Potentiometry: Ion-Selective Electrodes

Determination of the sodium monofluorophosphate content of a toothpaste sample using a fluoride ion-selective electrode.

1. Aims

The aims of the experiment are to:

1.1 Calibrate a fluoride ion-selective electrode (FISE) and determine over what range of fluoride ion concentrations the electrode has a Nernstian response.

1.2 Use the calibrated FISE to determine the amount of sodium monofluorophosphate present in a toothpaste sample, and see if the levels are consistent with the amount reported by the manufacturer.

1.3 Characterise inteferences to the FISE, including interferences from chloride ions, iron (III) ions and pH variations.

2. Background

Ion-selective electrodes are potentiometric electrodes with a high degree of specificity for a single ion or class of ions. They are used in conjunction with a reference electrode and a high impedance voltmeter such as the EA165 pH/mV Amp, to complete the measuring circuit in **Figure 2.1.**
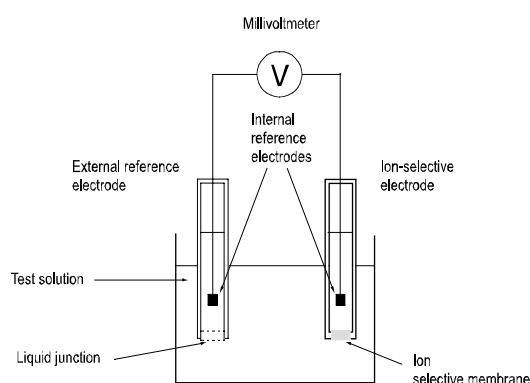

Figure 2.1 Potentiometric measuring circuit

The measured potential (E) of the ion-selective electrode is given by the Nernst equation

$$E = E^0 + \left(2.3\frac{RT}{nF}\right)\log a_i$$

where E^0 (standard potential) is a constant dependant upon the type of measuring and reference electrodes being used, R is the universal gas constant, T is the temperature in Kelvin, F is the Faraday constant, n is the valence of the ion and a_i is the ionic activity of the ion being measured.

The ionic activity, a_i, of a solution is related to the analytical concentration, [i], by the following relationship

$$a_i = \gamma_i\left[i\right]$$

where γ_i is the ion activity coefficient.

In dilute solutions, γ_i is frequently close to unity, thus activity and concentration can often be used interchangeably. However in most analytical situations, γ_i varies significantly from unity, and is principally a function of the ionic strength of the solution.

Ionic strength adjustment buffers are often used in conjunction with an ion-selective electrode to fix the ionic strength of the solution high enough to make the activity coefficients of unknowns and standards virtually identical. These buffers are carefully selected to have a pH that favours the free form of the ion, and often contain complexing agents that preferentially complex with interfering ions, releasing the analyte ion. Adjusting the pH and activity coefficients to optimum and constant values allows the concentration of an ion to be interpreted from measurements of ion activity.

Fluoride ion selective electrodes (**Figure 2.2**) consist of a tube with a lanthanum fluoride (LaF_3) crystal membrane forming an interface between the external solution and the internal electrolyte. The internal electrolyte consists of 0.1 M NaCl, 0.1 M NaF and saturated AgCl, all in contact with the internal Ag/AgCl reference electrode and LaF_3 crystal membrane.
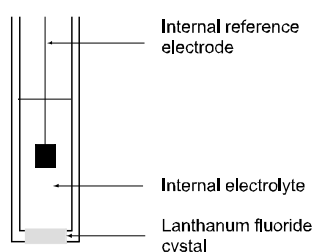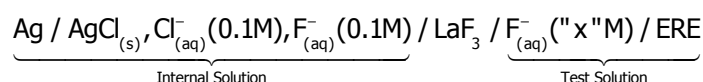

Figure 2.2 Fluoride ion-selective electrode showing lanthanum fluoride membrane and internal electrode construction.

The cell notation for the electrode is:

$$\underbrace{Ag \,/\, AgCl_{(s)}, Cl^-_{(aq)}(0.1M), F^-_{(aq)}(0.1M)}_{Internal\ Solution} \,/\, LaF_3 \,/\, \underbrace{F^-_{(aq)}("x"M)}_{Test\ Solution} \,/\, ERE$$

The overall cell potential is the result of several contributions, but only activity of the fluoride in the test solution is variable. A change in the fluoride ion concentration in the test solution results in a change of potential over the LaF3 crystal membrane. This membrane potential is the result of a dynamic exchange of fluoride ions between both the test solution and internal filling solution, and the crystal membrane. This change in potential is measured in the experiment and calibrated against fluoride ion concentration.

3. Hardware Required

Per Group:

- a computer system
- an e-corder unit
- an EA165 pH/mV Amp
- a fluoride ion-selective electrode with BNC connector
- a Ag/AgCl reference electrode with 4 mm banana plug connector
- 17 x 150 mL polypropylene beakers*
- 19 x 100 mL volumetric flasks*
- 1 x 25 mL pipette
- 1 x 10 mL pipette
- 1 x 5 mL pipette
- 2 x stainless steel spatulas
- a small glass funnel
- a pipette bulb
- a magnetic stirrer with 20 mm stirrer bar
- a retort stand with two boss heads and clamps attached
- a permanent marker pen
- a wash bottle filled with distilled water
- a thermometer

* Less may be used, however they will need to be rinsed thoroughly with deionised water between uses.

Per Class:

- a microwave oven
- oven mitts
- an electronic balance (0.0001 g readability)
- a printer

4. Reagents Required

- a tube of toothpaste with sodium monofluorophosphate as the active ingredient

- sodium monofluorophosphate (Na_2FPO_3)

- 1 M sodium fluoride (NaF) solution

- sodium chloride (NaCl)

- Total Ionic Strength Adjustment Buffer (TISAB)

- 0.2 M potassium nitrate solution (KNO_3)

- distilled water

- 0.01 M iron chloride $FeCl_3$ solution

- 1.0 M HCl solution

- 1.0 M NaOH solution

5. Safety Notes & Instrument Care

- Wear gloves and protective eyewear throughout the experiment

- Take care removing contents from the microwave oven, use the oven mitts supplied

- Avoid spilling liquids on the hardware by mixing reagents away from the units

- Avoid touching the lanthanum fluoride membrane of the FISE

6. Hardware Setup

6.1 Setup the e-corder and EA165 pH/mV Amp as per Instructions in the eDAQ hardware manuals found on the eDAQ installer CD. Connect the Amp to Channel 1 of the e-corder. Connect the FISE to the BNC input of the pH/mV Amp and the reference electrode into the 4 mm socket. The configuration should be warmed up for at least 10 minutes prior to the laboratory session.

6.2 Secure the electrode(s) to the retort stand with the clamps. Place magnetic stirrer unit below the electrodes and set to a medium rate of stirring. The polypropylene cups are placed on top of the unit and secured with another clamp connected to the retort stand.

7. Procedure

7.1. Preliminary Steps

7.1.1 Record the ambient temperature of the laboratory. For best results, all reagents should be equilibrated to the laboratory temperature.

7.1.2 Accurately weigh out around 400 mg of toothpaste in a 150 mL polypropylene beaker (remembering to tare out the mass of the beaker). Record the mass and

make a note of the reported sodium monofluorophosphate content of the brand of toothpaste.

7.1.3 Mix the toothpaste with 50 mL of TISAB and heat in a microwave oven at maximum power for two minutes. Wait for a minute and carefully remove the beaker from the oven.

WARNING: THE CONTENTS WILL BE HOT!

Set aside to cool to room temperature whilst carrying out the calibration of the FISE.

7.1.4 To determine the proportion of fluoride that is liberated from the sodium monofluorophosphate matrix, accurately weigh around 400 mg of pure sodium monofluorophosphate (record the exact weight), transfer powder to a 100 mL volumetric flask, and dilute to the mark with distilled water. Then serially dilute 5 mL of this solution in another 100 mL volumetric flask.

7.1.5 In another 150 mL polypropylene beaker, repeat the steps in **7.1.3** substituting the toothpaste with 5 mL of the sodium monofluorophosphate solution prepared in **7.1.4**.

7.1.6 Calculate and make a note of the theoretical fluoride ion concentration of the solution prepared in **7.1.4**, if 100% of the fluoride bound in the sodium monofluorophosphate matrix is converted to fluoride during the digestion step.

7.1.7 Open Chart software and hide all channels except Channel 1. Use the following settings throughout the rest of the experiment.

Range	200 mV
Sampling Speed	2 /s
Filtering	Select a 1 Hz digital filter in the input amplifier dialog box for the pH/mV Amp
Trigger	Set Chart to record a 5 min block of data when prompted by the user. This should be enough time for the response of the FISE to stabilise. Adjust the recording time if it takes longer than 5 minutes for the signal to stabilise.

7.2. FISE Calibration

7.2.1 From the 1 M NaF top standard, prepare fluoride standards by serial dilution with concentrations of 10^{-1}, 10^{-2}, 10^{-3}, 10^{-4}, 10^{-5}, 10^{-6} and 10^{-7} M. This can be conveniently achieved by diluting 10 mL of the previous higher concentration standard to 100 mL in a volumetric flask.

7.2.2 The fluoride standards should be analysed from least to most concentrated. Pipette 25 mL of the 10^{-7} M standard and 25 mL of TISAB buffer into a 150 mL polypropylene beaker.

7.2.3 Put the stirrer bar into the beaker and place the beaker onto the magnetic stirrer set to a medium rate of stirring. Lower the electrodes into the solution.

7.2.4 Click on the Start button to begin recording a block of data. When the block of data has been recorded, lift the electrodes and the stirrer bar from the solution. Rinse the electrodes and stirrer bar with distilled water and pad dry with lint free tissue. Use the comment function of Chart to make a note of the fluoride concentration with the corresponding block of data.

7.2.5 Repeat steps **7.2.2** to **7.2.4** with the next standard, until all standards have been analysed.

7.2.6 Adjust the view buttons so that all the blocks of data collected for the standards can be seen on the screen. With the mouse, highlight an area that encompasses the voltage response for all the standards. With the area highlighted, select MPCalibration from the Channel Function pop-up menu to display the Multipoint Calibration dialog box.
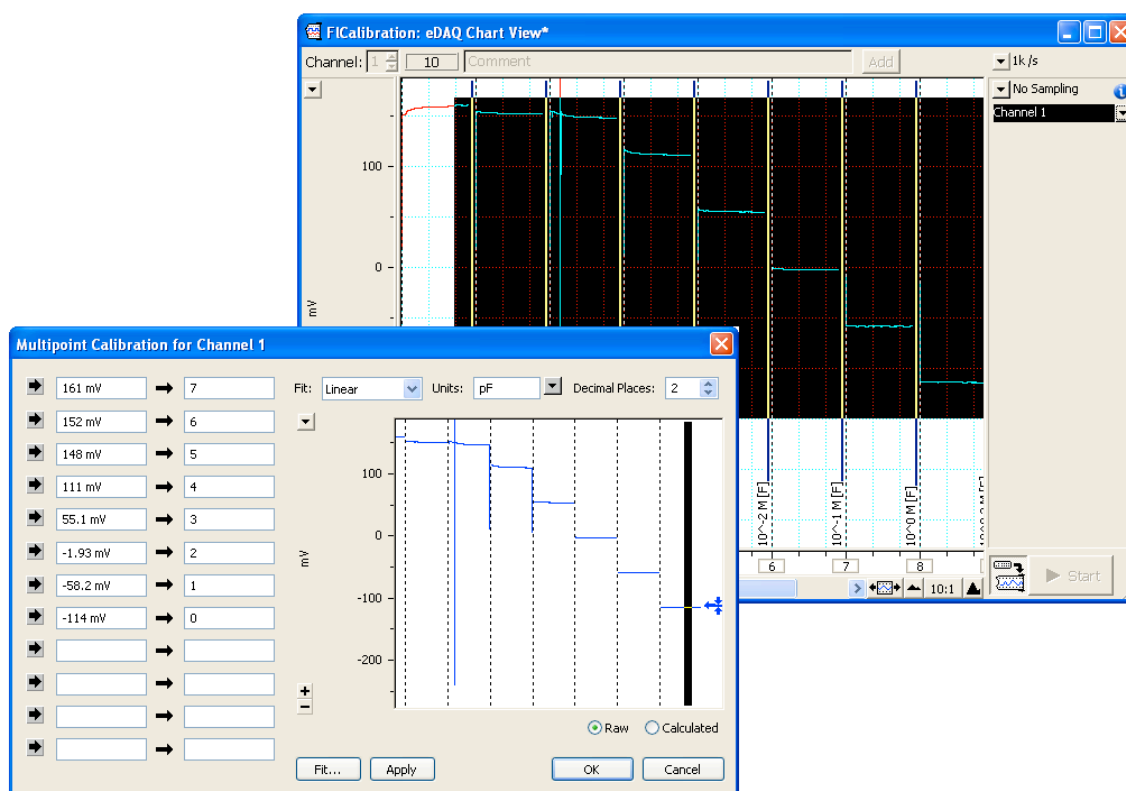

Figure 7.1 Typical electrode response for NaF standards and the Multipoint Calibration dialog box.

7.2.7 For each block of data, highlight a region where the signal has stabilised, i.e. towards the end of the block. With the region highlighted, click on one of the arrows on the far LHS of the Multipoint Calibration dialog box. This enters the average millivolt reading for the selected data into the left hand column. Enter the corresponding pF for that solution in the right hand column. If Chart has not been previously used to measure pF from a FISE, you will need to define the unit pF.

$$pF = -\log\left[F^-\right]$$

7.2.8 Click on the fit button in the Multipoint Calibration dialog box and select a linear fit. Inspect the resulting fitted curve and determine over which range of pF the electrode has a linear response (i.e., Nernstian response). A full fluoride standard range sample is given in **Figure 7.2**. Print the fitted curve over the full standard range for inclusion in your report.
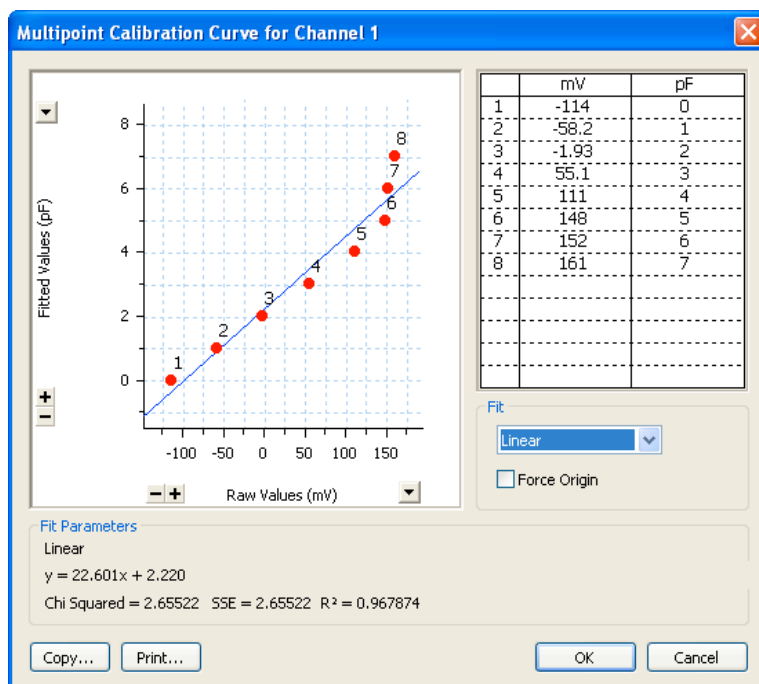

Figure 7.2 Linear fit over the full standard range.

7.2.9 In the Multipoint Calibration dialog box, delete the data points with pF values above which there is no longer a Nernstian response (probably the lowest 2 or 3 fluoride standards) In the case shown in Figure 5, the Nernstian response appeared to break down above a pF of 4 (i.e. [F$^-$] below 10^{-4} M). Click on fit again and inspect the new fitted linear curve for the reduced number of data points. Print the fitted curve over the Nernstian response range for inclusion in your report.
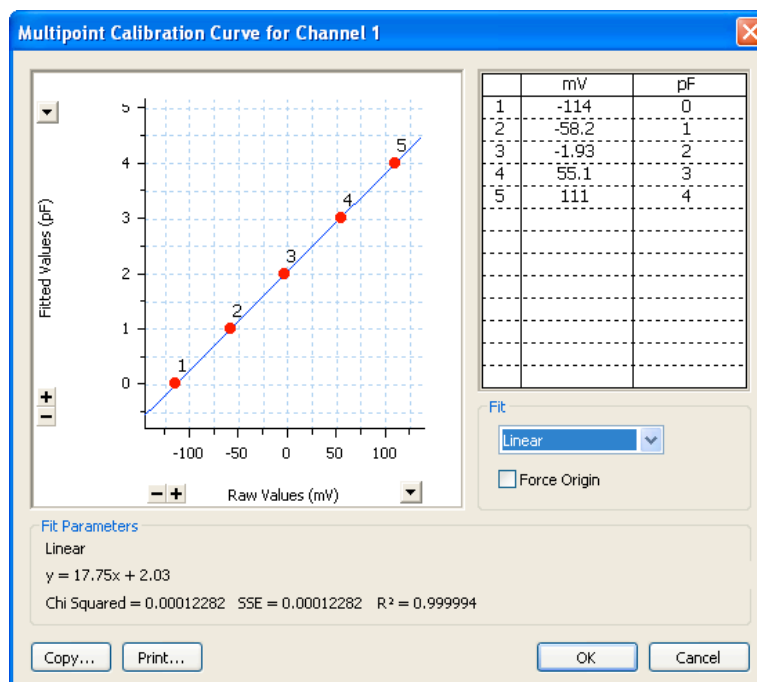
Figure 7.3 Linear fit over the Nernstian range.

7.2.10 Use the Nernst equation to calculate the theoretical FISE Nernstian response and use this value to calculate the percent Nernstian response for the curves obtained in **7.2.8** and **7.2.9**. Note that the slope of the equation in the Multipoint Calibration Fit window is in pF.mV^{-1}. Convert the slope to mV.pF^{-1} to calculate the percent Nernstian response.

$$\text{Hint: Theoretical Nernstian Slope} = \frac{2.3RT}{nF}$$

Upon returning to the Chart window, you will notice that the millivolt traces have been converted to pF traces. Chart has now been calibrated to record pF directly from the FISE.

7.3. Sample Dilution and Analysis

The toothpaste and sodium monofluorophosphate samples prepared in **7.1**, need to be diluted with TISAB prior to analysis.

7.3.1 Quantitatively transfer the cooled toothpaste sample to a 100 mL volumetric flask and dilute to the mark with distilled water.

7.3.2 Repeat steps **7.2.2** to **7.2.4**, substituting the standard with 25 mL of the diluted toothpaste sample. Note the pF value for the toothpaste sample when the electrode response has stabilised. Convert this value into a fluoride ion concentration.

7.3.3 With the sodium monofluorophosphate solution prepared in **7.1.4**. Repeat step **7.3.2** above, substituting the diluted toothpaste sample with 25 mL of sodium monofluorophosphate solution.

7.3.4 Compare the measured fluoride concentration in the sodium monofluorophosphate solution with the theoretical concentration calculated in **7.1.6**. Determine the percentage of fluoride liberated from the sodium monofluorophosphate matrix.

7.3.5 Assume that the percentage of fluoride liberated from the pure sodium monofluorophosphate sample is the same as the percentage liberated from the sodium monofluorophosphate in the toothpaste sample. Using this assumption, the measured fluoride concentration in **7.3.2** and the various dilution factors used throughout the experiment, calculate the sodium monofluorophosphate content of the toothpaste sample.

7.4. Interferences

7.4.1 Pipette 10 mL of the 10^{-1} M NaF standard into a 100 mL volumetric flask. Add 10 g of NaCl, swirl to dissolve and dilute to the mark with distilled water. Repeat steps **7.2.2** to **7.2.4** substituting the standard with 25 mL of the above solution. Report the mV value for the response, and compare with the value obtained for the 10^{-2} M standard in **7.2.4**. Turn off Multipoint Calibration to return to the raw mV recording.

7.4.2 Pipette 10 mL of the 10^{-1} M NaF standard into a 100 mL volumetric flask. To this flask add 5 mL of the Fe^{3+} solution and dilute to the mark with distilled water. Repeat steps **7.2.2** to **7.2.4** substituting the standard with 25 mL of the above solution. Report the mV value for the response, and compare with the value obtained for the 10^{-2} M standard in **7.2.4**.

7.4.3 Pipette 10 mL of the 10^{-1} M NaF standard into a 100 mL volumetric flask. To this flask add 10 mL of the 1 M HCl solution and dilute to the mark with distilled water. Repeat steps **7.2.2** to **7.2.4** substituting the standard with 25 mL of the above solution. Report the mV value for the response, and compare with the value obtained for the 10^{-2} M standard in **7.2.4**.

7.4.4 Pipette 10 mL of the 10^{-1} M NaF standard into a 100 mL volumetric flask. To this flask add 10 mL of the 1 M NaOH solution and dilute to the mark with distilled water. Repeat steps **7.2.2** to **7.2.4** substituting the standard with 25 mL of the above solution. Report the mV value for the response, and compare with the value obtained for the 10^{-2} M standard in **7.2.4**.

7.4.5 Repeat steps **7.4.1** to **7.4.4** substituting the TISAB solution with the 0.2 M KNO_3 solution as the supporting electrolyte. Report the mV value for the response, and compare with the value obtained for the 10^{-2} M standard in **7.2.4**.

8. Results

Brand of toothpaste: _____

Mass of toothpaste: _____ mg,   Reported Na2FPO3 content: _____

Mass of Na_2FPO_3: _____ mg,   100% dissolution concentration: _____ M

Range of FISE Nernstian response: _____ pF

Theoretical Nernstian slope: _____ $mV.pF^{-1}$

Percent Nernstian response of FISE: _____ %

Toothpaste sample solution fluoride concentration: _____ M

Na_2FPO_3 sample solution fluoride concentration: _____ M

% Na_2FPO_3 dissolution: _____ %

Measured Na_2FPO_3 content of toothpaste sample: _____

% Difference between measured and reported fluoride content of toothpaste sample: _____ %

Response 10^{-2} M standard with TISAB   _____ mV

Response 10^{-2} M standard with TISAB and NaCl   _____ mV

Response 10^{-2} M standard with TISAB and 1 M HCl   _____ mV

Response 10^{-2} M standard with TISAB and 1 M NaOH   _____ mV

Response 10^{-2} M standard with 0.2 M KNO_3 _____ mV

Response 10^{-2} M standard with 0.2 M KNO_3 and NaCl   _____ mV

Response 10^{-2} M standard with 0.2 M KNO_3 and 1 M HCl   _____ mV

Response 10^{-2} M standard with 0.2 M KNO_3 and 1 M NaOH   _____ mV

9. Questions

1. What is the Nerstian slope of an ideal pH electrode at 25 °C? Over what range of pH is the response of a pH electrode typically Nernstian? How does this range compare with the Nernstian response range of the FISE?

As the hydronium ion charge is +1, the Nernstian slope is opposite to the slope for a FISE, i.e. 59.160 $mV.pH^{-1}$. pH electrodes typically have a Nernstian response between pH 0 and 14, which is several orders of magnitude wider than the response of a FISE.

2. What is the purpose of using an ionic strength adjustment buffer when measuring fluoride ion concentrations in solution with a FISE? In **7.4.5** what influence does substituting the TISAB with 0.2 M KNO_3 have on the electrode response?

The purpose of the TISAB solution is threefold: to adjust pH to a constant value, to provide a background of constant ionic strength, and to release fluoride from its complexes with a range of metal ions, principally Al^{3+} and Fe^{3+}.

Substituting TISAB with 0.2 M KNO_3 increases interferences due to pH fluctuations, and the presence of Fe^{3+}.

3. To what degree do chloride ions interfere with a FISE signal? Propose a mechanism for the interference.

The presense of an excess of chloride ions causes a slight positive bias in the determination of total fluoride. Fluoride ions preferentially diffuse across the LaF_3 membrane, but other species such as chloride and other halogens do also to a lesser extent.

4. To what degree do Fe^{3+} ions interfere with a FISE signal? Propose a mechanism for the interference.

The addition of Fe^{3+} ions cause a negative bias in the determination of total fluoride. This is because FISE only respond to free fluoride, and Fe^{3+} tends to form complexes with fluoride. This effect is more pronounced in the sample without TISAB, because this reagent includes a much stronger metal complexing agent.

4. How does pH influence the response of the FISE? Propose a mechanism for the interference.

Low pH causes a negative bias, as the free fluoride concentration is reduced by the formation of HF and HF_2^-. High pH causes a positive bias as the hydroxide ion interferes with the LaF_3 membrane. This effect is more pronounced when TISAB is not used.

10. Instructors Notes

10.1 Computer System and Software

A PC (running Windows XP or later) or Mac (running OS X or later) computer with USB support is required. Chart must be installed along with the Multipoint Calibration extension, which is available for download from the eDAQ website:

> http://www.edaq.com/chart_extns_list.html

10.2 Availability of Fluoride Ion-Selective Electrodes

There are many companies that manufacture fluoride ion-selective electrodes. See the pH and ion-selective electrodes page on the eDAQ website for a list of some manufacturers:

> http://www.edaq.com/research_pH.html

The majority of FISE manufactured require an additional external reference electrode. A Ag/AgCl reference electrode is the most practical type to use in this experiment. Some companies manufacture combination FISE, but these tend to be more expensive than the standard type.

A common feature of both types of FISE is a single crystal lanthanum fluoride, LaF_3, membrane, which permits the transport of fluoride ions only. The crystal is doped with europous fluoride, EuF_2, in order to reduce its electrical resistance.

10.3 Potentiometers

This practical has been written assuming a EA165 pH/mV Amp is to be used with a standard FISE and reference electrode, however the EP303 pH Pod can be used with a combination FISEs. Most other standard pH meters with an analog output can also be used in this experiment.

To use the eDAQ pH/mV Amp, the FISE must be fitted with a standard BNC connector, and the reference electrode must be fitted with a 4 mm banana plug.

10.4 Reagents

The following solutions should be prepared prior to the laboratory session in quantities suitable for the size of the class. All reagents need to be prepared in deionised water.

- Total Ionic Strength Adjustment Buffer (TISAB)*

- 1 M NaF solution†

- 0.01 M FeCl3 solution

- 1.0 M HCl solution

- 1.0 M NaOH solution

* To Prepare 1 L of TISAB buffer, boil 500 mL of distilled water in a 1 L beaker, add 57 mL of glacial acetic acid, 58 g of NaCl and 2 g of 1,2–cyclohexlenedinitrotetraacetatic acid (CDTA). Stir

to dissolve solids and cool the solution to room temperature. Adjust the pH to between 5 and 5.5 by adding 5 M NaOH. Quantitatively transfer to a 1 L volumetric flask and fill to the mark.

†Solutions containing fluoride should be stored in polypropylene bottles.

NaCl and sodium monofluorophosphate powder also needs to be available to the class.

11. Bibliography

D. Midgley, and K.Torrance, *Potentiometric Water Analysis*, 2nd Edition.