Operating Instructions and Notes on Measuring Procedures
for all ELIT Ion-Selective Electrodes

(Last updated 11 May 2015 -- Chris C Rundle, BSc, PhD -- Nico2000 Ltd.)

For more information, visit: **www.nico2000.net - Technical Information** page**.**

CONTENTS

INTRODUCTION

ELIT solid state ion selective electrodes are fitted with either impregnated PVC or crystalline membranes, depending on which ion is to be detected. They are all mono electrodes which must be used with an appropriate separate reference electrode and must be inserted into an appropriate ELIT electrode head for connection to the measuring system.

A) QUICK GUIDE TO BASIC OPERATION

Note that these instructions are for the most common method of analysis, known as **Direct Potentiometry**. Details of the **Standard (known) Addition** and **Sample Addition** methods are given later.

1) Remove the black protective caps from the ISE and the reference electrode (note that the reference electrode cap contains liquid and must be kept upright) and insert the electrodes into the labelled sockets of the ELIT dual electrode head.

2) Install the electrode head in any standard electrode holder with an articulated arm, and connect the cable to the BNC socket of the ELIT Ion Analyser, or to a pH/mV/Ion meter.

3) Immerse the electrodes in the Preconditioning Solution (normally the 1000 ppm standard, but this is not critical. If you are working in moles then use a convenient dilution of your bulk standard which will give a similar concentration - say in the range 500 to 2000 ppm.) Leave to stand (swirling occasionally) for at least 10 minutes or until the millivolt output reaches a stable reading. Note that when first used or after prolonged storage this may take several hours – or even days in extreme cases.

4) Meanwhile, make up at least two standard solutions to cover the concentration range expected for the samples (say 1 & 10, or 10 & 100, or 5 & 50 ppm) – Note that these are concentrations of the ion to be measured, not the salt containing the ion, and they can be expressed in moles or milli-moles, or whatever units the analyst prefers – but it is easiest to calculate the slope and check the performance of the electrode if decades of concentration are used, e.g. 1 & 10 mMol etc.

5) When the mV reading is stable, remove the electrodes from the preconditioning solution, rinse with a jet of de-ionised water and dab dry with a paper tissue. WARNING: Do not leave the electrodes soaking in de-ionised water.

6) Lower the electrodes into the lowest concentration standard, stir with a magnetic stirrer at approx 100rpm, and wait for a stable reading (can take 5 or more minutes for the lowest concentrations of some ions) - then record the voltage. Note that for some electrodes it is better to switch off stirrer and measure in still solutions - as noted on individual specification sheets.

7) Repeat this procedure for the other standard(s). Note that for negative ions the voltage is inversely proportional to the concentration.

8) When all the standards have been measured, plot a graph of mV versus Log of Concentration (or mV versus concentration on semi-log paper) to provide the calibration data - this is done automatically by the ELIT ISE/pH Ion Analyser software.

9) Wash the electrodes as before and measure the samples in the same way as the standards.

10) Plot the sample data on the graph and read off the sample concentration - also done automatically by the ELIT software.

At the end of the analyses, wash and dry the electrodes and replace the caps - to prevent drying out of the external filling solution of the reference electrode and to protect the ISE from mechanical damage or atmospheric oxidation/corrosion.
For optimum precision and accuracy, recalibrate after every ten samples, or if the temperature changes by > 1°C.

If the samples are expected to have high Ionic Strength (i.e. > 0.01 Molar for monovalent ions or > 0.001 Molar for divalent ions) add Ionic Strength Adjustment Buffer equally to standards and samples before measuring – see later: Notes on Measuring Procedures, section B5, 3.

B) Detailed Instructions with Explanations and Discussion

B1) Installation

If the electrode is to be used with a conventional reference electrode, it must be inserted in a Mono Electrode Head (ELIT 101). This head fits in every standard electrode holder and is attached to a cable fitted with a BNC connector which can be connected to any ELIT Ion Analyser / computer interface, or to any pH/mV/Ion meter with a BNC socket. Alternative DIN, US, or S7 connectors can be supplied if required.
If the electrode is to be used in combination with an ELIT 8mm reference electrode, then both must be inserted into a Dual Electrode Head (ELIT 201). This system replaces conventional Combination Electrodes and has the advantage that the expensive low noise connectors and cables are not attached directly to the electrodes, the ISE or reference electrode can easily be exchanged independently and the electrode head can be re-used many times with any ELIT electrode. The black plastic protective caps must be removed from the electrodes before use. It is recommended that this is done before inserting the electrode into the electrode holder to avoid placing undue stress on the connecting pin.
NB: the reference electrode cap contains liquid and must be kept upright.

B2) Preconditioning

In order to obtain the most stable results, it is recommended that the electrodes are pre-conditioned by immersing both the ISE and the reference electrode in the 1000ppm standard for at least 10 minutes before use. If the voltage is monitored during this period and is seen to settle down to a sensible stable reading then this is a good indication that the system is operating correctly. For the most precise results, it is recommended that optimum wetting and pre-conditioning can be ensured by repeatedly removing the electrodes from the solution, washing and drying, and re-immersing (and waiting for at least two minutes for a stable reading) until three consecutive readings are within 1mV of each other. When the electrode is first used, or after prolonged storage, it may be that this procedure is insufficient and further soaking, overnight or over a weekend, may be necessary to achieve stable readings. In this case it is strongly recommended that the reference electrode is removed and the protective cap (containing outer filling solution) is replaced during this time to avoid unnecessary leaching of the filling solution. After preconditioning, rinse with a jet of de-ionised water and gently pat dry with a low-lint tissue.

Preconditioning/Standard Solution

To calculate the weight of salt to dissolve in 1 litre of de-ionised water for 1000ppm of any ion, simply divide the molecular weight of the salt in grammes (including any water of crystallization) by the molecular weight of the ion. This will give the weight of salt containing 1g of ion. ppm = mg/l.

B3) Calibration Theory.

The operation of ion selective electrodes is based on the fact that there is a linear relationship between the electrical potential developed between an ISE and a reference electrode immersed in the same solution, and the Logarithm of the **activity** (or "effective concentration") of the ions in the solution. This relationship is described by the Nernst equation:

$E = E^0 + (2.303RT/ nF) \times Log(a)$

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)

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 per mole).

Log(a) = the logarithm of the activity of the measured ion.

Note that 2.303RT/nF is the **Slope** of the line 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 - eg: at S=55, a 1mV error in reading will make about a 4% difference in concentration; at S=26 the difference will be more like 8%. Because of the logarithmic relationship, the slope can most easily be determined as the difference between the voltages measured in two solutions which differ by one order of magnitude - usually expressed as mV/decade. The theoretical value for the slope at 25°C is 59.2 for mono-valent ions and 29.6 for di-valent ions - but in practice these can vary considerably. 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.

The **activity** of an ion in solution is a measure of the number of ions taking part in any given reaction, in this case those interacting with the ISE membrane. It is always less than the actual number of ions present in the solution (i.e. concentration) because the mobility of the ions is reduced by the presence of other ions in the solution.
The higher the concentration of other ions, whether the same or different from the species being measured, (i.e. the Ionic Strength of the solution) then the stronger is this retarding effect and the greater the difference between activity and concentration. However, it must be noted that in dilute solutions with low Ionic Strength this difference is small and can be ignored in many practical applications – i.e. the calibration can be made and sample results calculated using the more convenient concentration units.

The relationship between activity and concentration is defined by the **Activity Coefficient** (f = a / c). This is dependent on the **Ionic Strength** of the solution, and the valency and ionic radius of the ion being measured. Note that the activity coefficient is always less than one, and the lower the value the bigger the difference between activity and concentration.
The **Ionic Strength** (I) can be calculated from $I = 0.5 \times \text{Sum} (ci \times Zi^2)$
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 ISEs cannot be used reliably above this concentration.
For samples with high ionic strength, there are five possible methods that 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. It must be noted, however, that most recipes for the addition of ISAB only produce an increase of 0.1M and this procedure will only be effective if the Ionic Strength of the original sample is significantly below this.

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 matrix** which does not contain the detected ion, or any ion which would interfere with the measurement.

4) Use the Activity Coefficient to calculate the concentration from the activity.
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 (sample) is added to a larger measured volume of sample (standard) so that the ionic strength is essentially the same for both the calibration and the unknown measurement. These methods also

have the added advantage that the electrodes remain immersed in the same solution for both measurements, thus minimising any errors due to temperature differences or hysteresis or variations in the liquid junction potential of the reference electrode, and thus can potentially yield more precise results than direct potentiometry; even for low-ionic-strength samples (see later - Section C).

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 – but also see below, section B5,3.

Activity Coefficients and likely Error (i.e. under-estimate) in Concentration for various Ions in 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%

B4) Calibrating the Electrode in Practice

For a complete calibration, a 10,000 or 1,000 ppm standard solution (or 0.1 or 0.01 molar solution, whatever is most convenient) can be diluted sequentially to produce concentrations of, for example, 100ppm, 10ppm & 1ppm or 1, 0.1 & 0.01 mMol (or even lower for some electrodes – see electrode specification sheet). Note that these are concentrations of the ion to be measured, not the salt containing the ion. The easiest way to do this is by serial dilution - i.e. pipette 10mls of the higher concentration solution into a 100ml flask, dilute to 100ml with deionized water and mix thoroughly. Then transfer this solution into a 150ml polypropylene beaker ready for analysis. Then wash and re-use the pipette and flask, taking the next aliquot from the previous beaker.

However, if the approximate concentration range of the samples is known then a complete calibration will not be necessary and two standards should be made which closely bracket the sample range. Note that large errors may occur if samples are measured by extrapolation beyond the range of the calibration and it is easiest to calculate the slope, and check the performance of the electrode, if decades of concentration are used, e.g. 10 & 100 ppm or 1 & 10 mmol etc. - because the slope is simply the difference between the millivolts in two solutions which differ by one order of magnitude. Three or more calibration points 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. Once the slope has been confirmed in the range of the sample concentrations, subsequent re-calibrations can be made more quickly with a single standard in the middle of the sample range (at least on the same day and probably over a longer period for less precise measurements). This is relatively easy using the ELIT ISE/pH Ion Analyser software.

The temperature of the calibrating solutions and the samples should be the same within a tolerance of ±1°C. If ISAB is required then this must be added in equal proportions to all standards and samples. Note that if the electrode specification sheet indicates that ISAB should be added, for example, "2% v/v" then it should be realised that these are only approximate proportions and the critical factor is that all solutions, samples and standards, must be treated in the same way. Thus it is generally easiest to add 2ml of ISAB to 90ml of standard solution, (remaining after serial dilution), after the appropriate concentration standards have been made. In this case, 10ml must be removed from the lowest standard to make it the same as the others, and only 90mls of sample should be used.

When the calibrating standard solutions are ready they should be measured in the same way as the samples (see Notes on Measuring Procedures, below) - working from the lowest concentration standard to the highest in order to minimise cross contamination. The mV reading must then be plotted against the Logarithm of the concentration (or against the concentration on a Log scale) on graph paper or computer graphics package.

This is done automatically if an ELIT ISE/pH Ion Analyser is used instead of a conventional mV/ion meter. The mV reading for the samples can then be used to read the concentration of the samples from the calibration graph. Again done automatically by the ELIT software.
For the most precise results it is best to measure samples soon after calibration; ideally, calibrate before every sample. This can be done initially with two standards to define the slope, then, to save time, with a single standard using the same slope.

In practice, the operator must decide what is the best compromise between the increased time needed for frequent re-calibrations and the precision required for his measurements. For many applications, calibrating once every hour or every 20 samples should be sufficient - but much less frequently if monitoring long term changes in a single solution.

B5) Notes on Measuring Procedures

The basic method of measuring standards and samples is as given in the Quick Guide (above). Nevertheless, for the most precise results, the operator should be aware of a number of factors and alternative methods which may affect the quality of the analyses. Thus, if the highest possible precision is required, it is recommended that, before starting a new type of sample, the operator should test the various alternative methods (below) to see which will give the most reproducible results with his particular samples and electrode system.

It must be stressed however, that whichever method is adopted, it is essential that the same method is used for all standards and samples.

1) Stirring the solution during measurement ?

There are several schools of thought as to the best way to take measurements. Some authorities suggest that the solutions should be stirred gently with a magnetic stirrer (at ~100rpm) during immersion of the electrodes. The main advantage of this is that, in most electrode systems, the mV reading will stabilise quicker than without stirring. Stirring will also prevent the build up of layers within the solution or around the electrodes. The disadvantages are the extra time taken, the possibility of cross contamination when inserting and removing the stirrer, and the possibility of heat exchange between the stirrer and the solution. Moreover, stirring requires at least 50ml (100ml is better) of sample and is not practical if only small samples are available. Some users 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 note that with some electrode systems and some samples there is a considerable and fairly rapid change in the voltage when the solution stops moving.

Alternatively, in many cases 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.

2) How long to wait after immersion, before taking a reading?

The time at which the measurements are taken can vary depending on the characteristics of the particular type of electrode system being used, the nature of the sample, and the balance between time constraints and precision requirements. For the most precise results it is probably best to wait for a stable mV reading. This could take between 3 and 5 minutes for most electrode systems - though often longer at low concentrations near the detection limit. Some authorities say you need to wait 15 mins for all samples!

Alternatively, it may be more convenient (and quicker) to take all readings after a pre-specified time after immersion. Normally the measured voltage changes fairly rapidly and falls (or rises) by several millivolts during the first 30 seconds after immersion but then the change gradually gets slower and slower. Taking a reading after 2 – 5 minutes (depending on electrode system) will ensure that the initial equilibration of the ISE is completed and the reading is taken in the shallow part of the curve where the final stabilisation of the reference electrode liquid junction potential is only making small changes to the measured voltage.

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.

3) To use ISAB or not ?

If it is not certain that ISAB is required to counteract the effect of samples with high Ionic Strength then a simple check can be made as follows: First make a normal 2-point calibration with pure standards, then measure a typical sample by the Standard Addition method. Then use the first mV reading (in the pure sample) to calculate/read the concentration from the normal Direct Potentiometry calibration graph. If the concentration by SA is significantly higher than that by DP then the sample has high IS and ISAB must be added to standards and samples and a new calibration made before continuing with DP.

As noted above (section B3,1) the addition of ISAB is only effective if the samples have ionic strengths well below 0.1 Molar. Above this, only the SA method will give reliable results.

Nevertheless, most electrode systems will stabilise more quickly when ISAB is present and some authorities recommend that ISAB is always used. Furthermore, special ISABS to control the pH or suppress interfering ions should always be added no matter what the ionic strength of the samples.

4) Cleaning between samples?

For some analyses, particularly if only approximate results are required or where large volumes of sample are available, simply shaking off any droplets of the previous sample or dabbing with a paper towel may be sufficient to avoid significant cross contamination. But for more precise work it is recommended that the electrodes are rinsed by spraying with a jet of deionised water and dabbed dry with a low-lint laboratory tissue between measurements. For the most precise results, it may help to minimise hysteresis effects if, after rinsing, the electrodes are soaked in deionised water for 20 or 30 seconds, (and then dried to prevent dilution of sample) before every measurement. This should ensure that each reading is always approached from the same direction. Alternatively, some authorities recommend that, when measuring samples with similar concentrations, the mV signal will stabilize more quickly if the electrodes are not rinsed, but simply dabbed dry between samples.

C) STANDARD ADDITION AND SAMPLE ADDITION METHODS.

The **Standard Addition** method (also known as "Known Addition") involves adding a small volume of a concentrated standard (e.g. 2 or 5 ml) to a much larger volume of sample (e.g. 50 or 100 ml). The volume and concentration of the standard must be chosen to cause a significant and measurable change in the concentration of the detected ion (and hence in the measured voltage) but should not cause a significant dilution of the sample matrix (so that the ionic strength remains essentially unchanged). The voltage is first measured in a measured volume of the pristine sample. Then a measured volume of standard is added, the solutions are mixed well and a second reading is taken before calculating the concentration of the sample.

The **Sample Addition** method is used in exactly the same way as Standard Addition, except that a small volume of sample is added to a larger volume of standard. The main advantage of these methods is that calibration and sample measurement are both made essentially at the same time and in the same solution. Thus temperature and ionic strength differences are not significant and ISAB is not required.

An additional advantage, however, is that 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) and therefore this source of measurement error is also avoided. Furthermore, once the approximate concentration for the samples is known, the calibration (electrode slope) can be "fine tuned" by making up a standard which lies within the range of the samples and analysing it by whichever "Addition" method is to be used and then adjusting the slope and re-calculating the results until the standard gives the correct answer. These measurements and calculations can be made quickly and easily using the **ELIT ISE/pH Ion Analyser Software**.

Alternatively, the **Double Standard Addition Method** can be used to measure the slope at the same time and in the same solution as the sample measurement and further reduce any errors which may be due to differences in Ionic Strength between samples and standards. In this way, these Addition methods can be used even with old or worn electrodes which are not completely linear over their whole range, or even over a decade of concentration, as long as the slope is stable and reproducible over the limited range of the samples.

These methods can potentially yield more precise results than Direct Potentiometry, even in low-ionic-strength samples. For a detailed description, including an Excel spreadsheet for making the calculations, please visit http://www.nico2000.net/datasheets/staddl.html.

D) INTERFERING IONS.

The biggest limitation and difficulty with Ion Selective Electrode measurements is the problem of interference from other ions. ISEs are not ion-specific. All are sensitive to some other ions to some extent. In many cases the interferences are trivial and can be ignored but in some extreme cases 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 absent, or only present in very low concentrations relative to the primary ion.
In some systems the interfering ion can be removed by chemical means and special chemicals can sometimes be added to the appropriate Ionic Strength Adjustment Buffer.

The interfering ions and their Selectivity Coefficients (SC=1 if electrode is equally sensitive to both the primary and interfering ions, 0.1 if ten times less sensitive to the interfering ion, etc.) are clearly shown on the individual electrode data sheets. Unfortunately the Selectivity Coefficient is not constant and is dependent on a number of factors such as total ionic strength of the solution, temperature and the actual and relative concentrations of each ion. Thus it cannot be used to make precise corrections for the interference. Nevertheless, the Chemtools package in the ELIT software can be used to calculate the order of magnitude of the likely interference effects for all ELIT ISEs as a guide for the user in deciding whether or not ISE measurement would be suitable for his application.

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 it's 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. See the on-line version of this document (on the Technical Information page of www.nico2000.net) for a practical example. 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.

E) STORAGE AND MAINTENANCE

After use, the electrodes should be rinsed with de-ionised water and dried with a paper towel. If the electrodes are in regular use and are kept permanently plugged into the electrode head, then it is not necessary to replace the plastic cap for the ISE after every analytical session. It can just be left hanging in the air. If unused for long periods however, (overnight or for prolonged storage) it is necessary to replace the cap to protect the membrane from atmospheric oxidation/corrosion or mechanical damage.

The cap for the reference electrode however, should be replaced after each session of use, in order to prevent drying out of the filling solution. Reference electrodes should be stored wet, with the protective cap containing the same solution as the outer filling solution. Loss of solution is minimised by keeping a plug of absorbent material, such as cotton wool, in the bottom of the cap. This should be checked frequently and the solution replenished if necessary.

Alternatively, for short breaks during regular use, both electrodes can be immersed in a standard solution with similar concentration to the samples to be measured.

SPECIAL NOTES:

1) Electrodes should never be left in pure distilled or de-ionised water (or any solution which does not contain the target ion) for more than a few minutes at a time - to avoid leaching effects.

Blank measurements are not necessary or appropriate for ISE work because the voltage measured when there are no target ions present is the sum of various liquid and solid junction potentials in the circuit which can be highly variable and unstable and change when the target ion is introduced.

2) It is strongly recommended that the electrode is removed from the electrode head before attempting to remove or replace the cap, in order to prevent unnecessary force being applied to the joint between the electrode body and the connecting pin.

3) In order to maximise the life of the electrode, it is best to avoid touching the membrane surface and avoid strong acid or alkaline solutions, detergents, surfactants, and PVC solvents. Also avoid prolonged exposure of the electrode to solutions containing interfering ions which may poison the membrane.

F) FAULT FINDING

Important Diagnostic Note: It is quite normal for the measured voltage in a particular concentration standard to differ from a previous calibration (on the same day or days or weeks before) or from another ISE for the same ion. This does not necessarily indicate a fault.
The potential difference between the ISE and the Reference Electrode can vary by several mV each time they are immersed in a new solution, due to variations in the liquid junction potential of the RE. Also the speed of stirring (if used), the age and amount of use of the electrodes, the precise laboratory conditions (eg: temperature, stray electro-magnetic fields, humidity), and slight variations during the manufacturing process can all have an effect.

Thus the actual value of the mV reading is almost irrelevant. The two important factors are:
a) the mV reading should reach a stable value in a reasonable time;
b) the difference in mV between two solutions of known concentration (the Slope) is within specification in the concentration range of the samples and stable and reproducible. If this is the case then there is no fault in the measuring system.

1) If the electrode shows a slow response or a low slope, the membrane may be poisoned or coated with a film. In this case PVC membranes may be rejuvenated by carefully washing in pure ethanol, then de-ionised water. Thick deposits can be washed off with a jet of deionised water from a wash bottle. As a last resort, try gentle wiping with a soft wet tissue or lint-free cloth - but be very careful not to scratch the membrane. Protein deposits can be removed by rinsing in a HCl/Pepsin cleaning solution available from several chemical suppliers.
Crystal membranes can also be rejuvenated by gently polishing with very fine, wet emery paper, using a circular motion, to remove all stains and blemishes, then washing in deionised water.
After cleaning, the electrode must be pre-conditioned again before use - but note that it may take several hours to regain a stable reading.

2) If there is low slope but no deposit then the membrane may be oxidised or leached. In this case the ISE should be soaked in 1000ppm standard solution overnight or even for several days to ensure complete impregnation.

3) If the ISE is being used with an ELIT 8mm reference electrode and the signal is very erratic and jumps by tens or even hundreds of millivolts then this is probably due to minute bubbles in the reference electrode gel electrolyte. These can develop during transport or prolonged storage. This can normally be cured by holding the reference electrode firmly with the active tip pointing downwards and shaking down several times with a flick of the wrist, as with old medical mercury thermometers (i.e. down vigorously but up gently so that the gel is propelled towards the ceramic frit and any bubbles away from it).

4) If the reading when immersed in the 1000ppm standard is 0 mV or an unchanging high value then it is likely that the gel electrolyte in the reference electrode has completely dried out. This may be because there has been insufficient filling solution in the plastic cap or the cap has not been replaced after use. In this case a new RE will be required.

5) Large deviations in the mV reading may also be due to poor connections in the wiring or moisture on the contacts and in this case all connections should be checked, cleaned and dried. Random deviations of a few millivolts may be due to contamination of the ISE membrane or to external electrostatic fields. In the latter case, if the operator or passers-by are wearing static-producing clothing, it may help to ensure that every one remains still for a few seconds whilst the reading is taken.