3.1 General Principles

An ion-selective electrode (ISE) is an indicator electrode that responds (produces a potential) when it is placed in a solution containing a certain ion. There is now a large variety of ion-selective electrodes available which selectively respond to particular cations and anions, and certain gases; pH electrodes are by far the best known. These may be utilised for many novel and diverse applications in chemical analysis.

All ISEs have a basic similarity in their design: the ion-sensing part consists of a membrane (which may be plastic, glass or an ionic crystal) which has sites which are capable of adsorbing the analyte ion. On either side of the membrane is a solution containing the ion of interest: one of these is the test solution, the other is a standard solution within the electrode itself. Inside the electrode body there is an electrical connection – a wire or a reference electrode – to monitor the response from the membrane. This is shown in Figure 3.1.

The ion-sensing membrane has sites on each surface where the analyte ion can bind in an equilibrium process: the higher the concentration of ions in solution, the more sites will be occupied. When the electrode is placed in a different solution, the number of adsorbed ions will change. This does affect the new solution, but by an undetectable amount. This is shown in Figure 3.2.

### Class Exercise 3.1

*Which solution has the higher analyte concentration in Figure 3.2?*

<table>
<thead>
<tr>
<th>the internal solution or test solution 1</th>
<th>test solution 1 or test solution 2?</th>
</tr>
</thead>
<tbody>
<tr>
<td>test solution 1 or test solution 2?</td>
<td>test solution 1 or test solution 2?</td>
</tr>
</tbody>
</table>
The difference in the number of sites on the inner and outer surface of the membrane causes a voltage that is related to the difference in concentration between the two solutions, as shown in Equation 3.1. You should be able to see how the Nernst equation is behind this equation.

\[ E_{ISE} = K + \frac{59}{n} \log_{10}[X] \]  

_**Eqn 3.1**_

where \( E_{ISE} \) is the potential of the ISE in millivolts, \( K \) a constant, \( n \) the charge of the analyte ion and \([X]\) the activity of the analyte.

We do not use this equation to determine analyte concentration, for the same reasons that the original Nernst equation could not be used: junction potentials and activity variations. The only practical uses for this equation are that:

- there is a straight-line relationship between voltage and log (concentration), which we will use in the quantitative analysis section later
- the \((59/n)\) term describes the slope of this straight line, and is used as measure of how well the electrode is actually working; \(59/n\) is known as the **theoretical sensitivity**, while the graph slope is the **working sensitivity**; the sensitivity is the change in millivolts for a 10 x time change in concentration

**Class Exercise 3.2**

*What is the theoretical sensitivity of the following ISEs?*

<table>
<thead>
<tr>
<th>ISE</th>
<th>Ion charge</th>
<th>Theoretical sensitivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>+1</td>
<td>(59 + +1 = +59)</td>
</tr>
<tr>
<td>fluoride</td>
<td></td>
<td></td>
</tr>
<tr>
<td>sodium</td>
<td></td>
<td></td>
</tr>
<tr>
<td>sulfide</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

An ISE functions like any indicator electrode – it must be connected to a **voltmeter** together with a **reference electrode** to complete the cell, and produce a useful result. You may think of pH electrodes, and how they don’t seem to need either a voltmeter or a reference electrode! However, that isn’t the case: a pH meter is just a specialised voltmeter, and most modern pH electrodes are designed with their own inbuilt reference electrodes.

### 3.2 Electrode Errors

The S in ISE stands for selective, not specific. This means that the electrode is designed (via its membrane) to respond to one ion. However, none are perfect, so will respond to other ions, generally of a similar charge – for example, the pH electrode responds to \(H^+\), of course, but also weakly to other \(1^+\) ions, particularly Na\(^+\). Some ISEs are more prone to these **electrode errors**: the error caused by the extra response from a matrix ion.

The degree to which a particular ISE will respond to other ions is documented in the manufacturer’s specification for the ISE, so you get advance warning of what might cause problems. There is a numerical measure of the level of interference for each matrix species, so it can be determined whether a particular sample matrix will cause problems. This value is called the **selectivity coefficient**, and in simple terms, the smaller the value, the less the error. A more detailed listing of selectivity coefficients for common electrodes is given in the section covering the types of electrodes in use. However, Table 3.1 here lists those for the nitrate ISE.
TABLE 3.1 Selectivity coefficients for the nitrate ISE

<table>
<thead>
<tr>
<th>Matrix ion</th>
<th>Selectivity coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>perchlorate</td>
<td>1000</td>
</tr>
<tr>
<td>iodide</td>
<td>40</td>
</tr>
<tr>
<td>bromide</td>
<td>0.1</td>
</tr>
<tr>
<td>nitrite</td>
<td>0.1</td>
</tr>
<tr>
<td>chloride</td>
<td>0.03</td>
</tr>
</tbody>
</table>

CLASS EXERCISE 3.3

Which matrix ion causes the most error in the measurement of nitrate?

What does the value of the selectivity coefficient mean? It means that the electrode is *that many times as responsive to the interferent ion as the analyte ion*. For example, the nitrate ISE responds 1000 times more strongly to perchlorate than nitrate. In fact, the nitrate ISE would be better marketed as a perchlorate ISE!!

Equation 3.2 estimates how much extra “analyte” would be detected by the presence of a given interferent. The example below shows how the selectivity coefficient can be used to estimate errors (if approximate levels of the various species known).

Extra electrode response = sel. coefficient x matrix ion conc.  
*Eqn 3.2*

EXAMPLE 3.1

*A nitrate ISE is used to measure the concentration of effluent, where the typical levels of analyte are 5 mg/L, and the only significant interferent is chloride, at levels of 10 mg/L. How much error is caused by the matrix?*

Extra response = 0.03 x 10 = 0.3 mg/L

Therefore, the electrode “sees” an extra 0.3 mg/L of “nitrate” that is really due to the chloride. Therefore, the nitrate result would be 5.3 mg/L. The relative error is equal to 100 x 0.3 / 5 = 6% in error.

CLASS EXERCISE 3.4

(a) *What relative error is caused to a measurement of 20 mg/L nitrate by 0.1 mg/L of iodide?*

(b) *For nitrate samples of around 10 mg/L, what is the concentration of perchlorate that gives a relative error of 5%?*
Errors can also be caused by the analyte ion not being sensed by the ISE, because it is not in the correct chemical form. ISEs can only respond to the free, dissociated ion: if it is bound to something else in a complex or a weak acid/base, then it cannot be detected. These are called method errors, and are generally much easier to deal with, than the electrode errors. Normally sample treatment is all that is required to “free” up the analyte: a change in pH or addition of a species that breaks up a complex. We will cover sample treatment in detail in a later section.

3.3 Applications Of Ion-Selective Electrodes

Ion-selective electrodes are used in all areas of chemical analysis. The most common is, of course, the pH electrode, which responds to free H⁺. Other common used electrodes are for fluoride, nitrate, calcium, chloride, sodium and carbon dioxide. Many others are available.

The most significant advantages of analysis by ISE are:

- **relative cheapness** – typically $500-800,
- **portability** - for analysis in the field or placement in situ for continuous measurement of water,
- **limited sample preparation** for solutions - in some cases the sample is totally unchanged,
- **wide working range** - typically 1-10⁻⁵ M: accuracy decreases at the high end of the range since activity diverges significantly from concentration, and at the lower end due to solubility of the membrane or response to other species,
- **ability to analyse very small samples** – chloride ISE has been used to test perspiration as it emerges on this skin, and
- **ability to analyse difficult species** – H⁺ and fluoride are not readily analysed at low levels by other methods

These advantages have meant that ISEs have become extremely valuable analytical tools in the last thirty years. They are widely used for analysis in the environmental, food, health, medicine and biochemical areas. There are however some problems associated with their use, including:

- **non-specificity** – causing the electrode to respond to other species,
- **slow response times** – in some cases, up to ten minutes before each reading can be taken,
- **limited lifetime** – typically twelve months,
- **response limited to free ions** – complexed or otherwise bound ions do not produce any response, and
- **response governed by ion activity not concentration** – the response from two solutions with the same analyte concentration can be different due to different levels of background electrolyte
- **limited accuracy** – apart from the pH electrode, other ISEs are accurate to no more than ±5%

Some electrodes are less prone to problems than others, and certain samples cause less problems. The decision to use an ISE is very much case-by-case, but their convenience makes indispensable for field testing. For accurate analysis of alloying elements, such as copper or zinc, in steel an atomic absorption spectrophotometer would be a better choice, but for calcium in milk, an ISE would be at least as good as an AAS, though sample preparation to free the calcium from complexes would still be needed.

Rapid-response ISEs are used as indicator electrodes in potentiometric titrations, as discussed in the previous chapters. The most common is the pH electrode, but the Ca and Cl electrodes are also used for this purpose.

3.4 Quantitative Analysis

Because of the various errors, such as activity differences and junction potentials, Equation 3.1 can’t be used for single measurements of potential to determine concentration. The electrode must be calibrated with standards of known concentration before accurate results can be obtained.

With a pH electrode and meter, this normally means adjusting the meter reading to match the standard pH values. With some of the newer meters, something similar can also be done with other electrodes, where the concentration value for a number of standards is entered, and the meter calibrates itself internally.
With older meters and electrodes, the reading is in mV, and cannot be calibrated internally. The process is then similar to calibrating a spectrophotometer: record the response, plot a graph, and use this to determine the sample concentrations.

In this case, there is one difference in the graph. Because concentration and voltage are not directly proportional – doubling the concentration does not double the voltage – the calibration graph is a plot of mV versus \( \log_{10}(\text{concentration}) \), as shown in Figure 3.3.

FIGURE 3.3  A typical ISE calibration graph

CLASS EXERCISE 3.5
Plot a calibration graph for the following data form a nitrate ISE.

<table>
<thead>
<tr>
<th>Concentration (mg/L)</th>
<th>log (conc)</th>
<th>mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-225</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>-282</td>
<td>-</td>
</tr>
<tr>
<td>50</td>
<td>-320</td>
<td>-</td>
</tr>
<tr>
<td>-40</td>
<td>-20</td>
<td>-</td>
</tr>
<tr>
<td>-20</td>
<td>-0</td>
<td>-</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>20</td>
<td>0.5</td>
<td>-</td>
</tr>
<tr>
<td>40</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>60</td>
<td>1.5</td>
<td>-</td>
</tr>
<tr>
<td>80</td>
<td>2</td>
<td>-</td>
</tr>
<tr>
<td>100</td>
<td>2.5</td>
<td>-</td>
</tr>
<tr>
<td>120</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>140</td>
<td></td>
<td>-</td>
</tr>
</tbody>
</table>

It was mentioned in Section 3.2 that the slope of the calibration graph for an ISE was equal to the working sensitivity, which is a measure of how well the electrode is working, by comparison with the theoretical sensitivity.

The simplest way to calculate the slope of the graph is shown in Equation 3.3.

\[
\text{Slope of graph} = \text{mV}_{(\log = 1)} - \text{mV}_{(\log = 0)}
\]

Eqn 3.3

EXAMPLE 3.2
(a) Calculate the slope of the calibration graph in Figure 3.3.

The scale is a bit small, but estimating the mV at log = 1 and log = 0 gives 60 and 125, respectively.

Slope = 60 – 125 = - 65.

(b) How well is the electrode working?

It is a fluoride electrode with a theoretical sensitivity of –59, so –65 is not too bad.
CLASS EXERCISE 3.6

*Determine the working sensitivity for the electrode in Exercise 3.5, and assess how well it is working.*

Using a calibration graph to determine the sample concentration is again similar to that for a spectroscopic analysis:

- draw a horizontal line from the mV axis corresponding to the sample value until you reach the calibration graph,
- drop a vertical line to the horizontal axis

The difference comes when you take the value from the horizontal axis. This is not the concentration, but the log of the concentration. To get the concentration that we want, use the antilog or $10^x$ button on your calculator.

EXAMPLE 3.3

*Determine the sample concentration from Figure 3.3.*

The sample response is shown as 40 mV. This gives a log (conc) value on the horizontal axis of about 1.3. This corresponds to a concentration of 20 mg/L ($= 10^{1.3}$).

CLASS EXERCISE 3.7

*A 10.25 g sample of soil is analysed for nitrate using the electrode calibrated in Exercise 3.5. It is extracted into 100 mL of solution and measured with the ISE. The response is –269 mV.

(a) *Determine the concentration of nitrate in the solution.*

(b) *Calculate the mass of nitrate in the sample.*

(c) *Calculate the concentration of nitrate in the soil as mg/kg.*
For more difficult matrices, standard addition is used to reduce error. In practical terms, it is done the same as in any other analysis: add a known amount of analyte to a known amount of sample, and remeasure. Very commonly, a very small volume (e.g., 100 µL) of a concentrated standard is added to the sample, and it is assumed that the volume is unchanged.

The calculations are much different, because of the log relationship between potential and concentration. Instead of a number of standard additions plotted on a graph, a single one is done, and a formula used – Equation 3.4.

$$C_x = \frac{\Delta C}{10^{\frac{\Delta E}{S}} - 1}$$  \hspace{1cm} \text{Eqn 3.4}

where

- $C_x$ is the concentration of analyte (in mg/L) in the analysed sample
- $\Delta C$ is the increase in concentration (in mg/L) due to the standard addition
- $\Delta E$ is the change in electrode potential as a result of the addition
- $S$ is the electrode’s working sensitivity

**Notes**

1. $\Delta E$ and $S$ must be the same sign – both positive or both negative, otherwise the equation fails.
2. $\Delta C$ is calculated by the dilution equation $C_1V_1 = C_2V_2$, where $C_1$ and $V_1$ refer to the aliquot of added standard, $V_2$ is the sample volume and $C_2$ is the result for $\Delta C$

**Example 3.4**

*The free calcium concentration in milk is determined by ISE using standard addition. The response of a 25 mL aliquot of milk is measured at +34 mV. 100 µL of 5000 mg/L Ca is mixed into the sample, and the potential rises to 48 mV. The electrode sensitivity is known to be 31 mV/decade.*

Calculating $\Delta C$:

- $5000 \text{ mg/L} \times 0.1 \text{ mL} = \Delta C \times 25 \text{ mL}$
- $\Delta C = 20 \text{ mg/L}$

$$\Delta E = \text{mV}_\text{after} - \text{mV}_\text{before}$$
- $= 48 - 34$
- $= 14$

Substituting into Eqn 3.4

$$C_x = \frac{20}{10^{\frac{14}{31}} - 1} = 10.9 \text{ mg/L}$$
**CLASS EXERCISE 3.8**  
The fluoride concentration in soil was analysed by standard addition using an ISE, which had been previously calibrated, given a sensitivity of –54.

10.0374 g of soil was mixed with water, filtered and made up to 100 mL. A 25 mL aliquot of this solution was prepared for measurement, giving a result of –234 mV. A 200 µL of 1000 mg/L standard was added, and the solution re-measured, giving a reading of –259 mV.

What is the concentration of fluoride in the soil, in mg/kg?

---

### 3.5 Practical Aspects

Some ISEs exhibit what is known as a **memory effect**. This means that if a low concentration solution is measured immediately after one of a higher concentration, the electrode will give a response which is affected by some ions from the higher concentration solution remaining adsorbed on the electrode membrane. Thus, a misleading result would be obtained. Thus, calibration standards should be measured in **ascending order of concentration**, and samples measured near standards of similar concentration. If the sample has a completely unknown concentration, standard addition could be used, where the problem is eliminated entirely.

**CLASS EXERCISE 3.9**  
*Why does standard addition avoid any memory effect?*

---

As mentioned above, ISEs respond to ion activity, not concentration. Since ionic strength affects activity, all solutions (standards and samples) should have the same ionic strength, which reduces one source of matrix error. One method of doing this is to add a high concentration of electrolyte to each solution. This is known as **ionic strength adjustment (ISA)**, and must be done with an ionic species to which the ISE is completely unresponsive. This also helps to ensure that the junction potential is constant for all solutions. An example is the use of 0.1 M NaCl solutions for Ca ISEs.

**pH levels** are significant in many ISE analyses, since the electrode may be affected or respond to high levels of H⁺ or OH⁻. One of the main interferent ions for the fluoride ISE is hydroxide ion, so pH levels must be kept below 10. However, high H⁺ concentration would cause the formation of HF, which would cause a loss of response. Thus, a buffer solution is required to ensure that all solutions are kept at a certain pH.
3.  Ion-Selective Electrodes

The ISE will only respond to the analyte ion in its **free, unbound form**. Fluoride as HF, Ca as a complex, covalently-bonded chlorine in organic species will all fail to produce a response by their respective ISE. This may be an advantage if the free ion concentration is the required result, but will otherwise give a low result. For example, the calcium in milk as determined by ISE is less than 5% of the total calcium. The interfering matrix must be destroyed or chemically modified to release the analyte ion. In the case of fluoride, a strong ligand such as EDTA (or its close relative, CDTA) is added to form complexes with cations such as aluminium or iron (III) which would otherwise bind the fluoride.

Finally, each electrode has its own characteristic **response time**, during which the sensing membrane interacts with the test solution and reaches equilibrium. pH electrodes are almost instantaneous, whereas for other types of electrodes, it is typically between thirty seconds and five minutes.

### 3.6 Types of Electrodes

There are the three basic types of ion-sensing membranes used in ISEs:
- **glass** – special glass that is sensitive to cations, especially hydrogen ions
- **ionic crystal** – where one of the ions in the compound is the analyte
- **liquid membrane** – a special plastic which is impregnated with a solution of a selective ion-exchange compound

Examples of the latter two classes, and some of their characteristics are given in Tables 3.1 and 3.2.

#### TABLE 3.1 Important crystal electrodes

<table>
<thead>
<tr>
<th>Ion</th>
<th>Working Range $(M)$</th>
<th>pH Range</th>
<th>Interferences (selectivity coefficients)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>$10^{-7} - 10^{-6}$</td>
<td>5 - 9</td>
<td>OH$^-$ (0.1)</td>
</tr>
<tr>
<td>Cl</td>
<td>$10^{-1} - 10^{-5}$</td>
<td>1 - 10</td>
<td>S$^{2-}$, NH$_3$ must be absent; CN$^-$ (400), I$^-$ 20, Br$^-$ (1.2)</td>
</tr>
<tr>
<td>S$^{2-}$</td>
<td>1 - 10$^{-6}$</td>
<td>13 - 14</td>
<td>Hg$^{2+}$ must be absent</td>
</tr>
<tr>
<td>Cu</td>
<td>1 - 10$^{-6}$</td>
<td>1 - 6</td>
<td>Ag$^+$, Hg$^{2+}$ must be absent; Pb$^{2+}$ (0.007)</td>
</tr>
<tr>
<td>I</td>
<td>1 - 10$^{-8}$</td>
<td>0 - 14</td>
<td>S$^{2-}$ (30), CN$^-$ (0.01)</td>
</tr>
</tbody>
</table>

#### TABLE 3.2 Common liquid membrane ISEs

<table>
<thead>
<tr>
<th>Ion</th>
<th>Working Range $(M)$</th>
<th>pH Range</th>
<th>Interferences (selectivity coefficients)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>1 - 10$^{-6}$</td>
<td>3.5 - 12</td>
<td>K$^+$ &amp; Na$^+$ (2-3 x 10$^{-4}$), Sr$^{2+}$ (0.01)</td>
</tr>
<tr>
<td>water hardness (2+ ions)</td>
<td>1 - 10$^{-5}$</td>
<td>2.5 - 11</td>
<td>K$^+$ &amp; Na$^+$ (0.01)</td>
</tr>
<tr>
<td>NO$_3$</td>
<td>1 - 10$^{-5}$</td>
<td>2.5 - 11</td>
<td>ClO$_4^-$ (1000), I$^-$ (40), Br$^-$ &amp; NO$_2^-$ (0.1), Cl$^-$ (0.03)</td>
</tr>
<tr>
<td>K</td>
<td>1 - 10$^{-5}$</td>
<td>2.5 - 11</td>
<td>Cs$^+$ (1), H$^+$ &amp; Na$^+$ (0.01)</td>
</tr>
</tbody>
</table>
The **pH electrode**

Glass is an non-crystalline three-dimensional arrangement of SiO$_4$ (silicate) joined by the sharing of one oxygen between pairs of groups. Glasses vary by the nature of the cations (most commonly Na and Ca) which are present to balance the negative charge of the silicate. These cations are not tightly bound and can be replaced by others, particularly at the glass surface when immersed in a solution containing certain cations. Most glass electrodes these days are constructed of lithia glass (which contains some Li and Ba in place of Na and Ca). The lithium ions are readily replaced by H$^+$ from solution.

The glass electrode comprises a thin-walled bulb of cation-responsive glass sealed to a stem of non-responsive glass. In this manner, the cation response is confined to the area of the special glass membrane, eliminating any variance caused by the depth of immersion. Glass electrodes are completely indifferent to the presence of anions.

As shown in Figure 3.4, the membrane separates the solution to be measured from a standard HCl solution (saturated in KCl, and AgCl if a Ag/AgCl internal reference electrode is employed) in the bulb (typically 0.1 M), and the potential that develops across the glass membrane is directly related to the difference in concentration of H$^+$ (in solutions of pH < 10 at least). At the centre of the glass electrode is a wire which provides the connection between the voltmeter and the glass membrane.

In most pH electrodes available these days the external reference electrode is physically enclosed with the glass electrode, meaning that only one electrode unit is required.

![FIGURE 3.4 Schematic diagram of a combined pH electrode](image)

In order to function, the membrane of a new glass electrode must be soaked in dilute acid to hydrate the outer layer (typically to the extent of 50-100 mg of water per cm$^2$ of glass). This allows the loosely bound Li atoms to become aquated (complexed with water) and exchange with H$^+$ ions from the surrounding solution. Once this occurs the electrode is fully functional. This outer hydrated layer of the glass undergoes ion exchange with the contact solutions, replacing bound ions with solution H$^+$ until an equilibrium is reached. This produces the measurable electrode response.

Glass electrodes respond to not only H$^+$, but other cations, particularly singly-charged ions, such as Na$^+$. The response is as follows: H$^+$ $>>$ Na$^+$ $>$ K$^+$, Rb$^+$, Cs$^+$ $>>$ Ca$^{2+}$. As a consequence in alkaline solutions, where the hydrogen ion concentration is very low, and normally much less than that of other cations, the electrode will register a higher concentration value than it should, since it is responding to cations other than H$^+$, and therefore give a lower pH value: this is known as the **alkaline error**: at 0.1 M NaOH, the pH would read about 11.7, instead of the true 13.

At the other end of the pH scale, glass electrodes give higher pH values in acidic solutions than should be expected. The reasons for this **acid error** are not understood. The consequences of these so-called alkaline and acidic errors is to limit the usefulness of pH electrodes for accurate measurement: *most glass electrodes are suitable for measurements between pH 1-12*.

The glass electrode is not subject to interferences by redox reagents, but will be affected by HF or strong alkaline solutions, both of which dissolve glass. Prolonged immersion in alkali or non-
aqueous solvents is to be avoided as is leaving the electrode exposed to the air, as these disrupt the hydration of the outer layers. Immersion in 6 M HCl is recommended if the electrode fails to calibrate correctly. If this doesn’t work, a one minute soak in 20%w/w NH₄HF₂ removes a surface layer of the electrode, and will either rejuvenate or ruin it.

**Gas Sensing Electrodes**

These electrodes are capable of monitoring gases molecules in the gas phase, or dissolved in solution. Their name is rather misleading, since the electrode does not detect the presence of a molecular gas, but rather an ion into which the gas is converted after it passes through an outer membrane.

The permeable membrane is the key to the electrode’s gas selectivity. It is made of a hydrophobic porous plastic that prevents water or ions from entering the pores or passing through the membrane. The gas in the sample solution diffuses through the membrane and comes to equilibrium with a liquid film inside the electrode, where it chemically reacts with some substance to form ions. These are detected by an ion selective electrode inside the gas sensing electrode.

Among the commonly used gas sensing electrodes are those for CO₂ and NH₃, which use a pH electrode to measure the change in internal solution pH as a result of the absorption of the acidic CO₂ or basic NH₃. Other electrodes include H₂S and HCN (sulfide solid-state electrode), nitrogen oxides (nitrate or pH electrode), SO₂ (pH electrode) and HF (fluoride).

The filling solution varies from one electrode to another, and may be pH buffered to ensure appropriate reaction of the gas. The pH conditions of the test solution are very important. In many cases, for example ammonia and carbon dioxide, the dissolved gas may be in the form of ions in the sample if the pH is around 7. Adjustment of the pH will be required to liberate the gas so that it can pass through the electrode membrane. if this may result in loss of analyte, then a closed system is used. The pH of course should be adjusted immediately prior to analysis. The normal calibration requirements (similar matrix, ionic strength) rules are equally important here, because they affect the solubility of the gas.

The electrode should be stored for long periods by removing the membrane and filling solution, but for short-term storage, the electrode should be immersed in a solution the same as the inner solution. The membrane has a limited lifetime, and is readily blocked by solid particles and grease, so it must never be touched with bare fingers.

---

**What You Need To Be Able To Do**

- describe the construction of an ISE
- explain how the ISE responds to the analyte
- describe the general sources of error in the use of ISEs
- define the term selectivity coefficient
- use the selectivity coefficient to estimate errors
- draw and use calibration graphs to determine analyte concentration
- calculate the theoretical and working sensitivity
- determine analyte concentration using standard addition
- explain the practical requirements of using ISEs
- list the three types of sensing membranes
- give examples of each type of electrode
- outline the principles of use of the pH electrode
- explain how gas-sensing electrodes work
3. Ion-Selective Electrodes

Practice Questions
1. Briefly outline how an ion-selective electrode works.
2. What is the theoretical sensitivity of a (a) calcium and (b) nitrate electrode?
3. Describe how the methods of calibration standards and standard addition are applied to analysis by ISE.
4. Determine the concentration of calcium in river water, given the following data.

<table>
<thead>
<tr>
<th>Solution</th>
<th>mV</th>
<th>Solution</th>
<th>mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 mg/L</td>
<td>-21</td>
<td>50 mg/L</td>
<td>+33</td>
</tr>
<tr>
<td>1 mg/L</td>
<td>-17</td>
<td>100 mg/L</td>
<td>+40</td>
</tr>
<tr>
<td>10 mg/L</td>
<td>+12</td>
<td>Sample</td>
<td>+22</td>
</tr>
</tbody>
</table>

5. Calculate the sensitivity for the Ca ISE in Q4, and compare it to the theoretical value.

6. Determine the concentration of nitrate in soil, given the following data: a 1.2812 g sample of soil was dried, and slurried with 75 mL of water to dissolve any nitrate. The mixture was filtered into a 200 mL volumetric flask, 100 mL of 0.2 M sodium sulfate for ionic strength adjustment, and made up to the mark. Compare the sensitivity to the theoretical value.

<table>
<thead>
<tr>
<th>Solution</th>
<th>mV</th>
<th>Solution</th>
<th>mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 mg/L</td>
<td>+190</td>
<td>50 mg/L</td>
<td>+85</td>
</tr>
<tr>
<td>10 mg/L</td>
<td>+127</td>
<td>100 mg/L</td>
<td>+69</td>
</tr>
<tr>
<td>20 mg/L</td>
<td>+111</td>
<td>Sample</td>
<td>+91</td>
</tr>
</tbody>
</table>

7. The calcium level in wine was analysed using the ISE from Q4. A 10 mL aliquot of wine was diluted to 100 mL, and the response of a 20 mL aliquot of this measured at 21 mV. A 200 uL aliquot of 250 mg/L Ca standard was added, the solution mixed and re-measured at 29 mV.

8. The response from the nitrate ISE in Q6 for a 25 mL aliquot of river water was -5 mV. A 100 uL addition of 100 mg/L NO₃ decreased the reading by 25 mV. What was the nitrate concentration in mg/L?

9. A 0.1023 g sample of butter was mixed with water to extract the salt, and made up to 100 mL. 25 mL aliquots were pipetted into two 50 mL volumetric flasks, and 0 and 10 mL of 20 mg/L Na added, one addition to each flask and then made up to the mark. The solutions were then measured with a Na ISE, and the responses found to be +11 and +31 mV, respectively. The electrode sensitivity was known to be +55 mV. Calculate the Na concentration in %w/w.

10. Explain the need for pH control, ionic strength adjustment and recording calibration standards from lowest to highest concentrations.

11. Explain the following observations from fluoride ISE measurements, and explain how the error would be corrected:
(a) a 10 mg/L F solution in pure water gives a lower response than 10 mg/L F in 5% NaCl solution.
(b) a sample is measured twice, once before and once after a 100 mg/L standard. The readings are +50, -75, -15 mV, respectively.
(c) A 0.01 mg/L standard and 1 mg/L standard gave a difference in response of 30 mV.

12. What is meant by the term “alkaline error” in terms of a pH electrode?

13. Interferences in ISEs are often given the general terms “method” and “electrode”, which refer to errors due to the sample preparation and errors due to electrode response. Give an example of each type of interference.

14. What percentage error would expected for the following:
(a) potassium electrode: 10 mg/L K, 1 mg/L Na
(b) chloride electrode: 10 mg/L Cl, 1 mg/L Br

15. How do gas-sensing electrodes differ from other ISEs?

16. Comment on the use of an ISE to monitor nitrate levels in waste water from a fertiliser plant.

17. Why would an AAS be better than an ISE for analysis of copper in steel?