

CHAPTER III

EXPERIMENTALS



3.1 Chemicals

Chemicals used for chemical analyses described in this thesis are listed and grouped under the heading of each constituent in the salt sample determined. All chemicals are of analytical reagent grade or otherwise stated.

Determination of Calcium and Magnesium

disodium ethylene diamine tetraacetate ($C_{10}H_{14}N_2Na_2O_8 \cdot 2H_2O$, Merk, AR grade)

hydrochloric acid HCl, Sp. gr. 1.19, Riedel De Haen, AR grade

sodium hydroxide (NaOH, Mallinckrodt, AR grade)

potassium cyanide (KCN, BDH, AR grade)

zinc metal (Zn, Merk, AR grade)

hydroxylamine hydrochloride ($NH_2OH \cdot HCl$, BDH, Lab grade)

2-hydroxy-1 - (2 - hydroxy - 4 - sulfo - 1- naphthylazo)

-3- naphthoic acid) (Riedel-De-Haen AG)

Eriochrome Black T (Riedel-De-Haen AG)

ammonia solution (Sp. gr. 0.899, BDH, AR grade)

ammonium chloride (NH_4Cl , Hopkin and Williams, General purpose grade)

Determination of Potassium

potassium chloride (KCl, BDH, AR grade)

sodium chloride (NaCl, Mallinckrodt, AR grade)

Determination of Chloride

silver nitrate (AgNO_3 , Mallinckrodt, AR grade)

sodium chloride (NaCl, Mallinckrodt, AR grade)

Determination of Sulfate

acetic acid (CH_3COOH , Sp gr. 1.048, May and Baker, AR grade)

ammonia solution (Sp. gr. 0.899, BDH, AR grade)

barium chromate (BaCrO_4 , BDH, Lab grade)

calcium chloride ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, BDH, AR grade)

ethyl alcohol ($\text{C}_2\text{H}_5\text{OH}$, Riedel-De-Haen AG, AR grade)

hydrochloric acid (HCl, Sp. gr. 1.19, Riedel-De-Haen AG,
AR grade)

potassium sulfate (K_2SO_4 , BDH, AR grade)

Distilled water used in this work was the double-distilled water

3.2 Apparatus

Atomic Absorption Spectrophotometer, model AA-5, Varian Techtron was used for the analysis of potassium.

Spectrophotometer, model 635, Varian Techtron equipped with a Varian Techtron Recorder, model 7040 A was used for plotting the visible spectra and measuring absorbance for the determination of sulfate.

pH meter, model Radiometer Copenhagen, type PEM 23 equipped with a silver electrode, model Beckman and a saturated calomel electrode was used for the potential measurement in the determination of chloride by potentiometric titration.

3.3 Sampling Method

Samples of rock salt were taken from core logs of drill holes. The location of drill holes are shown in the map no. 1.2. The samples to be analysed were taken through the length of the core logs in the range of 10 feet per sample as shown in Figure 3.1.

Recommended Method for Salt Analysis

In this thesis, the Salt Analyzing Methods of the Japan Monopoly Corporation (JMC's method) were recommended and adopted with some modification for the preparation of salt samples, sample solution and for the analysis of the rock salt. The actual methods for determining of each constituent described in this work are listed in Table 3.1

In Chloride determination, a potentiometric titration was used instead of the recommended Mohr's method because the potentiometric method had some advantage over the Mohr's method. Firstly, the potentiometric method using silver electrode is applicable to a turbid solution (20,25) and it is almost the only practical method for argentometric titration (24). Secondly, it provides an inherent more accurate data, and finally the end point of the method can be located precisely than the corresponding Mohr's method(14,20,25)

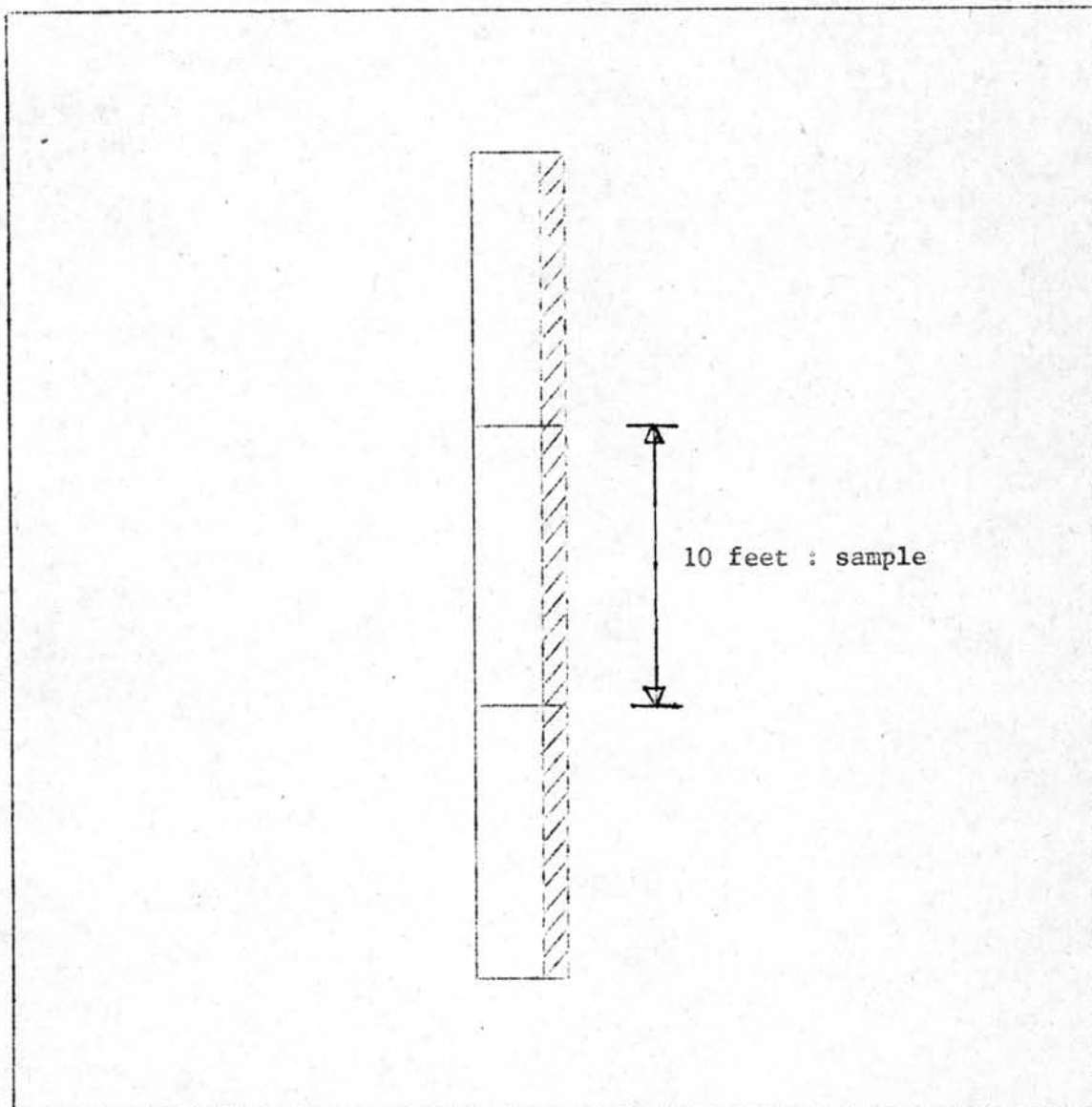


Figure 3.1 Sampling Method

Table 3.1 Methods for determining of each constituent in rock salt samples

Constituent to be determined	JMC'S method	Method used in this thesis
Moisture content	Heating in an electrical drying oven	Same
Water insolubles	Filtration method	Same
Calcium and Magnesium	Complexometric titration with EDTA	Same
Potassium	Flame photometric method	Atomic absorption spectroscopy
Chloride	Mohr's method	Potentiometric titration with silver nitrate
Sulfate	Photometric method	Spectrophotometric method

In determination of potassium, atomic absorption spectrophotometry was used instead of recommended flame photometry.

Atomic absorption spectroscopy is much more sensitive than flame photometry because atomic absorption spectroscopy is based upon a much larger population, it then might be expected to be the more sensitive procedure (20,21). The sensitivity of both techniques are also dependent on the type of instrument used. Atomic absorption spectroscopy has another advantage over flame photometry in quantitative analysis. The relation between absorption and concentration is nearly linear that Beer's law is obeyed on wide range of concentration (21). Flame photometry need more careful calibration than atomic absorption spectroscopy and it is more subject to chemical and spectral interferences (18,21)

3.4 Preparation of Salt Samples

Salt samples for analysis obtained from the Department of Mineral Resources in plastic bags were well and thoroughly mixed and then kept in a desiccator containing dried silica gel as a drying agent. The particle size of salt sample was obtained by sieving it through a 40 mesh sieve.

This sample was consequently used in the following sections.

3.5 Preparation of Sample Solution

There are two methods for preparation of sample solution depending on constituents to be determined.

3.5.1 Preparation of Salt Sample for Determination of Calcium and Magnesium

10 G. of the salt sample (previously prepared from 3.4) was weighted accurately then dissolved in 100 cm³ of double distilled water and 50 cm³ of 0.1 M hydrochloric acid. The solution was heated to boiling about 2 minutes. After cooling, it was filtered through a Whatmann filter paper No.1 and made up to 250 cm³ with distilled water.

3.5.2 Preparation of Salt Sample for Determination of Potassium, Chloride and Sulfate

10 G. of the salt sample (previously prepared as mention in 3.4) was weighted accurately and dissolved in 100 cm³ of double distilled water. After standing for about 15 hours, the residue was filtered off using Whatmann filter paper No.1 and the solution was diluted to 250 cm³ with distilled water.

The relationship between the dissolving times and amount of dissolved sulfate is in Table 3.2 with the graph presentation in Figure 3.2.

Table 3.2 The relationship between dissolving time and amount of dissolved sulfate

Dissolving times (hr.)	%SO ₄
1	1.8730 ± 0.0171
3	2.1240 ± 0.0075
5	2.2374 ± 0.0000
7	2.3643 ± 0.0052
10	2.4486 ± 0.0025
15	2.4284 ± 0.0000
20	2.4849 ± 0.0704

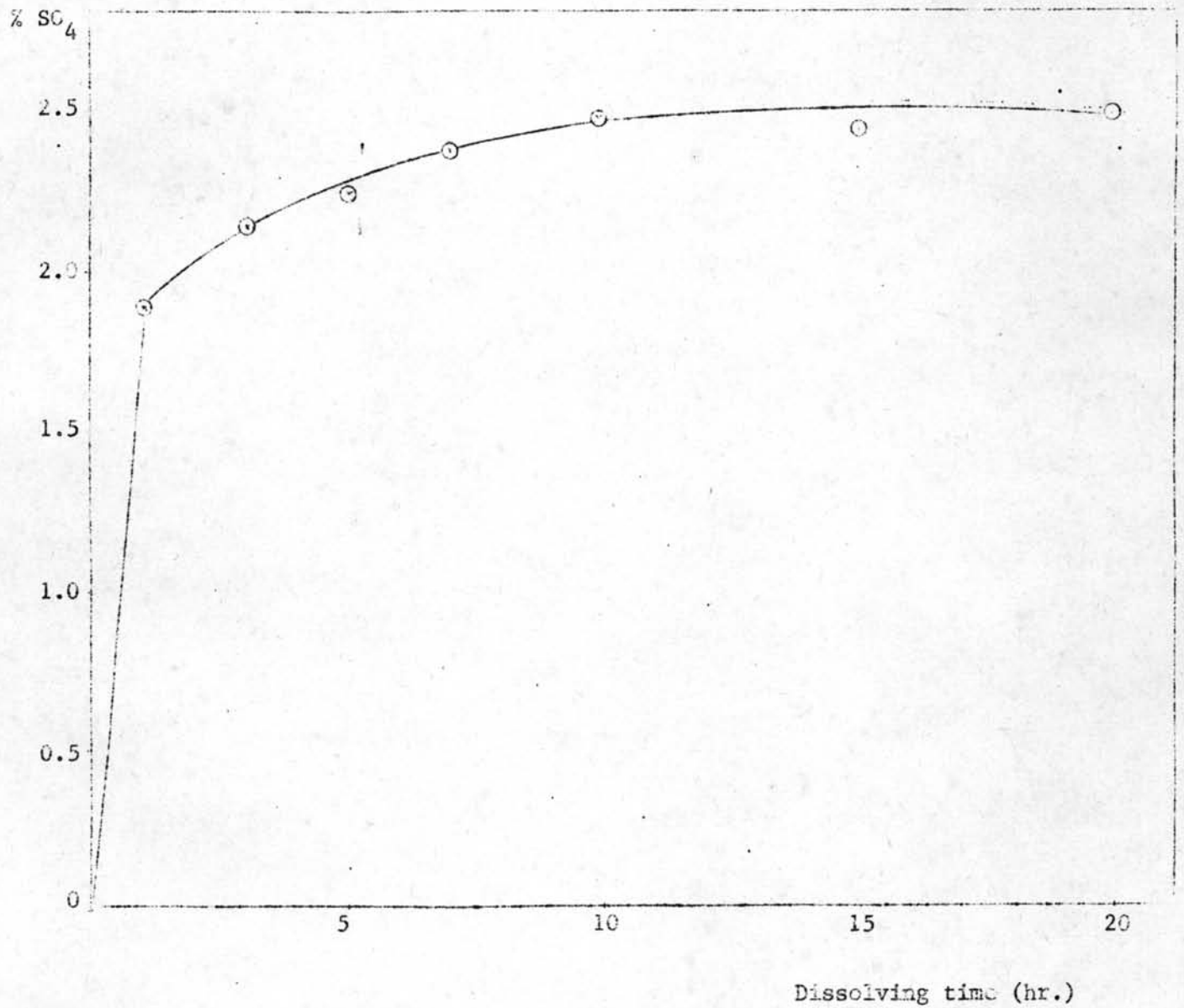


Figure 3.2 The correlation between dissolving time and dissolved sulfate

The effect of dissolving times on analytical result was studied only in the case of sulfate determination because the constituents present in rock salt are appreciably soluble in water or brine except calcium sulfate. Calcium sulfate in rock salt is present as the mineral anhydrite, the anhydrous form of CaSO_4 and is ordinarily considered to be a primary mineral in rock salt. Gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is also present in rock salt. Anhydrite is slowly soluble in water and in dilute brine. Its solubility in 5% brine is 6 g/1000cm³(1). If the salt is ground extremely fine and digested for a long time in brine, all of the anhydrite will eventually be dissolved eventually to the limit of its solubility in that particular strength of brine (1, 26).

From the Figure 3.2, it can be seen that the salt sample should be dissolved in water and left for at least 15 hours before carrying out the spectrophotometric determination of sulfate.

3.6 Method for Determination of Moisture Content

Approximately 10 g of the salt sample (as from 3.4) was transferred to a weighting bottle and weighed accurately. It was then placed in an electric drying oven previously temperature controlled at $140 \pm 2^\circ\text{C}$ and dried for 90 minutes. After cooling in the desiccator, the salt sample was re-weighed accurately. The percentage of the moisture content is calculated from the following relationship.

$$\% \text{Moisture} = \frac{\text{Weight loss on drying (g)} \times 100}{\text{Weight of salt sample (g)}}$$

3.7 Method for Determination of Water Insolubles

Approximately 10 g of salt sample (prepared in accordance with 3.4) was weighed accurately. It was then transferred into a 250 cm³ beaker and 100 cm³ of distilled water was added. The content was stirred continuously by a glass stirring rod for about 5 to 10 minutes. The solution was left about 20 minutes prior to filtration.

A sintered-glass crucible (porosity no.3, capacity 30 cm³) was prepared and dried at 110 ± 2°c for an hour in an electrical drying oven. It was then cooled in a desiccator to the room temperature and weighed accurately.

The mixture in the beaker above was filtered through the crucible with the aid of Buchner suction system. The beaker was rinsed two or three times with 15 cm³ portion of distilled water. The sintered glass crucible was consequently dried for an hour in an electrical drying oven controlled at 110 ± 2°c and finally let it cool in a desiccator to the room temperature. The crucible was weighed again. The percentage of water insolubles is calculated as follows.

$$\% \text{Water insolubles} = \frac{\text{increase in glass-filter crucible weight (g)} \times 100}{\text{weight of salt sample (g)}}$$

3.8 Method for Determination of Calcium

3.8.1 Preparation of Reagents

(1) Standard Zinc Chloride Solution

Accurately weighed 1 g of zinc metal was dissolved in 10 cm³ of concentrated hydrochloric acid and heated to evaporate and diluted to 1000 cm³ with distilled water. 1 cm³ of standard zinc chloride solution equals 1.00 x f_{Zn} (mg). The f_{Zn} is the factor obtained by the following equation.

$$f_{\text{Zn}} = \frac{\text{amount of zinc weighed (g)} \times \text{purity of zinc (\%)}}{1.000 \quad 100.00}$$

(2) Standard EDTA Solution

3.9 G of EDTA (disodium salt) was dissolved in 1000 cm³ of distilled water and stored in a polyethylene bottle.

The calcium titer F_{Ca} (mg) for 1 cm³ of this solution was determined as follows.

Exactly 10 cm³ of standard zinc chloride solution was titrated with standard EDTA solution, using 5 cm³ of buffer solution (see 3.9.1 (3)) and 3 - 4 drops of indicator. (see 3.9.1 (2)) The end point of this titration was made at the time when the red color turned blue completely.

The calcium titer F_{Ca} (mg) is obtained by the following equation.

$$F_{Ca} \text{ (mg)} = \frac{1.00 \times f_{Zn} \times 10}{\text{Consumption of standard EDTA solution (cm}^3\text{)}} \times 0.613$$

where $\frac{Ca}{Mg} = 0.613$

(3) Indicator

0.5 G of 2 - hydroxy - 1 - (2 - hydroxy - 4 - sulfo - 1 - naphthylazo) - 3 - naphthric acid and 10 g. of sodium sulphate dehydrate was ground together and was kept in a brown colored bottle and stored in a desiccator.

(4) Sodium Hydroxide Solution (4 % W/V)

(5) Hydroxylamine Hydrochloride Solution (5%W/V)

(6) Potassium Cyanide Solution (2 % W/V)

3.8.2 Procedure

Exactly 25 cm³ of sample solution (from 3.5.1) was pipetted and transferred into an Erlenmeyer flask. It was then added 10 cm³ of sodium hydroxide solution (4 %) and stirred thoroughly for about an hour by magnetic stirrer so as to adjust the pH to 12. After warming to about 50°C, it was added 1 cm³ of hydroxylamine hydrochloride solution (5 %) and 2 cm³ of potassium cyanide solution (2 %) and approximately 0.1 g of indicator powder. The solution

was titrated with the standard EDTA solution. The end point of this titration was made at the time when the color turned from red to pure blue. The consumption of the titrant is then indicated by 'B' cm³. The percentage of calcium is calculated from the following relationship.

$$\%Ca = \frac{F_{Ca} \times B \times \frac{100}{1000}}{\text{weight of salt sample (g)} \times \frac{25}{250}}$$

where F_{Ca} = calcium titer (mg)
 B = consumption of EDTA titrated
 1.069 = correction factor of calcium

The correction factor for calcium was obtained by testing the accuracy of the method. The primary standard solutions were prepared to the closest approximation as in the rock salt sample and carried out analysis according to the procedure in 3.8.2. The correction factor is then calculated from the following equation.

$$\text{correction factor} = \frac{100 + x}{100}$$

where $x = \frac{\sum (\%c)}{n}$
 $x = \frac{\sum \left(\frac{a - b}{a} \right)}{n} \times 100$

x = mean of percent relative error

%c = percent relative error

a = theoretical value

b = practical value

n = number of analysis

An example for the determination of the percent relative error for calcium and magnesium may be illustrated as follows.

weight of NaCl	3.83964 g
weight of CaCO_3 (MW. 100.09)	0.11417 g
weight of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (MW. 246.37)	0.04647 g
total weight	4.00028 g
% calcium in sample	$= \frac{40.08 \times 0.11417}{100.09 \times 4.00248} \times 100\%$
	$= 1.143$
% magnesium in sample	$= \frac{24.31 \times 0.04647}{246.37 \times 4.00248} \times 100\%$
	$= 0.1146$

From the experiment

% calcium found (obtained from duplicate analysis)

$$= 1.06 \%$$

% magnesium found (obtained from duplicate analysis)

$$= 0.112 \%$$

$$\text{the relative error of \% calcium} = \frac{(1.143-1.06)}{1.143} \times 100$$

$$= 7.26$$

$$\text{the relative error of \% magnesium} = \frac{(0.1146-0.112)}{0.1146} \times 100$$

$$= 2.27$$

The value of relative error of 10 samples are shown in

Table 3.3

Table 3.3 The mean value of relative error for calcium

Sample No.	Calculated value (Theoretical) a	From * analysis (Practical) b	% Relative error $c = \frac{(a - b)}{a} \times 100\%$
1	1.143	1.06	7.26
2	1.110	1.02	8.11
3	1.084	1.02	5.90
4	1.054	0.99	6.10
5	1.026	0.94	8.40
6	1.536	1.43	6.90
7	1.504	1.40	6.91
8	1.460	1.37	6.16
9	1.430	1.33	6.99
10	1.391	1.31	5.82
			$\frac{\sum c}{n} = 6.86$

* obtained from duplicate analysis

Table 3.4 The mean value of relative error for magnesium

Sample No.	Calculated value (Theoretical) d	From analysis (Practical) e	% Relative error $f = \frac{(d - e)}{d} \times 100\%$
1	0.1146	0.112	2.27
2	0.1123	0.109	2.94
3	0.1090	0.106	2.75
4	0.1058	0.100	5.48
5	0.1028	0.100	2.72
6	0.0230	0.022	4.35
7	0.0165	0.016	3.00
8	0.0143	0.014	2.10
9	0.0138	0.013	5.80
10	0.0183	0.018	1.60
			$\frac{\sum (\%f)}{n} = 3.30$

* obtained from duplicate analysis

From table 3.3 and table 3.4, it is shown that the result of analysis of calcium and magnesium obtained by the method described above was lower than the true value with the relative error of 6.86 and 3.30 respectively. In case of calcium, if the result determined is 100% the true value is $100 + 6.86 = 106.86$. So the correction factor that must multiply the result of analysis for % calcium is 1.069 . Similarly, the correction factor of percentage magnesium is 1.033.

3.9 Method for Determination of Magnesium

3.9.1 Preparation of Reagents

(1) Standard EDTA Solution

The EDTA solution used for calcium determination was used and the magnesium titer F_{Mg} (mg) for 1 cm^3 of this solution is calculated from the equation

$$F_{Mg} \text{ (mg)} = F_{Ca} \times 0.606$$

where $\frac{Mg}{Ca} = 0.606$

(2) EBT Indicator

0.5 G of EBT (Eriochrome Black T) and 4.5 g of hydroxylamine hydrochloride were dissolved in 100 cm^3 of anhydrous methyl alcohol and stored in a brown bottle in a cool and dark place.

(3) Buffer Solution

70 G of ammonium chloride was dissolved in 570 cm³ of ammonia solution and diluted to 1000 cm³ with distilled water.

(4) Hydroxylamine Hydrochloride Solution (5% W/V)

(5) Potassium Cyanide Solution (2% W/V)

3.9.2 Procedure

Exactly 25 cm³ of sample solution (in item 3.5.1) was transferred to a erlenmeyer flask and 5 cm³ of buffer solution was added to adjust the pH to 10. It was then added 1 cm³ of hydroxylamine - hydrochloride solution (5 %) and three or four drops of indicator and titrated with the standard EDTA solution. The end point of the titration was from red to pure blue. The consumption of the titrant is indicated by A cm³. The percentage of magnesium is calculated as follows.

$$\% \text{ Mg} = \frac{F_{\text{Mg}} \times (A - B) \times \frac{100}{1000}}{\text{weight of salt sample(g)} \times \frac{25}{250}} \times 1.033$$

where

F_{Mg} = magnesium titer (mg)

A = consumption of EDTA titrated with calcium and magnesium.

B = consumption of EDTA titrated with calcium only (from 3.8.2)

1.033 = correction factor of magnesium (obtained as described in 3.8.2)

3.10 Method for Determination of Potassium

3.10.1 Preparation of Reagents

(1) Potassium Chloride Solution

1.907 G of potassium chloride was weighted accurately, dissolved in water and diluted to 1000 cm^3 with distilled water. This solution contains $1000 \mu\text{g}/\text{cm}^3$ of K. and was diluted to $100 \mu\text{g}/\text{cm}^3$ of K.

(2) Sodium Chloride Solution

2.4 G of sodium chloride was weighed, dissolved in water and made up to 250 cm^3 with distilled water.

The concentration of standard potassium solution, amount of potassium chloride, and sodium chloride solution used to prepare 100 cm^3 of standard potassium solution are summarized in table 3.5

3.10.2 Procedure

Potassium content was determined by atomic absorption spectrophotometry. Absorbance of the sample solution was measured and the concentration was determined by comparing to the potassium concentration in the calibration curve of standard solution. The operation condition of the instrument was as follows

light source	K - lamp
lamp current	5 mA
wave length	766.5 nm

slit width	300 μ
oxidant/fuel	acetylene - air
flame stoichiometry	oxidising flame

Effect of major component in rock salt sample (NaCl) on analytical method was studied. Two sets of standard potassium chloride, with and without sodium chloride solution were prepared. The absorbance of both sets were measured and the correlation between the absorbance and concentration are shown in Table 3.6 and 3.7 and Figure 3.3 respectively.

$$\% K = \frac{\mu\text{g/cm}^3 \text{ of K from graph}}{\text{weight of sample(g)}} \times \frac{25.00 \times 250}{\text{required amount of sample}} \times 100\%$$

Table 3.5 Preparation of standard potassium solutions of various concentration.

Concentration of standard potassium concentration $\mu\text{g}/\text{cm}^3$	Potassium chloride solution (100 $\mu\text{g}/\text{ml}$ K) (cm^3)	Sodium chloride solution (cm^3)
0.25	2.50	10.00
0.50	5.00	10.00
0.75	7.50	10.00
1.00	10.00	10.00
1.25	12.50	10.00
1.50	15.00	10.00
1.75	17.50	10.00
2.00	20.00	10.00

Table 3.6 Relationship between absorbance and concentration of standard potassium solution (without addition of sodium chloride)

Concentration $\mu\text{g}/\text{cm}^3$	Absorbance		
	I	II	average
0.25	0.000	0.000	0.000
0.50	0.002	0.001	0.001
0.75	0.005	0.003	0.004
1.00	0.008	0.008	0.008
1.25	0.009	0.009	0.009
1.50	0.010	0.012	0.011
1.75	0.018	0.018	0.018
2.00	0.020	0.020	0.020

Table 3.7 Relation between absorbance and concentration of standard potassium solution (with addition of sodium chloride)

Concentration $\mu\text{g}/\text{cm}^3$	Absorbance		
	I	II	average
0.25	0.020	0.020	0.020
0.50	0.039	0.038	0.0385
0.75	0.053	0.052	0.0525
1.00	0.071	0.070	0.0705
1.25	0.081	0.085	0.083
1.50	0.095	0.095	0.095
1.75	0.107	0.108	0.1075
2.00	0.120	0.120	0.120

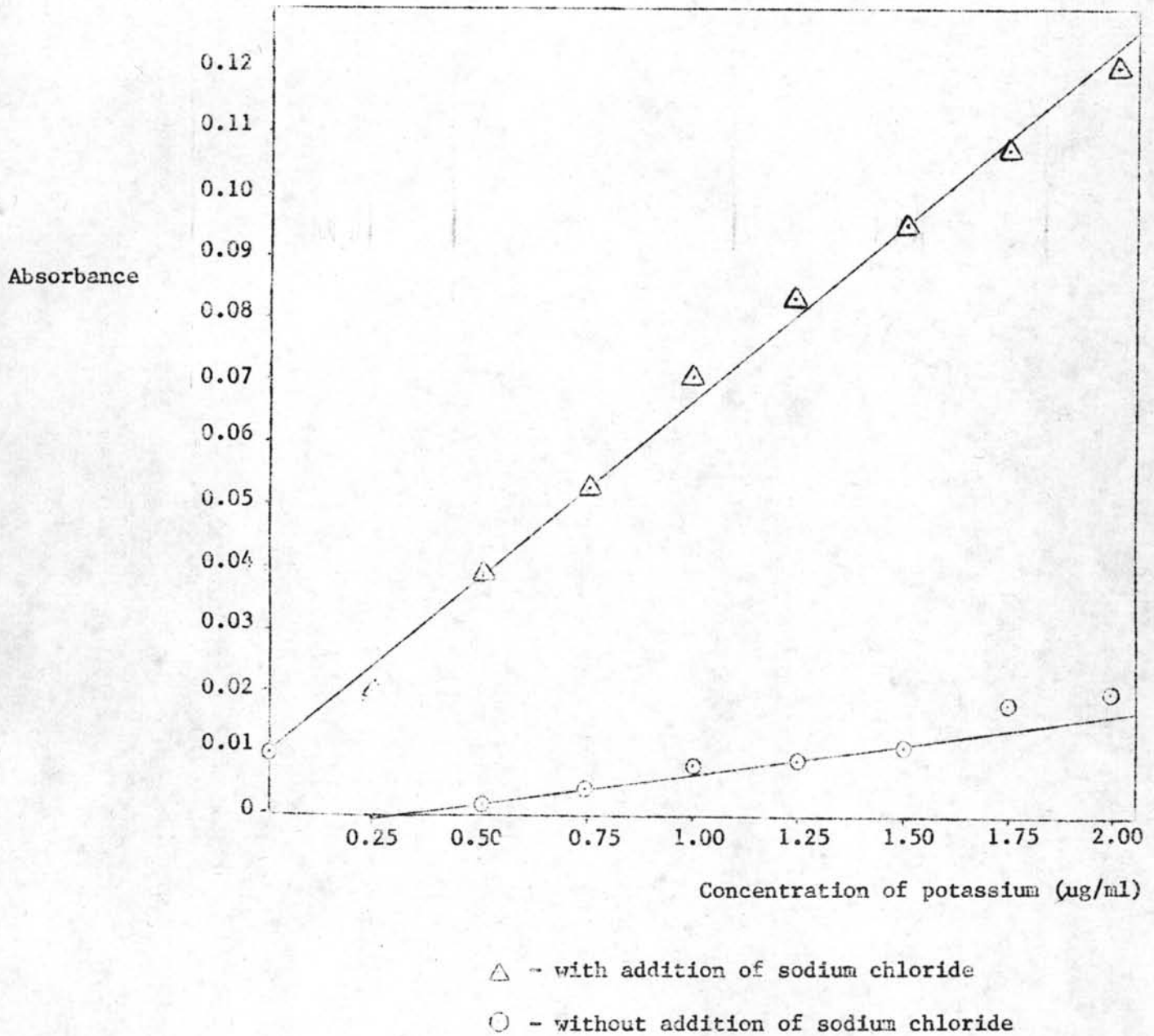
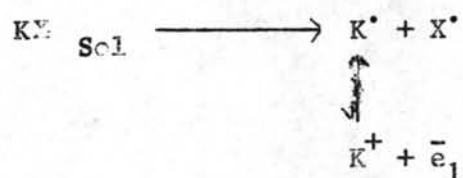


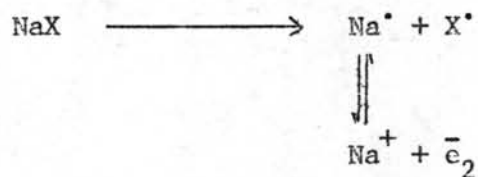
Figure 3.3 Relationship between absorbance and concentration of standard potassium solution with and without addition of sodium chloride

Effect of sodium chloride which is the major component of rock salt on determination of potassium content was studied. It is shown in Figure 3.3 that standard potassium solution with addition of sodium chloride gives higher absorbance than that of standard potassium alone. It can be explained that when solution of potassium chloride and sodium chloride are introduced in the flame, the ionization process is likely to occur. (22)

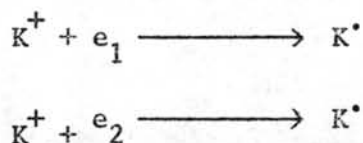
The ionization of alkali metal, potassium in the flame can be represented by the following equation.



The absorption value may be lowered due to the decrease of potassium ground state atom through ionization process. In the presence of another alkali of lower ionization potential (e.g. sodium), the following equation may be occurred.



The partial pressure of the electrons in the flame displace the ionization equilibrium and partial pressure of ground state atoms of potassium increase as



The concentration of K^+ is dependent partially on the electron concentration present. The electron concentration in turn depends on the ionization potential of alkali metal used. In case when sodium has lower ionization potential than potassium, the electron concentration is increased to a greater extent and hence with shift the equilibrium in favour of the production of potassium.

3.11 Method for Determination of Chloride

3.11.1 Preparation of Reagents

(1) Standard Sodium Chloride Solution

A portion of sodium chloride was heated at 500 - 650°C for 40 - 50 minutes and cooled in a desiccator. Approximately 5.85 g of treated sodium chloride was weighed accurately and dissolved in 1000 cm³ of distilled water. One cm³ of this solution contains $3.5453 \times f_{NaCl}$ (mg) chloride ion.

f_{NaCl} is the factor which is obtained by the following equation.

$$f_{NaCl} = \frac{\text{amount of sodium chloride taken(g)}}{5.8443} \times \frac{\text{purity of sodium chloride (\%)}}{100.00}$$

(2) Standard Silver Nitrate Solution

17.0 G of silver nitrate was dissolved in 1000 cm³ of water and stocked in a brown colored bottle.

The chloride titers $F_{(Cl)} \text{ (mg)}$ for 1 cm³ of this solution was determined as follows.

Exactly 25 cm³ of standard sodium chloride solution was titrated with standard silver nitrate solution the end point was detected according to item 3.11.2.

The chloride titers $F_{Cl(mg)}$ is obtained by the following equation.

$$F_{Cl} = \frac{25.00 \times f_{NaCl} \times 3.5453}{\text{consumption of standard silver nitrate solution(cm}^3\text{)}}$$

3.11.2 Procedure

The chloride content was determined by the potentiometric titration. 5 cm³ of sample solution (prepared in accordance with 3.5.2) was measured quantitatively and diluted with distilled water to about 25 cm³. The solution was titrated with standard silver nitrate solution. The potentials of the solution after each addition of standard silver nitrate were recorded. The end point was obtained from the second derivative plot of a potentiometric titration curve. The percentage of chloride is calculated from the following equation.

$$\% Cl = \frac{F_{Cl(mg)} \times \text{consumption of AgNO}_3 \times \frac{100}{1000}}{\text{weight of salt sample(g)} \times \frac{5}{250}} \times 0.9939$$

The correction factor for chloride is 0.9939 which was obtained by carrying out the experiment and calculating in the same manner as described previously in the case of calcium and magnesium in 3.8.2.

Table 3.8 The mean value of relative error for chloride

Sample no.	Weight of NaCl(g) g	From * analysis (Practical) h	% Relative error $j = \frac{(h-i)}{i} \times 100 \%$
1	3.7597	61.137	0.6319
2	3.7992	61.125	0.6205
3	3.8199	61.143	0.6486
4	3.8434	61.154	0.6669
5	3.8608	61.073	0.5356
6	3.8810	61.085	0.5552
7	3.9023	61.078	0.5426
8	3.9206	61.132	0.6316
9	3.9421	61.153	0.6652
10	3.9665	61.127	0.6232
			$\frac{\sum (\% j)}{n} = 0.6128$

i = theoretical value

= % Cl in NaCl = 60.746%

* obtained from duplicate analysis

3.12 Method for Determination of Sulfate

3.12.1 Preparation of Reagents

(1) Suspended Barium Chromate Solution

2.5 G of barium chromate was added to mixed solution of 100 cm³ of acetic acid* (1 + 35) and 100 cm³ of hydrochloric acid (1 + 50).

(2) Ammoniac Water Containing Calcium

1.85 G of calcium chloride was dissolved in 500 cm³ of ammoniac water (1 + 4) and stored in a polyethylene bottle.

(3) Standard Sulfate Solution

1.81 G of potassium sulfate previously heated at 110 ± 2°c for an hour was weighed accurately and diluted with distilled water to 1000 cm³. In every time to use, 50 cm³ of this stock solution was measured out and diluted to 500 cm³. 1 cm³ of this solution contains 0.1 mg of sulfate ion.

3.12.2 Procedure

A required amount of sample solution (prepared in item 3.5.2) was transferred quantitatively to a 50 cm³ volumetric flask. 3 cm³ of suspended barium chromate solution was added and the content was shaken thoroughly for one minute and settled for two minutes. The shaking procedure was repeated again. 1 cm³ of the

* acetic acid(1+35) means one volume of concentrated acetic acid diluted with 35 volumes of water

clear supernatant of the ammonia water containing calcium and 10 cm³ of ethyl alcohol were added and the content was diluted with distilled water to the 50 cm³ marked line. The solution was then shaken thoroughly for one minute and settled for ten minutes. The solution was filtered with a filter paper (Whatman filter paper No. 46). The absorbance of the filtrate was measured at 375 nm. The content of sulfate was obtained by comparing with the known amount of sulfate on a calibration curve. The calibration curve was prepared as follow.

1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5 and 5 cm³ of the standard sulfate solution (in item 3.12.1(3)) (each solution contains 0.10, 0.15, 0.20, 0.25, 0.3, 0.35, 0.4, 0.45 and 0.5 mg of sulfate) was pipetted and transferred to 50 cm³ volumetric flasks, and added with distilled water to 25 cm³. The procedure was conducted in accordance with 3.12.2. The relationship between the absorbance and the amount of sulfate was then established.

The percentage of sulfate is calculated from the following equation.

$$\%SO_4 = \frac{\text{amount of } SO_4 \text{ from graph(mg)} \times \frac{1}{1000} \times 100\%}{\text{weight of sample(g)} \times \frac{\text{required amount of sample solution(cm}^3\text{)}}{250}}$$

Effect of the major component (NaCl) on result of percentage sulfate determined by photometric method was studied. It is revealed that the absorbance of the standard solution with and without addition of sodium chloride were almost equal. It is concluded that sodium chloride does not interfere in the method as shown in Table 3.9 and Figure 3.4.

Table 3.2 Effect of sodium chloride in sulfate determination

Sulfate Content (mg)	Absorbance I	Absorbance II
0.1	0.195	0.210
0.2	0.315	0.310
0.3	0.415	0.405
0.4	0.495	0.510
0.5	0.625	0.640

I without addition of sodium chloride

II with addition of sodium chloride

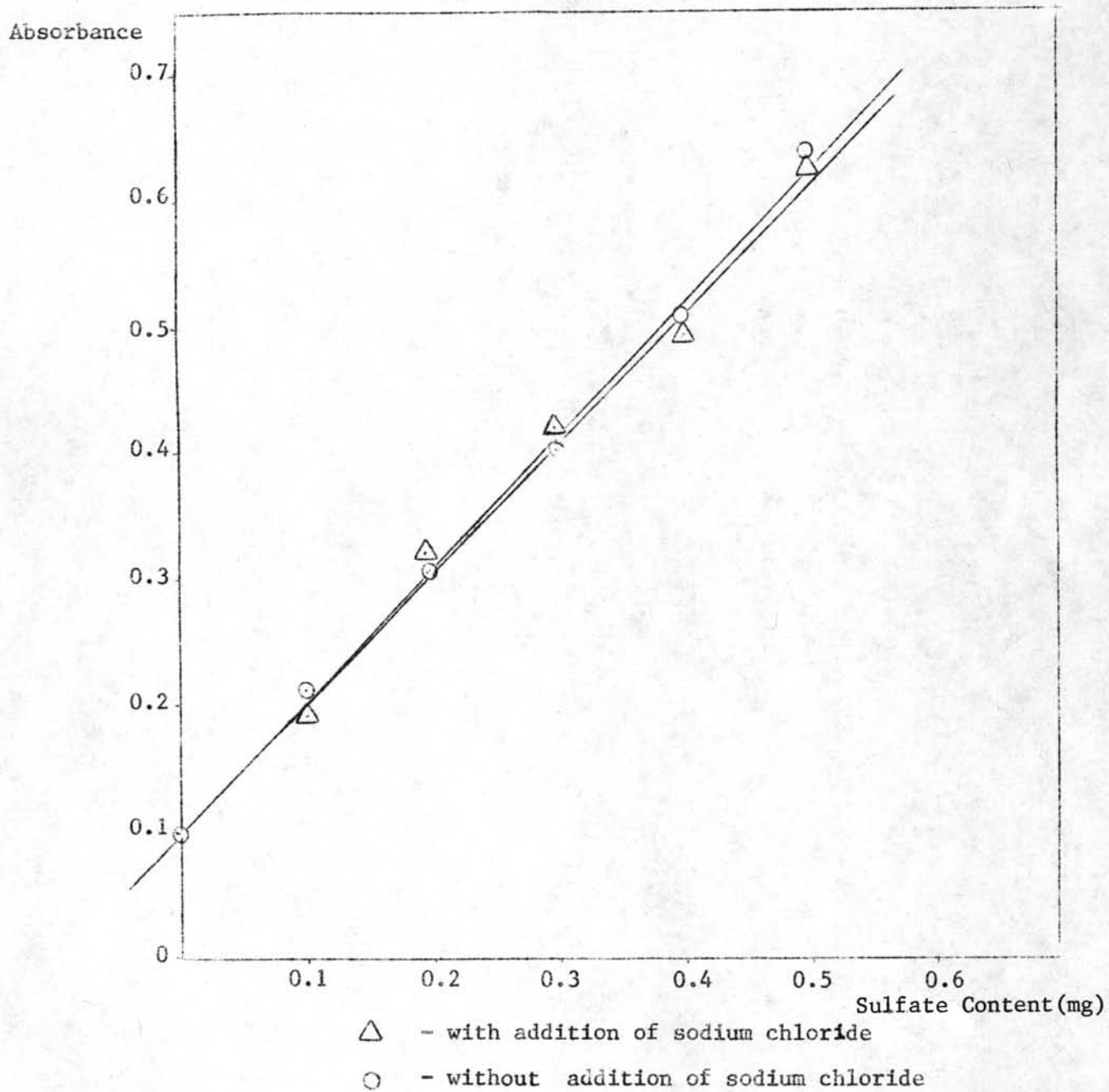


Figure 3.4 Effect of sodium chloride in sulfate determination

3.13 Calculation of Percentage of Sodium Chloride

Sodium chloride content is obtained by calculating from the ionic content found by analysis.

The value of α is calculated from the following equation

$$\alpha = (\% \text{Ca}^{2+}) \times 2.92 + (\% \text{Mg}^{2+}) \times 4.81 - (\% \text{SO}_4^{2-}) \times 1.22$$

if α is positive

$$\% \text{NaCl} = (\% \text{Cl}^-) \times 1.648 - (\% \text{K}^+) \times 1.49 - \alpha$$

if α is negative

$$\% \text{NaCl} = (\% \text{Cl}^-) \times 1.648 - (\% \text{K}^+) \times 1.49$$

The coefficient of each ion (in percent) is the equivalent of the corresponding ion to NaCl; namely,

$$\text{Coefficient of Cl}^- = \frac{\text{NaCl}(58.443)}{\text{Cl}(35.453)} = 1.648$$

$$\text{Coefficient of Ca}^{2+} = \frac{2\text{NaCl}(58.443 \times 2)}{\text{Ca}(40.08)} = 2.92$$

$$\text{Coefficient of Mg}^{2+} = \frac{2\text{NaCl}(58.443 \times 2)}{\text{Mg}(24.305)} = 4.81$$

$$\text{Coefficient of SO}_4^{2-} = \frac{2\text{NaCl}(58.443 \times 2)}{\text{SO}_4(96.062)} = 1.22$$

$$\text{Coefficient of K}^+ = \frac{\text{NaCl}(58.443)}{\text{K}(39.102)} = 1.49$$

3.14 Calculation of Percentage of Sodium

According to section 3.13 , if

if α is positive

$$\%Na = \%NaCl \times 0.3934$$

if α is negative

$$\%Na = (\% NaCl + \alpha) \times 0.3934$$

The coefficient of sodium is the equivalent of NaCl to
 $\%Na$; namely,

$$\frac{Na (22.990)}{NaCl (58.443)} = 0.3934$$