Potentiometric analysis

Basic principle

An ion selective electrode is an electrochemical device that responds to the presence of a single specific ion in solution. This is a highly selective device.

It generates a potential that follows the Nernst equation.

$$E = E^{o} - \frac{RT}{nF} \ln Q_r \qquad (1)$$

$E°$: standard potential (V)
R: ideal gas constant (8.314 $J.K^{-1}.mol^{-1}$)
Q_r: ratio [product]/[reactant]
T: Ideal temperature (K)
F: Faraday constant (96485 C/mol e^-)
n: mole e^- / mol chemical

Therefore, it provides a potential corresponding to the logarithm of the concentration of the ion. Since two half reactions are required to obtain a potential, the selective ion electrode also needs a reference electrode. When the two are combined together in one single electrochemical device, it is called a "combined electrode". It is the case, for example, for most pH electrodes.

<u>Metal cation electrode having a reversible redox potential in water</u>

The copper ion electrode is one of the simplest example to describe the principle of the ions selective electrode. Figure 1 show an electrochemical setup use to measure the Cu^{2+} concentration in a water sample.

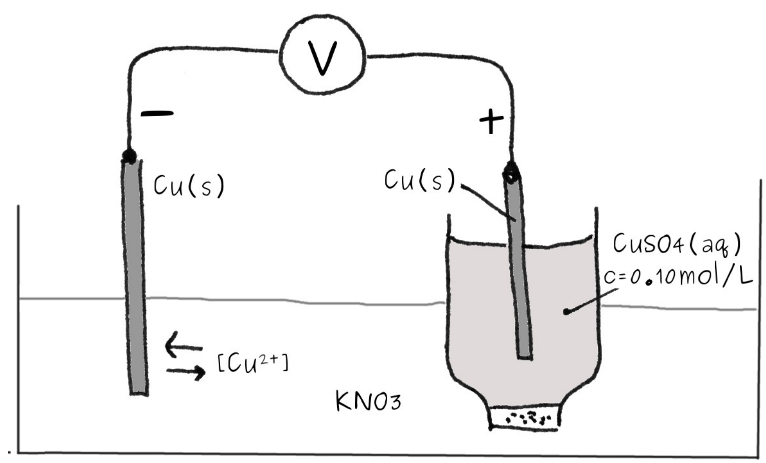

Figure 1. Copper ion selective electrode (left) with a similar electrochemical reference system (right).

This selective electrode works with a reference electrode using the same electrochemical reaction. The line representation for this electrochemical system is given by:

$$Cu(s) \mid Cu^{2+}(aq, c = ?), KNO_3(aq) \mid\mid CuSO_4(aq, c = 0.10\ M) \mid Cu(s)$$

Since the same reaction is present on both electrodes:

Anode (left)	oxidation	$Cu(s) \rightleftharpoons Cu^{2+}(sol) + 2\ e^-$	E° = −0.342 V
cathode (right)	reduction	$Cu^{2+}(ref) + 2\ e^- \rightleftharpoons Cu(s)$	E° = +0.342 V
Complete cell		$Cu^{2+}(ref) \rightleftharpoons Cu^{2+}(sol)$	E°(cell) = 0 V

With $E = E^o - \frac{RT}{nF} \ln Q_r$

Since the sum of the two standard potentials E° cancel out, the equation of this system is:

$$E = \frac{-0.05916\,V}{2} \log \frac{[Cu^{2+}(sol)]}{[Cu^{2+}(ref)]} \quad \text{at 25 °C} \tag{2}$$

Therefore, any change in the Cu^{2+}(sol) concentration by a factor of 10 will also change the electrode potential by 29.6 mV.

Example

The system shown at figure 1 is used to determine the copper ion concentration in an aqueous solution at 25 °C. Use this system to calculate the copper ion concentration [Cu^{2+}], when the potential of the system is 0.148 V.

From equation (2):

$$E = -\frac{0.0592\,V}{2} \log \frac{[Cu^{2+}(sol)]}{[0.10]} \quad \Rightarrow \quad 0.148\,V = -\frac{0.0592\,V}{2} \log \frac{[Cu^{2+}(sol)]}{[0.10]}$$

$$[Cu^{2+}] = \quad (0.10\,\text{mol/L}) \times 10^{(0.148)(-2/0.05916)} \quad = 1.0 \times 10^{-6}\ M$$

An increase in the concentration of the copper ion in the solution will also decrease the potential of the system. Consequently, the system becomes less spontaneous (less positive potential).

At low concentrations, it is reasonable to assume that the activity and concentration are the same. This is why a potentiometric technique is an excellent method for measuring very low concentrations, often on the order of ppm.

To be able to perform a measurement with a stable potential, an electrolyte must be added to increase the conductivity of the solution. Even in the absence current, a highly resistive solution will be sensitive to any electromagnetic disturbance making the potential reading unstable.

Detection of anions (Type II electrode)

It is sometime difficult to measure the concentration of a specific species for practical reasons like ions that produces gas in a redox reaction.

For example, the chloride ion $Cl^-(aq)$ determination is a good example:

$$2Cl^-(aq) + 2e^- \rightleftharpoons Cl_2(g) \quad \text{with} \quad E° = 1.358 \text{ V vs. NHE}$$

Also, the potential of this reaction is close to the water oxidation. Furthermore, chlorine gas is highly corrosive. A system using $Cl_2(g)$ will not be a practical one. In this case, a type II electrode, reversible to this anion, is more appropriate:

$$AgCl(s) + 1e^- \rightleftharpoons Ag(s) + Cl^-(aq) \quad \text{with} \quad E° = 0.222 \text{ V vs. NHE}$$

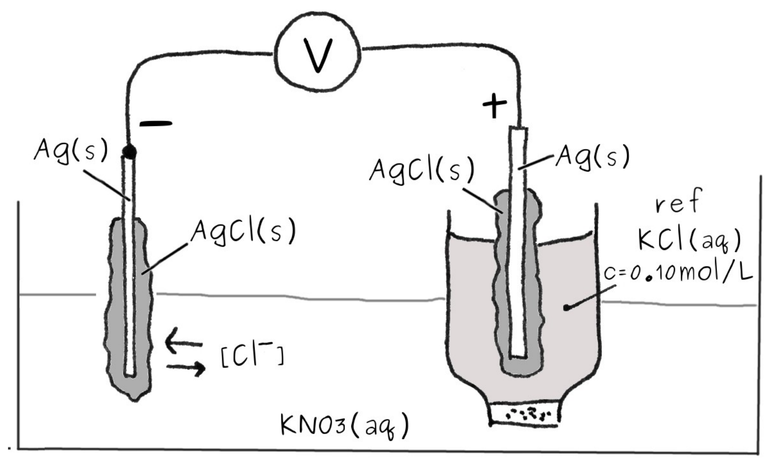

Figure 2. Chloride ion selective electrode (anode) with a silver chloride reference electrode (cathode)

An electrochemical cell using AgCl is reversible to Cl^- ions. If the concentration of Cl^- in the cathode (right electrode) is kept constant with KCl, then the change of potential of this cell is attributable solely to $[Cl^-]$ in the solution.

Once again, both electrodes are using the same red−ox reaction $Ag/AgCl/Cl^-$, therefore, their combined $E°$ values cancel out: $E°$(anode) + $E°$(cathode) = $E°$(cell) = 0.

Obviously, any other reference system can be used. However, in this case, $E°$ will not be zero but still, $E°$(cell) will be constant. The Nernst equation is then:

$$E = E^o - \frac{RT}{nF}\ln Q_r \quad \Rightarrow \quad E = \frac{-0.0592\text{V}}{1}\log\frac{[\text{Cl}^-(\text{ref})]}{[\text{Cl}^-(\text{sol})]} \quad \text{at 25 °C with } E° = 0 \tag{3}$$

Note that equation (3) is similar to equation (2) except for the number of electrons exchanged.

Also, in a spontaneous electrochemical cell, the electrons move from the anode (left) to the cathode (right), even though there is no current flowing. In this case, the oxidation of silver to produce AgCl(s) at the anode will "consume" $Cl^-(aq)$. Therefore, the $[Cl^-(sol)]$ on the left side of the cell is a reactant.

The ion selective membrane

Another way to measure the concentration of a species in solution is by using a selective membrane. In this case, the electrochemical reaction is not the only source of potential of a cell. The accumulation of ions, therefore of charges at an interface also create a potential corresponding to the ion concentration. This phenomenon is called junction potential "E_j" which is a capacitive phenomenon.

$$E_{\text{measured}} = E_{Nernst} + E_{\text{junction}} \tag{4}$$

E_{junction} is not the result of an oxidation−reduction process. This concept is shown in Figure 3.

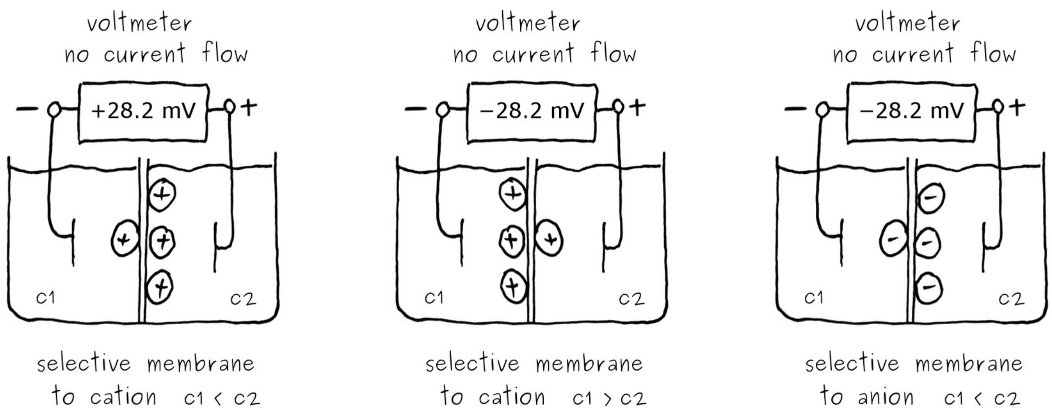

Figure 3. Junction potential at selective membrane according to the concentration and nature of the ions.

The junction potential follows the Nernst equation even in the absence of a redox reaction:

$$E_{\text{junction}} = -\frac{0.05916\ \text{V}}{z}\log\frac{c_1}{c_2} \quad \text{at 25 °C} \qquad z \text{ is the charge of the ion} \tag{5}$$

The fluoride electrode is used to explain the mechanism of a selective membrane. It is made of an ionic conductive crystal specific to fluoride ions. It has a transport number of t(F^-) = 1, made of lanthanum fluoride, doped with europium fluoride ($LaF_3 + EuF_2$). This ionic structure has vacancies in its crystal lattice that only allows fluoride ions to move through the structure.

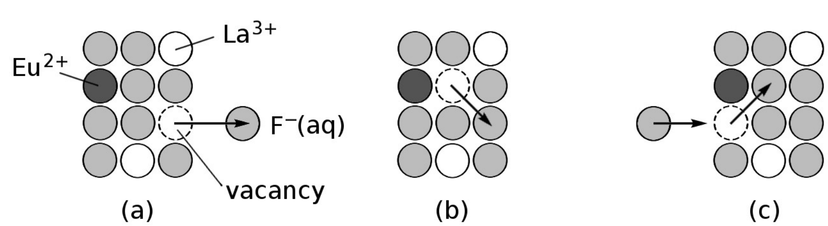

Figure 4. Transport mechanism of a fluoride ion in an $LaF_3 + EuF_2$ fluoride crystal.

a. Fluoride ion dissolution creating a vacancy

b. Diffusion−migration of the fluoride ion in the crystal

c. Adsorption of a fluoride ion at the crystal surface to fill the vacancy.

However, the fluorine transport rate through the crystal is small enough to maintain the concentration of F^-(aq) constant on both sides of the membrane.

The thermodynamic equilibrium is reached generally after ≈30 s.

Since only fluoride can be transported by the membrane or crystal, the following consequences arise:

1- Fluorides are naturally adsorbed and concentrate on both side of the surface membrane / crystal.

2- It allows ionic conductivity, the diffusion of the ion is slow so a stable potential can be measured.

3- Its ionic selectivity makes the electrode invisible to other ions.

A fluoride electrode can measure "free fluoride" in a solution as low as $c = 10^{-6}$ mol/L or 0.02 ppm.[1]

The ion selective general equation

Actually, any electrochemical measurement still relies on the use of two electrodes (here with some redox activity). Figure 5 is an example of an actual selective electrode setup:

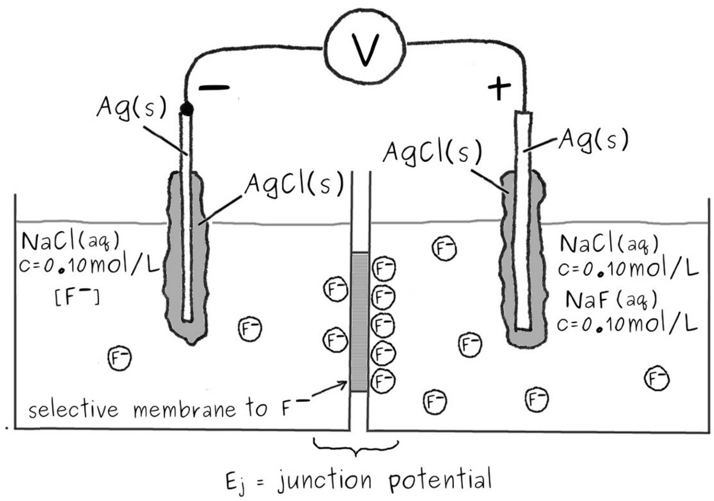

Figure 5. Potential at a fluoride ion selective membrane

This cell has the same electrochemical system Ag / AgCl / Cl^-(aq, 0.10 M) on both sides.

However, rather than using a salt bridge, a selective membrane is present. It is conductive and is designed to be permeable to a single type of ion. Also, two electrochemical systems, must be present to carry out the measurements. If there is no current flow, the general equation for potentiometry is:

$$E = offset + \frac{0.05916\text{ V}}{z}\log[\text{ion}] \quad \text{at } 25\ °\text{C} \qquad (6)$$

The "offset" value takes into account all the stable and constant parameters of the system: concentration of the standard solution, difference of potential between the two electrochemical systems used, junction potential not attributed to the ion studies, etc.

The positive sign in the equation can change for a negative one according to the charge of the ion studied. It can either be positive (cation) or negative (anion) which "flip" the potential of the cell. The polarity of the connections when the calibration is made can also affect the sign.

There is no electron exchanged in the process, therefore, "*n*" is replaced by "*z*" which is the charge of the ion. Also, since there is no flow of electrons, there is no cathode, anode, reactant or product.

For this reason, a selective electrode must be calibrated with standard solutions before use to set the sign in the equation (6).

1 Fischer Scientific: www.thermofischer.com

Limitations of potentiometric analysis with a selective membrane.

1− The potential measured corresponds to the activity of the ion in solution not the concentration. At high concentrations, the activity coefficient is not 1 anymore. Also, an electrolyte is added to the solution to increase the conductivity. Therefore, an high ionic strength (charge density in the solution) can also modify the activity coefficient of the ion studied.

2− Some interfering ions can decrease the adsorption of ions on the membrane. They can even cause a competitive reaction.

3− At low concentrations (ppm), another equilibrium reaction could be present. They can form ionic complexes with the "free ion" under study, making it undetectable. Often, the use of a buffer to control the pH is necessary.

Selective electrode exercise 1

Fluoride is added to the drinking water of a city. A fluoride selective electrode is used to measure the concentration of $F^-(aq)$. First, the electrode is calibrated with two solutions. The electrode potential is zero when the electrode is plunge in a 0.100 mg $F^-(aq)$/L standard solution. Then, it reads −17.8 mV when a 0.200 mg $F^-(aq)$/L solution is analyzed.

If this same fluoride electrode indicates E = −60.6 mV when immersed into the drinking water of the city, does the water exceed the legal authorized concentration of 1.5 mg F^-/L?

Solution:

The two standard solution are used to determine the "offset" and the sign of the general formula (6):

$$E = offset + \frac{0.05916\ \text{V}}{-1}\log[F^-] \qquad (z = -1 \text{ since } F^-)$$

First, the data are placed in a table (easier to read):

sample	E / mV	F^- concentration	$[F^-]$
a.	0.0	0.100 mg $F^-(aq)$/L	5.26×10^{-6} M
b.	−17.8	0.200 mg $F^-(aq)$/L	1.05×10^{-5} M
c.	−60.6	?	?

When the concentration of $F^-(aq)$ increases (sample "a" vs. "b") the potential decreases. Therefore:

$$E = offset\ \mathbf{-}0.05916\ \text{V} \log[F^-]$$

The sample "a" is used to determine the offset:

$$0.0\ \text{V} = offset - 0.05916\ \text{V} \log[5.26\times10^{-6}] \quad \Rightarrow \quad \text{offset} = -0.3123\ \text{V}$$

Therefore, $[F^-]$ in sample "c" is: $-0.0606\ \text{V} = -0.3123\ \text{V} - 0.05916\ \text{V} \log[F^-]$

$$[F^-] = 10^{\frac{-0.0606\ \text{V}+0.3123\ \text{V}}{-0.05916\ \text{V}}} = 5.57\times10^{-5}\ \text{mol/L}$$

Finally: $(5.57\times10^{-5}$ mol/L) × 19.0 g/mol × 1000 mg/g = **1.06 mg/L** , consequently, does not exceed.

Table 1. Potentiometry analysis of some ions with solid−state crystalline electrodes

Analyte Ion	Concentration Range mol/L	Major interferences
Br^-	1 to 5×10^{-6}	CN^-, I^-, S^{2-}
Cd^{2+}	0.1 to 10^{-7}	Fe^{2+}, Pb^{2+}, Hg^{2+}, Ag^+, Cu^{2+}
Cl^-	1 to 5×10^{-5}	CN^- , I^-, Br^-, S^{2-}, OH^-, NH_3
Cu^{2+}	0.1 to 10^{-8}	Hg^{2+}, Ag^+, Cd^{2+}
CN^-	0.01 to 10^{-6}	S^{2-}, I^-
F^-	Sat'd to 10^{-6}	OH^-
I^-	1 to 5×10^{-8}	CN^-
Pb^{2+}	0.1 to 10^{-6}	Hg^{2+}, Ag^+, Cu^{2+}
Ag / S^{2-}	Ag^+: 1 to 10^{-7}	Hg^{2+}
	S^{2-}: 1 to 10^{-7}	
SCN^-	1 to 5×10^{-6}	I^-, CN^-, S^{2-}

From Orion Guide to Ion Analysis. Boston, MA: Thermo Electron Corp. , 1992.

The selective membrane

- It can be a crystal, a glass, a gel, a liquid or an ion exchange polymer membrane
- It ensures the ionic conductivity of the cell. However, it is often highly resistive (100 kΩ).
- It generally allows only one type of ion to be transported across the membrane.
- The diffusion−migration of the ions is slow, allowing them to built−up at the interface.
- The difference of ion concentrations on both surfaces of the interface create a junction potential.

Desired characteristic of ion selective electrodes

- Minimal solubility of the membrane
- Electrical (ionic) conductivity to promote the ion diffusion−migration through the membrane
- Highly selective to one specific ion.

Selective electrode exercise 2: The case of a non−symmetrical system.

When two different electrochemical systems are used to perform the analysis, a “cell” potential combining the potential of the two different system is present. In this case, at least two standard solutions must be used to calibrate the system. However, knowledge of this “cell” potential is not necessary because it is constant and will therefore be part of the offset in the equation.

$$E = offset + \frac{0.05916\ \text{V}}{z}\log[\text{ion}] \qquad (6)$$

Additionally, regardless of the cell configuration, polarity of the voltmeter connection, etc., a second standard solution is required to account for the polarity of the electrode connections.

Calculate [Sn^{2+}] present in the unknown solution from the following data:

Solution	[Sn^{2+}] concentration	Potential measured E vs SCE
Standard 1	2.000×10^{-4}	0.2698 V
Standard 2	1.000×10^{-7}	0.1721 V
unknown	?	0.2224 V

The system is a combination of a calomel reference electrode (SCE) and a tin wire (Sn) both in the same solution. From this table, the potential decreases when the Sn^{2+} concentration also decreases. Therefore, the sign of the equation (6) must reflect the actual connection of this setup. Here:

$$E = offset + \frac{0.05916\ \text{V}}{+2}\log[\text{ion}]$$

the “offset” value is calculated with any of the two standard solutions.

If the solution 1 is used:

$$0.2698\,\text{V} = \text{offset} + \frac{0.05916\,\text{V}}{2}\log[2.000\times10^{-4}]$$

solving for the offset = +0.3792 V

The unknown concentration can then be calculated for this system with the complete equation:

$$E = 0.3792\,\text{V} + \frac{0.05916\,\text{V}}{2}\log[Sn^{2+}]$$

Unknown solution: E = 0.2224 V $\Rightarrow$ $10^{(0.2224-0.3792)\times(\frac{2}{0.05916})}$ = **5.002×10^{-6} mol/L**

Verification:

The standard 2 should give the same “offset” than the first one:

$$0.1721 = \text{offset} + \frac{0.05916\,\text{V}}{2}\log[1.00\times10^{-7}] \Rightarrow \text{solving for offset} = +0.3792\ \text{V}.$$

therefore, the system is Nernstian.

Problems: Selective electrode.

T = 25 °C unless state otherwise. All potentials are compared to NHE reference unless stated otherwise.

1. A cyanide ion−selective electrode obeys the equation:

$$E = offset - 0.05916 \log[CN^-].$$

The potential was −0.230 V when the electrode was immersed in 1.00 mM NaCN.

   a. Evaluate the *"offset"* in the equation.

   b. Using the result from part (a), find $[CN^-]$ unknown if $E = -0.300$ V.

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2. By how many millivolts will the potential of an ideal Mg^{2+} ion-selective electrode change if the electrode is removed from 1.00×10^{-4} M $MgCl_2$ and placed in 4.88×10^{-3} M $MgCl_2$ at 25 °C?

Hint: The offset is constant, so you can use any value you want.

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3. To measure the K_{sp} of AgBr, a saturated solution of AgBr is made. The solution also contains an electrolyte of KNO_3 (c = 0.10 M) to improve the conductivity. An electrochemical system made up of silver electrode vs. SCE reference (cathode) is used to perform the measurement.
An $AgNO_3$ (c = 2.25 mM) solution is used to determine the offset of the system.

Solution	$[Ag^+]$ concentration	Potential measured E vs SCE
$AgNO_3$	2.25×10^{-3}	0.269 V
AgBr	?	0.062 V

Hint: $[Ag^+](AgNO_3) >> [Ag^+](AgBr)$

Calculate the K_{sp} of AgBr(s). Note: solubility product = $K_{sp}(AgBr) = [Ag^+][Br^-]$ (use equation 6)

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4. A fluoride ion selective electrode was used to determine F^-(aq) concentration in the city water of Dorval, QC. The electrode potential was found to be 60.6 mV more negative than that of a standard solution containing 0.100 mg F^-/L. Knowing that $[F^-]_{standard} < [F^-]_{water}$, will the fluoride concentration in Dorval water exceed the maximum recommended level of 1.5 mg F^-/L? Assume Nernstian behavior of the electrode (Hint: Nernstian = slope: 59.16 mV/z log [c])

Answers

1. a. offset = −0.408 V

   b. $[CN^-]$ = 0.0149 mol/L

2. ΔE = 49.8 mV (the sign cannot be known, not enough information.)

3. $K_{sp}(AgBr) = 5.10\times10^{-13}$

4. 1.06 mg/L

Problems: Potentiometric analysis (Complete solution)

All the problems are at 25 °C unless state otherwise. All potentials are compared to NHE reference unless stated otherwise.

Problem 1

a) $-0.230V = E' - 0.05916 \log [1.00\times10^{-3} M]$

$E' = -0.230V + 0.05916 \log (1.00\times10^{-3}] = -0.408V$

b) $-0.300V + 0.408V = -0.05916 \log [CN^-]$

$$10^{\frac{0.108V}{-0.05916V}} = [CN^-] = 0.0149 \text{ mol/L}$$

Problem 2

$$E = \text{offset} - \frac{0.05916V}{2} \log [Mg^{2+}]$$

$$\Delta E = \left(\text{offset} - \frac{0.05916V}{2} \log [1.00\times10^{-4}]\right) - \left(\text{offset} - \frac{0.05916}{2} \log [4.88\times10^{-3}]\right)$$

$$\Delta E = \frac{-0.05916V}{2} \log \frac{[1.00\times10^{-4}]}{[4.88\times10^{-3}]}$$

$$\Delta E = -29.58 mV \log (0.02049) \Rightarrow \Delta E = 49.9 mV$$

$$E = \text{offset} + \frac{0.05916\ V}{z} \log [C]$$

in $AgNO_3$ solution :

$$0.269\ V = \text{offset} + \underbrace{\frac{0.05916\ V}{+1} \log [2{,}25 \times 10^{-3}]}$$

$$0.269\ V = \text{offset} + (-0.1566\ V)$$

$$\text{offset} = 0.269 + 0.1566 = 0.425\underline{6}\ V$$

Therefore :

$$E = 0.4256\ V + 0.05916\ V \log [Ag^+]$$

in $AgBr$ solution :

$$0.062\ V = 0.4256\ V + 0.05916\ V \log [Ag^+]$$

$$\frac{0.062\ V - 0.4256\ V}{0.05916\ V} = \log [Ag^+]$$

$$[Ag^+] = 10^{-6.146} = 7.14 \times 10^{-7}$$

Since $K_{sp} = [Ag^+][Br^-]$ same concentrations

$$K_{sp} = (7.14 \times 10^{-7})^2$$

$$K_{sp} = 5.10 \times 10^{-13}$$

$\Delta E = +0.0606\ V$ between the two measurements

$$\Delta E = E_{Dorval} - E_{standard} = +0.0606\ V$$

$$\Delta E = \left(E' - \frac{0.0592\ V}{z} \log \frac{[Dorval]}{[Ref]} \right) - \left(E' - \frac{0.0592\ V}{z} \log \frac{[standard]}{[Ref]} \right)$$

Since E' and $[Ref]$ are constant

$$\Delta E = -\frac{0.0592\ V}{z} \log \frac{[Dorval]}{[standard]}$$

$$0.0606\ V = \frac{-0.0592\ V}{-1} \log \frac{[Dorval]}{[0.100\ mg/L]}$$

Ratio $\dfrac{mol/L}{mol/L}$ is the same as Ratio $\dfrac{mg/L}{mg/L}$

Solving for $[Dorval] = 1.06\ mg/L$

The water $[F^-]$ concentration does not exceed the maximum