APPENDICES

Appendix 1. Potentiometry

Potentiometric method in analytical chemistry is based on the relationship between the potential of electrochemical cells and the concentrations or activities of the chemical species in the cell. Applications of potentiometry generally involve the use of an electrochemical cell composed of a reference electrode, which maintains a constant potential, and indicator electrode, which responds to the sample composition. A salt bridge often used to prevent mixing of the sample and the reference solution to minimize the liquid junction potential.

a) The Nernst equation

All electrochemical cells are considered to be a combination of two half cells, one for the reduction reaction and the other for the oxidation reaction. To have a current flow in any electrochemical system both oxidation and reduction reactions must occur. Any half-cell reaction can be written as either an oxidation or reduction by convention, that is

$$\mathrm{Ox} + n e^- \rightleftharpoons \mathrm{Red} \qquad (1.1)$$

The potential is given by the generalized form the Nernst equation

$$E = E^0 - \frac{RT}{nF}\ln\frac{a_{red}}{a_{ox}} = E^0 - \frac{2.303RT}{nF}\log\frac{a_{red}}{a_{ox}} \qquad (1.2)$$

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Where E^0 = standard electrode potential in volts

R = molar gas constant (8.314 J/K-mol)

T = absolute temperature in Kelvins

a_{red} = activity of the reduced form

a_{ox} = activity of the oxidized form

If numerical values are inserted for the constants and the temperature is 25 °C, the Nernst equation becomes

$$E = E^0 - \frac{0.05916}{n}\log\frac{a_{red}}{a_{ox}} \qquad (1.3)$$

Pure phases have unit activity, solvent containing even very large quantities of dissolved solutes are generally assumed also to have unit activity .The partial pressure of the gases and the molarities of uncharged solutes are used for the activities in equation 1.2, when they appear in half-reaction. The molarities of charged solutes differ too much from the activities to be rigorously in equation 1.3 directly. The activity and the concentration are related by

$$a = f_iC_i \qquad (1.4)$$

Where a = activity

f_i = activity coefficient of ion

C_i = concentration of ionic species

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The Nernst equation can be written as follows when the component of the half-cell reaction are solutes;

$$E = E^0 - \frac{RT}{nF}\ln\frac{f_{red}\left[Red\right]}{f_{Ox}\left[Ox\right]} = E^0 - \frac{RT}{nF}\ln\frac{f_{red}}{f_{Ox}} - \frac{RT}{nF}\ln\frac{\left[Re\right]}{\left[Ox\right]} = E^0 - \frac{RT}{nF}\ln\frac{\left[Re\right]}{\left[Ox\right]} \qquad (1.5)$$

Where $E^{0'}$ = formal electrode potential

The departure of activity from concentration for charged species is a function of ionic strength, I, of the solution:

$$I = \frac{1}{2}C_iZ_i^2 \qquad (1.6)$$

Where C_i = concentration of ionic species " i "

Z_i = charge on that ion

The activity coefficient, f_i , can be estimated from the ionic strength using equation developed with Debye Huckel theory. With the point-charge approximation, an assumption that ions do not interact in solution ($I < 0.01$), and a solvent of water at 25 ^{0}C, Debye Huckel limiting law can be used to estimate f_I :

$$-\log f_i = 0.5Z_i^2 I^{1/2} \qquad (1.7)$$

For solution of higher ionic strength, the form

$$\log f_i = \frac{0.5Z_i^2 I^{1/2}}{1 + I^{1/2}} \qquad (1.8)$$

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b) Indicator Electrode: Fluoride Ion Selective Electrode

Fluoride electrode consists of a slice of a single crystal of lanthanum fluoride as the membrane that has been doped with europium (II) fluoride to improve its conductivity and bonded into a glass or an epoxy body. The cell may be represented by

$$\text{Ag/AgCl, Cl}^-\text{(0.3 M), F}^-\text{(0.1 M) /LaF}_3\text{ / Test Solution/Reference Electrode} \quad (1.9)$$

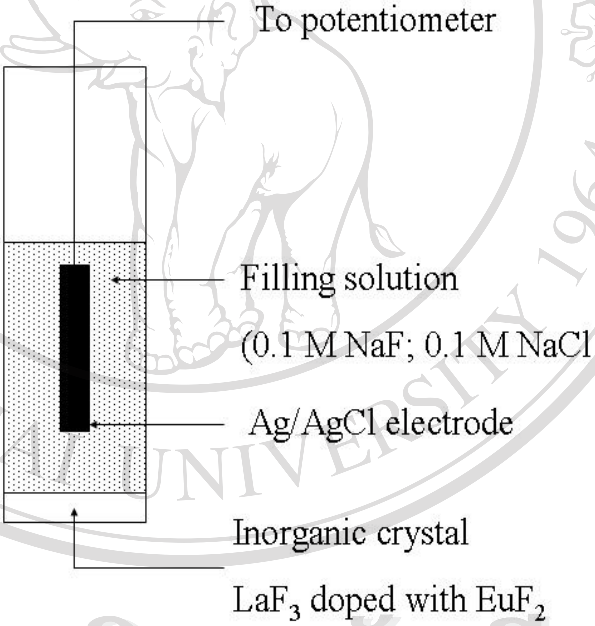

Figure A1 Fluoride ion selective electrode

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Only fluoride ions are mobile in the ionic conductor crystal. When the membrane comes in contact with a solution containing fluoride ions, a potential develops across the membrane. This potential is measured against an external or internal constant reference potential with a standard pH/mV meter or an ion meter and depends on the level of free fluoride ions in the solution. The Nernst equation describes the level of fluoride ions in the solution corresponding to the measured potential.

$$E = E_o + S\log X \qquad (1.10)$$

Where E = measured electrode potential

E_0 = reference potential (a constant)

S = electrode slope

X = level of fluoride in the solution

The activity, X represents the effective concentration of free fluoride ion in the solution. Total fluoride concentration C_t may include some bound as well as free fluoride ions. Since the electrode only responds to free ions, the concentration of the free ions, C_f is found by

$$C_f = C_t - C_b \qquad (1.11)$$

Where C_b represents the concentration of all bound or complexed fluoride ions

The activity is related to the free ion concentration by the activity coefficient, γ by

$$X = \gamma C_f \qquad (1.12)$$

Activity coefficients vary, depending on total ionic strength, I defined as;

$$I = 1/2 \sum C_x Z_x^2 \qquad (1.13)$$

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Where C_x = concentration of ion X

Z_x = charge of ion X

Σ = sum of all the types of ions in the solution

c) Specifications of Fluoride–Ion Selective Electrode

The fluoride ion selective electrode is selective for fluoride ion over other common anions. It is simple procedure for direct measurement of a large number of samples. The specifications of fluoride ion selective electrode are listed in Table A1.

Table A1 Specifications of Fluoride Ion Selective Electrode

Order	Detail
Concentration range	Saturated solution to 1.0 x 10^{-6} M or 0.02 mg/l
pH range	5–7 at 1.0 x 10^{-6}M Fluoride ion (0.02 mg/l) 5–11 at 1.0 x 10^{-1} M Fluoride ion (1900 mg/l)
Temperature range	0–80 °C (80–100 °C intermittent use)
Reproducibility	± 2%
Size	110 mm length, 12 mm diameter, 1 m cable length
Buffer solution	TISAB (Total Ionic Strength Adjustment Buffer)
Storage	Fluoride standard with TISAB solution
Electrode slope at 25° C	57 ± 2 mV/ decade
Preconditioning time	3 minutes
Minimum feasible sample - volume	5 ml

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Appendix 2. International Standard for Drinking Water

Table A2 International Standards for Drinking Water

Order	Maximum acceptable concentration	Maximum allowable concentration
1.Physical properties		
- Color, Pt-Co unit	5	15
- Turbidity, NTU	5	20
- Taste	accepted	accepted
- Odour	accepted	accepted
- pH	6.5-8.5	≤9.2
- Conductivity, µS/cm	700	2200
2.Chemical properties(mg/l)		
- Total Solids	500	1500
- Iron	0.5	1.0
- Manganese	0.3	0.5
- Copper	1.0	1.5
- Zinc	5.0	1.5
- Total hardness (as $CaCO_3$)	300	500
- Calcium	75	200
- Magnesium	50	150
- Sulfate	200	250
- Chloride	250	600
- Fluoride	0.7	1.5
- Nitrate as NO_3	45	454
3. Toxic substances(mg/l)		
- Mercury	0.0001	-
- Lead	0.05	-
- Arsenic	0.05	-
- Selenium	0.01	-

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Table A2 (continued)

Order	Maximum acceptable concentration	Maximum allowable concentration
- Chromium	0.05	-
- Cadmium	0.01	-
- Cyanide	0.2	-
- Radionuclides (gross beta activity)	1000	-
4. Chemical indicators of pollution indicator (mg/l)		
- Chemical oxygen demand (COD)	10	-
- Biochemical oxygen demand	6	-
(BOD)	1	-
- Total nitrogen exclusive of NO_3		
- NH_3	0.5	-
- Carbon Chloroform (CCE:Organic pollutants)	0.5	-
- Grease	1	-

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