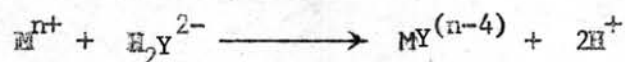
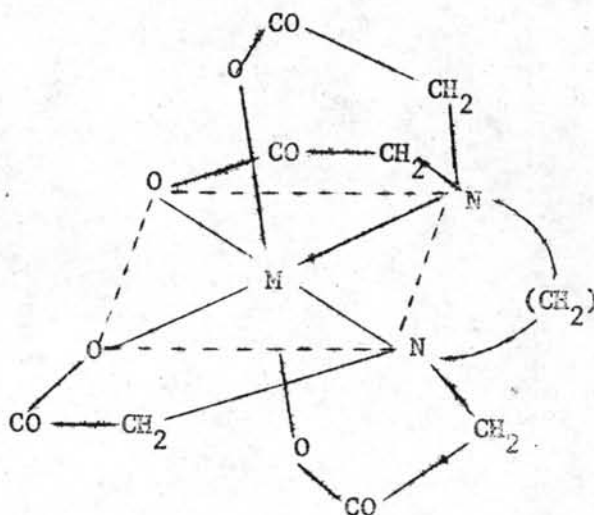


A pair of free electrons capable of complexing with a metal ion is contained on each of the two nitrogens and each of the four carbonyl groups. It is usually used in the form of its disodium salt. In aqueous solution, the H_2Y^{2-} ion is the complex forming species. This ion reacts with cation to form 1:1 complex according to the equation



The three dimensional structure of metal - EDTA chelate may be illustrated as follows (17)

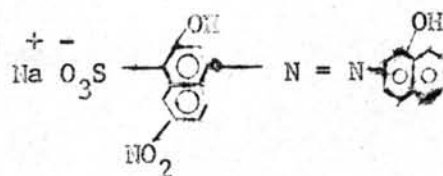


A wide variety of end point detection methods can be applied to the titration with EDTA. The use of metal indicator is the most common which is represented by the following expression

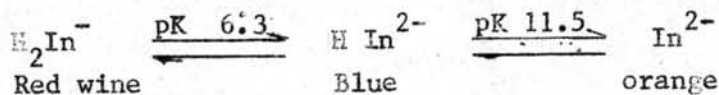


This reaction will proceed if the metal ion indicator complex (M - In) is less stable than the metal - EDTA complex (M - EDTA). The former dissociates to a limit extent and during the titration the free metal ions are progressively complexed by the EDTA until ultimately the metal is displaced from the complex M - In to leave the free indicator (In)

One of metal - indicators used in EDTA titration is Eriochrome Black T. Chemically it is sodium 1-1 (hydroxy - 2 - naphthylazo) - 6 - nitro - 2 - naphthyl - 4 - sulfonate, with the structure

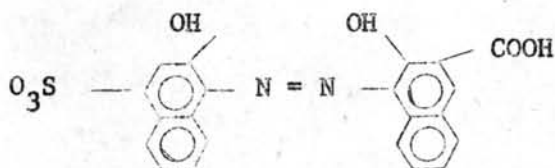


It is an acid-base indicator with two sensitive regions of color change. Representing the anion by the formula H_2In^- , the equilibrium are as follow.



Eriochrome Black T. is usually employed in EDTA titration of calcium and magnesium

The other metal indicator is Patton and Reeder's indicator of 2 - Hydroxy - 1 - (2 - Hydroxy - 4 - Sulfo - 1 - Naphthylazo) - 3 - Naphthoic acid. The name may be abbreviated to HESMNA. (16) The structure is



The sharp color change from wine-red to pure blue is obtained when calcium is titrated with EDTA at pH between 12 and 14

In titration of calcium and magnesium with EDTA using Eriochrome Black T as the indicator, the titration is carried out at a pH of 10, a low enough value to avoid the formation of $Mg(OH)_2$ and where the indicator is largely in the H_2In^{2-} form (15). The equilibrium is represented as

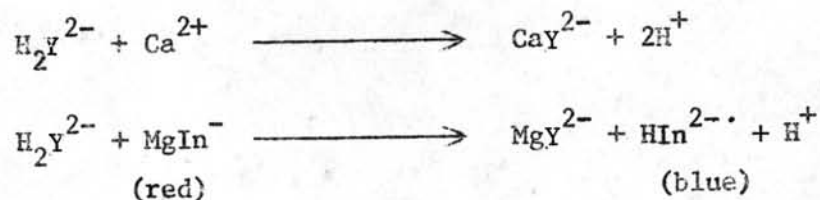


During the titration, EDTA first combines with free calcium, next with free magnesium ion and finally at the end point the EDTA extracts magnesium from magnesium-dye complex to cause the color change from wine-red to blue. The mechanism of this complex formation may be explained by the use of formation constants and sequences as shown in Table 2.1

Table 2.1 Formation Constant

Complex	Log K
EDTA - Ca	10.59
EDTA - Mg	8.69
Mg - Erio T	7.0
Ca - Erio T	5.4

The overall titration is represented by the principle and indicator reactions respectively,



In titration of calcium, the pH is raised to about 12 cause the precipitation of magnesium II as $\text{Mg}(\text{OH})_2$. The titration with EDTA serves to determine calcium alone using Patton and Reeder's indicator. It produces a sharp color change from wine red to pure blue when calcium is titrated with EDTA at pH values between 12 and 14 (16). Subtracting the amount of calcium determined by the above method from amount of calcium plus magnesium determined by EDTA titration using Eriochrome Black T as the indicator, the magnesium content is therefore evaluated.

Atomic Absorption Spectrophotometry

Atomic absorption spectrophotometry is a method for determining the concentration of an element by measuring the absorption of radiation in atomic vapour produced from the sample at a specific wavelength of each element. The characteristic wavelength corresponds to the electronic transition between the first allowable energy level and the ground state of the atoms.

If the radiation of radiant power P_0 at frequency ν incident on an atomic vapour of thickness b cm and if P_ν is the radiant power of the transmitted radiation then, the absorption coefficient, K_ν , of the vapour at frequency ν is defined by the relation (18).

$$P_\nu = P_0 e^{-K_\nu b}$$

where K_ν varies with ν since the absorption line has a finite width, the integrated absorption or the total degree of absorption in atomic absorption (18,19) is given by the relation

$$\int K_\nu d\nu = \frac{\pi e^2}{mc} N_\nu f$$

where

- K_ν = absorption coefficient at frequency
- e = charge of an electron
- m = mass of an electron
- N_ν = number of absorbing atoms
- c = speed of light
- f = oscillator strength of the absorption line
which is the average number of electrons
per atom capable of being excited by
incident radiation.

From the above equation, it is seen that the integrated absorption is therefore proportional to the concentration of free atoms in the absorbing medium.

In this study, potassium content in the sample is determined by atomic absorption spectrophotometry. The partial energy level diagram for potassium atom is shown in Figure 2.1.

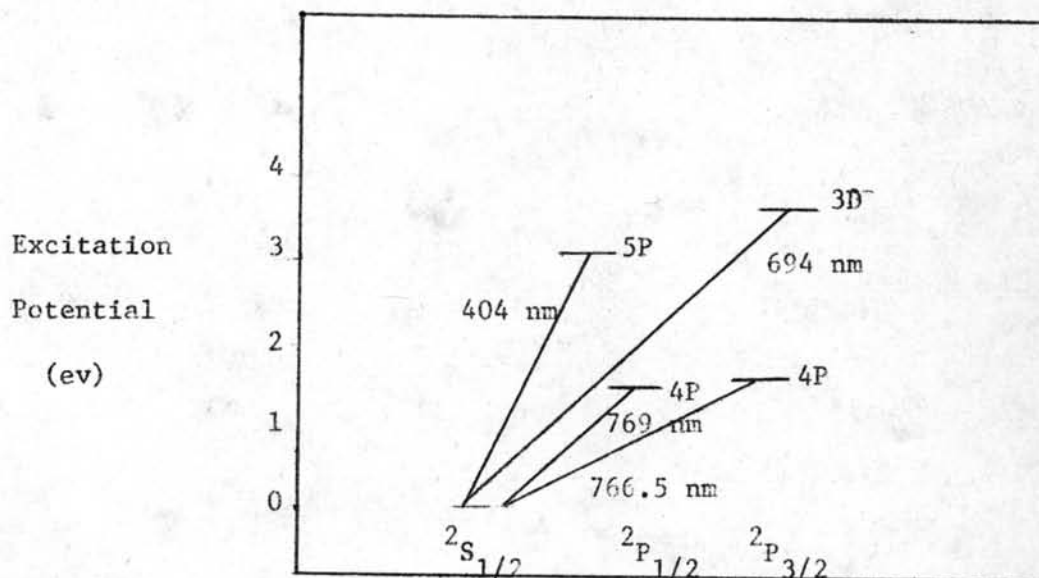
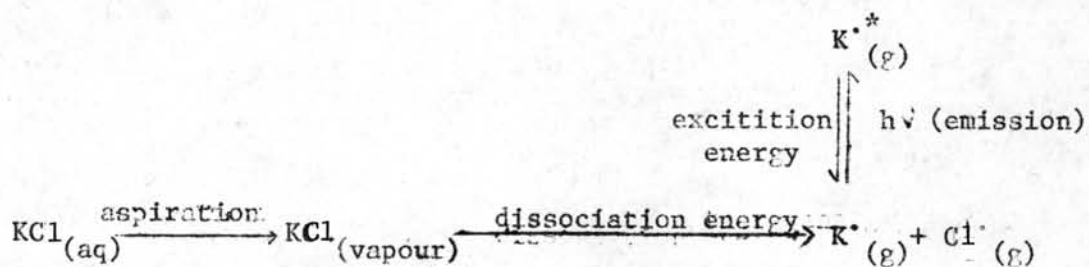


Figure 2.1 The partial energy level diagram for Potassium

The **resonance line** used for the analysis of potassium is 766.5 nm Potassium in the sample is in the form of potassium chloride. The production process of potassium atom may be shown in successive steps as follows:-



*
 $\text{K}^*_{(g)}$ - excited state potassium atom

Spectrophotometric Method

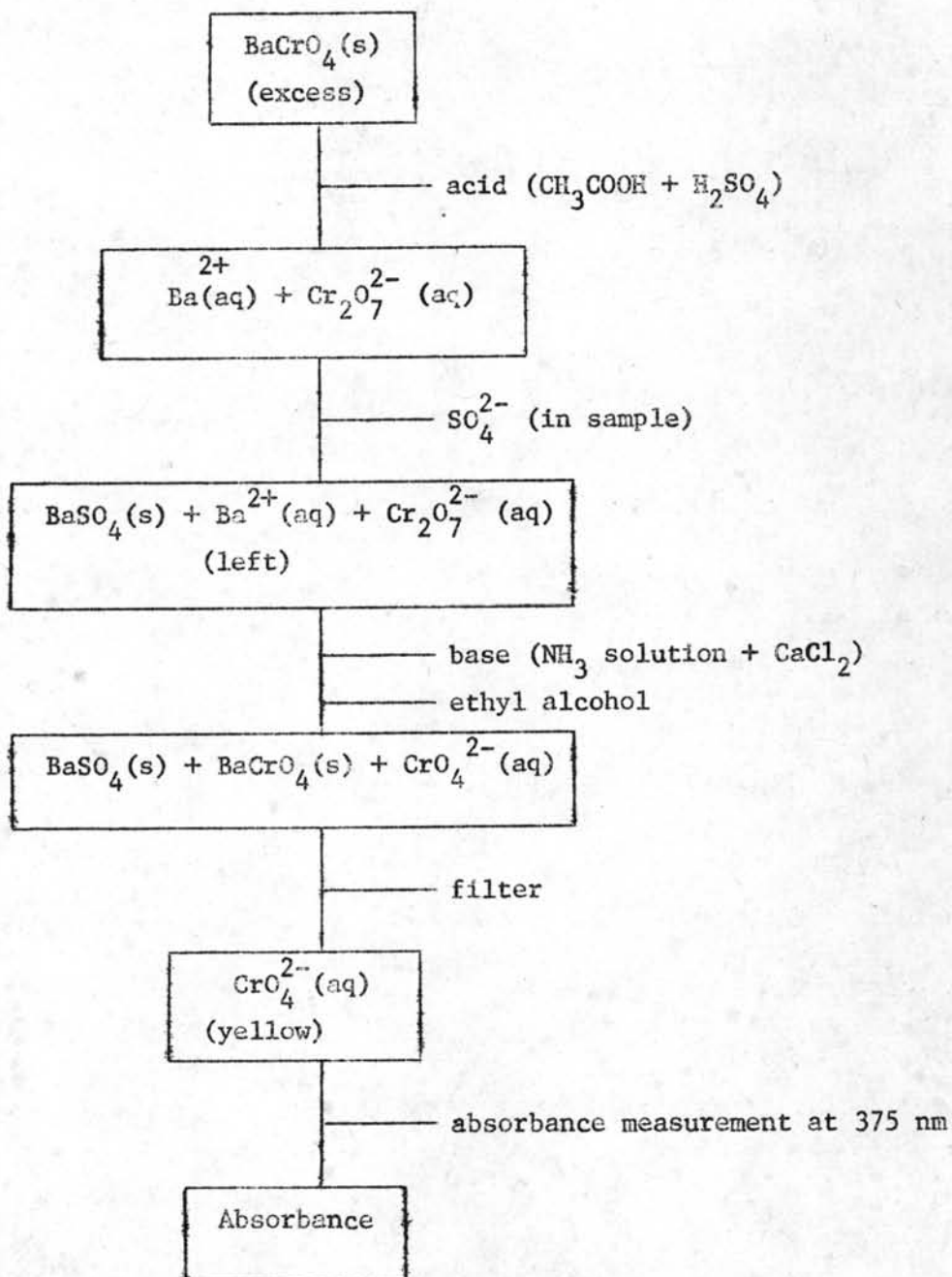
Spectrophotometry is based on the measurement of absorption of electromagnetic radiation. In visible or ultraviolet region, absorption process is a result of an electronic arrangement in atom or molecule. The intensity of absorption depends on the concentration of the absorbing species (c), optical path length (b) and the molar absorptivity (ϵ). From Beer - Lambert's law

$$A = \epsilon \cdot b \cdot c.$$

A is the absorbance which is equal to logarithmic ratio between the intensity of the incident and transmitted radiant power. Most spectrophotometric record the spectrum as the absorbance versus wavelength.

The spectrophotometric determination of sulfate is shown schematically as illustrated in Figure 2.2. The acidic suspension of barium chromate is added to the sample containing sulfate and then the white precipitate of barium sulfate is formed. The reaction solution is subsequently added with ammonia solution followed by ethyl alcohol. The content is filtered and the filtrate is collected. The greenish yellow filtrate is carried out absorbance measurement at 375 nm. The concentration of sulfate is determined by comparing to the sulfate from the corresponding calibration curve.

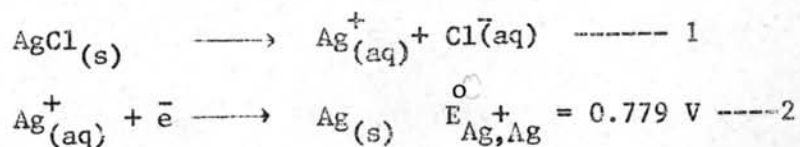
Figure 2.2 Flow-chart of sulfate determination by spectrophotometric method



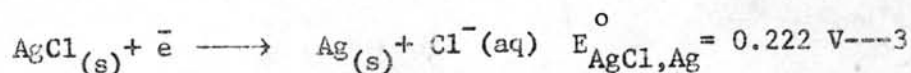
Potentiometric Titration

In many cases, the completion of a reaction can be easily and accurately determined potentiometrically. The method depends on measurement of potential of a suitable electrode during the titration. Since the potential is a function of the ionic activity or concentration if other conditions are constant (23,24). The potential of a metal and a solution containing ions of the same metal is given by the Nernst Equation which indicates that a change of a potential will occur as the concentration of the metal ion changes. The sharp change of the potential undergoes when there is the marked change in the concentration of one of the reacting species, indicates the equivalent point of titration. It is difficult to measure the single potential but it is more convenient to make the comparison against another electrode (reference electrode) which has a constant potential.

In determination of chloride ions, the silver electrode is used as the indicator electrode and the saturated calomel electrode is used as a reference electrode. The potential of a silver electrode will accurately reflect the concentration of chloride ions in a solution that is saturated with silver chloride. Here are two equilibria governed the electrode behavior.



combining equation 1 and 2



from Nernst Equation

$$E = E_{\text{AgCl},\text{Ag}}^{\circ} - \frac{2.303RT}{F} \log a_{\text{Cl}^{-}} \text{-----} 4$$

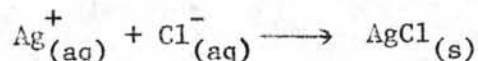
$$\therefore a_{\text{Cl}^{-}} = K_{\text{sp}} / a_{\text{Ag}^{+}}$$

$$E = E_{\text{AgCl},\text{Ag}}^{\circ} - \frac{2.303RT}{F} \log K_{\text{sp}} - \frac{2.303RT}{F} \log \frac{1}{a_{\text{Ag}^{+}}} \text{-----} 5$$

which is similar to

$$E = E_{\text{Ag}^{+}/\text{Ag}}^{\circ} - \frac{2.303RT}{F} \log \frac{1}{a_{\text{Ag}^{+}}} \text{-----} 6$$

In solution containing a mixture of silver ions and chloride ions such as a titration of chloride with silver solution, the concentration of each of these at equilibrium will be such that the potential can be calculated by equation 4 and 5. At equilibrium, the potential of one half-reaction must be equal to the potential of the other in a chemical reaction. Equation 2 and 3 are the two half reaction in this case. The overall chemical reaction is obtained by subtracted one from the other



From equation 2 and 3 the potential of the silver electrode will vary and it is directly proportion to pAg or pCl . An end point may be located more precisely by the first derivative plot which plotting successive values of the rate of change of potential versus each increment of titrant. The rate of change of the potential is maximal at the end point. It can be even more precisely to locate the end point from the second derivative curve, which is obtained by plotting the potential - volume acceleration versus the volume of titrant added. At the end point, the second derivative becomes numerically zero as the value of the ordinate rapidly changes from a positive to a negative number.

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