## Problem 1: Separation and Identification of Ions

A student studied the chemical reactions between cations, $A^{2+}$, $B^{2+}$, $C^{2+}$, $D^{2+}$, $E^{2+}$ in nitrate aqueous solutions and anions $X^-$, $Y^-$, $Z^-$, $Cl^-$, $OH^-$ in sodium aqueous solutions as well as an organic ligand L. Some precipitation (ppt) products and colored complexes were found as shown in Table 1:

**Table 1**

| | $X^-$ | $Y^-$ | $Z^-$ | $Cl^-$ | $OH^-$ | L |
|---|---|---|---|---|---|---|
| $A^{2+}$ | *** | *** | *** | *** | White ppt | *** |
| $B^{2+}$ | Yellow ppt | White ppt | *** | *** | *** | $BL_n^{2+}$ Complex |
| $C^{2+}$ | White ppt | Brown ppt | Brown ppt | White ppt | Black ppt | $CL^{2+}$, $CL_2^{2+}$ Complexes |
| $D^{2+}$ | *** | Red ppt | *** | *** | *** | *** |
| $E^{2+}$ | *** | Red ppt | White ppt | *** | *** | *** |

*** = No reaction,

1-1 Design a flow chart for the separation of $A^{2+}$, $B^{2+}$, $C^{2+}$, $D^{2+}$, $E^{2+}$ in a nitrate aqueous solution by using various aqueous solutions containing anions $X^-$, $Y^-$, $Z^-$, $Cl^-$, $OH^-$, respectively, as testing reagents. Write down the product of the chemical reaction for each step in the flow chart.

1-2 Design a flow chart for the separation of anions $X^-$, $Y^-$, $Z^-$, $Cl^-$, $OH^-$ in a sodium aqueous solution by using various aqueous solutions containing cations $A^{2+}$, $B^{2+}$, $C^{2+}$, $D^{2+}$, $E^{2+}$, respectively, as testing reagents. Write down the product of the chemical reaction for each step in the flow chart.

1-3 The white ppt $BY_2$ and brown ppt $CY_2$ have low solubilities in water with solubility products (Ksp) of $3.20 \times 10^{-8}$ and $2.56 \times 10^{-13}$, respectively at $25\,^{o}C$.

1-3-1 Calculate the solubility of $BY_2$.

1-3-2 Calculate the solubility of $CY_2$.

1-4 A series of solutions containing $B^{2+}$ and L were prepared in 50 mL volumetric flasks by adding a 2 mL of $8.2 \times 10^{-3}$ M solution of $B^{2+}$ to each flask. Varying amounts of a $1.0 \times 10^{-2}$ M solution of the ligand L are added to each flask. The solution in each volumetric flask was diluted with water to the mark (50 mL). The absorbance (A) of Complex $BL_n$ was measured at 540 nm for each solution in a 1.0 cm cell. The data are summarized in Table 2. (Both $B^{2+}$ and ligand L show no absorption (A = 0) at 540 nm.) [Mole Ratio Method]

1-4-1 Calculate the value of n (Coordination number) in the complex $BLn^{2+}$.

1-4-2 Calculate the formation constant ($K_f$) of complex $BLn^{2+}$.

**Table 2**

| Added L<br>$V_L$ (mL) | Absorbance<br>(A) | Added L<br>$V_L$ (mL) | Absorbance<br>(A) |
|---|---|---|---|
| 1.00 | 0.14 | 2.00 | 0.26 |
| 3.00 | 0.40 | 4.00 | 0.48 |
| 5.00 | 0.55 | 6.00 | 0.60 |
| 7.00 | 0.64 | 8.00 | 0.66 |
| 9.00 | 0.66 | 10.00 | 0.66 |

1-5 Solid NaY (soluble) was added very slowly to an aqueous solution containing 0.10 M in $B^{2+}$ and 0.05 M in $C^{2+}$ prepared from their respective nitrate aqueous salts.

1-5-1 Which cation ($B^{2+}$ or $C^{2+}$) precipitates first? What is the $[Y^-]$ when this happens? ($K_{sp} = 3.20 \times 10^{-8}$ for $BY_2$ and $K_{sp} = 2.56 \times 10^{-13}$ for $CY_2$, at 25 °C.) [Separation by Precipitation]

1-5-2 What are the concentrations of $Y^-$ and the remaining cation when complete precipitation of the first precipitating cation has occurred (assume that the concentration of the first cation in solution after complete precipitation is $\leq 10^{-6}$ M)? Is it possible to separate $B^{2+}$ and $C^{2+}$ by the precipitation method with $Y^-$ ion as a precipitating agent?

## Problem 2: Preparation and Applications of Radioisotopes

Radioisotopes can be used in medical diagnosis and therapy as well as industrial analysis. Many radioisotopes, e.g. P-32 (Mass number = 32) and Co-60 can be generated by the irradiation of neutrons in a nuclear reactor. However, some radioisotopes in nature, e.g. C-14 and T-3 (Tritium), can be produced by the bombardment of nitrogen N-14 atoms in the atmosphere by neutrons in the cosmic ray. (Atomic numbers of T & H, C, N, P, Co and neutron are 1, 6, 7, 15, 27 and 0, respectively. P-32 can be denoted as $^{32}_{15}P$)

2-1 Write down the equations for the nuclear reactions for the production of C-14 and T-3 by the bombardment of nitrogen N-14 atoms in the atmosphere with neutrons in the cosmic ray.

Radioisotope C-14 can be used as a reagent in C-14 dating. The activity (A) in terms of counts per minute (cpm) of the radioisotope C-14 is proportional to the number (N) of C-14 atoms as follows : [C-14 Dating]

$$A = \varepsilon \lambda N \qquad (1)$$

Where $\varepsilon$ is the detection coefficient of a detector for C-14 and $\lambda$ is the decay constant of C-14. An initial amount ($N_o$) of C-14 can be reduced to the amount (N) of C-14 by decay after a given time (t) as follows:

$$N = N_o e^{-\lambda t} \qquad (2)$$

The half life ($t_{1/2}$) of C-14 is 5730 years which is defined as the time required for 50% of the number of the radioisotope C-14 atoms in a sample to undergo decay, that is $N = 1/2\ N_o$. It is well known that activity ($A_o$) of C-14 in a living animal or plant is kept to be around 16.5 cpm/g of carbon. After the death of the animal or plant, the activity (cpm/g of carbon) of C-14 in the body of the living animal or plant is decreased by the time passed.

2-2-1 Give the equation showing the relation between the original activity ($A_o$) and final activity (A) as function of time for a living animal or plant.

2-2-2 The activity of C-14 in an ancient wood boat is found to be 10.2 cpm/g of carbon. Calculate the age of the ancient boat.

2-3 The radioisotope P-32 is a very important leveling reagent for biological research and can be produced by the bombardment of P-31 by a neutron in a nuclear reactor. The production rate (Rp) of P-32 can be estimated as :

$$Rp = N\Phi\delta \qquad (3)$$

Where N and $\delta$ are the number of atoms and neutron capture cross section ($\approx 0.9 \times 10^{-24}$ $cm^2$/atom) of P-31, respectively, and $\Phi$ is the neutron flux (neutron / ($cm^2$ sec)) of the nuclear reactor. If the detection efficient ($\varepsilon$) of the detector for P-32 is 1.0, the decay rate (Rd) and the activity (A) of P-32 in the nuclear reactor can be approximately estimated as a function of the number (N*) of P-32 atoms as follows:

$$Rd = N\Phi\delta\ (e^{-\lambda t}) \qquad (4)$$

and

$$A = \lambda N^* = Rp - Rd \qquad (5)$$

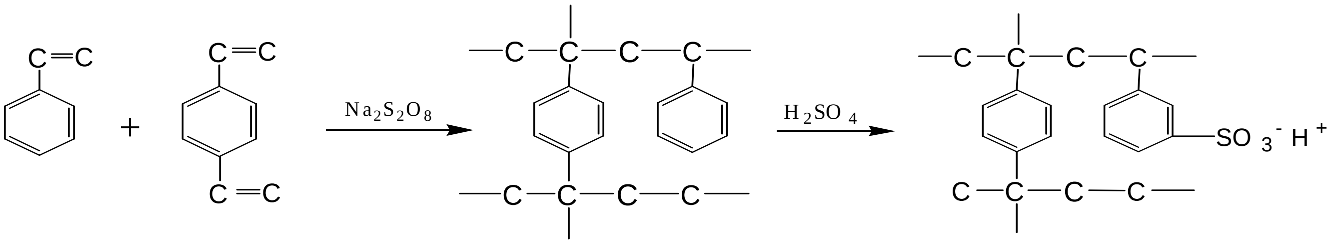
Where $\lambda$ is the decay constant of P-32, t is the neutron irradiation time in the nuclear reactor and the half life ($t_{1/2}$) of P-32 is 14.3 days.

2-3-1 A 10 mg sample of pure $H_3PO_4$ is irradiated by neutrons with a neutron flux of $1.00 \times 10^{13}$ n $cm^{-2}sec^{-1}$ for one hour in a nuclear reactor. Calculate the activity of the sample in cps (counts / second) and Ci. (Ci = Curie, 1 Ci $\approx 3.7 \times 10^{10}$ cps, atomic weight: H=1, P=31, O=16)

2-3-2 The radioisotope P-32 can be used to measure the volume of water in a pool or the blood volume of an animal. A 2.0 mL solution of 1.0 Ci/mL P-32 was injected into a pool. After mixing well, the activity of 1.0 mL of water in the pool was found to be 12.4 cps (counts / second). Calculate the volume of water (L) in the pool. (Ci = Curie, 1 Ci $\approx 3.7 \times 10^{10}$ cps)

## Problem 3: Ion Exchangers

Ion exchangers can be employed to adsorb and separate cations and anions. They can be prepared from organic or inorganic materials. An organic, cationic ion exchanger can be synthesized by the polymerization of styrene / divinyl benzene followed by sulfonation with $H_2SO_4$, as shown in Scheme 1:



[ polymer ]

[ cationic exchanger ]

$R^-H^+$

**[Scheme 1]**

Cationic ion exchanger (denoted as $R^-H^+$) can be employed to adsorb the cations, $M^+$,the chemical reaction and the equilibrium constant Kc as well as the distribution coefficient Kd can be expressed as follows:

$$R^-H^+ + M^+ = RM + H^+, \quad Kc = [RM][H^+] / ([M^+][RH]) \qquad (1)$$

$$K_d = [RM] / [M^+] \qquad (2)$$

The cationic ion exchanger $R^-H^+$ can be transformed into the ion exchanger $R^-M^+$ or $R^-M^{z+}$ by the reaction of $R^- H^+$ with a metal hydroxide (M(OH)z). The approximate equations are:

$$R^-H^+ + MOH = R^-M^+ + H_2O \qquad (3)$$

and

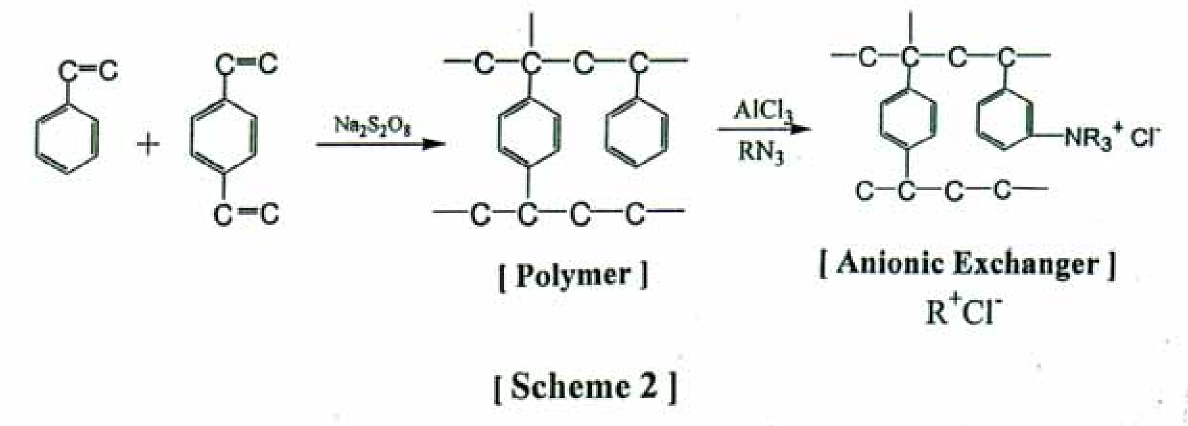
$$z\,R^-H^+ + M(OH)_z = (R^-)_zM^+ + z\,HCl \qquad (4)$$

3-1 A cationic ion exchanger $R^-Na^+$ was employed to remove $CaCl_2$ in tap water,

3-1-1 Give the chemical equation for the adsorption of $Ca^{2+}$ by the cationic ion exchanger $R^-Na^+$.

3-1-2 If another ion exchanger $R^-H^+$ is employed instead of $R^-Na^+$. (a) Give the chemical equation for the adsorption of $Ca^{2+}$ by the ion exchanger $R^-H^+$ and (b) tell which ion exchanger, $R^-H^+$ or $R^-Na^+$, is suitable for drinking purpose and give the reason.

3-2 An organic, anionic ion exchanger (denoted as $R^+Cl^-$) can also be synthesized by the polymerization of styrene / divinyl benzene followed by the reaction of the resulting polymer, poly (styrene / divinyl benzene), with the Lewis acid $AlCl_3$ and tertiary amine $NR'_3$, as shown in Scheme 2:



[ Scheme 2 ]

The anionic ion exchanger $R^+OH^-$ can be obtained from the chemical reaction of the ion exchanger $R^+Cl^-$ with 3.0 M of NaOH by the equation:

$$R^+Cl^- + NaOH = R^+OH^- + NaCl \qquad (5)$$

3-2-1 Tell how the removal of $H^+$ from a solution of HCl can be achieved with an anionic ion exchanger and give the chemical equation for the process.

3-2-2 Tell how the amount of $SO_4^{2-}$ in tap water can be estimated by using an anionic ion exchanger $R^+OH^-$. Give all of the chemical equations involved in the process.

The capacity (S) of the cationic ion exchanger $R^-H^+$ for an adsorbed ion can be expressed in moles of the adsorbed ion per gram of the ion exchanger in 1.0 mL of aqueous solution and can be calculated by using the following equation:

$$S = ([RM] + [RH]) \times 10^{-3} \qquad (6)$$

The capacity (S) of the cationic ion exchanger $R^-H^+$ for $M^+$ ions in an aqueous solution can be estimated from the equilibrium constant Kc, the distribution coefficient Kd and the concentrations of $M^+$ and $H^+$ ions in the aqueous solution.

3-3 Show that the relationship between Kd, S, Kc, $[M^+]$ and $[H^+]$ as shown by the equation:

$$1 / Kd = [M^+] / (S(10^3)) + [H^+] / (S\,Kc(10^3)) \qquad (7)$$

3-4 Ion exchangers can be employed as stationary phase materials in liquid chromatography to adsorb and separate various ions. For example, the anionic ion exchanger $R^+OH^-$ can be used to separate $X^-$ and $Y^-$ ions with the eluent NaOH. The chromatogram for separation of $X^-$ and $Y^-$ ions using a 30 cm of anionic ion exchange column is shown in Figure 1.

Where $t_1$, $t_2$ and $t_o$ are the retention times ($t_R$) for $X^-$, $Y^-$ and the pure eluent (NaOH) to traverse the column, respectively. $\omega 1$ and $\omega 2$ are the peak-widths for $X^-$ and $Y^-$. The number of theoretical plates N and the plate height H (height equivalent of the theoretical plates) of the column can be estimated as shown below:

$$N = 16\,(t_R / \omega)^2 \qquad (8)$$

and

$$H = L / N \qquad (9)$$

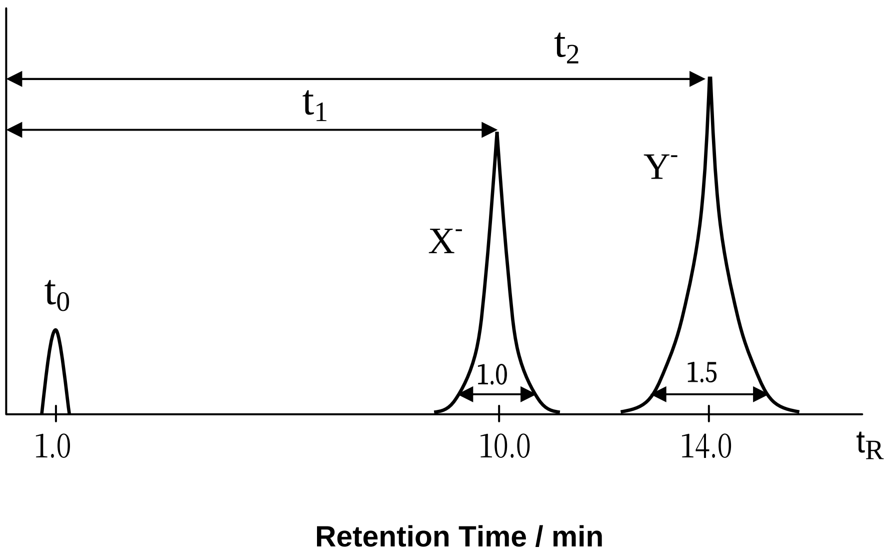


**Figure 1. Liquid Chromatogram for $X^-$ and $Y^-$ ions**

where L is the length of the column. The resolution (R) of the column and the separation factor ($\alpha$) for $X^-$ and $Y^-$ also can be estimated using the following equations:

$$R = 2\,(t_2 - t_1) / (\omega_1 + \omega_2) \qquad (10)$$

and $$\alpha = (t_2 - t_0) / (t_1 - t_0) \qquad (11)$$

3-4-1 Calculate the average number of theoretical plates N of the column.

3-4-2 Calculate the plate height H of the column.

3-4-3 Calculate the resolution (R) of the column for $X^-$ and $Y^-$ ions.

3-4-4 Calculate the separation factor ($\alpha$) for $X^-$ and $Y^-$ ions.

3-5 Some ion exchangers are derived from inorganic matters. Zeolites $[(M^{z+})(Al_2O_3)_m / (SiO_2)_n]$ ($M^{z+}$ = $Na^+$, $K^+$ or $Ca^{2+}$, $Mg^{2+}$) are the best known examples of inorganic ion exchangers. Some examples of Zeolites are shown in Figure 2.

A $Na^+$-Zeolite (denoted as Z-$Na^+$) with a pore size of 13 Å is an important ion exchanger for the removal of $Ca^{2+}$ or $Mg^{2+}$ ion from tap water. Zeolites with definite pore sizes also behave as highly selective adsorbents for various molecules, e.g. $H_2O$ and iso-butane. Thus, the zeolite can be used as a molecular sieve. The zeolite can also be used as a catalyst by adsorption of a petroleum component, e.g. iso-butane, in petroleum resulting in the enhancement of rate of the cracking of the adsorbed component.

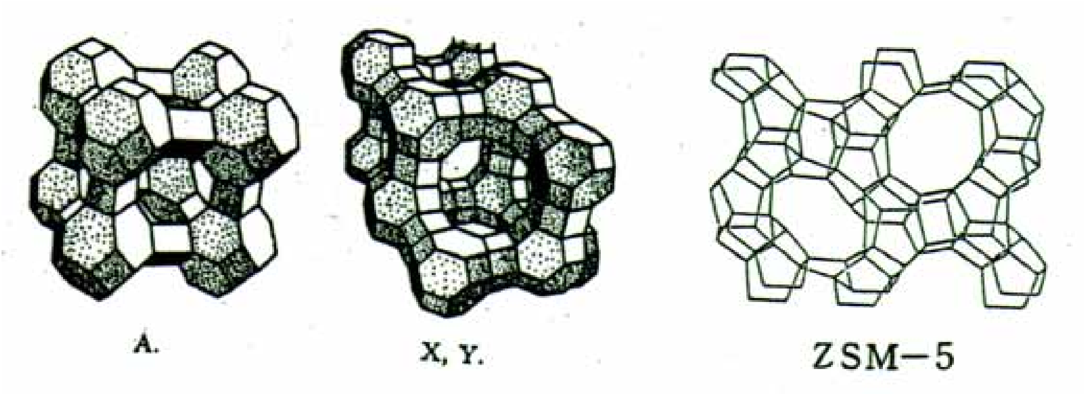


**Figure 2. Various types of Zeolites**

3-5-1 Give the chemical equation for the removal of $Ca^{2+}$ ions from tap water with Z-$Na^{+}$ zeolite ion exchange column.

3-5-2 Give the chemical equation for the adsorption of $K^{+}$ with Z-$Na^{+}$ zeolite.

## Problem 4: Determination of Calcium Ion by Precipitation Followed by Redox Titration

The calcium content of an aqueous sample can be determined by the following procedure:

Step 1 A few drops of methyl red are added to the acidified aqueous sample, followed by thorough mixing with $Na_2C_2O_4$ solution.

Step 2 Urea ($(NH_2)_2CO$) is added and the solution gently boil until the indicator turns yellow (this typically takes 15 min). $CaC_2O_4$ precipitates out.

Step 3 The hot solution is filtered and the solid $CaC_2O_4$ is washed with ice-cold water to remove excess $C_2O_4^{2-}$ ions.

Step 4 The insoluble $CaC_2O_4$ is dissolved in hot 0.1 M $H_2SO_4$ to give $Ca^{2+}$ ions and $H_2C_2O_4$. The dissolved $H_2C_2O_4$ is titrated with standardized $KMnO_4$ solution until the purple end point is observed.

Relevant reactions and equilibrium constants:

$$CaC_2O_{4(s)} \rightarrow Ca^{2+}_{(aq)} + C_2O_4^{2-}{}_{(aq)} \qquad K_{sp} = 1.30\times10^{-8}$$

$Ca(OH)_{2(s)} \rightarrow Ca^{2+}{}_{(aq)} + 2OH^{-}{}_{(aq)}$ $K_{sp} = 6.50 \times 10^{-6}$

$H_2C_2O_{4(aq)} \leftrightarrow HC_2O_4^{-}{}_{(aq)} + H^{+}{}_{(aq)}$ $K_{a1} = 5.60 \times 10^{-2}$

$HC_2O_4^{-}{}_{(aq)} \leftrightarrow C_2O_4^{2-}{}_{(aq)} + H^{+}{}_{(aq)}$ $K_{a2} = 5.42 \times 10^{-5}$

$H_2O \leftrightarrow H^{+}{}_{(aq)} + OH^{-}{}_{(aq)}$ $K_w = 1.00 \times 10^{-14}$

4-1 Write a balanced equation for the reaction that takes place upon the addition of urea (Step 2).

4-2 The calcium content of a 25.00 mL aqueous sample was determined using the above procedure and found to require 27.41 mL of a $2.50 \times 10^{-3}$ M $KMnO_4$ solution in the final step. Find the concentration of $Ca^{2+}$ ions in the sample.

4-3 Calculate the solubility of $CaC_2O_4$ in an aqueous solution buffered at pH 4.0. (Neglect activity coefficients)

In the above analysis, a possible source of error was neglected. The precipitation of $CaC_2O_4$ in Step 1 will be incomplete if an excess of $C_2O_4^{2-}$ ions is added, due to the following reactions:

$Ca^{2+}{}_{(aq)} + C_2O_4^{2-}{}_{(aq)} \rightarrow CaC_2O_{4(aq)}$ $K_{f1} = 1.0 \times 10^{3}$

$CaC_2O_{4(aq)} + C_2O_4^{2-}{}_{(aq)} \rightarrow Ca(C_2O_4)_2^{2-}{}_{(aq)}$ $K_{f2} = 10$

4-4 Calculate the equilibrium concentrations of $Ca^{2+}$ and $C_2O_4^{2-}$ ions in solution after optimal precipitation of $CaC_2O_4$ is reached.

4-5 Calculate the concentrations of $H^{+}$ and $Ca^{2+}$ in a saturated solution of $CaC_2O_4$. (Neglect activity coefficients. Any assumptions made during calculation must be clearly stated.)

## Problem 5: Nitrogen in Wastewater

In natural water and waste water, the forms of nitrogen of greatest interest are nitrate, nitrite, ammonia, and organic nitrogen. All these forms of nitrogen, as well as nitrogen gas, are biochemically interconvertible and are components of the nitrogen cycle.

5-1 The Macro-kjeldahl method, in combination with a titration method, is often used in the determination of organic nitrogen in wastewater. In the first step, $H_2SO_4$, $K_2SO_4$, and $HgSO_4$ are added to the sample solution. After digestion, the solution is neutralized by the addition of concentrated NaOH. The gas liberated by the treatment is then distilled into a solution of excess boric acid and the latter subsequently titrated with 0.02 N $H_2SO_4$.

5-1-1 Identify the product formed in the digestion step.

5-1-2 Identify the gas liberated upon the addition of NaOH.

5-1-3 Write a balanced equation for the reaction between the liberated gas and boric acid.

5-1-4 Write a balanced equation for the final titration step.

5-1-5 Which of the following indicators is most suitable to be used in the final titration step:

Methyl orange (transition range pH 3.1 - 4.4), phenolphthalein (transition range pH 8.0 - 9.6) is chosen as the indicator. Explain your choice.

5-2 Nitrite is known to cause the illness methemoglobinemia in infants. In the laboratory, nitrite can be determined by a colorimetric method. The method requires the preparation of a series of standard nitrite solutions. However, nitrite is readily oxidized in the presence of moisture and hence standardization of the stock nitrite solution is required in order to achieve high accuracy in the subsequent analysis. The standardization is carried out by adding a known excess of standard $KMnO_4$ solution and $H_2SO_4$ solution are added into the nitrite stock solution. The purple color of the solution due to the presence of excess permanganate was subsequently discharged by the addition of a known quantity of $Na_2C_2O_4$ and the mixture back titrated with standard permanganate solution.

5-2-1 Write a balanced equation for the reaction of the nitrite solution with $KMnO_4$.

5-2-2 Write a balanced equation for the back titration.

5-2-3 Write a mathematical equation for calculation of nitrogen concentration.

A: mg/ml N in stock $NaNO_2$ solution
B: total ml standard $KMnO_4$ used
C: molarity of standard $KMnO_4$
D: total ml standard $Na_2C_2O_4$ solution
E: molarity of standard $Na_2C_2O_4$
F: ml stock $NaNO_2$ solution taken for titration

## Problem 6: Use of Isotopes in Mass Spectrometry

Many elements in the periodic table have more than one isotope. The atomic mass of an element is calculated based on the relative abundance of the isotopes. As an example, the atomic mass of chlorine is about 35.5 because the abundance of $Cl^{35}$ is about three times the abundance of $Cl^{37}$. In mass spectrometry, instead of average atomic mass, the isotope peaks are observed. ($Cl^{35}$ 75.77%, $Cl^{37}$ 24.23%, $C^{12}$ 98.9%, $C^{13}$ 1.1%, $Br^{79}$ 50.7%, $Br^{81}$ 49.3%)

Isotopes are quite useful in quantitative mass spectrometry.

6-1 In addition to the retention time (migration time), the ratio of M and M+2 ions was used as the qualitative criteria in the analysis of 2,3,7,8, tetra chlorinated dioxin (2,3,7,8-TCDD) by gas chromatography / mass spectrometry. Calculate the theoretical ratio of the two ions. The intensities of the isotopic species can be found by applying the following formula: $(a+b)^n$, where a is the relative abundance of the light isotope, b is the relative abundance of the heavy isotope, and n is the number of chlorine atoms present.

6-2 Molecular ion is often selected in quantitative analysis. The intensity of the molecular ion needs to be corrected if the signal is interfered by other compounds. In the analysis of a non-halogenated compound with a molecular weight of 136, the molecular ion was selected for quantitative analysis. Propose a mathematical equation for calculation the corrected signal, if the analyte co-elutes (same migration time) with the compound n-butyl bromide.