

# **A GUIDE TO ION SELECTIVE MEASUREMENT**

## INTRODUCTION

The measurement of the concentration or activity of an ion in a solution by means of an Ion Selective Electrode is as simple as making a routine pH measurement. A pH electrode is only a rather special case of an almost perfectly selective Ion Selective Electrode but the principles and practice are the same in both cases. The chief difference between the pH electrode and other electrodes is that the latter, generally speaking, are not as selective as the pH electrode and some account must be taken of possible interferences in an analytical situation.

Sophisticated, microprocessor-controlled Ion meters have operational modes which enable concentration results to be obtained directly from sample solutions. Calibration is automatic and the ability of the Ion meter to retain this data in memory dispenses with the drawing of calibration curves.

The information contained in this booklet should enable the reader to understand the principles of operation and methods of analysis involving Ion Selective Electrodes.

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## SECTION 1 Ion selective measurement

### Basic theory

An ion selective electrode generates a difference in electrical potential between itself and a reference electrode. The output potential is proportional to the amount or concentration of the selected ion in solution.

The concentration is a measure of the number of ions in a specific volume. The definition assumes that all of those ions behave in the same manner. However, ions do not always behave similar to one another: some are effective i.e. exhibit properties associated with that ion, and some are not effective. The number of effective ions is called the activity of the solution. It is therefore reasonable to assume that the electrode will measure the activity rather than the finite concentration of the ions. In dilute solutions though, the ionic activity and concentration are practically identical but in solutions containing many ions, activity and concentration may differ. This is why dilute samples are preferred for measurement with ISE's.

It is possible to 'fix' the solution so that activity and concentration are equal. This can be done by adding a constant concentration of an inert electrolyte to the solutions under test. This is called an Ionic Strength Adjustment Buffer (I.S.A.B.). Thus the ion selective electrode will measure concentration directly. Activity can also be an important quantity to measure; for instance, it is the activity of calcium in blood that is physiologically important, and not the concentration.

The measured electrode potential,  $E$ , is related to the activity of an ionic species by the **Nernst equation**.

$$E = E_o + 2.3 \frac{RT}{nF} \log \text{ACTIVITY}$$

Where  $E_o$  = a constant for a given cell

$R$  = the gas constant

$T$  = the Temperature in Kelvin

$n$  = the ionic charge

$F$  = the Faraday constant

and the expression  $\frac{RT}{nF}$  is termed the **Slope Factor**

For example, when measuring Potassium ions, (i.e.  $n = +1$ ), the slope factor at 298K (25°C) has a value of 59.16 mV. This is termed the **Ideal Slope Factor**, and means that for each ten-fold change in Potassium concentration, an ideal measuring system will sense a mV change of 59.16.

The measurement of slope factor gives an indication of the performance of the electrode system.

If ion selective electrodes are not cleaned after use, and are subject to long term neglect, then the accuracy of the system is lost. This loss of performance can be monitored by a steady decrease in measured slope value during the calibration of a system.

A number of factors including reference junction blockage, electrolyte loss, electrode interference and the use of incorrect calibration solutions will all contribute to 'low slope values'. All of these must be considered when there are doubts about the system performance.

Ionic charge	Slope	Example
+2	29.58	Ca <sup>2+</sup> , Mg <sup>2+</sup>
+1	59.16	K <sup>+</sup> , Na <sup>+</sup>
-1	-59.16	F <sup>-</sup> , Cl <sup>-</sup>
-2	-29.58	S <sup>2-</sup>

Table 1 gives the ideal slope values for monovalent and divalent anions and cations.

Table 1

Direct measurements are particularly useful for ions which have specifically designed electrodes. However, the accuracy can be increased by using different methods of measurement, e.g. standard addition, known subtraction or titration. It is possible to use the ion selective electrode as an end point indicator, just as litmus or universal indicator can be used as indicators for acid/base titrations.

Furthermore, it is even possible to measure the concentration of an ion for which there is no specific electrode, e.g. the measurement of aluminium concentration where there is no aluminium electrode. By carefully considering the chemistry of ions such as aluminium one can create a system by which it is possible to determine their concentrations. For example, aluminium fluoride is insoluble, therefore the addition of a sodium fluoride solution precipitates the aluminium out of solution as aluminium fluoride. Using a fluoride ISE, the concentration of sodium fluoride added to aluminium solution can be measured. At first there will be no potential as the fluoride precipitates with aluminium. When all the aluminium has reacted further additions of fluoride will provide a sudden change in electrode potential. By drawing a graph of electrode potential versus amount of sodium fluoride added, the concentration of sodium fluoride required to react with the aluminium can be calculated. Therefore, if one knows the ratio in which the aluminium and fluoride react, the aluminium concentration can be found.

## Selectivity, interferences, activity

As the name suggests, ion selective electrodes are selective to one ion but not specific for it. This means that other ions in solution may also be sensed by an ISE although it is not designed to do so.

The ion that is to be determined is referred to as the determinant and other ions to which an electrode responds are known as Interferents or interfering ions. It is possible to calculate the preference of an electrode for the determinant over the interferent. This is called the selectivity of the electrode. The preference, expressed as a ratio is called the selectivity coefficient, or

ratio. Each electrode has its own set of selectivity coefficients. For example:

$$K_{K^+/Na^+} = 2.6 \times 10^{-3}$$

determinant      interferent

Meaning that the preference for  $K^+$  (potassium) over  $Na^+$  (Sodium) for this electrode is 1 to  $2.6 \times 10^{-3}$  or 385:1. This means that the electrode is 385 times more selective to  $K^+$  than  $Na^+$ .

These coefficients are not always constant and the manufacturer's specification should be consulted.

The 'pH glass-electrode' or hydrogen selective electrode is the most responsive of all ISE's, yet measurements of pH to better than  $\pm 0.01$  pH are known to require considerable care: this corresponds to an uncertainty of  $\pm 2\%$ . However, accuracy of 2% or even down to 0.5% can be achieved if the operator follows good laboratory procedures.

It is possible to increase accuracy by using different measuring techniques. Methods known as known addition, sample addition, etc., have been devised to improve accuracy. These techniques reduce the effect on the result of errors in single readings and consequently a balance must be found between accuracy and convenience in the choice of technique.

## Types of electrode

There are four types of ion selective electrode whose construction and mode of operation differ considerably. These are:

1. **Glass body electrode**
2. **Solid state (crystalline membrane)**
3. **Liquid ion exchange (polymer membrane)**
4. **Gas sensing type**

### 1. Glass body electrodes

The most common ISE is the glass-bodied pH combination electrode. The sodium ( $Na^+$ ) combination has a similar construction which houses a glass bulb that is sensitive to sodium ions in solution.

### 2. Solid state ion selective electrode

The electrode potential of standard and sample solutions is measured across a solid, polished crystalline membrane. The crystalline material is prepared from a single compound or a homogeneous mixture of compounds (for example, the fluoride ISE has a Lanthanum Fluoride crystal).

### 3. Polymer membrane ion selective electrode

These electrodes use a replaceable membrane cap which has a solid, polymeric membrane containing a selective ion exchanger. The electrode potential of solutions is measured by their effect on the ion exchange material. Due to the complex properties of the ion exchangers, they are subject to more interferences than other ion selective electrodes.

### 4. Gas sensing type

Electrodes, including the ammonia ISE, use a gas sensing mode of operation. In the case of ammonia, a caustic solution is added to the sample solution to liberate ammonia. The gas permeates through a membrane and changes the pH of the filling solution. The change in pH is proportional to the ammonia concentration. This gives a quantitative measurement of the ammonia in the sample solution.

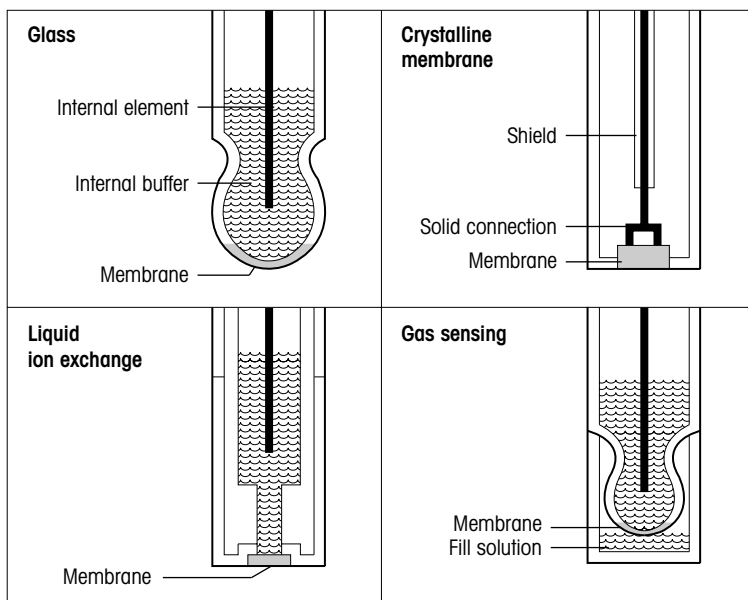
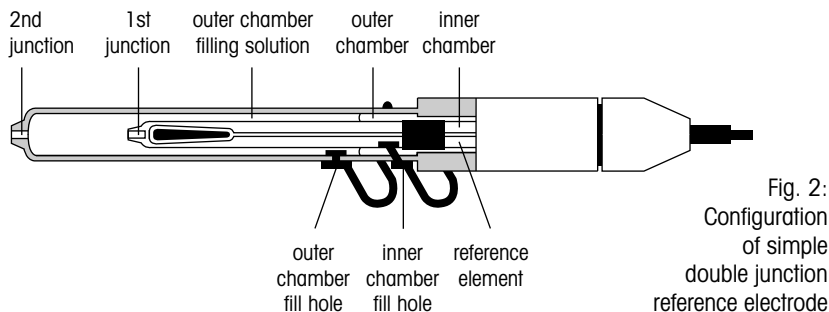


Fig. 1: Construction of the sensing portion on the 4 main types of Ion-selective/gas sensing electrodes

## Reference electrodes

The potential of an Ion Selective Electrode can only be measured against a suitable reference electrode in contact with the same test solution. Reference electrodes are electrochemical half cells whose potentials are maintained at a constant value by the chemical equilibria maintained inside them.



It is preferable to use a double-junction reference electrode for ISE applications. Standard reference half cells have KCl based electrolyte filling solutions. This is a distinct disadvantage when, for example, potassium or chloride is being measured. To overcome this, a double junction reference is used in which the escaping KCl is retained in a second chamber containing a non-interfering electrolyte, which in turn escapes into the test solution at the second junction.

Bridge solutions for the outer chamber are listed in Table 2. The filling solution for the inner chamber of a double junction reference electrode is 4M KCl saturated with AgCl for a silver/silver chloride electrode.

Sensing electrode	Ref. outer bridge solution	Sensing electrode	Ref. outer bridge solution
Barium	0.1M NaNO <sub>3</sub>	Nitrate	1.0M (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>
Bromide	1.0M KNO <sub>3</sub>	Potassium	0.1M TEACl
Calcium	1.0M KNO <sub>3</sub>	Silver	1.0M KNO <sub>3</sub>
Chloride	1.0M KNO <sub>3</sub>	Sodium	0.1M CaCl <sub>2</sub>
Copper	1.0M KNO <sub>3</sub>	Sulphide	1.0M KNO <sub>3</sub>
Cyanide	1.0M KNO <sub>3</sub>	Thiocyanate	1.0M NaNO <sub>3</sub>
Fluoride	1.0M KNO <sub>3</sub>	Water hardness	0.1M KNO <sub>3</sub>
Iodide	1.0M KNO <sub>3</sub>		

Table 2: Bridge solutions for the outer chamber

## SECTION 2: Methods of analysis

There are a number of methods of analysis with ion selective electrodes and some examples are given in this section. Microprocessor based instruments are programmed with direct concentration modes of operation. Calibration and sample measurement are carried out automatically. The traditional drawing of calibration graphs is no longer necessary.

### Direct potentiometry

This is the simplest and most widely used method of obtaining quantitative results using Ion Selective Electrodes. Standard solutions are prepared by serial dilution of a concentrated standard. The recommended Ionic Strength Adjustment Buffer, (ISAB), is added to each standard as well as to the unknown samples. The system is calibrated and the information stored in the microprocessor memory. The electrode potential of each of the unknown solutions is then measured and the concentration of the ion read directly from the meter.

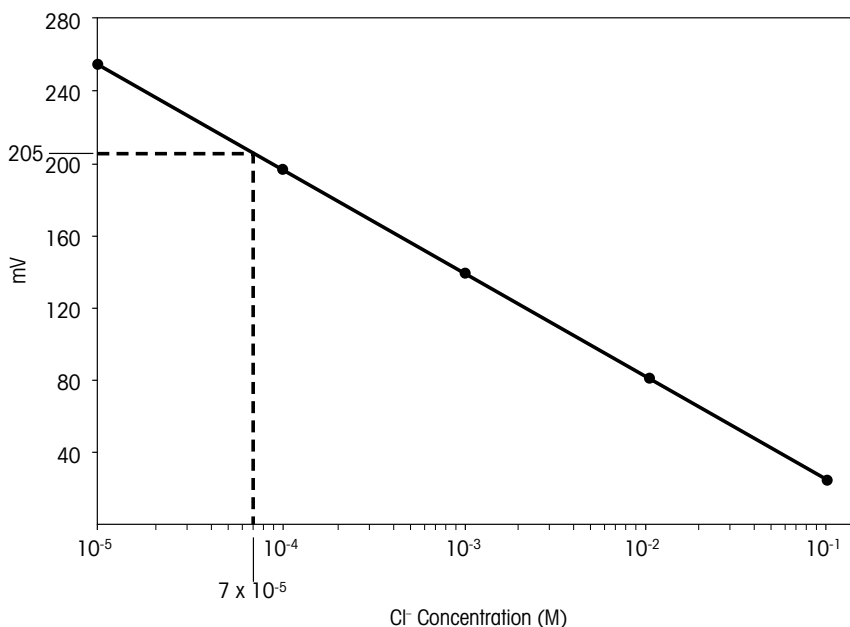


Fig. 3: Chloride electrode calibration graph held in microprocessor memory

The chief advantage of direct potentiometry is its ability to rapidly analyse solutions of widely differing concentrations.

For example: Measurement of chloride in natural water, using the chloride ion selective electrode, by direct potentiometry.

1. Prepare standard solutions of  $1 \times 10^{-1}$ ,  $1 \times 10^{-2}$ ,  $1 \times 10^{-3}$ ,  $1 \times 10^{-4}$  and  $1 \times 10^{-5}$  M NaCl in distilled water.
2. Mix each of the above standards with an equal volume of 1M NaNO<sub>3</sub> (ISAB).
3. Connect the ISE and the double junction reference electrode to the meter. Programme the meter with the standard solution concentration values.
4. Immerse the electrodes in each of the standards in turn, starting with the least concentrated, and calibrate the system.
5. The calibration curve will be constructed and stored in the memory of the meter.
6. Prepare unknown samples in the same way as the standard solutions. Immerse electrodes and read the unknown concentration on the display of the meter.

Notes:

- (i) Once the calibration process has been completed subsequent measurements are rapid and this method is most suitable where large numbers of similar samples need to be analysed. Sampling rates of up to 60 per hour are possible.
- (ii) The electrode may be calibrated below  $10^{-5}$  M but the response will show some curvature owing to chloride ions being dissolved from the surface of the membrane. This phenomenon ultimately limits the usable range of any electrode. Roughening or scratching of the surface of the membrane causes the solubility to increase and so further reduce the linear range and increase the response time. Care should be exercised, therefore, in the handling and storage of the electrode.
- (iii) The volume of sample taken has no influence on this method of measurement, in contrast with the techniques described later.
- (iv) The temperature of both standards and samples should be within 2 degrees of each other.
- (v) This technique is most useful when samples exhibit a wide range of concentrations. There is no need to change the meter range or to have knowledge of the sample concentration.

## One point calibration

Once the slope of an electrode is calculated it is then possible to measure an unknown concentration. By recording the electrode potential in the unknown solution (E<sub>1</sub>) and a standard solution (E<sub>2</sub>), the difference between these two potentials ( $\Delta E$ ) can be used to calculate the unknown concentration.

where:  $C_u = C_s \times 10^{\Delta E/S}$   
 $C_u$  = the unknown concentration;  
 $C_s$  = the standard concentration;  
 $S$  = the slope of the electrode;  
 $\Delta E = E_1 - E_2$

Thus, if the electrode slope is -57.5 mV and the potential in an unknown solution is +170 mV and in  $10^{-2}$ M solution is +83 mV, the unknown can be calculated as follows:

$$\begin{aligned} C_u &= 10^{-2} \times 10^{87/-57.5} \\ &= 10^{-2} \times 10^{-1.51} \\ &= 10^{-2} \times 0.03 \\ &= 3 \times 10^{-4}\text{M} \end{aligned}$$

Naturally the precision in such a determination is dependent upon knowing the exact electrode slope and having a meter resolution of  $\pm 0.1$  mV. The use of the ionic strength adjustment buffer is necessary to eliminate 'activity effects'.

## Incremental techniques

### Known addition

In analytical situations where a large number of very different measurements have to be made with different electrodes, it would be laborious to calibrate at several points for only two or three samples. In such situations the incremental addition techniques are more suitable.

In principle, all incremental addition techniques operate on the same basis. The electrode potential of a known volume of unknown solution is measured. A small volume of a known solution is added to the first volume and the electrode potential re-measured, from which the potential difference ( $\Delta E$ ) is found. By solving the following equation the unknown concentration can be found:

$$C_u = C_s \left[ \frac{V_s}{V_u + V_s} \right] \left[ 10^{\Delta E/S} - \frac{V_u}{V_s + V_u} \right]^{-1}$$

where:  $C_u$  = concentration of the unknown;  
 $C_s$  = concentration of the standard;  
 $V_s$  = volume of the standard;  
 $V_u$  = volume of the unknown;  
 $\Delta E$  = change in electrode potential in mV;  
 $S$  = slope of the electrode in mV.

If the same volumes of standard and sample are always used, e.g. 100 ml of sample and 10 ml of known addition, this equation can be considerably simplified and reduced to a parabolic curve of Q against  $\Delta E$  where Q is a factor such that:

$$C_u = QC_s$$

A more convenient way to use this formula is from a table of  $\Delta E$  and  $Q$  values which is given below.

$\Delta E$	$Q$	$\Delta E$	$Q$	$\Delta E$	$Q$
0 mV	1.000	10 mV	0.160	20 mV	0.0716
1	0.696	11	0.145	21	0.0671
2	0.529	12	0.133	22	0.0629
3	0.423	13	0.121	23	0.0591
4	0.351	14	0.112	24	0.0556
5	0.297	15	0.1030	25	0.0523
6	0.257	16	0.0952	26	0.0494
7	0.225	17	0.0884	27	0.0466
8	0.199	18	0.0822	28	0.0440
9	0.178	19	0.0767	29	0.0416

Table 3: Known Addition Table for a 10 ml addition to a 100 ml sample volume, and a monovalent ion

Example: The determination of calcium in beer by Incremental Addition.

A sample of aerated, pH adjusted (pH 5.5-6.0) beer is required. Pipette 30 ml of this solution into a beaker and measure the electrode potential of a calcium electrode. Add 1.0 ml of standard (0.1M) calcium solution and measure the new electrode potential. Use the Known Addition formula to calculate the unknown calcium concentration.

These techniques are programmed into modern ion meters. The equation for incremental techniques is stored in memory. Sample and standard volumes are keyed into the meter and as the electrode potentials are measured, the concentration of unknown samples is read on the display of the meter.

**Known subtraction:** In this case a small volume of a reagent which complexes or precipitates the primary ion is added to the known volume of the sample. This produces a decrease in ion concentration and a corresponding change in  $\Delta E$ . Provided the stoichiometry of the complexing or precipitation reaction is known (usually 1:1) the same equation as that used for Known Addition applies.

The advantages of this technique are apparent in those applications where standard solutions of the ion to be measured are unstable, of interdeterminable concentration, or toxic such as cyanide. In the last case, an addition of hypochlorite will oxidise the cyanide, thus eliminating the necessity for the handling and pipetting of potentially lethal standard cyanide solutions.

**Sample addition:** In this case a small known volume of the sample is added to a known volume of a more dilute standard solution and the electrode potential difference  $\Delta E$  measured. The equation in this case is:

$$C_u = C_s \left[ \frac{V_u + V_s}{V_u} \right] \left[ 10^{\Delta E/S} - \frac{V_s}{V_s + V_u} \right]$$

This technique finds application when the samples to be measured are of rather high concentration and the known addition procedure produces very little change in the electrode potential.

**Sample subtraction:** A small volume of unknown sample is added to a larger, known volume of a standard solution of an ion with which the sample will react to form a complex or precipitate. The electrode used is sensitive to the ion in the standard solution and not the sample solution.  $\Delta E$  is again measured and the same equation used as for sample addition. The advantage of this technique is that measurements can be made of an ion for which no electrode exists provided a measurable reagent can be found which reacts with the ion.

Example: Determination of Sulphate by Sample Subtraction

There is no electrode at the present which will respond to sulphate ion, but a technique using a barium ion selective electrode can be used. The technique is as follows:

- a) Make up a solution of  $10^{-4}M$  barium chloride containing about 25% ethanol or methanol and pipette 100 ml into a beaker on a stirrer and measure the electrode potential with a barium selective electrode.
- b) The sample solution should be in the range  $10^{-4}$  to  $10^{-3}M$  (if it is stronger use correspondingly stronger  $BaCl_2$ ). Add 10 ml of the sulphate sample slowly to the standard solution while stirring. Measure the electrode potential again once it has reached a constant value and compute  $\Delta E$ . The concentration of the unknown sulphate can then be determined using the sample addition equation.

### Advantages and disadvantages of the incremental methods

1. Incremental methods are particularly useful for the 'one-off' analysis since they generally require only one standard solution and two potential measurements.
2. Since the standard solution is always in at least 10:1 excess, the effects of the matrix in the sample are practically eliminated. Ionic strength adjustors are not necessary.
3. Temperature differences between the sample and the standard become unimportant since again the dilution effect will quickly reduce the sample temperature to that of the standard.
4. An increased range of species can be measured using the Sample Subtraction technique since measurements can be made on samples for which there is no ion selective electrode.
5. A disadvantage of all incremental addition methods is the fact that the approximate value of the 'unknown' concentration must be known so that the correct standard solution can be used.
6. The use of incremental techniques also introduces the need for the accurate measurement of volumes of both sample and standard.

## Multiple sample addition

Microprocessor driven ion meters can be programmed for a multiple sample addition technique. A routine sample addition experiment is set up. The volume ( $V_s$ ) and concentration ( $C_s$ ) of the standard solution are keyed into the meter. The electrode potential of the standard solution is measured.

The sample solution ( $V_{U1}$ ) is then pipetted into the standard solution and the electrode potential remeasured. The change in electrode potential ( $\Delta E$ ) is calculated. The meter solves the incremental technique equation and the concentration of the unknown sample ( $C_{U1}$ ) is displayed.

When the volume of the first sample ( $V_{U1}$ ) is keyed into the meter, the volumes of additional samples can also be put into memory.

The presence of  $V_{U2}$  in memory triggers the multiple sample addition software routine. Experimentally, the beaker now contains the standard solution mixed with the first sample solution.

The meter calculates the volume of the mixture ( $V_s + V_{U1}$ ) and uses the following equation to calculate the concentration of the mixture in the beaker:

$$C = \frac{C_s V_s + C_{U1} V_{U1}}{V_s + V_{U1}}$$

Now by adding the known volume of the second sample solution to the beaker and remeasuring the electrode potential, the meter can calculate the concentration of the second sample.

This mode of operation allows a large number of samples to be analysed using only one standard solution contained in a beaker.

The ability to carry out such an experimental technique is due to the innovative software of modern ion analysers.

## Titrimetric procedures

One of the major limitations of analysis with ion selective electrodes by any of the preceding methods is their relative imprecision. An accuracy of 2-8%, while adequate for a great many applications may not be sufficient for some measurements. For these analyses it may be possible to use a titration procedure in which the ion selective electrode is only used as the indicator and the accuracy is derived from the classical titration process which can yield answers to within 0.1-0.5%.

The principle of ion selective electrode titrations is based on the fact that in a stoichiometric reaction between two species in solution, the end point of the reaction is characterised by the total disappearance of one of the species or first appearance of a product of the reaction. Figure 4 shows the concentrations of the ions involved during the course of a titration reaction between calcium ions and EDTA.

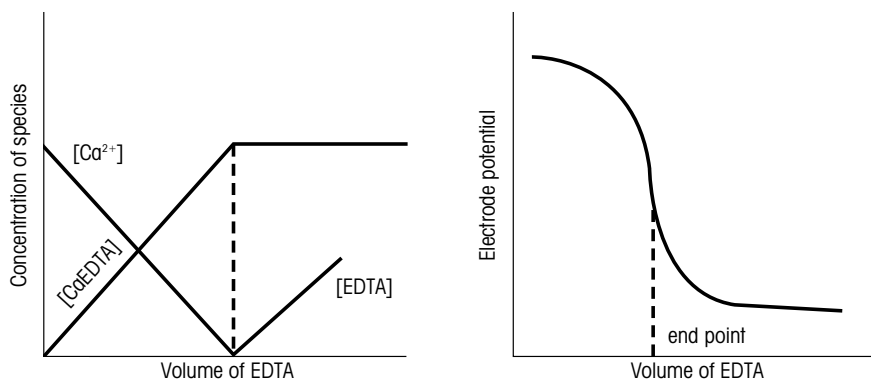


Fig. 4: Titration of calcium with EDTA

As the EDTA solution is added to the calcium solution, the EDTA-Ca complex is formed in which the calcium will not react with an ion selective electrode. At the end-point the concentration of calcium approaches zero and as the dissociation constant of Ca-EDTA complex is very small (less than  $10^{-10}M$ ), the net result is a sudden and significant change in the electrode potential. From this the end-point volume of EDTA and hence the concentration calcium can be calculated. Since the volume of titrant can be measured to 0.05 ml quite easily, this gives precisions of 0.2% in volumes of 25 ml. Modern microprocessor-based automatic titrators can carry out the complete process including addition of reagent, location of the end-point and calculation of the result.

Apart from increasing the precision of ISE measurements, titrimetric methods also extend the range of species which can be measured. Thus, aluminium cannot be analysed by direct potentiometry but by titrating with sodium fluoride and monitoring with a fluoride selective electrode, aluminium solutions can be measured quite readily.

While titration methods are generally quite straightforward, producing accurate, precise and rapid results, there can be occasions when problems occur. The usual cause of such problems is a failure to understand either the chemical equilibrium principles or the kinetics behind the titration reaction.

## SECTION 3: Laboratory measurements

To use an ISE successfully, a number of preparative steps need to be made before a simple concentration measurement can be taken. The experimental procedure must be evaluated. All glassware must be clean and any analytical equipment set up according to the manufacturer's instructions.

Step 1. The calibration curve needs to be prepared. This is achieved by measuring the electrode potentials developed in a range of solutions of known concentration.

Step 2. The range of solutions with known concentration are called 'standard solutions'. A solution consisting of, for example, 1000 parts per million or ppm of a species can either be accurately made up by weighing and dissolving in distilled water or bought directly from the manufacturers of the ISE. This is called a 'stock' solution; it is always the most concentrated solution.

Step 3. A number of different solutions which are less concentrated are prepared from the stock solution by dilution. This is known as serial dilution and is exemplified by the following: take 10 ml of 1000 ppm stock in a 100 ml class A volumetric flask and dilute to 100 ml with distilled water. This gives a 100 ppm solution.

A typical range of solutions could be 0.1, 1, 10, 100 and 1000 ppm in concentration. These are standard solutions.

Step 4. It is now necessary to adjust the solution so concentration can be determined. This is achieved by the addition of an 'Ionic Strength Adjustment Buffer' (ISAB). An example would be in potassium determinations. It is necessary to add 2 ml of 2M Ammonium Sulphate ISAB per 100 ml of potassium standard or sample.

Step 5. Place the ion selective electrode and reference electrode into a known quantity of the least concentrated standard (e.g. 100 ml, suitably adjusted by ISAB). Allow sample to reach room temperature and pressure. Stir gently. Measure the electrode potential which is stored in the memory of the ion meter.

Step 6. Rinse the electrodes with distilled water and repeat steps 4 and 5 using the next concentration of standard solution, in succession, until all the standards have been measured.

Step 7. The ion meter will store the calibration curve and indicate the slope efficiency of the system.

Step 8. Take the same volume of sample as standards (suitably adjusted by ISAB) and place both electrodes in that sample; stir and allow to reach room conditions. The electrode potential of the unknown sample is measured and the concentration displayed on the meter. Using this method, known as direct measurement, it is possible to determine the concentration of numerous samples in a very short time.

(Note: The drawing of calibration curves is restricted to those analysts who are using a mV meter to measure electrode potentials of standard and sample solutions)

## SECTION 4: Ions determined by ion selective electrode

The following table lists ion selective electrodes which are readily available, concentration ranges, selectivity ratios to the major interfering ions and the recommended outer bridge solutions for double junction reference electrodes.

Electrode	Type	Concentration range	Selectivity ratios	Reference/ Filling solutions
<b>Barium</b> <b>Ba<sup>2+</sup></b>	Liquid ion exchange	10 <sup>0</sup> - 5 x 10 <sup>-5</sup> M	Pb <sup>2+</sup> = 2.4 Ca <sup>2+</sup> = 0.025 Na <sup>+</sup> = 0.0004 K <sup>+</sup> = 0.0009	Double junction Bridge solution 0.1M NaNO <sub>3</sub>
<b>Bromide</b> <b>Br<sup>-</sup></b>	Solid state	10 <sup>0</sup> - 5 x 10 <sup>-6</sup> M	OH <sup>-</sup> = 3 x 10 <sup>-5</sup> Cl <sup>-</sup> = 2.5 x 10 <sup>-3</sup> I <sup>-</sup> = 5 x 10 <sup>3</sup> NH <sub>4</sub> <sup>+</sup> = 3 x 10 <sup>-1</sup> CN <sup>-</sup> = 1.2 x 10 <sup>4</sup> S <sup>2-</sup> may be present in traces only	Double junction Bridge solution 1.0M KNO <sub>3</sub>
<b>Calcium</b> <b>Ca<sup>2+</sup></b>	Liquid ion exchange	10 <sup>0</sup> - 5 x 10 <sup>-5</sup> M	Mg <sup>2+</sup> = 2.5 x 10 <sup>-4</sup> Ba <sup>2+</sup> = 3 x 10 <sup>-3</sup> Pb <sup>2+</sup> = 0.1 Zn <sup>2+</sup> = 1.0 Fe <sup>2+</sup> = 0.8 Na <sup>2+</sup> = 1.46 x 10 <sup>-4</sup> K <sup>+</sup> < 10 <sup>-6</sup>	Double junction Bridge solution 1.0M KNO <sub>3</sub>
<b>Chloride</b> <b>Cl<sup>-</sup></b>	Solid state	10 <sup>0</sup> - 5 x 10 <sup>-4</sup> M (5 x 10 <sup>-5</sup> with careful calibration)	OH <sup>-</sup> = 1.25 x 10 <sup>2</sup> Br <sup>-</sup> = 3 x 10 <sup>2</sup> I <sup>-</sup> = 2 x 10 <sup>6</sup> S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> = 10 <sup>-2</sup> CN <sup>-</sup> = 5 x 10 <sup>6</sup> NH <sub>4</sub> <sup>+</sup> = 8.3 S <sup>2-</sup> in traces only	Double junction Bridge solution 1.0M KNO <sub>3</sub>
<b>Copper</b> <b>Cu<sup>2+</sup></b>	Solid state	10 <sup>0</sup> - 10 <sup>-6</sup> M	Pb <sup>2+</sup> = 5 x 10 <sup>-3</sup> Ca <sup>2+</sup> = 1 x 10 <sup>-4</sup> Ni <sup>2+</sup> = 1.6 x 10 <sup>-4</sup> Co <sup>2+</sup> = 7.6 x 10 <sup>-5</sup> Mg <sup>2+</sup> = 6.4 x 10 <sup>-5</sup> Sr <sup>2+</sup> = 1.3 x 10 <sup>-5</sup> Cu <sup>+</sup> , Ag <sup>+</sup> , Hg <sup>2+</sup> in traces only	Double junction Bridge solution 1.0M KNO <sub>3</sub>
<b>Cyanide</b> <b>CN<sup>-</sup></b>	Solid state	10 <sup>-2</sup> - 10 <sup>-6</sup> M	OH <sup>-</sup> = 10 <sup>-8</sup> Cl <sup>-</sup> = 10 <sup>-6</sup> Br <sup>-</sup> = 2 x 10 <sup>-4</sup> S <sup>2-</sup> , I <sup>-</sup> in traces only	Double junction Bridge solution 1.0M KNO <sub>3</sub>
<b>Fluoride</b> <b>F<sup>-</sup></b>	Solid state	10 <sup>0</sup> - 10 <sup>-6</sup> M	OH <sup>-</sup> = 10 <sup>-1</sup>	Double junction Bridge solution 1.0M KNO <sub>3</sub>
<b>Iodide</b> <b>I<sup>-</sup></b>	Solid state	10 <sup>0</sup> - 10 <sup>-5</sup> M	OH <sup>-</sup> = 10 <sup>-8</sup> Cl <sup>-</sup> = 10 <sup>-6</sup> Br <sup>-</sup> = 2 x 10 <sup>-4</sup> CrO <sub>4</sub> <sup>2-</sup> = 7 x 10 <sup>-10</sup> AsO <sub>4</sub> <sup>3-</sup> = 3 x 10 <sup>-10</sup> PO <sub>3</sub> <sup>3-</sup> = 3 x 10 <sup>-10</sup> Fe(CN) <sub>6</sub> <sup>3-</sup> = 4 x 10 <sup>-6</sup> S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> = 10 <sup>-5</sup> SCN <sup>-</sup> = 3 x 10 <sup>-5</sup> CN <sup>-</sup> = 2.5 S <sup>2-</sup> in traces only	Double junction Bridge solution 1.0M KNO <sub>3</sub>
<b>Nitrate</b> <b>NO<sub>3</sub><sup>-</sup></b>	Liquid ion exchange	10 <sup>0</sup> - 5.10 <sup>-5</sup> M (10 <sup>-5</sup> with careful calibration)	Cl <sup>-</sup> = 9.4 x 10 <sup>-3</sup> Br <sup>-</sup> = 5 x 10 <sup>-2</sup> F <sup>-</sup> = 10 <sup>-6</sup> I <sup>-</sup> = 4.1 NO <sub>2</sub> <sup>-</sup> = 3 x 10 <sup>-2</sup> SO <sub>4</sub> <sup>2-</sup> = 3.5 x 10 <sup>-3</sup> PO <sub>4</sub> <sup>3-</sup> = 10 <sup>-6</sup> ClO <sub>4</sub> <sup>-</sup> = 16.2	Double junction Bridge solution 1M (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>

Table 4: Operating parameters for ion selective electrodes

Electrode	Type	Concentration range	Selectivity ratios	Reference/ Filling solutions
<b>Potassium K<sup>+</sup></b>	Liquid ion exchange	10 <sup>0</sup> - 5.10 <sup>-5</sup> M	Li <sup>+</sup> = 2.1 x 10 <sup>-2</sup> Na <sup>+</sup> = 2.6 x 10 <sup>-3</sup> Rb <sup>+</sup> = 1.9 Cs <sup>+</sup> = 0.38 NH <sub>4</sub> <sup>+</sup> = 0.3 Ca <sup>2+</sup> = 2.5 x 10 <sup>-3</sup> Mg <sup>+</sup> = 1.9 x 10 <sup>-3</sup>	Double junction Bridge solution 0.1M TEACl
<b>Silver Ag<sup>+</sup></b>	Solid state	10 <sup>0</sup> - 10 <sup>-6</sup> M	Hg <sup>2+</sup> in traces only	Double junction Bridge solution 1.0M KNO <sub>3</sub>
<b>Sodium Na<sup>+</sup></b>	Glass	10 <sup>0</sup> - 10 <sup>-6</sup> M	K <sup>+</sup> = 3 x 10 <sup>-2</sup> NH <sub>4</sub> <sup>+</sup> = 2 x 10 <sup>-2</sup> H <sup>+</sup> if PH <sub>2</sub> pNa +3	Double junction Bridge solution 0.1M CaCl <sub>2</sub>
<b>Sulphide S<sup>2-</sup></b>	Solid state	10 <sup>0</sup> - 10 <sup>-5</sup> M	Hg <sup>2+</sup> trace only or absent completely	Double junction Bridge solution 1.0M NaNO <sub>3</sub>
<b>Thiocyanate SCN<sup>-</sup></b>	Solid state	10 <sup>0</sup> - 10 <sup>-5</sup> M	OH <sup>-</sup> = 3 x 10 <sup>-5</sup> Cl <sup>-</sup> = 2.5 x 10 <sup>-3</sup> I <sup>-</sup> = 5 x 10 <sup>-3</sup> S <sup>2-</sup> may be present in traces only	Double junction Bridge solution 1.0M NaNO <sub>3</sub>
<b>Water hardness</b>	Liquid ion exchange	10 <sup>-1</sup> - 10 <sup>-4</sup> M (5 x 10 <sup>-5</sup> with careful calibration)	Na <sup>+</sup> = 2 x 10 <sup>-2</sup> Fe <sup>2+</sup> = 3 x 10 <sup>-3</sup>	Double junction Bridge solution 0.1M KNO <sub>3</sub>

Table 4: Operating parameters for ion selective electrodes (continued)

The following tables describe the range of ions which may be measured using ion selective electrodes and the composition of the recommended Ionic Strength Adjustment Buffers, (I.S.A.B.).

Some species can be determined by both Direct Potentiometry and Potentiometric Titration; the latter will usually give more accurate results.

Species	Direct potentiometry			Potentiometric titration			Minimum Conc. M
	Elec.	pH range	ISAB	Elec.	Titrant	ISAB	
<b>Aluminium</b>				F <sup>-</sup>	NaF	A	10 <sup>-3</sup>
<b>Barium</b>	Ba <sup>2+</sup>	5-9	B				
<b>Bromide</b>	Br <sup>-</sup>	2-12	C	Ag <sup>+</sup>	AgNO <sub>3</sub>	None	10 <sup>-5</sup>
<b>Cadmium</b>				S <sup>2-</sup>	Na <sub>2</sub> S <sub>(5)</sub>	None	10 <sup>-4</sup>
<b>Calcium</b>	Ca <sup>2+</sup>	6-8	B	Ca <sup>2+</sup>	EDTA <sub>(3)</sub>	None	10 <sup>-4</sup>
<b>Chloride</b>	Cl <sup>-</sup>	2-11	C	Ag <sup>+</sup>	AgNO <sub>3</sub>	None	10 <sup>-4</sup>
<b>Cyanide</b>	CN <sup>-</sup>	11-13	D	Ag <sup>+</sup>	AgNO <sub>3</sub>	None	10 <sup>-4</sup>
<b>Fluoride</b>	F <sup>-</sup>	5-8	E	F <sup>-</sup>	La(NO <sub>3</sub> ) <sub>3</sub>	F	10 <sup>-3</sup>
<b>Iodide</b>	I <sup>-</sup>	3-12	C	Ag <sup>+</sup>	AgNO <sub>3</sub>	None	10 <sup>-5</sup>
<b>Lead</b>				Cl <sup>-</sup>	NaCl <sub>(6)</sub>	None	10 <sup>-3</sup>
<b>Lead</b>				S <sup>2-</sup>	Na <sub>2</sub> S <sub>(5)</sub>	None	10 <sup>-4</sup>
<b>Lithium</b>				F <sup>-</sup>	NH <sub>4</sub> F	F	10 <sup>-1</sup>
<b>Magnesium</b> <sub>(1)</sub>	W.H <sub>(2)</sub>	6-8	C				
<b>Mercury</b> <sub>(4)</sub>	I <sup>-</sup>	2-3	G	I <sup>-</sup>	NaI	None	10 <sup>-5</sup>
<b>Nitrate</b>	NO <sub>3</sub> <sup>-</sup>	3-10	K	NO <sub>3</sub> <sup>-</sup>	(Ph <sub>2</sub> Tl) <sub>2</sub> SO <sub>4</sub>	None	10 <sup>-2</sup>
<b>Phosphate</b>				F <sup>-</sup>	NaF	H	5 x 10 <sup>-3</sup>
<b>Potassium</b>	K <sup>+</sup>	3-10	I				
<b>Selenide</b>				Ag <sup>+</sup>	AgNO <sub>3</sub>	J	
<b>Silver</b>	Ag <sup>+</sup>	2-9	C	Ag <sup>+</sup>	NaI	None	10 <sup>-5</sup>
<b>Sulphate</b>				Ba <sup>2+</sup>	BaCl <sub>2</sub>	C	10 <sup>-4</sup>
<b>Sulphide</b>	S <sup>2-</sup>	13-14	J				
<b>Water hardness</b>	W.H <sub>(2)</sub>	5-8	B	W.H <sub>(2)</sub>	EDTA <sub>(3)</sub>	None	10 <sup>-3</sup>

Key: (1) Calcium activity must be removed. (4) Only applicable to mercurous not mercuric salts.  
(2) Water hardness electrode. (5) Adjust to pH 7-9.  
(3) Ethylenediamine tetracetic acid. (6) Heat to 60°C.

Table 5: Range of Ions which may be measured using ion selective electrodes

Note: For composition of ISAB, see Table 6.

Code	Name	Composition	ml/100 ml
A	2M acetate buffer	164.1 g/l CH <sub>3</sub> COONa (A.R.) titrated to pH 4.7 with glacial acetic acid	1
B	4M potassium chloride	300 g/l KCl (A.R.)	2
C	5M sodium nitrate	425 g/l NaNO <sub>3</sub> (A.R.)	2
D	10M sodium hydroxide	400g/l NaOH (A.R.)	1
E	TISAB (Total ionic strength adjustment buffer)	58.5 g/l NaCl (A.R.) 15 g/l CH <sub>3</sub> COOH (glacial) 66g/l CH <sub>3</sub> COONa (A.R.) 1 g/l CDTA (1,2 cyclohexylene diaminetetra-acetic acid)	100
F	Methanol	CH <sub>3</sub> OH (A.R.)	100
G	1M sodium perchlorate	120g/l NaClO <sub>4</sub> (A.R.)	10
H	Lanthanum buffer	Equal volumes of A and 866.0 g/l La(NO <sub>3</sub> ) <sub>3</sub> · 6H <sub>2</sub> O(A.R.)	2
I	10M TEACl	1837.2 g/l tetraethylammonium chloride	1
J	SAOB (Sulphide anti-oxidant buffer)	80g/l sodium hydroxide 320 g/l sodium salicylate 72 g/l ascorbic acid	100
K	2M ammonium sulphate	264.3 g/l (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> (A.R.)	2

Table 6: Composition of recommended ionic strength adjustment buffers

## SECTION 5: Applications

Ion Selective Electrodes are being used today in a wide range of applications and new uses are constantly being reported in the literature. Coloured or opaque solutions, or solutions full of suspended or colloidal matter, are equally suited to ion selective electrode analysis.

The following list is a brief survey of some of the major applications in which electrodes have been used.

### Agriculture

- a) Determination of nitrate, potassium, calcium and chloride in soils.
- b) Analysis of additives in animal feedstuffs.
- c) Analysis of plant materials for nitrate, potassium, chloride, fluoride, iodide, cyanide and calcium.
- d) Measurement of nitrate content of fertilisers.

### Biomedical and clinical laboratories

- a) Determination of various species including calcium, potassium, chloride in serum, blood, plasma and other body fluids. Electrodes are particularly suitable as they monitor ion activity which is considered to be more biologically significant than concentration.
- b) Analysis of fluoride in skeletal structures.
- c) Investigation of fluoride in dental studies.
- d) Sweat chloride measurement as a screening test for cystic fibrosis.

### Paper and pulp

- a) Sulphide is measured at every stage of the pulping and recovery cycle in liquors, as well as in mill effluents.
- b) Analysis of chloride in pulping liquors.

### Pollution monitoring

Levels of cyanide, fluoride, sulphide and chloride can be measured in effluents, natural waters and waste-matters. The use of electrodes for continuous, unattended and trouble-free monitoring makes them increasingly suitable for pollution monitoring.

### Detergent manufacture

- a) The measurements of calcium, water hardness and barium can be used to study the effects of detergents on water quality.

## **Education and research**

- a) Electrode of all types are being used as sensors in many experiments to study reaction mechanisms, kinetics, equilibria, activity coefficients and solubilities.
- b) Electrodes are simple and inexpensive enough to be used by undergraduates as part of analytical chemistry training.
- c) Electrodes are particularly suitable for nuclear applications since they are unaffected by radiation and can be remotely operated. Fluoride finds wide application in fuel reprocessing solutions.

## **Explosives**

Fluoride, chloride and nitrate have been measured in explosives and their combustion products.

## **Food processing**

- a) Determination of nitrate and nitrite in meat preservatives.
- b) Determination of salt content of meat, fish, milk, dairy products, fruit juices, beer and brewing water.
- c) Analysis of fluoride in drinking water, mineral drinks, fish protein, tea, beer and brewing water.
- d) Measurement of calcium in milk and dairy products and beer.
- e) Determination of potassium in fruit juices and wine-making.
- f) Monitoring the potential corrosive effect of nitrate in canned foods.
- g) Determination of water hardness in brewing water.

## **Metallurgy and electroplating**

- a) Analysis of etching baths for fluoride and chloride.
- b) Measurement of sulphate and aluminium in anodising baths.
- c) Monitoring of urinary fluoride concentrations in people involved in the extraction of aluminium.

## Examples of suggested methods

The following table outlines methods for the measurement of various ions in a number of media using ion selective electrodes.

Ion	Matrix/Sample	Electrode	Method	Sample preparation
<b>Aluminium</b>	Metals, alloys, solutions	Fluoride	Potentiometric titration with sodium fluoride	Dissolve sample (if solid) in HCl. Adjust pH to 4 with acetate buffer. Either end-point titration or titration to a fixed potential.
<b>Ammonia</b>	Biological materials	Ammonia	Direct or standard addition	Extract or macerate with 0.1M HCl; add NaOH to pH 11 or more.
<b>Ammonia</b>	Waters: Natural Waste Sea Fish tanks	Ammonia	Standard addition	Adjust pH to 11 with 10M NaOH. Spike with NH <sub>4</sub> Cl.
<b>Ammonia</b>	Boiler feed water	Ammonia	Direct	Add NaOH to exceed pH 11.
<b>Ammonia</b>	Beer	Ammonia	Standard addition	Adjust to pH 11 with NaOH.
<b>Arsenic</b>	As As <sup>3+</sup> In solution	Redox	Titration with potassium permanganate	
<b>Bromide</b>	Biological fluids	Bromide	Direct	
<b>Bromide</b>	Soils and plant materials	Bromide	Direct	Extract with 2M sodium nitrate.
<b>Bromide</b>	Wines	Bromide	Standard addition	Add buffer solution of H <sub>3</sub> PO <sub>4</sub> and KNO <sub>3</sub> .
<b>Cadmium</b>	Aqueous solutions	Cadmium	Direct or standard additions or titration with EDTA	
<b>Calcium</b>	Milk	Calcium	Standard addition	Dissolve in 0.1M sodium nitrate.
<b>Calcium</b>	Gastric juices	Calcium	Standard addition	
<b>Calcium</b>	Soils	Calcium	Direct	Extract dry soil using sodium acetate pH 8.2. Filter or centrifuge and use clear liquor.
<b>Calcium</b>	Sugar solutions	Calcium	Standard addition or direct	Standards and spiking solution should be made up in sucrose solution.
<b>Calcium</b>	Waters	Calcium	Direct	Use KNO <sub>3</sub> as ionic strength adjuster.

Ion	Matrix/Sample	Electrode	Method	Sample preparation
Calcium	Wines	Calcium	Standard addition	Dry ash sample and dissolve residue in HCl. Adjust pH to 6.5-7.0.
Chloride	Boiler feed water	Silver	Differential potentiometry	Add 5M nitric acid to sample water.
Chloride	Food samples	Chloride	Direct	Disperse sample in hot HNO <sub>3</sub> .
Chloride	Sugar solutions	Chloride	Direct or titration with silver nitrate	Prepare samples in sucrose background.
Chloride	Lubricating oils	Chloride	Direct	Extract with water after oxidation of sulphides adjust ionic strength with KNO <sub>3</sub> .
Chloride	Plant tissue	Chloride	Titration with acidified silver nitrate.	Shake sample in nitric acid.
Chloride	Serum	Chloride	Sample addition	Add to acidified chloride standard.
Chloride	Sea water	Chloride	Direct	Calibrate the electrodes in artificial sea water.
Chloride	Soils	Chloride	Direct or by silver titration	Leach oven dried samples with distilled water.
Chloride	Sweat	Chloride	Direct	
Chloride	Biological fluids	Chloride	Direct or titration	
Chloride	Pharmaceutical products	Chloride	Direct or titration	
Chloride	Electroplating baths	Chloride	Direct or titration	
Chloride	In sugar refining process	Chloride	Titration	Potentiometric titration.
Cyanide	Plating baths (brass)	Cyanide	Direct for total cyanide	Pass through ion-exchange column to remove Cu <sup>2+</sup> + Zn <sup>2+</sup> .
Cyanide	Waste water	Cyanide	Direct	Add KAg(CN) <sub>2</sub> indicator buffer.
Cyanide	In biological systems	Cyanide	Direct	
Cyanide	In atmosphere, drinking water and industrial waste	Cyanide	Direct	Covers the range 270 µg/ml to 270 mg/ml. Sulphide interferes with the measurement.
Cyanide	In pharmaceutical products	Cyanide	Direct or titration	Measurement at pH 11.
Fluoride	Air and stack gases	Fluoride	Direct	Collect fluoride on filter papers, extract with water and dilute with TISAB.

Ion	Matrix/Sample	Electrode	Method	Sample preparation
Fluoride	Bone	Fluoride	Direct	Dissolve ashed bone in HCl neutralise, buffer to pH 4.0.
Fluoride	Cement	Fluoride	Direct	Add acidified alum to sample, boil, dilute with water, add sodium citrate buffer.
Fluoride	Dental plaque	Fluoride	Direct	Dry sample, suspend in perchloric acid, add sodium citrate buffer.
Fluoride	Detergents	Fluoride	Known addition	Dilute with citrate buffer.
Fluoride	Drinking and natural waters	Fluoride	Direct	Dilute sample 1:1 with TISAB.
Fluoride	Faeces	Fluoride	Direct	Homogenize sample and ash aliquot at 550°C. Dilute 1:1 with TISAB.
Fluoride	Milk	Fluoride	Direct	Prepare samples in milk with TISAB.
Fluoride	Plant tissue	Fluoride	Direct	Fuse sample with CaO, fuse with Na <sub>2</sub> CO <sub>3</sub> /ZnO extract with water. Dilute with citrate buffer.
Fluoride	Saliva	Fluoride	Direct	Dilute 1:1 with TISAB.
Fluoride	Sea water	Fluoride	Direct	Dilute with TISAB. Calibrate in artificial sea water.
Fluoride	Serum and biological fluid	Fluoride	Direct	Ash with MgCl <sub>2</sub> /Na <sub>2</sub> CO <sub>3</sub> . Diffuse fluoride from ash at room temp. Neutralise.
Fluoride	Soils	Fluoride	Direct	Distil 2-5 g sample in perchloric acid/silver perchlorate, add TISAB to distillate.
Fluoride	Teeth	Fluoride	Direct	Dissolve in perchloric acid, add sodium citrate.
Fluoride	Toothpaste	Fluoride	Direct	Add water to paste mixture, use deoxygenated water for Stannous Fluoride samples.
Fluoride	Urine	Fluoride	Direct	Dilute 1:1 with TISAB.
Fluoride	Vegetation	Fluoride	Known addition	Digest dried samples in 2M KOH. Bring to pH 1.8 with H <sub>3</sub> PO <sub>4</sub> and HCl.
Fluoride	Waste water	Fluoride	Direct	Dilute 1:1 with TISAB.
Fluoride	Wine	Fluoride	Known additions	Add TISAB to sample.

Ion	Matrix/Sample	Electrode	Method	Sample preparation
<b>Iodide</b>	Feeds and plants	Iodide	Direct	Add hot water to ground dried sample, stir, cool, add 10% phosphate solution to adjust ionic strength.
<b>Iodide</b>	Pharmaceuticals and bile, not approved in vitro or in vivo diagnostic	Iodide	Direct	Adjust sample pH to 9-11 with sodium hydroxide, add aluminium metal (preactivated by boiling in sodium hydroxide) to reduce iodate use to iodide.
<b>Iodide</b>	Vitamins, minerals	Iodide	Direct	
<b>Iodide</b>	Organic and biological substances	Iodide	Direct	
<b>Iodide</b>	$I^{131}$ isotope in milk	Iodide		
<b>Iodide, Cyanide</b>	Mineral waters, comparative examinations of different compounds	Iodide	Direct	$10^{-3}$ - $10^{-6}Ml$ .
<b>Magnesium</b>	Natural and sea waters	Cadmium	Indicator titration with EDTA	Dilute sample 1 + 1 with ammonium hydroxide, add Cd EDTA indicator solution.
<b>Nitrate</b>	Baby foods	Nitrate	Direct	Remove interference with ion exchange resins.
<b>Nitrate</b>	Fertilisers	Nitrate	Direct	Extract with dilute $H_2SO_4$ .
<b>Nitrate</b>	Meat	Nitrate	Direct	Grind sample in a blender with distilled water, centrifuge, decant, measure supernatant.
<b>Nitrate</b>	Plant tissue	Nitrate	Direct	Extract ground, dried, sample, filter.
<b>Nitrate</b>	Sea water	Nitrogen Oxide ( $NO_x$ ) (nitrite) ( $NO_2$ )	Direct as $NO_2^-$	Reduce nitrate to nitrite, acidify.
<b>Nitrate</b>	Sewage	Nitrogen Oxide ( $NO_x$ ) (nitrite) ( $NO_2^-$ )	Direct as $NO_2^-$	Reduce nitrate to nitrite, acidify.
<b>Nitrate</b>	Soils	Nitrate	Direct	Disperse air-dried soil in extracting solution, alternate methods given.
<b>Nitrate</b>	Sugar beets	Nitrate	Direct	Dry sample in forced draft oven, grind, extract Nitrate with silver sulphate solution, filter or centrifuge.

Ion	Matrix/Sample	Electrode	Method	Sample preparation
<b>Nitrate</b>	Water: well and natural	Nitrate	Direct	If low level chloride, no pretreatment.
<b>Nitrate</b>	Foods	Nitrogen Oxide (NO <sub>x</sub> ) (Nitrite) (NO <sub>2</sub> <sup>-</sup> )	Direct	Extract ground sample with H <sub>2</sub> O, add buffer.
<b>Nitrite</b>	Soils	Nitrogen Oxide (NO <sub>x</sub> )	Direct	Add 2 ml acid buffer to 20 ml sample extract.
<b>Nitrite</b>	Water	Nitrogen Oxide (NO <sub>x</sub> ) (Nitrite) (NO <sub>2</sub> <sup>-</sup> )	Direct	Add 2 ml acid buffer to 20 ml sample.
<b>Potassium</b>	Fertilizer	Potassium	Known addition or direct	Extract pulverized fertilizer in acetate buffer at pH 4-4.5.
<b>Potassium</b>	Saliva (not approved for in vitro or in vivo diagnostic use)	Potassium	Sample addition	
<b>Potassium</b>	Serum	Potassium	Direct	Automated system can be used.
<b>Potassium</b>	Soils	Potassium	Direct	Mix dried, pulverized sample 1 + 1 with water, let stand 2 hours, filter.
<b>Potassium</b>	Urine (not approved for in vitro or in vivo diagnostic use)	Potassium	Sample addition	
<b>Potassium</b>	Wines	Potassium	Direct	Dilute 1 + 9 with water.
<b>Silver</b>	Low levels	Silver/Sulphide	Direct	Add anhydrous sodium nitrate.
<b>Silver</b>	Cyanide plating baths	Silver/Sulphide	Known addition of potassium silver cyanide complex	Dilute 1:100 or 1:1000.
<b>Silver</b>	Photographic fixing solution	Silver/Sulphide	Know addition of potassium silver	
<b>Sodium</b>	Plant tissue	Sodium	Direct	Extract with ISAB.
<b>Sodium</b>	Sea water	Sodium	Direct or sample addition	Calibrate electrodes in artificial sea water. No preparation necessary for sample addition.
<b>Sodium</b>	Serum	Sodium	Direct	
<b>Sodium</b>	Soluble saccharin	Sodium	Direct	Dissolve tablet in distilled water, adjust to pH 9 with ammonium hydroxide.

Ion	Matrix/Sample	Electrode	Method	Sample preparation
<b>Sodium</b>	Water-high purity for boilers	Sodium	Direct	
<b>Sodium</b>	Wine	Sodium	Direct	Dilute sample 1 + 9 with dilute ammonium hydroxide.
<b>Sulphate</b>	Natural waters	Lead	Titration with lead	Dilute 1 + 1 with methanol.
<b>Sulphate</b>	Watts nickel bath	Lead	Sample subtraction	Add sample to a reagent of 1:1 methanol/water containing known concentration of lead and 10-5M formaldehyde background.
<b>Sulphide</b>	Cigarette smoke	Silver/ Sulphide	Direct	Scrub smoke with solution of 0.2M Ascorbic acid in 2M NaOH, dilute 1 + 1 with water.
<b>Sulphide</b>	Natural waters	Silver/ Sulphide	Direct	Collect sample according to ASTM procedure D-510, dilute 1 + 1 with SAOB, filter if necessary.
<b>Sulphide</b>	Proteins	Silver/ Sulphide	Titration with silver nitrate	Dissolve sample in water or dilute nitric acid, reduce to thiol with NaBH <sub>4</sub> and EDTA, heat, acidify to pH 3.
<b>Sulphide</b>	Sediments	Silver/ Sulphide	Gran's plot titration with Cd(NO <sub>3</sub> ) <sub>2</sub>	Mix with SAOB, disperse ultrasonically.
<b>Sulphide</b>	Soils	Silver/ Sulphide	Direct	
<b>Sulphide</b>	Water	Silver/ Sulphide	Direct	Use buffer containing EDTA, NaOH; and ascorbic acid.
<b>Sulphide</b>	Wood chips	Silver/ Sulphide	Direct	Extract with 25% SAOB for 3 hours, add 0.5 g sodium sulphite to 3 ml solution.
<b>Thiocyanate</b>	Thiocyanate (SCN <sup>-</sup> )	Thiocyanate	Various	
<b>Thiocyanate</b>	Black nickel solution	Thocyanate	Direct	Dilute 10 ml sample to 100 ml, add 2 ml concentrated sulphuric acid
<b>Water hardness</b>	Water hardness (Ca <sup>2+</sup> , Mg <sup>2+</sup> )	Water hardness	Direct	Buffer to pH 8.

Table 7: Application methods for ion selective electrodes

## SECTION 6: Ion selective electrode systems

### Fault finding

This section deals with the types of problem that may be encountered with ISE equipment or difficulties with samples.

#### A) Equipment

Most of the pH/Ion analysers available have either a self test procedure (if microprocessor controlled) or a test procedure outlined in the manufacturer's manual which accompanies the instruments.

#### B) Reference electrode

Without doubt the reference electrode junction is the most frequent source of instability or drift. Should a large junction potential develop, it is normally due to a clogged junction or the use of an inappropriate filling solution. The junction potential may be tested by substituting a reference electrode, known to be functioning properly, in place of the questioned reference electrode.

#### C) Ion selective electrode

The most common source of error is that the slope of the electrode is incorrect. The test described here assumes a properly functioning pH meter and reference electrode. Observe the potential change between  $10^{-4}\text{M}$  and  $10^{-3}\text{M}$  standard solutions. The potential change or slope should be at least 52mV for a monovalent electrode and 22mV for a divalent electrode to consider it functioning properly.

#### D) Samples

Great care must be taken during sample preparation to avoid incorrect and unrepresentative results being produced:

Symptom	Probable cause
Low values	(i) Air oxidation of analyte (ii) Loss of gas sample (iii) Sample not preserved properly
High values	(i) Glassware is contaminated and is contributing to low level samples (ii) Interferences present (iii) Ionic strength adjustment not performed on sample
High or low values	(i) ISAB, decomplexing or pH adjustment needed (ii) Sample temperature varied (iii) Standards are contaminated

Table 8: Factors leading to incorrect sample results

## Troubleshooting guide

### A) Meter reading offscale or over-range

Table 9 shows the possible cause and the corrective procedure to be taken when the meter reading is offscale or digital display over-range shown.

Component	Possible cause	Procedure
<b>pH/Ion meter</b>	Instrument malfunction	Initiate self test function or test. Standardise according to manufacturer's instructions.
<b>Reference electrode</b>	Not filled Electrode junction blocked or dry Test junction potential.	Fill with appropriate filling solution. See manufacturer's instructions for unclogging.
<b>ISE (exchangers)</b>	Defective sensor	Test electrode span with standard solutions.
<b>ISE (all types)</b>	Defective body or cable	Using an ohmmeter verify continuity of inner cable and open circuit between inner and outer conductors.
<b>ISE (gas sensor)</b>	Insufficient internal filling solution Defective inner body	Add appropriate fill solution, recharge using new membrane. Verify proper operation.
<b>Sample</b>	Potential out of range	Recalibrate or dilute sample.

Table 9: Factors leading to offscale sample readings

### B) Low slope values

The major reasons for the generation of low slope values in ISE determinations are outlined below.

Component	Possible cause	Procedure
<b>ISE (exchangers)</b>	Poisoned module Defective module	Soak overnight in appropriate standard. Test electrode span with standard solutions. Replace module.
<b>ISE (gas sensors)</b>	Membrane failure Defective inner body	Replace membrane. Verify proper operation by reference to manufacturer's instructions.
<b>Solutions</b>	Standards contaminated or incorrectly made Presence of interferences ISAB not used Standard used as ISAB	Prepare fresh standards. Remove interference. Use appropriate ISAB.

Table 10: Factors leading to low electrode slope values

### C) Unstable readings

The possible causes of unstable readings and the steps that should be taken for rectification are given below in Table 11.

Component	Possible cause	Procedure
pH/Ion meter	Instrument malfunction	Initiate self test function or test. Standardise according to instructions.
	Stirrer not earthed	Earth meter on stirrer.
Reference electrode	Junction dry or clogged	See manufacturer's instructions for unclogging. Test junction potential.
ISE (exchangers)	Air bubble on membrane	Remove bubble by agitation.
	Module not secure	Tighten module to finger tightness.
	Insufficient filling solution	Add appropriate filling solution.
	Bottom cap loose	Secure the cap.
Sample	ISAB not used	Use recommended ISAB.
Stirrer drift	Tip of probes too close to magnetic field of stirrer	Use more solution. Move electrodes away from stirrer bar.

Table 11: Factors leading to unstable sample readings

### D) Wrong answer

Wrong answers are usually a function of the solutions used or the calculations being performed. These problems may be overcome by operating the procedures given in Table 9.

Component	Possible cause	Procedure
Solutions	Complexing agent in sample	Use standard addition titration or decomplexing procedure.
	Interfering ions present	Remove interferents.
	"Bad samples"	Be sure preservative and ISAB are added to sample.
Manual Calculations	Incorrect scaling of lin/log paper	Verify proper procedure.
	Wrong units used	Apply correct conversion factor.
	Incorrect sign	Wrong sign used for $\Delta E$ or S in calculations.

Table 12: Factors leading to incorrect sample readings

### E) Drift

Drift is one of the most common faults associated with ISE determinations and can be caused by a variety of factors. Table 13 lists these factors and outlines how the fault may be eliminated.

Component	Possible cause	Procedure
<b>pH/Ion meter</b>	Instrument malfunction	Initiate self test function or test. Standardise according to instructions.
<b>Reference electrode</b>	Incorrect fill solution	Use appropriate fill solution.
<b>ISE (solid state)</b>	Membrane dirty, oxidised or etched	Polish membrane.
	Membrane leakage	Replace membrane.
<b>ISE (gas sensor)</b>	Internal filling solution leakage	Verify proper assembly.
	Incorrect internal solution	Refill outer electrode body.
	Membrane failure	Replace membrane.
	Defective inner body	Verify proper operation. See manufacturer's instructions.
<b>ISE (exchangers)</b>	Unseasoned or poisoned module	Soak overnight in appropriate standard.
<b>Samples</b>	Incorrect pH	See recommended pH values.
	Glassware contribution to trace level	Use plastic disposable labware.
	Samples and standards at different or changing temperatures	Allow solution to come to room temperature before measurement.
	Gas evolution due to level of dissolved species being too high	Dilute solution.
	Loss of gas over a period of time	Use beakers that reduce surface area to volume ratio, use slower stirring rate and avoid high temperatures.

Table 13: Factors leading to experimental drift

### F) Wildly erratic readings

Wildly erratic readings are generally caused by the factors listed in Table 11. The source of the error should be firstly isolated and then corrected using the methods outlined.

Component	Possible cause	Procedure
pH/Ion meter	Instrument malfunction	Initiate self test function or test. Standardise according to instructions.
	Poor connection inside lead connectors	Repair or replace plug.
Reference electrode	Incorrect fill solution	Use recommended filling solution.
ISE	Air bubble trapped inside membrane unit or outside on the surface of the membrane	Remove air bubble.
Samples	Excessively violent stirring	Slow down stirring rate.

Table 14: Factors leading to erratic readings

## SECTION 7: Conditioning, maintenance and storage

### Electrode conditioning

On receiving an ion selective electrode, the following conditioning steps should be carried out to ensure successful, experimental ion measurement.

#### 1. Glass body electrode

Inspect the glass bulb and body for damage. For combination electrodes ensure that the level of reference electrolyte is above the reference element. Soak the glass bulb in a solution of the appropriate ion ( $10^{-1}\text{M}$ ) for an hour. Check that the electrode potential remains constant, when measured against a double-junction reference electrode. If constant, the electrode is ready for use. If not, repeat the soaking procedure and retest.

#### 2. Solid state ion selective electrode

The electrode should be inspected for damage, particularly to the highly polished membrane which forms the sensing end of the electrode. Place the electrode with its sensing end in a solution of the appropriate ion ( $10^{-1}\text{M}$ ) for about two hours or until the electrode potential, when measured against a double-junction reference electrode, remains constant. Overnight soaking is recommended. After this conditioning the electrode is ready to use.

Contamination of these electrodes is caused by relatively small concentrations of poisons (for example,  $10^{-7}\text{M}$   $\text{Hg}^{2+}$  will poison a silver ISE). Strong reducing agents should be avoided for halide electrodes as these agents reduce the silver of the silver halide crystal.

#### 3. Polymer membrane ion selective electrode

Prior to use the electrode should be inspected for damage, particularly to the delicate, membrane which forms the sensing end of the electrode. Remove the membrane cap and add the specific internal filling solution. Remove air bubbles from inside the membrane unit and reconnect it to the electrode body. Any sign of solution seeping around the membrane indicates a damaged membrane unit and a replacement should be fitted.

High concentrations of interfering ions will poison the electrode. The exposure of the membrane to organic solvents will strip the ion exchanger from the membrane and destroy the electrode.

#### 4. Gas sensing type

Inspect the electrode body and membrane cap for damage. Add filling solution to the membrane cap and ensure that all bubbles are removed. Connect the membrane cap to the electrode body. Check for electrolyte leakage from the membrane cap. Carry out an electrode potential check to ensure that a constant reading is obtained from a standard solution.

## Maintenance and storage

To ensure optimum electrode performance, the Ion Selective electrodes must be maintained and stored correctly. Table 16 lists the procedures for short and long term storage.

Electrode type	Short term	Long term
<b>Glass body electrode</b>	Immerse glass bulb in lowest standard solution. Do not allow glass bulb to dry by exposure to air.	Wash with distilled water. Replace protective cap, containing a few drops of internal filling solution, to ensure that glass bulb remains wet.
<b>Solid state (Crystalline membrane)</b>	Store in lowest standard solution used during analysis. Protect from scratching and abrasion.	Wash with distilled water. Dry. Replace protective cap to prevent damage to ion selective membrane. The electrode membrane surface should be kept shiny by polishing it occasionally with a soft cloth or fine abrasive.
<b>Liquid ion exchange</b>	Store in lowest standard solution.	Wash with distilled water. Dry. Return to packing container to prevent damage to membrane.
<b>Gas sensing type</b>	Wash with distilled water. Dry. Immerse electrode in 0.05M $\text{NH}_4\text{Cl}$ to prevent drying of membrane.	Remove membrane module. Rinse electrode body with distilled water. Dry. Store electrode and module in packing container.

Table 16: Storage procedures for ion selective electrodes

### Double-junction reference electrode

For optimum electrode performance, a new electrode should be soaked before use. Remove wetting cap and open the side filling apertures. Fill outer salt bridge two-thirds full with appropriate non-interfering electrolyte. Soak complete electrode in a beaker of 4M KCl overnight. For short-term storage, place the electrode in a beaker containing the type of salt bridge solution being used. For longer term storage, discard salt bridge solution. Flush outer salt bridge with distilled water and place it in a beaker of distilled water for a few minutes to flush ceramic junction. Dry outer salt bridge. Replace the wetting cap, filled with filling solution, and close the side filling aperture. Store in a cool place.

Always ensure that the level of the inner reference filling solution is covering the internal element. Fill the inner electrode via the side aperture with the correct filling solution. Filling solution has a tendency to creep and encrust the exterior of the inner electrode with salt. This in no way harms the electrode, but it should be removed periodically with distilled water for maximum accuracy and to prevent contamination of the bridge solution. Closing the inner electrode side filling aperture when not using the electrode will reduce the tendency of the salt to creep over the surface of the electrode.

## SECTION 8: Standard solutions for ISE analysis

The ability to determine ionic constituents in any sample matrix depends upon the quality of the standard solutions that have been used to calibrate the measuring system. The inability to prepare accurate standard solutions leads to erroneous analytical results. The aim of this section is to inform the analyst of the standard solutions that should be used with each ion selective electrode.

### The range of standards

The most commonly used technique in ISE analysis is direct potentiometry. The preparation of standards for this analysis is carried out by preparing a concentrated stock solution of the ion determinant (usually by dissolving a salt). From this stock solution a range of standards of decreasing concentration are prepared by serial dilution. The concentration range of these standards must be sufficiently wide to accommodate the expected sample concentration. Table 17 outlines the recommended concentrations of stock solution covering the most widely used ion selective electrodes.

Electrode		Salt	Stock solution
Ammonia	NH <sub>3</sub>	NH <sub>4</sub> Cl	1,000 ppm
Bromide	Br <sup>-</sup>	NaBr	10,000 ppm
Calcium	Ca <sup>2+</sup>	CaCl <sub>2</sub> .2H <sub>2</sub> O	1,000 ppm
Chloride	Cl <sup>-</sup>	NaCl	1,000 ppm
Cyanide	CN <sup>-</sup>	KCN	1,000 ppm
Fluoride	F <sup>-</sup>	NaF	1,000 ppm
Iodide	I <sup>-</sup>	NaI	10,000 ppm
Nitrate	NO <sub>3</sub> <sup>-</sup>	KNO <sub>3</sub>	1,000 ppm
Potassium	K <sup>+</sup>	KCl	1,000 ppm
Silver	Ag <sup>+</sup>	AgNO <sub>3</sub>	1,000 ppm
Sodium	Na <sup>+</sup>	NaCl	1,000 ppm
Sulphide	S <sup>2-</sup>	Na <sub>2</sub> S.9H <sub>2</sub> O	Saturated

Table 17: Stock solutions

## Preparation of stock solutions

1. Ensure that the chemical to be used is of analytical reagent grade. Use class A glassware.
2. For complete accuracy it may be necessary to dry the salt before weighing. Heating in an oven for 1 hour at 110°C is usually sufficient for most salts (but the melting point of the solid must not be exceeded).
3. Accurately weigh the dried salt on a balance with an accuracy of  $\pm 0.0005$  g. Use a weighing boat or glass beaker.
4. Place the weighing boat into the top of a volumetric flask. Wash the salt into the flask using deionised water. If any salt or salt solution is lost, the standard should be discarded.
5. If a glass beaker is used, the salt should be transferred into the volumetric flask via a wide mouthed glass funnel. Ensure that the weighing vessel is rinsed thoroughly.
6. Stopper the flask and mix by inversion. Ensure that all of the solid is dissolved. Remove the stopper and dilute to the mark with deionised water.
7. Replace the stopper and mix the stock standard thoroughly by inversion. Label the flask clearly.

## Serial dilution

When a range of standards of decreasing concentration are to be prepared, the technique of serial dilution is performed. When direct potentiometry is being performed it is recommended that four standards are prepared. Each should be ten times less concentrated than the last (e.g. 1000, 100, 10 and 1 ppm).

1. Using a volumetric pipette extract 10 ml of the stock standard (e.g. 1000 ppm sodium). Pipette into a clean 100 ml volumetric flask.
2. Dilute to the mark with deionised water. Stopper and mix thoroughly by inversion. Label the flask 100 ppm sodium.
3. Extract 10 ml of the 100 ppm sodium standard and pipette into a clean 100 ml volumetric flask. Repeat step 2 and label the flask 10 ppm sodium.
4. Extract 10 ml of the 10 ppm sodium standard and pipette into a clean 100 ml volumetric flask. Repeat step 2 and label the flask 1 ppm sodium.

## ppm stock solutions and Molar equivalents

A list of stock solutions was given in Table 17. Details of their preparation is given in Table 18. The Molar equivalents of these ppm stock standards are listed for reference.

Stock standard	Preparation	Molar equivalent
1,000 ppm NH <sub>3</sub>	Dissolve 3.146 g NH <sub>4</sub> Cl in deionised water and dilute to 1,000 ml. (See Note 1).	0.0588M NH <sub>4</sub> <sup>+</sup>
10,000 ppm Br <sup>-</sup>	Dissolve 12.88 g NaBr in deionised water and dilute to 1,000 ml.	0.1258M Br <sup>-</sup>
1,000 ppm Ca <sup>2+</sup>	Dissolve 3.668 g CaCl <sub>2</sub> ·2H <sub>2</sub> O in deionised water and dilute to 1,000 ml.	0.0249M Ca <sup>2+</sup>
1,000 ppm Cl <sup>-</sup>	Dissolve 1.648 g NaCl in deionised water and dilute to 1,000 ml.	0.0282M Cl <sup>-</sup>
1,000 ppm CN <sup>-</sup>	Dissolve 2.505 g KCN in deionised water and dilute to 1,000 ml.	0.0385M CN <sup>-</sup>
1,000 ppm F <sup>-</sup>	Dissolve 2.21 g NaF in deionised water and dilute to 1,000 ml.	0.0526M F <sup>-</sup>
10,000 ppm I <sup>-</sup>	Dissolve 11.81 g NaI in deionised water and dilute to 1,000 ml.	0.0788M I <sup>-</sup>
1,000 ppm NO <sub>3</sub> <sup>-</sup>	Dissolve 1.631 g KNO <sub>3</sub> in deionised water and dilute to 1,000 ml.	0.0161M NO <sub>3</sub> <sup>-</sup>
1,000 ppm K <sup>+</sup>	Dissolve 1.91 g KCl in deionised water and dilute to 1,000 ml.	0.0256M K <sup>+</sup>
1,000 ppm Ag <sup>+</sup>	Dissolve 1.575 g AgNO <sub>3</sub> in deionised water and dilute to 1,000 ml.	0.0093M Ag <sup>+</sup>
1,000 ppm Na <sup>+</sup>	Dissolve 2.56 g NaCl in deionised water and dilute to 1,000 ml.	0.0435M Na <sup>+</sup>
Saturated S <sup>2-</sup>	Add approximately 100 g Na <sub>2</sub> S·9H <sub>2</sub> O to 100 ml deionised water. Stopper and shake well. Allow to stand overnight (see Note 2)	Saturated S <sup>2-</sup>

Table 18: Preparation of stock solutions

Note 1 This corresponds to a 1059 ppm solution of NH<sub>4</sub><sup>+</sup>. Before analysis the addition of 10M NaOH (1 ml to 100 ml sample) converts the solution to 1,000 ppm NH<sub>3</sub>.

Note 2 To prepare stock sulphide solution pipette 1 ml of the saturated solution into 50 ml of Sulphide Anti-Oxidant Buffer (see Table 6) and dilute to 100 ml with deionised water. The concentration of this stock solution must then be determined by electrode titration using either 0.1M lead perchlorate or 0.1M cadmium nitrate as titrant.

## SECTION 9: Glossary of terms

### Absolute mV

A mode of operation of a pH/mV meter or ISE analyser in which the actual potential of the electrode is displayed. In this mode the calibration control, sometimes referred to as the asymmetry control, does not change the readings.

### Accuracy

A measure of the closeness of a result to the theoretical value.

### Activity

The effective amount of a free ion in solution. The chemical effectiveness of an ion is influenced by the amount and type of other ions in the solution, so that varying the solution composition makes a fixed concentration of a given ion more or less "active". In dilute solutions, ionic activity and concentration are practically identical, but in solutions containing many ions, activity may differ from concentration by as much as a factor of five. Ionic activity, not concentration, determines both the rate and the extent of chemical reactions.

### Activity coefficient

A factor which relates the activity to the concentration of a species in solution, such that:

$$A_x = F_x \cdot C_x$$

where:  $A_x$  = Activity of the species x

$C_x$  = Concentration of the species x

$F_x$  = Activity coefficient of the species x

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

### Anion

A negatively charged ion ( $\text{Cl}^-$ ,  $\text{S}^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{CO}_3^{2-}$ , etc.)

### Calibration

A process of normalising electrode output by measuring a series of two or more known concentration solutions. The ion analyzer then calculates the offset and slope characteristics of the electrode and uses them to compute the concentration of unknown samples.

## Calibration curve

A plot of electrode potential versus activity in two or more standardising solutions. Unknown sample activity is determined by converting electrode potential to activity using the curve.

## Cation

A positively charged ion ( $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{NH}_4^+$ , etc.)

## Complexing agent

Any species that combines with an ion to form an undissociated species; the resulting complex stays in solution and does not precipitate. Complexing agents are used as titrants and to bind ions that may interfere with direct measurements. For example hydrogen ions complex fluoride and acetate ions, and ammonia complexes with copper and cadmium.

## Concentration

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

## Decomplexing agent

A species that is added to a solution to liberate bound ions. The decomplexing agent is a strong complexing agent for the species binding the ions, and is added in excess in order to free all the complexed ions. Examples of decomplexing agents are CDTA, which liberates fluoride complexed to aluminium, and NaOH, which liberates  $\text{CN}^-$  from HCN and  $\text{S}^{2-}$  from  $\text{H}_2\text{S}$  and  $\text{HS}^-$  (CDTA-1.2 cyclohexylene diaminetetra acetic acid).

## Dilution

The effect of changing the concentration of a species in solution by the addition of a solvent. Note that a 1:10 dilution means 1 volume of original solution plus 9 volumes of the solvent.

## Divalent ion

A doubly charged ion ( $\text{Ca}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{S}^{2-}$ , etc.)

## Drift

A slow change in the measured potential of an electrode pair. When the electrode system reaches equilibrium the drift should be nominal and within defined limits.

## Electrolyte

A substance which ionizes in aqueous solution; or a solution containing ions. Weak electrolytes are only slightly dissociated into ions in solution (acetic acid) and strong electrolytes are highly dissociated (HCl, NaCl). Strong electrolytes are good conductors of electricity, and conductance measurements correlate with electrolyte strength.

## Filling solution

Solutions inside sensing or reference electrodes which are replenished periodically. The composition of the reference electrode filling solution, which connects the reference element to the sample, is chosen to maximise stability of the potentials developed at the reference element to filling solution interface and the filling solution to sample junction.

## Interference

The effect, of any species in the sample solution, that causes either a positive or negative measurement error. Electrode interference can result from any species, other than the ion being measured, which changes the sensing electrode potential. In glass and ion exchange electrodes, interferences are "mistaken" by the electrode for the ion of interest and, a positive error results. In solid-state electrodes the interference reacts chemically with a constituent of the sensing membrane resulting, in either positive or negative errors, or electrode failure. Electrode function can usually be restored by cleaning the membrane surface. Method interference may be caused by any species in the sample solution that precipitates, complexes, oxidizes or reduces the ion being measured. Interference effects may be minimised by appropriate sample preparation.

## Ionic strength

This is a measure of the effective concentration of ions in solution. It is calculated according to the following formula:

$$\text{Ionic strength} = \frac{1}{2} \sum_{x=1}^n C_x Z_x^2$$

where:  $C_x$  = the concentration of ion  $x$ ;

$Z_x$  = the charge of ion  $x$ ;

$n$  = the number of species present in the solution.

The ionic strength determines the activity coefficient of each ion in the solution. Conductivity measurements give an estimate of ionic strength.

## **Ionic strength adjustment buffer (ISAB)**

A solution of high ionic strength used to dilute samples and standard solutions. The ISAB minimises differences in ion strength from solution to solution, making the activity coefficient of the ion approximately the same in all solutions. Multi-purpose ISAB's may contain pH adjusters, decomplexing agents or species that remove interferences. Examples of such solutions are Total Ionic Strength Adjustment Buffer (TISAB) for fluoride measurements and Sulphide Anti-Oxidant Buffer (SAOB) for sulphide measurement.

## **Ion meter**

A meter that converts the mV potential developed between an ion selective electrode and double-junction reference electrode, to a concentration value. It is programmed with direct concentration and incremental technique modes of operation to give the analyst greater experimental flexibility.

## **Known addition**

A method for determining the concentration of an ion by adding a known volume of standard to the sample. The electrode potentials of the sample before and after addition are compared.

## **Monovalent ion**

An ion with a single positive or negative charge, e.g.  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ , etc.

## **Nernst equation**

The response of an electrode varies with respect to the logarithm of the activity of the measured ion. The Nernst equation is a mathematical description of the electrode behaviour.

$$E = E_0 + \frac{2.3RT}{nF} \cdot \log A$$

- where:
- E = Total potential, in mV, developed between the sensing and reference electrodes.
  - $E_0$  = The sum of the junction potentials in the electrode pair. This will vary with the choice of reference electrode.
  - R = The gas constant 8.314 joules/deg/mol.
  - T = The temperature of the solution in degrees Kelvin.
  - n = The charge of the ion including sign.
  - F = The Faraday constant, 96,500 coulombs.
  - A = Activity of the ion measured.

## **pH electrode**

An ion selective electrode, made of glass, that responds to hydrogen ion activity. pH electrodes function over the activity range  $1\text{ M H}^+$  (pH 0) to  $10^{-14}\text{ M H}^+$  (pH 14). Special purpose electrodes are made for very acidic or very alkaline solutions; solutions containing high levels of other cations; high temperature operation; and industrial and medical applications. pH electrodes may be subject to acid error in strongly acidic solutions and alkaline error caused by a response to sodium or other cations in basic solutions.

## **pH**

A convenient way of expressing hydrogen ion activity, where:

$$\text{pH} = -\log_{10}\text{H}^+$$

Thus a solution of pH 7 has an activity of  $1 \times 10^{-7}\text{ M H}^+$ .

## **pH meter**

A meter that converts the mV potential developed between a sensing and reference electrode pair, to a corresponding pH value.

## **Poisoning**

The chemical conversion of the surface of a solid state electrode to a form which is less responsive to changes in ionic activity. In many cases, electrode function may be restored by physically removing a thin layer of the sensing element or by reversing the poisoning reaction chemically.

## **Precipitation**

The removal of one or more species from solution by forming water insoluble compounds.

## **Precision**

A measure of the reproducibility of a method, when multiple measurements are made on the sample under identical conditions. The observed values may differ from the true values without affecting the precision.

## **Reference electrode**

The half of an electrode pair which provides a constant potential, regardless of the sample composition. The potential developed by a sensing electrode is measured against this reference to give a potential which can be converted to the activity of ion under analysis.

## Reference internal element

The part of a reference electrode which reacts with the filling solution to produce a constant reference potential. The most common element is silver/silver chloride.

## Relative mV mode

A mode of operation of a pH/mV meter in which the displayed electrode potential can be changed by means of the calibration (asymmetry potential) control. After restandardization, this control is used to correct for electrode drift so that readings may be taken without redrawing the calibration curve.

## Reproducibility

A measure of the closeness of replicate measurements on the same sample, using the same measurements technique, under the same conditions. Reproducibility can be limited by many factors, including instrument or electrode stability, loss of the substance being measured during sample operation and contamination.

## Slope

The gradient of the line formed by plotting the change in the electrode response against change in activity of the ion measured. Theoretical Nernstian slope at 25°C is 59.16 mV per decade change in activity for a monovalent ion and 29.58 mV per decade change for a divalent ion. Slope values are often stated in % efficiency terms (an ideal slope of 59.16 mV for a monovalent ion = 100% slope efficiency). Slope values of less than 90% efficiency may be indicative of electrode contamination. However, many other factors will contribute to a loss of system performance.

## Solubility

The concentration of a given species dissolved in a solvent when the solution is saturated with respect to that species. Solubility depends on the nature of the solute and the solvent, temperature and, for gases, pressure. Solubility is measured at 25°C and expressed in g/l solvent.

## Spiking

The process of adding a known amount of the ion being measured to a sample in order to determine the original sample concentration by the known addition technique, or to determine the accuracy of a direct measurement technique.

## Total ionic strength adjustment buffer (TISAB)

A reagent used in measuring total fluoride concentration. It contains a sodium acetate/acetic acid buffer to liberate fluoride bound to hydrogen and CDTA or citrate to liberate fluoride from aluminium, iron and other cations. It stabilises the fluoride ion activity coefficient by its high ionic strength.

## Titrant

A reagent containing a species that either complexes or liberates the species being determined. An ideal titrant should react instantaneously, completely, and stoichiometrically with the species being determined. The titrant is added in measured increments from a burette and the sample concentration determined from the amount of titrant needed for complete reaction.

## Titration

A quantitative analytical technique for measuring the concentration of a species by incremental addition of a reagent (titrant) containing a species that either complexes or liberates the sample species.

## Trivalent ion

An ion with three positive or negative charges, e.g.  $\text{PO}_4^{3-}$ ,  $\text{Al}^{3+}$ .

## Troubleshooting

The process of determining which part of a system is responsible for a problem.

## Units of concentration

Units of number, volume, or weight of a substance dissolved in a given volume or weight of solvent, e.g.:

- grams per litre (g/l) - the weight in grams of a species dissolved in a litre of solvent;
- parts per million (ppm) - the weight of a species in a given volume of solvent, (e.g. mg per litre);
- moles per litre (mol/l) - the atomic weight of a species dissolved in a litre of solvent.
- equivalents per litre (Eq/l) - the equivalent weight of a species per litre of solvent. The equivalent weight is the weight in grams of a species which will react with one gram of hydrogen or eight grams of oxygen. (This is not an S.I. unit);
- %Volume/Volume (%V/V) - the percentage of the total volume contributed by the volume of the species added to the solution;
- %Weight/weight (%W/W) - the percentage of the total solution weight contributed by the weight of the dissolved species.

## NOTES

## NOTES