APPENDIX I

The mixed solution methods[29]

These methods yield more reliable value of $K_{A,B}$ than seperate solution method. The fixed interference method consists of the measurement of E_{cell} for solution containing the same activity of interferent a_B and varying the activity of the determinand ion a_A. This method is preferred over the converse method of holding a_A constant and varying a_B although the latter has been used when the hydrogen ion is the interfering ion. The fixed interference method, however, more closely resemble the situation in the samples. The method depends upon the interpolation from the graph of E_{cell} versus log c_A, that concentration of A at which the electrode is responding equally to both ions. If this interpolated concentration of A is c_A, and assuming constancy for the activity coefficients under conditions for which E_{cell} is measured, the equation

$$E_{cell} = \text{constant} + \frac{k}{Z_A}\log\left[a_A + K_{A,B}(a_B)^{Z_A/Z_B}\right] \qquad (1)$$

becomes

$$c_A = K_{A,B}(c_B)^{Z_A/Z_B} \qquad (2)$$

In the presense of an interfering ion the graph of E_{cell} versus log c_A ideally has two near segments interconnected by a curve section. The first of these linear segments is obtained when the range of concentrations of determinand A is such that the electrode yields a Nernstian response, indicating that the concentration of the interferent B is too low to alfer this response. The second linear portion is caused when the concentration of A is low so that the electrode responds only to B, and, since the concentration of the latter has been kept constant throuhtout, the cell potential will also remain constant. The point of intersection when those two linear points are extrapolated yields log c_A from which $K_{A,B}$ may be calculated by eqution (2). It should again be emphasized that the range of concentrations of the determinand should lie whithin the range of Nernstian response for the electrode when B is absent.

An alternative method of locating the midpoint of the curved section corresponding to a condition of equal response of the electrode toward A and B must be used if the expected zero electrode response due to the invariant concentration of B cannot be established experimentally. Such acase is represented in figure 1 on which the point Y represents the lower limit of response when the electrode is calibrated with solution containing the determinand alone. At point X the interferent B starts to cause the electrode to deviate from the linearity observed along the line TX. The concentration at point P is below that at which the response of the electrode departs from linearity at point Y and thus the linear segment of zero electrode response cannot be established. That point R yields the concentration at which the electrode responds equally to the determinand and the interferent is deducible as follow: The concentration corresponding to R is given by equation (2) which, when substituted in a modified equation (1) yields

$$E_{cell} = \text{constant} + \frac{k}{Z_A} \log 2c_A$$

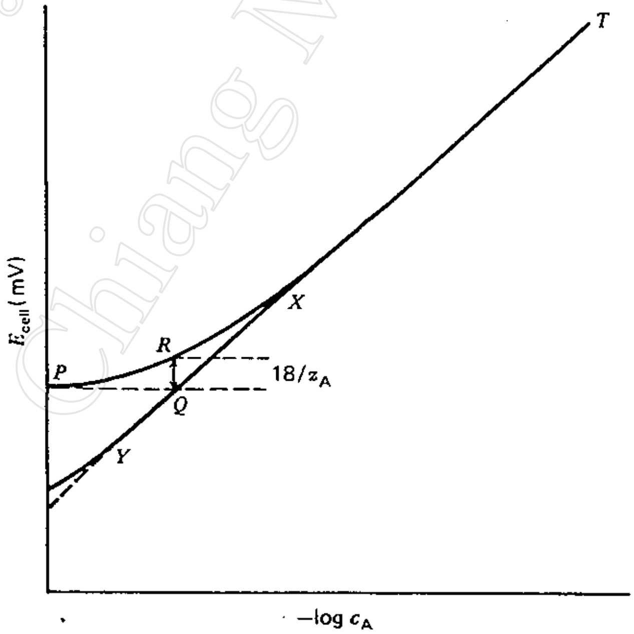

Figure 1. Location of that point (R) at that which the A ion selective electrode responds equally to species A and interferent B.

On the other hand, point Q represents the response of the electrode to a solution of concentration c_A when the interferent is absent. The change in E_{cell} between R and Q is given by

$$\Delta E = \frac{k}{Z_A}(\log 2c_A - \log c_A)$$

$$= \frac{k}{Z_A}\log 2$$

$$\approx \frac{18}{Z_A} \quad \text{mV} \quad \text{at} \quad 25°\text{C}$$

Thus the midpoint of the curved section at R can be found from a plot of the data by extrapolating the linear portion TX toward Y and then selecting the value of log C_A at which the linaer XP differ from XY by $18/Z_A$ mV. The antilogarithm of this value is C_A from whence the selectivity coefficient can be calculated from

$$K_{AB} = \frac{(c_A)^{Z_B}}{(c_B)^{Z_A}}$$

VITA

Name : Miss Wilailuck Suebpimpawong

Date of Birth : March 22th, 1969

Academic status : -MS.3 Certificate holder from Sirindhorn School, Surin (1984)

-High School Certificate holder from Sirindhorn School, Surin (1987)

-B.Sc. Degree holder from Chiang Mai University, Chiang Mai (1991)

Scholarship : Teaching Assistant at Chiang Mai University (1993,1994)