surface open to the air but protected by a clean dry beaker. For prolonged storage in a cupboard or drawer, the membrane should be protected by covering with the rubber or plastic cap which is normally provided with the electrode. After extensive use the membranes may become coated with a deposit or scoured with fine scratches which may cause a slow or reduced response (low slope) or unstable readings.

Crystal membranes can be regenerated by washing with alcohol and/or gently polishing with fine emery paper to remove any deposit or discoloration, then thoroughly washing with de-ionised water to remove any debris. After this, they may require soaking in the concentrated standard solution for several hours before a stable reading can be re-established. It must be noted, however, that prolonged immersion of crystal membranes in aqueous solutions will eventually cause a build up of oxidation products on the membrane surface and thus inhibit performance and shorten the active life. Conversely, PVC membranes should not even be touched, let alone polished, and can be often be regenerated by prolonged (several days) soaking in the standard solution, after removing any deposit with a fine jet of water, or rinsing in alcohol.

REFERENCE ELECTRODES

In order to measure the change in potential difference across the ion-selective membrane as the ionic concentration changes, it is necessary to include in the circuit a stable reference voltage which acts as a half-cell from which to measure the relative deviations.

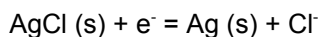
a) The Silver / Silver Chloride Single Junction Reference Electrode.

The most common and simplest reference system is the silver / silver chloride single junction reference electrode. This generally consists of a cylindrical glass tube containing a 4 Molar solution of KCl saturated with AgCl. The lower end is sealed with a porous ceramic frit which allows the slow passage of the internal filling solution and forms the liquid junction with the external test solution. Dipping into the filling solution is a silver wire coated with a layer of silver chloride (it is chloridised) which is joined to a low-noise cable which connects to the measuring system.

In electrochemical terms, the half-cell can be represented by:



and the electrode reaction is:



The electrode potential for this half-cell is + 0.2046 V relative to the Standard Hydrogen Electrode at 25°C

b) Double Junction Reference Electrodes.

One problem with reference electrodes is that, in order to ensure a stable voltage, it is necessary to maintain a steady flow of electrolyte through the porous frit. Thus there is a gradual contamination of the test solution with electrolyte ions. This can cause problems when trying to measure low levels of K, Cl, or Ag, or when using other ISEs with which these elements may cause interference problems. In order to overcome this difficulty the double junction reference electrode was developed. In this case the silver / silver chloride cell described above forms the inner element and this is inserted into an outer tube containing a different electrolyte which is then in contact with the outer test solution through a second porous frit. The outer filling solution is said to form a "salt bridge" between the inner reference system and the test solution and is chosen so that it does not contaminate the test solution with any ions which would effect the analysis.

Commonly used outer filling solutions are:

potassium nitrate - for Br, Cd, Cl, Cu, CN, I, Pb, Hg, Ag, S, SCN.

sodium chloride - for K,

ammonium sulphate - for NO₃,

magnesium sulphate - for NH₄,

Note that double junction reference electrodes are named after their outer filling solutions.

One disadvantage with double junction reference electrodes is that they introduce an extra interface between two electrolytes and thus give the opportunity for an extra liquid junction potential to develop.

c) Liquid Junction Potentials.

It must be noted that the standard voltage given by a reference electrode is only correct if there is no additional voltage supplied by a liquid junction potential formed at the porous plug between the filling solution and the external test solution. Liquid junction potentials can appear whenever two dissimilar electrolytes come into contact. At this junction, a potential difference will develop as a result of the tendency of the smaller and faster ions to move across the boundary more quickly than those of lower mobility. These potentials are difficult to reproduce, tend to be unstable, and are seldom known with any accuracy; so steps must be taken to minimise them. Using 4 Molar KCL as the inner filling solution has the advantage that the K^+ and Cl^- ions have nearly equal mobilities and hence form an equi-transferent solution. Also, in the single junction electrodes, the electrolyte concentration is much higher than that of the sample solution thus ensuring that the major portion of the current is carried by these ions. A third factor in minimising the junction potential is the fact that there is a small but constant flow of electrolyte out from the electrode thus inhibiting any back-diffusion of sample ions - although this is less important with modern gel electrolytes.

As indicated above, all these problems are doubled when double junction reference electrodes are used and an additional problem arises in the case of the last three listed above (Sodium Chloride, Ammonium Sulphate, Magnesium Sulphate) because the filling solutions are not equi-transferent and hence have a stronger tendency to form liquid junction potentials. It must be noted here that Nico2000 Ltd have recently introduced a novel Lithium Acetate reference electrode which overcomes most of these problems and can be used with all but one of the ELIT range of ISEs. This is because it contains ions which are very nearly equi-transferent and which do not interfere with any of the commonly used ISEs - the only known interference being that of acetate on the carbonate electrode.

It must be noted that the E^0 factor in the Nernst equation is the sum of all the liquid junction potentials present in the system and any variation in this during analyses can be a major source of potential drift and error in measurements.

d) Combination Electrodes

The majority of pH electrodes are produced in the form of combination electrodes in which the reference system is housed in the same cylindrical body as the sensor head. This produces a simple, compact unit for immersing in the test solution and has the added advantage that the two cells are in close proximity (with the reference cell normally completely surrounding the sensor element) - thus minimising the effect of any stray electrostatic fields or any inhomogeneity in the test solution. The main disadvantage of this arrangement is the fact that it is the reference element which is the most likely to cause problems or fail, long before the ISE head does, but the whole unit has to be replaced when failure does occur.

In contrast to pH electrodes, some ISEs are produced as mono-electrodes for use with separate reference systems. One reason for this is because ISE membranes have a far lower impedance than pH sensors and are less susceptible to stray electrostatic fields. Thus it is not necessary to screen the sensor head by surrounding it with the reference system. More importantly, the membranes and internal construction of ISEs are generally far more expensive than pH sensors and it is much more cost-effective to have separate units in which the reference system can be replaced independently from the ISE.

e) Multiple Electrode Heads: Separable Combinations.

A new concept for combination electrodes has recently been introduced. Both the ISEs and the reference electrodes are made in the form of 8mm diameter tubes fitted with a gold plated plug-in connector.

These can be inserted separately into special multiple electrode heads which are fitted with the cables and connectors for attaching to the measuring system. The rigid plastic head ensures that the ISE and reference system remain firmly linked together at a regular distance apart during operation, but either one can easily be replaced in the event of failure or need to change the analysis. Moreover, the replacement electrodes are relatively inexpensive compared to conventional electrodes because they do not incorporate the expensive low-noise cables.

The ELIT Electrode Head System

A practical and cost effective way to combine Ion Selective and Reference Electrodes

ELIT Electrode Heads are manufactured from a robust plastic material and fitted with low noise cables and connectors which are compatible with any standard mV/pH/ion meter.

The standard version, for use with an ELIT Ion Analyser / Computer Interface, has a BNC plug, but DIN, US or S7 versions are available if required.

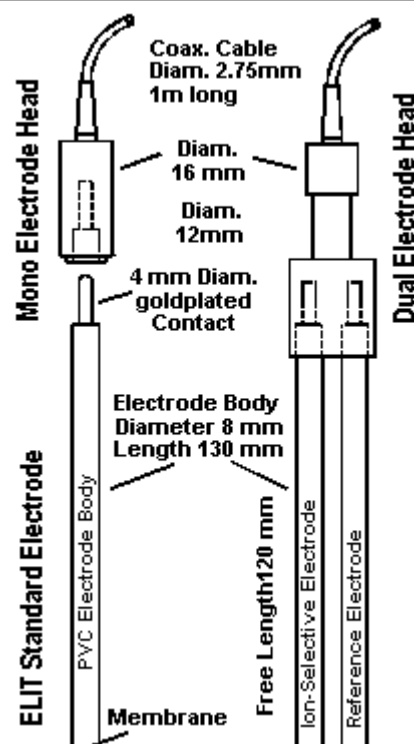
The sockets on the head and the pins on the plug-in electrodes are gold plated to assure good contact.

Advantages of this 'electrode combination' over conventional combination electrodes:

- Use of one reference electrode for several ion-selective electrodes.
- Replacement of a defective reference system without sacrificing the more expensive ISE.
- Expensive low-noise cable and connector are attached to the re-usable head and do not need to be replaced if the ISE becomes defective.
- ISE is less expensive than conventional types with cable & connectors permanently attached.
- ISE can be stored dry and the RE wet.
- Increased distance between the ISE and the reference system reduces electrical interference and increases the precision of measurement.

Five types of Heads are currently available:

- **Mono Head** for inserting one ELIT ISE or Redox electrode, for use with a conventional reference electrode (or a combination pH electrode).
- **Dual Head** for use as an **electrode combination**: one ISE or Redox and one ELIT reference electrode.
- **Triple, Four or Seven-electrode head** for connecting up to six sensors with one reference, for use in simultaneous multi-component analysis using an ELIT four or eight-channel computer interface.



Beginners Guide to ISE Measurement. Chapter 6.

PROBLEMS WITH ISE MEASUREMENTS

The three main problems with Ion Selective Electrode measurements are the effect of **interference** from other ions in solution, the effect of the **ionic strength** of the solution reducing the measured activity relative to the true concentration at high concentrations, and **potential drift** during a sequence of measurements.

a) Ionic Interference and Selectivity Coefficients.

ISEs are not ion-specific. All are sensitive to some other ions to some extent. For many applications these interferences are insignificant (unless there is a high ratio of interfering ion to primary ion) and can often be ignored. In some extreme cases, however, the electrode is far more sensitive to the interfering ion than to the primary ion and can only be used if the interfering ion is only present in trace quantities or even completely absent. In some systems the interfering ion can be removed by chemical means (chiefly precipitation or complexing) and many manufacturers can supply detailed instructions and special reagents to accomplish this, but this can be a laborious and time-consuming process and most analysts prefer to avoid this if possible.

The ability of an ion-selective electrode to distinguish between different ions in the same solution is expressed as the Selectivity Coefficient. If the primary ion for which the electrode is sensitive is A and the interfering ion is B then a selectivity coefficient of 0.1 would mean that the electrode is ten times more sensitive to A than to B. If the coefficient is 1 then the electrode is equally sensitive to both. Unfortunately the selectivity coefficient is not constant and depends on several factors including the concentration of both elements, the total ionic strength of the solution, and the temperature. According to the British Standards Specification for Ion-Selective Electrodes, all manufacturers should provide details of the conditions under which the SC was measured, including concentrations of both ions, for all ISEs which they supply. This should assist potential users in properly evaluating the significance of this limitation for their own particular application - but all this information is not always available. Thus the value quoted in the electrode specifications is necessarily only a general guide and cannot be used to make accurate corrections for the interfering ion in any simple manner.

Nevertheless, if the analyst is unsure if an interfering ion will be a problem, or if he wishes to make a correction for its presence, then it is possible to measure the SC directly in a typical sample and obtain a more accurate assessment of the interference. First measure the concentrations of the primary ion and the interferent in the sample, using the appropriate ISE for each ion. Then add more interferent - sufficient to ensure a significant (say 10%) increase in the signal for the primary ion. The amount to add can be calculated from the initial concentration measurements and the indicative SC quoted in the electrode specifications. Then measure the apparent concentration of the primary ion again and calculate the SC for the interferent from the increase caused by the known amount added. e.g. if the added interferent increased its concentration by 10ppm and this produced a 1 ppm increase in the measured value of the primary ion then the SC would be 0.1. Subsequent sample measurements can then be made by measuring both the primary ion and interferent and using the measured SC to make a more reasonable correction for the interference. These measurements can be made by Direct Potentiometry or Standard Addition, with or without ISAB, depending on what is the chosen method for the samples. However, it must be noted that the accuracy and precision of this correction may be quite variable and will need to be tested for validity and reliability for each particular application before being used on a routine basis.

Possible Alternative to using Selectivity Coefficient: If the interfering ion is fairly constant in the samples and is not too concentrated (ie will not cause too much of an error in the measured ion concentration - say not more than 100%) Then it may help to minimize this error by spiking the standards with the same concentration of interfering ion as in the samples. But this will inevitably lead to a raising of the lower limit of concentration for reasonable routine measurements.

Probably the most common example of interference is that of potassium on ammonium and vice-versa. Potassium is a very common element and is present in most natural substances. The selectivity coefficient for K of the NH₄ electrode is approximately 0.1. This means that if there are equal concentrations of NH₄ and K in a solution, then the K will contribute about 10% to the NH₄ signal. To put it another way, if a sample contains ten times more K than NH₄ then the ISE analysis will give an apparent concentration for NH₄ of approximately twice as much as is actually present. A further complication is that NH₄ also has a slight effect on the K electrode which may become significant at high NH₄ to K ratios. Until recently, these interferences have limited the use of the ammonium ISE to only those applications where a high NH₄ to K ratio can be guaranteed. It must be noted, however, that recent advances in ISE measurement and data processing using computer interfaces

and neural network software have made it possible to make reasonably precise corrections for these interferences and hence permit the measurement of NH_4 in the presence of a larger amount of K (See: A new Approach to Ammonium Analysis Using Ion-Selective Electrodes - available at www.nico2000.net/datasheets/ammopaper.html).

Another typical example of interference is that of the chloride ion on the nitrate electrode. In this case the selectivity coefficient is only about 0.003. This means that an equal concentration of chloride would only add about 0.3 % to the nitrate signal. Nevertheless, in many natural waters the Cl/NO_3 ratio can be as high as 50:1 or even more, thus causing a possible 15 or 20% increase in the apparent NO_3 signal. In this case however, the chloride ion can be removed from solution by precipitating as the sparingly soluble silver chloride. So, by adding measured quantities of the appropriate reagents to samples and standards, the analyst can overcome this problem in the laboratory. Nevertheless, it must be noted that silver salts are relatively expensive and so adopting this procedure can add significantly to the cost of analysis.

b) Ionic Strength and Activity Coefficients: Activity versus Concentration.

Ion selective electrodes measure the concentration of ions in equilibrium at the membrane surface. In dilute solutions this is directly related to the total number of ions in the solution but at higher concentrations, inter-ionic interactions between all ions in the solution (both positive and negative) tend to reduce the mobility and thus there are relatively fewer of the measured ions in the vicinity of the membrane than in the bulk solution. Thus the measured voltage is less than it would be if it reflected the total number in the solution and this causes an erroneously low estimate of the concentration in samples with a high concentration and/or a complex matrix.

Ionic Strength is a measure of the total effect of all the ions in a solution. It is the sum of the molar concentration multiplied by the square of the valency of all the ions. The effective concentration measured at the electrode head is known as the **activity** of the ion. In general chemical terms it is the number of ions taking place in any chemical reaction – measured in concentration units. The **activity coefficient** is the ratio of the activity divided by the concentration. This is a variable factor and depends on the valency and ionic radius of the measured ion and the total ionic strength of the solution.

The activity coefficient is always less than one and becomes smaller as the ionic strength increases; thus the difference between the measured activity and the actual concentration becomes higher at higher concentrations. This effect causes two main problems in ISE measurement. Firstly, when constructing a calibration graph using concentration units, the line is seen to curve away from linearity as the concentration increases (it remains straight, up to the highest concentrations if activity units are used). Thus, if concentration units are used, it is necessary to measure many more calibration points in order to define the curve more precisely and permit accurate interpolation of sample results. Secondly, it is most likely that the sample solutions will contain other ions in addition to the ion being measured and the ionic strength of the samples may be significantly higher than that of the standards. Thus there will be an incompatibility between the calibration line and the measured samples leading to errors in the interpolated results.

It is possible to calculate the activity coefficient for the primary ion in a simple pure solution where the composition and relative concentration of all the ions is known. Thus the measured activity can be converted into concentration results for simple solutions - but in most practical applications this is not possible, or very difficult and time-consuming.

The Ionic Strength (I) can be calculated from $I = 0.5 \times \text{Sum} (c_i \times Z_i^2)$
Where c is the concentration in Moles and Z is the valency.

The Activity Coefficient (f) can then be found from:

$$-\text{Log}(f) = [(0.51 \times Z^2 \times \text{SQR}(I)) / (1 + (3.29 \times d \times \text{SQR}(I)))] - (0.1 \times Z^2 \times I)$$

Where: Z = the ionic charge, I = the ionic strength of the solution, d = the ionic radius in nanometres.

Note that it is generally accepted that this formula is only accurate up to about $I = 0.1$ Molar. At higher ionic strength other factors come into play which make the calculation of activity coefficients virtually impossible and thus most ISE measurements cannot be made reliably above this concentration.

The table below can be used as a guide in deciding whether or not the samples to be measured have sufficiently low Ionic Strength that the activity effect can be ignored.

Activity Coefficients and likely error (i.e. under-estimate) in concentration measurement for different Ionic Strength Solutions.

Ion	Valency (Z)	Ionic Radius(nm)	Ionic Strength (mol/L)	Activity Coefficient	% error in Concentration
NH4, Ag	1	0.25	0.5	0.664	34%
			0.1	0.762	24%
			0.01	0.899	10%
			0.001	0.965	4%
			0.0001	0.988	1%
K, Cl, Br, I, CN, NO2, NO3	1	0.3	0.5	0.688	31%
			0.1	0.771	23%
			0.01	0.901	10%
			0.001	0.965	4%
			0.0001	0.988	1%
F, ClO4, SCN	1	0.35	0.5	0.710	29%
			0.1	0.779	22%
			0.01	0.902	10%
			0.001	0.965	3%
			0.0001	0.988	1%
Na	1	0.45	0.5	0.748	25%
			0.1	0.795	21%
			0.01	0.905	10%
			0.001	0.965	3%
			0.0001	0.989	1%
Pb, CO3	2	0.45	0.5	0.313	69%
			0.1	0.399	60%
			0.01	0.670	33%
			0.001	0.869	13%
			0.0001	0.955	5%
Ba, Cd, Hg, S	2	0.5	0.5	0.341	66%
			0.1	0.413	59%
			0.01	0.674	33%
			0.001	0.869	13%
			0.0001	0.955	5%
Ca, Cu	2	0.6	0.5	0.396	60%
			0.1	0.439	56%
			0.01	0.682	32%
			0.001	0.870	13%
			0.0001	0.955	4%

For samples with high ionic strength, there are five possible methods which can be used to avoid the error introduced by the difference between activity and concentration.

- 1) Bring the ionic strength to the same level in both the calibrating standard solutions and the samples by adding a suitable Ionic Strength Adjustment Buffer (ISAB) to both - see below, section c).
- 2) Dilute the samples to a level where the ionic strength effect is insignificant – but make sure that the detected ion is still within the linear range of the electrode.
- 3) For samples with complex but known matrix, make up the standards in a similar solution which does not contain the detected ion, or any which would interfere with the measurement.
- 4) Use the Activity Coefficient to calculate the concentration from the activity. As noted above, the activity coefficient can be calculated for simple solutions with known concentrations of all the ions, but this is not possible in many practical applications, where the samples may have a complex or unknown matrix.
- 5) Use the Standard Addition (or Sample Addition) Method where the voltage is measured before and after a measured small volume of standard (or sample) is added to a larger measured volume of sample (or standard) and the ionic strength is not altered significantly.
See later, Chapter 10.

c) Ionic Strength Adjustment Buffers.

The most common way of overcoming the effect of the variable ionic strength of the solutions is to attempt to make them all the same. Theoretically, this can be done by adding, equally to all standards and samples, another solution of high ionic strength which does not contain the ion to be measured, or any likely interferent. These solutions are known as Ionic Strength Adjustment Buffers (ISAB). The idea is that they are added in sufficient quantity to completely swamp the ionic effects of the host solutions and hence give a uniform ionic strength in all samples and standards. In this case the straight-line calibration curve can be constructed using concentration units and the unknown concentrations can be read directly from the calibration graph. Note that there is no need to recalculate the standard concentrations after adding ISAB as long as all standards and samples are treated in the same way.

It must be noted, however, that most recipes for the addition of ISAB only produce an increase in ionic strength of 0.1M and thus will only be effective if the IS of the original sample is much lower than 0.1M. Furthermore, the difference between activity and concentration is relatively small at low ionic strengths and can often be ignored in many practical applications – see table above.

Most ISE suppliers also supply ISABs. These vary in composition depending on the detected ion and occasionally contain other components which actively suppress interfering ions and/or control the pH value. In many cases the composition of these solutions are carefully guarded 'trade secrets' and the reagents are simply labelled as e.g. "ISAB for nitrate electrode".

d) Potential Drift.

The effect of potential drift can easily be seen if a series of standard solutions are repeatedly measured over a period of time. The results show that the difference between the voltages measured in the different solutions (i.e. the electrode slope) remains essentially the same but the actual value generally drifts in the same direction by several millivolts (ie, not random variation or instability). This is somewhat surprising in view of the fact that many ISE specifications quote a potential drift of less than 1 mV per day. However, it must be noted that this figure is an attempt to define the drift which is attributable to the ISE alone - but this is impossible to measure directly due to variations in other potential differences in other parts of the measuring system. The most significant of these is the liquid junction potential of the reference electrode.

Although the LJP does not drift significantly once stabilised in a solution at constant temperature, it can change by several millivolts every time a reference electrode is immersed in a new solution, or even re-immersed in the same one. Thus the quoted ISE drift factor only applies when the ISE and reference are constantly immersed in a 1000 ppm solution at constant temperature. Furthermore, constantly removing and replacing an ISE in different solutions will produce hysteresis (or memory) effects, the extent of which depends on the relative concentrations of the new and old solutions. Thus if the same solution is re-measured after measuring a different one it cannot be expected to give exactly the same millivolt reading the second time.

In view of these various sources of potential drift, some manufacturers include a more realistic figure of 3 mV per 8 hour working day in the electrode specifications.

For most ISE applications these effects are insignificant when compared to the overall reproducibility and accuracy requirements, but, for the most precise work, steps must be taken to try to minimise these effects - see Chapter 8.

CALIBRATION THEORY

Calibration is carried out by immersing the electrodes in a series of solutions of known concentration and plotting a graph of the mV reading versus the log of the activity (or the actual activity on a logarithmic X-axis). This should give a straight line over the whole linear concentration range. However, as noted above, activity is difficult to determine in complex solutions and it is generally more useful to plot concentration units. In this case the effect of variable activity coefficients in solutions with high ionic strength can be minimized by adding Ionic Strength Adjustment Buffer to all standards and samples - but note the limitations to this detailed in the previous chapter. Nevertheless, it must be noted that if the samples to be measured are likely to have a total ionic strength of less than about 0.01M for monovalent ions (0.001M for divalent ions) then the activity effect should be insignificant and it may not be necessary to add ISAB. However, it must be noted that ISAB may be useful when using a double junction reference electrode with a non-equi-transferent outer filling solution, in order to compensate for drift in the liquid junction potential, and in general, most ISE systems give stable readings more quickly in high ionic strength solutions.

The slope of the calibration graph is the mV response per decade of concentration change. This is typically around 54 mV/decade for monovalent ions and 27 for divalent ions and will have a negative value for negative ions - i.e. a higher concentration means more negative ions in solution and therefore a lower voltage.

a) Linear Range.

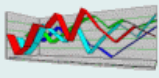
The linear range of the electrode is defined as that part of the calibration curve through which a linear regression would demonstrate that the data points do not deviate from linearity by more than 2 mV. For many electrodes this range can extend from about 0.1 Molar down to 10^{-6} or even 10^{-7} Molar.

b) Total Measuring Range.

The total measuring range includes the linear part of the graph as shown below together with a lower curved portion where the response to varying concentration becomes progressively less as the concentration reduces. Samples can be measured in this lower range but it must be noted that more closely spaced calibration points are required in order to define the curve accurately and the percentage error per mV on the calculated concentration will be progressively higher as the slope reduces.

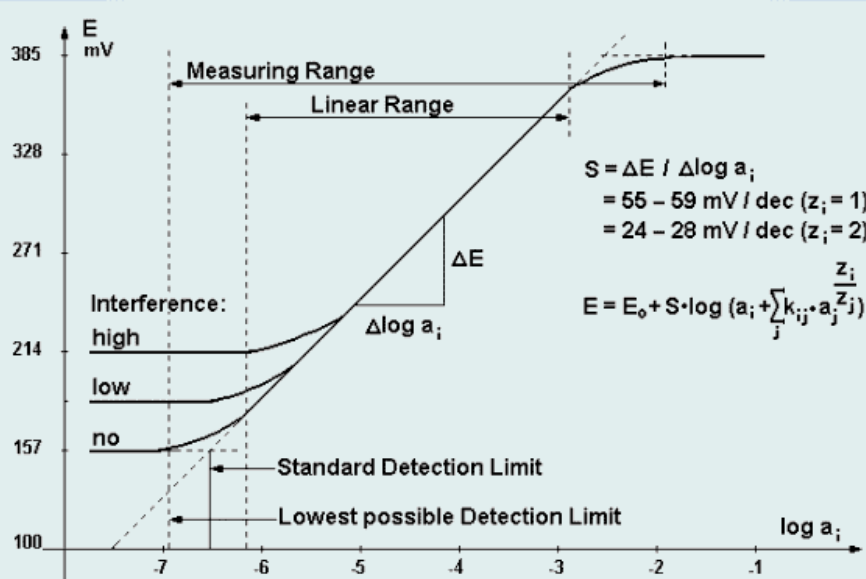
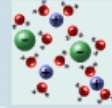
c) Limit of Detection.

For monovalent ions, the IUPAC definition is: that concentration at which the measured potential differs from that predicted by the linear regression by more than 18 mV. The practical limit of detection can be calculated by plotting a calibration graph using several standards at the lower end of the concentration range, and below it. Say 100, 10, 1, 0.1, 0.05, 0.01 ppm - i.e. at least two to define the linear slope and two to show the position of the horizontal section below the limit of detection, where the electrode is unresponsive to concentration change. The limit of detection is then defined by the crossing point of the two straight lines drawn through these points.



Typical ISE Calibration Graph

NB: X-axis units are the logarithm of the Molar Activity of the Ion



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CALIBRATION PRACTICE

a) Standard Solutions.

A single standard solution is usually diluted sequentially to produce concentrations of 1000 ppm, 100 ppm, 10 ppm, 1 ppm and even 0.1 ppm for a complete calibration (or this can be done using decades of Molarity units). However, if the approximate concentration range of the samples is known then the calibration should be made using standards which closely bracket this range. Large errors may occur if samples are measured by extrapolation beyond the range of the calibration. If you are confident that you are working in the linear range of the electrode then only a two point calibration is necessary. But three or more are recommended in order to confirm the linearity and to detect any errors in diluting the standards, or to define the curve in the non-linear range. Since the slope of the calibration line is temperature dependent, the temperature of the calibrating solutions and the samples should be the same within a tolerance of $\pm 2^{\circ}\text{C}$.

b) Minimising Drift Effects During Calibration

If more than three standards are being measured, it may help to minimise potential drift and hysteresis during measurement, if the solutions are measured twice, the second time in the reverse order (i.e. 1, 2, 3, 4, ..., etc. then ..., 4, 3, 2, 1 - all at regularly spaced intervals) and the average mV value taken to construct the calibration graph. In this case, having defined the calibration slope accurately, it may only be necessary to recalibrate using only one representative standard, nearest to the range of the sample concentrations, and simply normalise the rest of the points to this new value. For example, if a subsequent reading for the recalibration standard gives a millivolt reading of 2 mV below the initial (average) value, then you can either subtract 2 mV from all the other initial calibration data and re-plot the graph or, probably more easily, add 2 mV to any sample readings taken immediately after the recalibration and then read the concentrations directly from the original graph.

Alternatively (or possibly additionally) it may help (particularly for the lowest concentration standard and during sample measurement) to always immerse the electrodes in pure water for a short time, then drying, before immersing in the next solution. However, it must be noted that prolonged immersion in pure water may damage the electrodes and they should only be immersed for as long as it takes for the voltage to fall below that of the lowest standard (or rise above for negative ions).

Despite these possible improvements to the conventional calibration method, the most effective way of reducing potential drift is to use the Standard Addition method to measure two standards (which bracket the known range of the samples) to find the average slope and then measure the samples by Standard or Sample Addition methods - see Chapter 10.

c) Frequency of Calibration.

For the most precise results it is best to measure samples soon after calibration. Ideally each sample measurement should be immediately preceded by a calibration (see Chapter 11 for more details of how to achieve the most precise results). This is relatively quick and easy if only a one-point recalibration is employed as described above. Ultimately the operator must decide what is the best compromise between the time taken to make frequent calibrations and the precision requirements, but for many applications it will be sufficient to make just one calibration graph before taking a series of sample measurements over several hours.

MEASURING PROCEDURES

a) Adding ISAB

As noted above (Chap. 6) ISAB (Ionic Strength Adjustment Buffer) is normally added to samples and standards in order to ensure that all measured solutions have the same Ionic Strength and avoid errors due to differences between the measured activity and the actual concentration. Indeed, many ISE manufacturers advocate always adding ISAB to samples and standards, irrespective of whether the samples have high ionic strength or not, because this can help to stabilise the liquid junction potential of the reference electrode and hence reduce errors in measurement, and reduce the time taken to reach a stable reading - but this may not be necessary if the reference electrode has an "equi-transferring" filling solution (i.e. both ions have the same, or nearly the same, mobility - e.g. Lithium Acetate, or Potassium Nitrate).

Nevertheless, it must be noted that most electrode systems will give faster stabilisation with ISAB when measuring low concentration samples in the non-linear range.

For many applications, however, it may be unnecessary (for samples with IS below 0.01M for monovalent ions and 0.001M for divalent ions), or ineffective (for samples with IS greater than about 0.1M), or inconvenient, to add ISAB to all the samples and standards.

One simple way to avoid adding ISAB is to dilute the samples to a level where the activity effect is insignificant. But this requires a knowledge of the Ionic Strength of the samples, and care must be taken to avoid diluting so much that the measurements would fall within the non-linear range of the electrode. In some applications, where only the approximate concentration of the samples are required, or the differences between samples are more important than the actual concentrations, the effect of the ionic strength can often be ignored. Alternatively, if the highest possible precision and accuracy is required then using the Sample Addition or Standard Addition methods may be a better solution than adding ISAB.

If it is decided that ISAB should be added then the most important factor is that it should be added equally to standards and samples. Thus if the ISE instructions say, for example, that ISAB should be added "2%v/v" it must be recognised that this is only an approximate recommendation, and it will be more convenient to add 2ml of ISAB to 100ml of sample and standard (or 1ml to 50ml) rather than adding 2ml to 98ml.

b) Taking Readings and Minimising Drift Effects.

There are several schools of thought as to the best way to take measurements. Some authorities suggest that the solutions should be stirred slowly with a magnetic stirrer at 50 - 100 rpm during immersion of the electrodes - but care must be taken to ensure that there is no heat exchange between the stirrer and the solution and that the stirrer is always at the same speed. Big differences in mV readings can occur if the speed is varied. Moreover, the magnitude of this effect is related to concentration (most variation in dilute solutions) and hence will affect the slope of the calibration graph. Some prefer to take a reading whilst stirring, others suggest that it is better to switch off the stirrer and take a reading in a still solution - but this can greatly increase the time for the measurement because it may take several minutes for the mV reading to stabilise whilst stirring, and several more to stabilise after the stirrer is switched off. Alternatively, and more easily, the solution can simply be swirled manually after immersion of the electrodes (to ensure good, homogeneous contact between solution and membrane- i.e. no air bubbles) and then left to stand. This avoids the problems of heat transfer and the inconvenience of adding and removing the magnetic stirrer every time. It must be noted however that some electrode systems stabilise more quickly and give more reproducible measurements when stirred whilst others give better results in still solutions - this is sometimes mentioned in the electrode operating instructions.

The time at which the measurements are taken can also vary depending on the characteristics of the particular type of electrode system being used and the balance between time constraints and precision requirements. In some cases it is best to wait for a stable mV reading (this can take several minutes). In others it is better to take all readings after a pre-specified time after immersion. Generally, the mV reading changes rapidly in the first 10 or 20 seconds as the ISE membrane equilibrates with the solution, then more slowly and exponentially as the reference electrode liquid junction potential stabilises. Always taking a reading after say 1 or 2 minutes (depending on which electrode system is being used) should ensure that all are taken in the shallow part of the stabilisation curve where only small and insignificant changes are occurring. A third alternative is to observe the drift in reading as the electrodes equilibrate after immersion and then take a reading at the point where the direction of drift is definitely reversed - i.e. a different electrochemical process begins to dominate - but this last effect is not common.

If the highest possible precision is required then it is suggested that each operator should make his own simple experiments by comparing the reproducibility of repeated measurements on the same sample using each method discussed above, in order to determine which is most suitable for his particular application. But note that whichever method is preferred, the same procedure must be used for all standards and samples in order to ensure that the electrode response will be as uniform as possible.

c) Cleaning Electrodes and Minimising Hysteresis Between Samples.

The electrode tips must be rinsed by spraying with a jet of deionised water and gently dabbed dry with a low-lint laboratory tissue between measurements. For the most precise results, it may help to minimise hysteresis effects if the electrodes are soaked in deionised water for 20 or 30 seconds after rinsing, before every measurement, so that each new reading is approached from the same direction, (i.e. always from low concentration to high - as recommended for calibration measurements, to also minimise cross contamination) rather than just being dependent on the last sample measured.

METHODS OF ANALYSIS

a) Direct Potentiometry

Direct potentiometry is the simplest and most widely used method of using ISEs as described above in the Basic Theory and Calibration sections of this work. Simply measure the electrode response in an unknown solution and read the concentration directly from the calibration graph (either manually or using special computer graphics and calculations - see later) or from the meter display on a self-calibrating ion meter. A big advantage of this method is that it can be used to measure large batches of samples covering a wide range of concentrations very rapidly without having to change range, recalibrate or make any complicated calculations. Moreover, if ISAB is not being used, it is not necessary to measure the volume of the samples or standards. Quite acceptable results can be obtained for some elements by simply dangling the electrodes in a river or pond or effluent outflow without the need to take samples in small beakers.

b) Incremental Methods

There are three main types of incremental methods in general use:

Standard (or Known) Addition,
Sample Addition,
Sample Subtraction.

Standard Addition and Sample Addition Methods.

These methods involve measuring the voltage in a relatively large, accurately measured, volume of sample (for standard addition) or standard (for sample addition) then adding a much smaller volume of standard (or sample) and taking a second reading after the voltage has stabilised in the mixture. For full details see: www.nico2000.net/datasheets/staddl.html

Summary of Advantages over Direct Potentiometry:

- The electrodes remain immersed throughout the process so that there is little change in the liquid junction potential of the reference electrode (which can often be changed by several millivolts when the electrodes are removed from one solution and placed in another) between calibration and sample measurement - and therefore this source of measurement error is virtually eliminated.
- Calibration and sample measurement are both made essentially at the same time and in the same solution so that ionic strength and temperature differences between standard and sample are not significant and ISAB is not normally required.
- Once the approximate concentration for the samples is known, the calibration (slope) can be "fine tuned" by analysing a standard with a concentration that lies within the range of the samples (and is at the same temperature) and then adjusting the slope and re-calculating the results until the standard gives the correct answer. This "fine tune" procedure is very quick and easy using the ELIT ISE/pH Ion Analyser Software.
- Measuring the slope at or very near to the sample concentration means that these methods can be used with old or worn electrodes which may not be completely linear over their whole range, as long as the slope is stable and reproducible over the limited range of the samples.

Sample Subtraction method.

This involves adding a small amount of sample solution to a standard solution of an ion with which it will react stoichiometrically to form a complex or precipitate, thus reducing the concentration of both ions. The ISE used will be sensitive to the reactive ion in the standard, not the sample. The big advantage of this method is that it can extend the range of ions measurable by ISEs to others for which no ion-sensitive membranes are available. For example, there is currently no ISE capable of detecting the sulphate ion. However, sulphate can be removed from solution by precipitating as barium sulphate, and there is an ISE which is sensitive to barium. Therefore, sulphate can be measured by first measuring the voltage in a pure barium chloride standard. Then adding a known volume of a sample containing sulphate, wait for precipitation to be completed, and measure

the voltage on the barium electrode again. The amount of barium used can then be calculated using a similar equation to that used for Sample Addition and the sulphate content in the sample will be the same as this - since each sulphate ion will combine with one barium ion.

c) Potentiometric Titrations

Potentiometry is generally valuable as a technique for detecting the end-point of titrations where there is often a drastic change in the concentrations of the reactants and thus a big shift in the electrode potential. These end point determinations can often be made more precisely than other ISE methods because they depend on the accuracy of the volumetric measurements rather than the measurement of the electrode potential. For example, when a calcium solution is titrated against the complexing reagent EDTA there is a gradual decrease in the Ca concentration as more EDTA is added until the end point when all the Ca disappears from solution. The progress of this titration can be monitored using a calcium electrode.

This method can also be used to extend the range of ions measurable by ISEs. For example aluminium cannot be measured by direct potentiometry but it can be titrated by reacting with sodium fluoride and monitoring the reaction using a fluoride electrode. It can also be used for elements for which it is difficult to maintain stable standard solutions or which are toxic and it is undesirable to handle concentrated standard solutions. For example, cyanide solutions can be titrated against a hypochlorite solution which forms a complex with the cyanide ions and effectively removes them from solution. The amount of cyanide in the original solution is proportional to the amount of hypochlorite used from the start of the titration until the end-point when there is no further change in the cyanide electrode potential.

ACCURACY AND PRECISION OF SAMPLE MEASUREMENTS

a) General Discussion

The accuracy (how close the result is to the true value) and precision (= reproducibility; i.e. how close are a series of measurements on the same sample to each other) of ISE measurements can be highly variable and are dependent on several factors. The concentration is proportional to the measured voltage and so any error in measurement will cause an error in the concentration, but this is not directly proportional. It depends on the slope of the calibration line. For mono-valent ions with a slope of around 55 millivolts per decade of concentration, an error of 1 mV in measuring the electrode potential will cause a 4% error in the concentration, whereas for di-valent ions, with a slope of around 26, the error will be more like 8% per mV. It must also be noted that the slope becomes less at the lower end of the concentration range, in the non-linear area, and hence the error per mV can be even greater at low concentrations. Thus it is important to use a meter which is capable of measuring the millivolts accurately and precisely. With modern meter technology this is not normally the limiting factor, although for the most precise work it can be beneficial to adopt multiple-sampling techniques (i.e. by using an integrating voltmeter or computer interface) in order to ensure the most reliable voltage measurements.

Apart from the accuracy and precision of the measuring device (meter or computer interface), the most important factors in achieving the most **precise** results is controlling the electrode drift and hysteresis (or memory), and limiting the variability in the Liquid Junction Potential of the reference electrode, so that the measured voltage is reproducible. The amount of the drift and hysteresis effects can vary significantly between different ions and different electrode types, with crystal membranes being generally more stable than PVC - techniques for controlling or minimising drift and hysteresis are described elsewhere in this work (Chapter 9).

The most effective way of minimising the variation in LJP is by using Standard Addition or Sample Addition Techniques (see later - section d). Alternatively, but less effectively, by using reference electrodes with nearly equi-transferring filling solutions (in which both ions have the same mobility when diffusing through the ceramic tip) such as KNO₃ or Li Acetate - but this is not always possible (depending on likely interference effects).

The **accuracy** of the results is affected by several other factors:

- 1) The presence of interfering ions.
- 2) Any difference in ionic strength between the sample and standard solutions.
- 3) Any difference in temperature between sample and standards - A re-calibration should be made if the sample temperature changes by more than 1 degree C from the calibration temperature.
- 4) Any variation in the electrode slope in different parts of the curve. Although the calibration graph may show a straight line over several decades of concentration with an average slope of say 54.5 ± 2 mV/dec. it is highly unlikely that this will be exactly the same across the whole of this range. If separate two-point calibrations are made between two more closely spaced points at different concentration ranges then there may be a variation of several millivolts between the individual slopes. Thus, if samples are calculated using the overall slope then they will give results which will differ in concentration from those calculated using the appropriate individual slope by 4% times the difference in mV between the two slopes.

Therefore, for the most accurate results, it is recommended that the electrode slope is determined using two standards which closely span the expected range of the samples. It must be noted, however, that it is not beneficial to have standards too close together because the measured slope is dependent on the difference in voltages. So, for example, if the difference in mV is 50 then a 1 mV error in measurement will only cause a 2% error in the slope but if the difference is only 10 mV then the same measurement error will result in a 10% error in the slope. Thus it is normally recommended that calibration standards are about an order of magnitude different in concentration and should not be less than 20 mV difference in reading.

Nevertheless, whichever slope is used, the reproducibility of replicate measurements of the same sample should be the same.

By taking special precautions to overcome drift problems (such as frequent recalibration and ensuring that you wait for stable readings, or read after a regular time interval), and by adding special ISABs to equalise activity effects and remove interfering ions, direct potentiometry can give very reasonable results (reproducibility of ± 2 or 3%, one standard deviation, and accurate within these precision limits). Even without taking these precautions, it is possible to achieve satisfactory reproducibility and accuracy (± 10 to 15%) for many

applications where the highest accuracy is not necessary and ionic strength and interfering ions are not a problem.

b) Reproducibility Experiments using an Ammonium Electrode.

Some of the suggestions in the foregoing discussion, and the levels of accuracy and precision achievable with careful work, can be illustrated with the results of some experiments conducted by the author. Reproducibility tests were carried out using an 'ELIT' 8 mm diameter, solid-state ammonium electrode (PVC membrane) with a lithium acetate double junction reference electrode and pure ammonium solutions (no ISAB). Standard solutions containing 1 ppm and 10 ppm NH_4^+ were used for calibration and a 5 ppm solution was used as the test sample. Measurements were made after immersing the electrodes in approximately 50 mls of solution in a 100 ml beaker, swirling the solution for 5 secs. then leaving to stand for 20 secs. Each millivolt measurement was the average of ten readings taken at one second intervals. The electrodes were rinsed with a jet of de-ionised water, then soaked in a beaker of water for twenty seconds, then dabbed dry with a low-lint tissue between each measurement. The solutions were measured in the sequence 1 ppm, 5 ppm, 10 ppm, and this pattern was repeated six times. The data were obtained using a meterless PC interface and specially written software.

For this experiment, the concentration results were calculated with an EXCEL spreadsheet using the Nernst equation in the standard form for a straight line: $y = mx + c$.

Where: y is the measured voltage,

m is the electrode slope
(calculated from the two-point calibration data: $(V_1 - V_2) / ((\text{Log ppm}_1) - (\text{Log ppm}_2))$),

x is the logarithm of the concentration in the sample,

c , the intercept on the y axis, is E° .

The experimental data were processed in several different ways:

1) Using only the first measurement of the two standards to define the slope and intercept, six measurements of the 5 ppm sample, taken over approximately half an hour, gave an average of 4.71 ± 0.14 ppm ($\pm 2.96\%$ one standard deviation). However it was noticeable that successive measurements gave progressively lower values due to electrode drift after calibration (causing a difference of nearly 8% between the highest and lowest results).

2) The drift effect was compensated for by recalculating each result using different values for the slope and intercept as defined by the standards measured immediately adjacent to each sample measurement. This produced a significant improvement in the reproducibility and only a random variation in the results rather than a progressive drift downwards. This clearly demonstrates the importance of measuring samples soon after calibration. The average concentration this time was 4.90 ± 0.06 ppm ($\pm 1.20\%$, 1 S.D.) Although remarkably precise and very close to the true value, the accuracy of this average is not quite within the precision limits. As noted above, this can probably be explained by variation in the electrode slope and this suggestion is supported by examining the individual slope values which can be calculated from the various measurements. The average value for six determinations of the slope between 1 and 5 ppm was 55.92 ± 0.92 whereas that between 5 and 10 ppm was 58.21 ± 0.78 ; i.e. there is a significant difference in slope between the two adjacent ranges.

3) A third method of calculating these results, using the slope defined by the first calibration for all samples but a different intercept value as given by each successive two-point calibration, was less satisfactory and gave 4.87 ± 0.12 ppm ($\pm 2.35\%$) which is only slightly better than the results using only a single calibration at the beginning. Thus these data would appear to suggest that the effect of electrode drift is more significant in producing changes in the measured slope between different sample measurements rather than producing a change in the calculated value for the intercept. This conclusion is also borne out by examining the individual calibration data. Whereas the average slope between 1 and 10 ppm was 56.74 ± 0.51 ($\pm 0.90\%$) for six successive measurements and these showed a gradual drift downwards (57.49, 57.04, 56.84, 56.64, 56.49, 55.98) the associated intercept calculations showed a more random distribution and gave a much more precise average value of 346.18 ± 0.26 mV ($\pm 0.07\%$).

c) Reproducibility of Chloride Measurements.

A second experiment using the same techniques as above, but with a chloride (crystal membrane) electrode and calibration standards of 25 and 250 ppm also yielded very impressive results. Eight measurements of a 100 ppm test solution gave an average of 95.4 ± 0.6 ppm ($\pm 0.63\%$) when two-point calibrations were made immediately prior to each sample measurement. Again the relatively poor accuracy is probably due to the calibration standards being relatively far from the measured sample and thus the calculated slope was probably not exactly correct for the 100 ppm range.

d) Standard Addition and Sample Addition Methods

These methods can potentially yield even more accurate and precise results than direct potentiometry because the calibration and sample measurement stages are made essentially at the same time and in the same solution (so that Ionic Strength and temperature differences are not significant) - and the electrodes remain immersed throughout the measurements so that hysteresis, memory, and variations in the reference electrode liquid junction potential are eliminated. They are particularly useful for samples with high ionic strength or a complex matrix.

e) Conclusions from the Experimental Data.

These experimental results demonstrate that in order to obtain the best possible accuracy and precision, it is important to measure samples soon after calibration and to use standard solutions that closely bracket the expected range of sample concentrations. Furthermore, for direct potentiometry measurements, it is best to make a full two-point recalibration every time, in order to obtain the most precise value for the slope, rather than just making a single point recalibration and assuming that the slope is constant. This is not necessary for Standard and Sample Addition techniques because of the possibility of recalculating the results for a known standard to "fine tune" the slope measurement in the middle of the concentration range expected for the samples.

These results show that it is possible to obtain accuracy and precision levels of better than $\pm 3\%$ fairly easily, and better than $\pm 2\%$ by making more frequent calibrations or by using Standard or Sample Addition techniques (better than $\pm 1\%$ for some crystal membrane electrodes). Thus it has been shown that, with careful use and a full consideration of all the limiting factors, ISE technology can be compared favorably with other analytical techniques which require far more sophisticated and costly equipment.

Nevertheless, it must be stressed that these special considerations are only necessary to achieve the highest possible precision and accuracy. For many applications, a simple two-point calibration followed by one direct potentiometry measurement will probably be quite sufficient.

TYPES OF MEASURING DEVICES AND DATA PROCESSING

a) Analogue Meters

The earliest type of pH meters were simple analogue devices with a resolution of only one or two millivolts. The original meters were calibrated in millivolts and the corresponding pH value was read from a calibration graph as described earlier. However it was soon realised that pH electrodes are reasonably uniform and reproducible instruments with very similar slopes so that it is not necessary to have a unique calibration graph for each electrode. In this case the meters can be calibrated directly in pH units by the manufacturer and can simply be recalibrated each time they are used (to compensate for temperature changes or slight differences in electrode response) by immersing the electrode in just one pH buffer solution and adjusting the meter output to give the correct reading. This type of meter is very simple and quick to use and is perfectly adequate for many pH measurements because it requires a change of more than 5 mV in order to change the pH value by more than 0.1 pH units.

Nevertheless, as noted earlier, in the direct measurement of ionic concentration, a change of only 1 mV will represent a change of 4% in the concentration of mono-valent ions and 8% for di-valent ions. Therefore it is necessary to have a more precise measuring system in order to determine ionic concentrations and for the most precise pH measurements. Furthermore, Ion Selective electrodes are more variable in their response and do not have such uniform slopes so it is more important to make a complete multi-point calibration in order to determine the slope for each electrode, each time it is used. Thus simple pre-calibrated analogue meters are not appropriate for ISE measurements and in this case it was always necessary for the analyst to keep a record of the millivolt readings obtained in the standard and sample solutions. Then a calibration graph was plotted on semi-log paper, using concentration units on the logarithmic axis, and the sample results were read directly from this graph, with varying degrees of accuracy depending on the range of concentrations plotted and the skill of the operator.

b) Digital Meters

A major advance was made when digital meters were introduced with a resolution of 0.1 or even 0.01 mV. This enabled the analyst to measure and read the voltage with much greater accuracy and meant that the stability and reproducibility of the electrode response became the main limiting factor in determining the accuracy and precision. Nevertheless, although these meters were also capable of being calibrated in pH units, it was still necessary for the analyst to keep a log of the millivolt readings for ISE measurements and then plot the calibration on graph paper or using computer graphics. Sample results were then read from this graph, or calculated manually or by using computer spreadsheets, as with analogue meters.

c) Self-Calibrating, Direct-Reading Ion Meters.

The next major advance was when micro-processors were introduced which contained simple programs to calculate the slope and intercept from the calibration data and then use these to calculate the sample concentration from the millivolt reading in the sample. Thus the analyst can simply enter the concentrations of the standards and measure the millivolts, then immerse the electrodes in the sample and read the sample concentration directly from the meter. Nevertheless, these meters are often quite confusing to operate, with small keypads and multi-function switches, and they are not suitable for working in the non-linear range of the electrodes, or using different slopes for different parts of the calibration range, or for measuring more than one ion at a time. Furthermore, it is often difficult for the analyst to assess the quality of the calibration or detect errors in data entry and it is still necessary for the results to be transferred manually to a permanent record.

Most of these problems of data acquisition, transfer, processing, and storage have now been overcome with the introduction of meterless computer interfaces and sophisticated software packages which are the subject of the next section of this guide.

RECENT DEVELOPMENTS

a) Meterless Electrode-Computer Interfaces

The recent development of computer interfaces for connecting the sensor electrodes directly to a personal computer, without the need for a meter to measure the voltage, has revolutionised ISE data acquisition and processing. The earliest versions of this type of measuring system were designed in the form of a flimsy PCMCIA card which were specifically for use only with a lap-top or palm-top computer and with only one particular style of electrode with special connecting cables.

Later models are far more versatile and built in the form of a rugged electronic box connected to the computer and to the electrodes by standard cables and connectors. They can be used with any type of electrode plugged into the interface in the same way as for any conventional ion/pH meter. The electrode signals are processed by a low-noise amplifier and analogue-to-digital converter for direct transfer into any desk-top or lap-top computer. The user-friendly software will run on any computer using Windows operating system and is designed for maximum efficiency and versatility. Apart from the ease and speed of operation, the great advantage of this type of measuring system is that it virtually eliminates any possibility of operator error in recording and transferring data. It also facilitates far more sophisticated data processing, and display and archiving of results, once the raw data are securely recorded in the computer.

b) Data Processing Software

Data processing software is now available to carry out most of the functions previously done by the operator, and much more. The software basically carries out six main functions:

- 1) Hardware Set-up:** to configure the system for whichever sensors and reference electrodes are being used (e.g. temperature, pH, Redox, or any ISE) and give a full documentation of electrode types, serial numbers, operator details, date and time etc.
- 2) Signal measurement:** The software interprets the signal from the interface and uses a calibrating factor to produce an accurate display of the millivolts. The operator can select to take single readings, taking about one second each, or the average of multiple readings to "smooth" the data and give a more accurate reading.
- 3) Calibration:** the only operator entry required is of the concentration (or pH) of the calibration standards. For ISE measurements, calibration graphs are plotted automatically and instantaneously and can be assessed with various line-fitting techniques.
- 4) Sample calculation:** the sample results are calculated instantaneously with no possibility of operator error. All results are saved and displayed in data tables where sample numbers and comments can be added. Sample results can be calculated using partial slopes if the calibration in the range required is not completely linear. Concentration results can be reported as ppm or moles/l. Samples can be measured using direct potentiometry or by Sample Addition and Standard Addition methods.
- 5) Display, reporting and archiving of results:** all data can be stored, printed or imported to other software packages. Continuous recording of pH measurements can be displayed graphically, in real-time, to facilitate such activities as pH titrations or process monitoring.
- 6) Help and Advice for the Operator:** the software contains several help menus and drop-down hints and warnings which guide the operator reliably through the analysis. It also includes an off-line 'Chemtools' package which permits the simple calculation of various electrochemical parameters and provides information on interference factors and activity coefficients. Since the computer interfaces and software were designed to improve on existing ion meters, the initial concept was based on the most up-to-date ion meters available. These generally have two inputs, one for pH and one for ISE measurements. They contain microprocessors for making pH and ISE calibrations and reporting the results as millivolts, pH, or concentration. Some of these meters also include a temperature sensor. Thus the initial design for the interface was with two channels which could perform all of these functions, but better.

c) Multi-Component Analysis

The development of the two-channel interface to permit simultaneous measurement of pH and ionic concentration, naturally led to the possibility of adding extra channels to measure several other sensors at the same time. At the time of writing, four and eight channel versions are available. The main advantage of these multi-component systems is that they are ideal for monitoring changes in batch processes where several reaction vessels need to be monitored at the same time; without the interface each vessel would require a separate meter. They are also essential for the rapid determination of several components simultaneously in the same solution. However, they are not expected to give the highest possible precision. As discussed previously, because of the complexity and variation in ISE responses, this requires very careful and detailed work which is not appropriate for multi-component systems.

The multi-component software has been designed to exploit the simple and rapid aspects of ISE measurement and thus does not include such features as individual plotting and assessment of calibration graphs or incremental methods of analysis. Nevertheless, all channels can be calibrated with up to six calibrating solutions, depending on which sensor is selected, and the slope between each point is displayed so that the operator can detect any errors in calibration. To save time and effort, simultaneous calibration of several channels is possible, if several similar sensors are being used together or if mixed standard solutions are used.

Any sensor can be allocated to any channel and each can have its own reference system (for monitoring in different vessels) or all can be used with a single reference electrode (for simultaneous measuring in one solution). The sample measurement is based on direct potentiometry and it is not expected that calibrations will be made very frequently. Sample measurements and results are displayed in tabular form simultaneously for all channels. There are options to display the results in graphical form, in real-time, either as mV, pH, ppm, or moles/l for all channels together, or for one or more selected channels.

Biography for Dr Chris C Rundle, Nico2000 Ltd, London, UK



Chris Rundle worked for more than 25 years for the Natural Environment Research Council as a Geochronologist / Isotope Geochemist / Mass Spectrometrist, where a significant part of his work was the development of software for the automatic control of analysis, data acquisition and processing. His first degree in Chemistry and Geology was at the University of London (External joint honours BSc, 1968) and his PhD thesis was "The Chronology of Igneous Intrusion in the English Lake District", awarded by Birkbeck College, London, 1982.

After taking early retirement from NERC in 1994, Dr Rundle joined Nico2000 Ltd. in 1997 and started to work with Ion-Selective Electrodes. Since then he has helped develop measuring techniques and software for a unique range of electrode-computer interfaces (as an alternative to conventional pH/Ion meters) and written software manuals, analytical procedures and electrode operating instructions for ISE measurements. He also developed and maintains the company website at www.nico2000.net