DETERMINATION OF MAGNESIUM IN DOLOMITE

BY

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ABSTRACT

In this work, four methods have been tried in an effort to find the best method for the determination of magnesium in dolomite. The determination of the magnesium content of dolomite, the raw material for the production of cement, is very important in that the quality of cement depends on its magnesium content. The methods are: the Classical titration with hydrochloric acid and sodium hydroxide, the Complexometric titration with EDTA, Atomic Absorption Spectrometry and Absorption Spectrophotometry with Erio T and Titan yellow. A statistical analysis was carried out using the Student's t-test at 95% level of confidence and the Correlation coefficient. The Student's t-test showed that there is no significant difference between the results by the methods, except those between the Classical titration and Atomic Absorption - Direct Calibration and Absorption Spectrophotometry - Standard Addition methods. The methods also showed good correlation between them except the classical titration and Absorption Spectrometry - Standard Addition which showed poor correlation ($r < 0.90$). From the results of the statistical analysis and the difficulties encountered during the course of the analyses it has been decided that Atomic Absorption Spectrometry is the best of the four methods for routine quality control analysis. It has been found that it is more sensitive, has fewer interferences and requires the shortest time. However if the cost of an atomic absorption spectrometer is taken into consideration, the method

becomes very expensive. In that case the Complexometric titration with EDTA is the next best alternative.

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CHAPTER 1

GENERAL INTRODUCTION

In the cement industry dolomite is used mainly as a source of lime, which is an important component. Cement is used as a binder in the production of concrete which is used widely in the building industry. Apart from the major elements calcium and magnesium, dolomite rocks contain some silicon, aluminium and iron.

Cement itself is composed of a number of chemical constituents which control its behaviour[1]. The basic ones are:

lime (CaO)	63%
silica (SiO_2)	21%
alumina (Al_2O_3)	6%
iron (Fe_2O_3)	3%
magnesia (MgO)	1-6%
alkali oxides (Na_2O and K_2O)	less than 2%

These percentages are average values. These constituents exist as complex compounds of which the major ones are:

tricalcium silicate ($3CaO.SiO_2$)
dicalcium silicate ($2CaO.SiO_2$)
tricalcium aluminate ($3CaO.Al_2O_3$)
tetracalcium alumino ferrite ($4CaO.Al_2O_3.Fe_2O_3$)

The symbols used here are those which are used in the cement industry.

The hardening of cement depends upon calcium silicate compounds which, upon reaction with water, produce other compounds which give cement the stone-like quality. The rate of hardening, strength attained, durability and other properties of cement are controlled by the relative proportions of these compounds, for example, to produce a cement of low heat generation a relatively high dicalcium silicate and low tricalcium aluminate is desirable.

In dolomite rocks calcium and magnesium are present as carbonates ($CaCO_3$ and $MgCO_3$). When the dolomite is heated to about 1200 K, the carbonates are transformed to their oxides.

$$MCO_3 \xrightarrow{\text{heat}} MO + CO_2\uparrow$$

where M stands for either calcium or magnesium.

When lime and magnesia are mixed with water hydration occurs. The magnesia, also called periclase in the cement industry, hydrates more slowly than lime, and when it does, it undergoes volume expansion which is greater than that which occurs when lime combines with water. If a sufficient amount of magnesia hydrates within a hardened mass of cement paste or concrete, it can cause severe cracking and disintegration. These effects usually start showing after fifteen to twenty years. Good quality cement should, therefore, have a low magnesium content. Cement specifications give magnesium oxide a maximum of 5%[1] for Portland cement.

At Chilanga Cement Factory, Chilanga, Zambia, there are problems with the determination of magnesium in dolomite. The method used at present gives a range of not less than 1.5% after six or more replicate analyses. Whereas the method would be adequate for rocks with low magnesium content (less than 3% MgO), it is inadequate for rocks that contain more than 4% MgO. For such rocks an accurate and more precise determination of magnesium is important. The purpose of the present work is to find an accurate and precise method that can be used for routine analysis. Several methods for the determination of magnesium can be found in many reference books[2, 3, 4, 5] some of which have been investigated in the present work.

At Chilanga Factory the classical titration method[6] is employed. This method involves the dissolution of the rock sample in an excess of hydrochloric acid and back-titrating the excess acid with sodium hydroxide. This gives the total carbonate content. The magnesium is then precipitated with an excess of sodium hydroxide and the excess base back-titrated with acid. This gives the magnesium content.

The other methods that can be employed are atomic absorption spectrometry, quantitative absorption spectrophotometry, complexometric titration, gravimetric analysis, flame photometry and emission spectroscopy. Of the above methods, atomic absorption, absorption spectrophotometry, and complexometric titration have been investigated in the present work. The results found by these

methods are compared to those found by the classical titration method.

Of the three methods investigated, atomic absorption spectrometry is the most sensitive. The first problem with atomic absorption spectroscopy is that the resonance line which is used depends on the amount of magnesium[7,8,9].

Resonance line (nm)	Range of optimum level (ppm)	Sensitivity (ppm)
285.2	0.2-2	0.01
202.5	10 -500	2
279.5	100 -1000	5

The second problem encountered with this method is interference mainly from silicon, aluminium, sulphate and phosphate[2,8]. The results found by this method are also affected by such effects as ionization, composition of sample solution in comparison to the standard (matrix effects) and instrumental factors such as flame conditions and monochromator slit width. Hansen and Hall[10] have studied matrix interference and the effects of ionization suppression, lateral diffusion and flame conditions in the determination of magnesium, calcium and other metals. The findings led to the development of a single base solution, containing 0.4% caesium chloride and 2% hydrochloric acid, suitable for preparing sample and standard solutions.

Interferences, other than spectral, in atomic absorption can be minimized in three ways. The first way is to remove the interfering ions from the test solution. The second is to add to the test solution reagents which are commonly known as releasing reagents. The third way is by using a technique known as standard addition. In this technique equal volumes of the sample solution are added to the standards. This does not remove the interferences but the interferences affect all the solutions in the same manner up to the limiting concentration. A new approach to the standard addition technique was devised by Leiritie and Mattsson[11]. By means of a Y-shaped capillary tube, the sample ions are supplied continuously to the flame and the ions being determined, as a standard solution, are introduced simultaneously and automatically into the flame.

Absorption spectrophotometry has yet to find general application[2]. This is partly due to the lack of good reagents for magnesium and partly because of interference from other ions. However, with the discovery of new reagents the method is being used more widely. The interferences can be reduced by making use of masking and releasing reagents. Some releasing reagents have been found to form complexes with the reagents used which absorb strongly near the maximum light absorption wavelength of the required complex. An example of this is polyvinyl alcohol if the reagent used is Titan yellow. Other masking reagents have been found to affect the stability of the magnesium complexes[2]. Another way of eliminating interferences is by removing the responsible ions from the test solution by, for example, ion exchange.

In complexometric titration with ethylenedinitrilo-tetraacetic acid (EDTA; 1, 2-diaminoethanetetraacetic acid) [3, 12, 13, 14], interferences are mainly caused by the cations of iron, aluminium and manganese. Apart from reacting with EDTA if not masked, they react irreversibly with most recommended indicators. When present in more than trace amounts, even when masked they give rise to colour changes in the indicator, making endpoint detection difficult.

Several complexometric titration procedures are available. Sahai[15] gives the following procedure. The sample is brought into solution with hydrochloric acid. Hydrofluoric acid is added and the solution evaporated to dryness to remove silicon. The residue is fused with sodium carbonate and the product dissolved in hydrochloric acid. First calcium is determined in one aliquot by masking iron, aluminium and other heavy metals with 5% potassium cyanide in a 1:1 solution of 1 M potassium hydroxide and triethanolamine. The solution is titrated with EDTA using the Patton-Reeder indicator (2-hydroxy-1-(2-hydroxy-4-sulpho-1-naphthylazo)-3-naphthoic acid). To a second aliquot, hydroxylammonium chloride and the masking mixture are added. The solution is adjusted to pH 10 and titrated against EDTA using Eriochrome black T (Erio T) as indicator. This gives the total calcium and magnesium in the sample. The magnesium is found by difference.

Rahut et al[16] give procedures applicable to solutions containing up to 10 mg of magnesium and 15 mg of calcium. They

are based on the fact that calcium sulphate is insoluble in 60% ethanol, whereas magnesium sulphate is soluble and can be titrated with Erio T as indicator.

Budesinsky[17] used the following method for determining calcium and magnesium simultaneously. Firstly calcium is titrated with EDTA at pH 13 - 13.3 with antipyrinylazo III as indicator. After the endpoint has been reached, the orange-red colour is discharged by adding 40% hydroxylammonium chloride and magnesium is then titrated with EDTA at pH 10.2 - 10.5 with thymolphthalein complexan as indicator. The titrations can also be followed spectrophotometrically at 600 nm. Interfering ions such as iron and aluminium must be masked with cyanide. The ratio of magnesium to calcium must not exceed 1:1000, otherwise appreciable adsorption of calcium on magnesium hydroxide occurs.

Khalifa and Ismail[18] give a slightly different method to the usual EDTA titrations. To an aliquot, an excess of EDTA is added. Aluminium is either masked with fluoride or precipitated as aluminium hydroxide with boiling aqueous ammonia - ammonium nitrate and calcium is separated from magnesium as tungstate. The solution is then titrated with a mercuric salt solution at pH 11 using a silver amalgam electrode to determine magnesium.

The method used by Alvarez-Jimenez et al[19] is similar to most methods reported except for the use of palladiazo as indicator. This indicator forms a blue complex with both calcium and magnesium.

It is used in the same manner as Erio T to determine the total calcium and magnesium. But unlike Erio T it can still be used at high pH values to titrate calcium in the presence of magnesium hydroxide precipitate. The indicator is sensitive to the ionic strength of the solution and especially to the amount of hydrochloric acid used for sample dissolution. The endpoint becomes sharper as the ionic strength decreases but becomes difficult to detect with ageing of solutions.

Abramov et al[20] determined magnesium in dolomite using an automatic photometric titrator. The rock is dissolved in 20% hydrochloric acid. In one portion of the test solution, calcium is titrated at pH 14 in the presence of triethanolamine and sucrose with Acid chrome dark blue (C. I. Mordant 13) as indicator. In a second portion of the sample solution total calcium and magnesium are titrated similarly at pH 10 but without sucrose. The magnesium is found by difference.

Unlike atomic absorption, flame photometry[13] has not gained much popularity in the determination of magnesium. It is not commonly used because it requires the use of nitrous oxide-acetylene combination and not the commonly used air-acetylene. The excitation energy for magnesium is 415 kJ/mole which is much higher than that of sodium (204 kJ/mole) or calcium (283 kJ/mole) both of which can be easily determined using an air-acetylene flame. The air-acetylene flame has a maximum temperature of 2,525 K which is not high enough for the excitation of magnesium. A nitrous oxide-acetylene flame has a maximum temperature of 3,230 K which is high enough to reach the excitation state of magnesium.

In conclusion, with an air-acetylene flame, which is commonly used in flame photometry, it is not possible to determine magnesium. Furthermore, the sensitivity in flame photometry (0.003 mg/ℓ Mg) is lower than that in atomic absorption spectroscopy (0.0001 mg/ℓ Mg). In addition to this magnesium shows a strong self absorption[21] and its emission is weak compared with the flame background.

Gravimetric methods when used for the determination of magnesium, especially for rocks low in magnesium, usually give erratic results[2, 13]. For this reason they are not usually recommended.

Most of the procedures mentioned above deal only with the actual analysis without a mention of how the rock sample is brought into solution. To obtain accurate results, it is important that the sample be quantitatively brought into solution. Renard and Blane[22] studied the effects of acid, temperature and duration of attack on the dissolution of a rock sample. They found the optimum conditions to be treatment of the rock for two hours at 330 K with 1 M acetic acid. In the present work, however, the rock was, in all cases, dissolved in hydrochloric acid, since the rock worked on is a carbonate. It is also the way that Chilanga Factory Laboratories prepare their sample solution. Furthermore the procedure given by Renard and Blane requires a higher temperature and longer time which would make the procedure unduly long for routine quality control analysis.

CHAPTER 2

CLASSICAL TITRATION OF MAGNESIUM WITH SODIUM HYDROXIDE AND HYDROCHLORIC ACID

2.1. INTRODUCTION

In the classical titration of calcium and magnesium[6], the dolomite sample is dissolved in an excess of hydrochloric acid. The metal carbonates react with the acid to give water soluble chlorides.

$$MgCO_3 + 2HCl \rightarrow MgCl_2 + H_2O + CO_2\uparrow$$
$$CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2\uparrow$$

The residue carbon dioxide liberated can interfere with the subsequent determination and is therefore expelled by boiling the solution. The excess hydrochloric acid is then titrated with sodium hydroxide using phenolphthalein as indicator.

Excess sodium hydroxide is then added to precipitate magnesium as a hydroxide.

$$MgCl_2 + 2NaOH \rightarrow Mg(OH)_2\downarrow + 2NaCl$$

The calcium hydroxide does not precipitate under these conditions. The excess sodium hydroxide is then back-titrated with acid using thymolphthalein as indicator. The choice of the indicator for this titration should be made such that the indicator changes colour just when the excess hydroxide has been neutralized. It can be shown that, when the excess hydroxide has been neutralized, the pH of the solution is 10.4. Thymolphthalein, with a pH transition

interval of 9.0 - 10.5, is therefore a suitable indicator.

The total carbonates, as calcium carbonate, are obtained by noting the volume of hydrochloric acid used to dissolve the sample and the volume of sodium hydroxide required to neutralize the excess acid. The calcium carbonate content is determined by difference, after determining the magnesium carbonate content of the sample and converting it to the equivalent calcium carbonate.

Although the introduction above deals with the determination of both calcium and magnesium, the calcium determination was omitted. This was done since the primary objective of this work is the determination of magnesium.

2.2. EXPERIMENTAL

Reagents

Hydrochloric acid (ca 0.5 M): Approximately 42 cm^3 of the concentrated acid (specific gravity 1.18) were diluted to 1000 cm^3 with water.

Sodium hydroxide (ca 0.25 M): The solid reagent (10 g) was dissolved in water and diluted to 1000 cm^3.

Potassium hydrogen phthalate (0.05000 M): The solid reagent (2.0423 g) was dissolved in water and the volume brought to

the mark in a 200 cm^3 volumetric flask.

Phenolphthalein indicator: The solid reagent (2 g) was dissolved in 100 cm^3 of 95% ethanol.

Thymolphthalein indicator: The solid reagent (4 g) was dissolved in 100 cm^3 of 95% ethanol.

Standardization of Sodium Hydroxide

The standard potassium hydrogen phthalate solution (50.00 cm^3) was pipetted into a 250 cm^3 erlenmeyer flask. Three drops of phenolphthalein indicator were added and the solution titrated against sodium hydroxide until the colour changed from colourless to a faint pink. The titration was performed two more times (table 2.1).

Standardization of Hydrochloric Acid

The hydrochloric acid solution (20.00 cm^3) was pipetted into a 250 cm^3 erlenmeyer flask. Three drops of phenolphthalein indicator were added and the solution titrated against the sodium hydroxide until the colour changed from colourless to a faint pink. The titration was performed three more times (table 2.2)

DETERMINATION OF MAGNESIUM CARBONATE

About 5 g of the finely ground dolomite rock sample was dried in an electric oven at 390 K for one hour and cooled in a desiccator. About 0.1 g of the dried sample was weighed into each of six 250 cm^3 erlenmeyer flasks. For each sample the following procedure was followed. The sample was moistened with 1 cm^3 of water and then an excess of hydrochloric acid (20.00 cm^3) was added from a burette, rinsing the sides of the flask with water after the addition. The solution was then boiled on a hot-plate for three minutes and left to cool. Three drops of phenol-phthalein indicator were then added and the solution titrated against sodium hydroxide to the first permanent pink colour. The solution was again brought to the boil and four drops of thymol-phthalein indicator added. To the still hot solution an excess of sodium hydroxide (10.00 cm^3) was added and then the solution left to cool. The cool solution was titrated against hydrochloric acid until the blue colour just disappeared. The volume of acid required to neutralize the excess sodium hydroxide was recorded (table 2.3).

2.3. RESULTS AND DISCUSSION

The percentage of magnesium carbonate in the sample was found to be 3.74% with a standard deviation of 0.12%. The confidence limit for this value is ±0.13% at 95% level of confidence.

TABLE 2.1: Standardization of sodium hydroxide

TITRATION NO.	BURETTE READINGS		VOLUME OF NaOH USED (cm^3)	MOLARITY OF NaOH
	INITIAL	FINAL		
1	3.40	13.70	10.30	0.2427
2	13.70	24.00	10.30	0.2427
3	25.00	35.30	10.30	0.2427

TABLE 2.2: Standardization of hydrochloric acid.

TITRATON NO.	BURETTE READINGS		VOLUME OF NaOH USED (cm^3)	MOLARITY OF HCl
	INITIAL	FINAL		
1	0.00	39.35	39.35	0.4774
2	0.10	39.40	39.30	0.4770
3	0.10	39.45	39.35	0.4774
4	0.00	39.35	39.35	0.4774

TABLE 2.3: Determination of magnesium carbonate.

SAMPLE NO.	WEIGHT OF SAMPLE (g)	BURETTE READINGS		VOLUME OF HCl_3 USED (cm^3)	WEIGHT OF $MgCO_3$ (mg)	% $MgCO_3$
		INITIAL	FINAL			
1	0.1202	20.10	24.95	4.85	4.714	3.92
2	0.1010	0.50	5.40	4.90	3.683	3.65
3	0.1020	25.20	30.10	4.90	3.683	3.61
4	0.1000	0.50	5.40	4.90	3.683	3.68
5	0.0980	30.10	35.00	4.90	3.683	3.76
6	0.1225	29.80	34.65	4.85	4.714	3.85

A comparison of this value with that which was found at Chilanga Cement laboratory (3.61%) using Student's t-test at 95% confidence level shows that there is no significant difference in the two values.

A few problems are encountered during the course of the determination. The neutralization of excess hydrochloric acid after the dissolution of the sample does not present any problems as the endpoint is sharp and easy to detect. It is also easy to tell if one has overtitrated from the intensity of the colour of the solution. The endpoint for the titration of excess sodium hydroxide is, however, not as sharp and as easily detectable as that for the first titration. At the beginning of the titration the colour of the solution is blue. As the titration is continued the colour of the solution first turns pink and on addition of two to three drops of the titrant it becomes colourless. Before the addition of sodium hydroxide the solution is pink. This means that the titration should be proceeded only to the pink colour.

On addition of sodium hydroxide magnesium precipitates out as hydroxide. Some calcium hydroxide will co-precipitate with magnesium[12]. The co-precipitated calcium hydroxide redissolves slowly so that at the endpoint some calcium will still remain as a precipitate. This has the effect of reducing the amount of excess hydroxide available for titration thus raising the magnesium content of the sample. If the solution is allowed to stand for a few minutes after the endpoint some calcium comes back into solution

and a little more titrant could be added. However, after titrating the excess sodium hydroxide the pH of the solution will be lowered and, therefore, magnesium hydroxide will start redissolving. This means any extra titrant that will be added will also react with the hydroxide from the dissociation of magnesium hydroxide. This would make the apparent content of magnesium lower than the actual value.

Even when the correct endpoint is attained at the first appearance of the pink colour, the dissociation of magnesium hydroxide makes the solution turn blue on standing for less than twenty seconds. This makes it difficult to determine the correct endpoint since the reaction is rather slow as the endpoint is approached and the titration has to be carried on slowly to avoid overtitration. To get acquainted with the titration, several runs on synthetic solutions were made.

The other source of error arises from the sample solution preparation. After dissolving the sample in hydrochloric acid, some solid particles still remain. These undissolved particles, it is assumed, do not contain any imbedded magnesium carbonate in them. This assumption may lead to lower values of magnesium especially for silicate rocks. It has been suggested[15] that if the amount of undissolved material is at least 1% of the original sample, then the residue material should be fused with sodium carbonate at 770 K and the product of fusion dissolved in hydrochloric acid. In the present work the amount of undissolved

material was determined and found to be less than 0.6%.

2.4 CONCLUSION

The procedure followed in this titration is similar to that followed at Chilanga Cement Factory laboratory except for two deviations.

The first deviation lies in the procedure for the standardization of the solutions used. In the Chilanga Factory procedure the concentration of hydrochloric acid was determined, first, by adding an excess of the acid to a known weight of calcium carbonate. The excess acid was then back-titrated with sodium hydroxide, yet not standardized. The sodium hydroxide was then titrated against hydrochloric acid. The calculations for the concentration of hydrochloric acid and sodium hydroxide can be found in reference 6. In the procedure followed in this work, sodium hydroxide was first standardized against potassium hydrogen phthalate, a primary standard, and then used to standardize hydrochloric acid.

The second deviation lies in the precipitation of magnesium as hydroxide. In the case of the Chilanga Factory procedure, after bringing the solution to the boil, it was titrated against sodium hydroxide to the thymolphthalein endpoint. Then an excess of the base was added. In the present work, the base was immediately added in excess, without paying any special attention to the endpoint, because what is important here is to have the base in

excess. The indicator was added mainly to indicate the endpoint for the back-titration. After the first run, a constant volume of the base was being added to all the flasks.

The determination of total carbonates was also omitted although phenolphthalein indicator was added. Phenolphthalein was added so as to get an insight of the advantages and disadvantages brought about by its colour at the endpoint of the titration for magnesium. From the theoretical point of view, these changes should not affect the final result. Comparison of the final result found with that found by Chilanga Factory Laboratory confirms this.

CHAPTER 3

COMPLEXOMETRIC TITRATION

3.1. INTRODUCTION

In the titrimetric determination of magnesium with 1, 2 - diaminoethanetetraacetic acid (EDTA), magnesium forms a complex with the titrant. Both magnesium and calcium form stable complexes with EDTA at pH 10, whereas at pH 7.6 only the calcium complex is stable[2]. It is therefore theoretically possible, by choosing a pH just above 7.6 and a suitable indicator, to titrate calcium in the presence of magnesium, and then by raising the pH to 10 the magnesium is also titrated. In practice, however, calcium is titrated at a pH greater than 12 where the magnesium is precipitated as hydroxide and does not interfere. The complexometric determination of magnesium is therefore accomplished in two parts: determination of calcium plus magnesium and that of calcium alone, finding magnesium by difference.

Several indicators have been recommended for this titration. In the titration of both magnesium and calcium the most widely used indicator is Erio T[3]. Other indicators that can be used are Eriochrome blue black T and Calmagite. Indicators such as Erio T and Eriochrome blue black T are sensitive to the presence of iron and manganese. The metals must either be masked or removed from the test solution. In rocks with low magnesium content such as limestones and dolomites, acid alizarin black and methyl thymol blue can be employed for the titration of calcium[2]. Murexide has also been extensively used for such titrations. The indicators calcein, Cal-Red, Eriochrome blue black R have been used in the

determination of calcium even for rocks with approximately a 1:1 ratio of magnesium to calcium[2]. The Patton - Reeder indicator[15] has also been used for this titration. The indicator must, however, be added after the precipitation of magnesium hydroxide to avoid its coprecipitation as the pH is raised. Another indicator that can be employed is palladiazo[19]. This indicator is specifically used as a metallochromic indicator for calcium but it can also be used as an absorption reagent for both calcium and magnesium. It is especially sensitive to the amount of hydrochloric acid used for sample dissolution.

In the present work Erio T was used for the titration of the total calcium and magnesium. For the titration of calcium, murexide was employed.

3.2. EXPERIMENTAL

Reagents

Hydrochloric acid (HCl); Concentrated, Sp. Gr. 1.18

EDTA (0.01022 M) $Na_2H_2C_{10}H_{12}O_8N_2 \cdot 2H_2O$; The reagent (3.7984 g) was dissolved in water and diluted to volume in a 1000 cm^3 volumetric flask.

Sodium Hydroxide (NaOH, 1.00 M);

The reagent (4.00 g) was dissolved in water and diluted to volume in a 100 cm^3 volumetric flask.

Buffer solution (NH_4Cl - NH_4OH, pH 10)

Ammonium Chloride (70.00 g) was dissolved in about 300 cm^3 of water, then 570 cm^3 of ammonia solution (Sp. Gr. 0.910) was added and the mixture diluted to volume in a 1000 cm^3 volumetric flask.

Hydroxylamine hydrochloride solution ($NH_2OH.HCl$, 10% w/v);

The reagent (10.00 g) was dissolved in water and diluted to volume in a 100 cm^3 volumetric flask.

Triethanolamine solution ($N(C_2H_4OH)_3$);

Potassium cyanide (6.40 g) was dissolved in 60 cm^3 of water and then mixed with 40 cm^3 of triethanolamine.

Erio T indicator (1% w/v)

The reagent (0.20 g) was dissolved in a solution consisting of 15 cm^3 triethanolamine and 5 cm^3 of 95% ethanol. Fresh solutions were prepared every two weeks.

Murexide indicator;

A minimum amount of the reagent was dissolved in 10 cm^3 of water to give a saturated solution. Fresh solutions were prepared everyday.

Methyl red indicator (0.5% w/v)

The reagent (0.25 g) was dissolved in 50 cm^3 of 95% ethanol.

PROCEDURE

The finely ground rock sample (approximately 2 g) was dried in an electric oven at 380 K for one hour and cooled in a desiccator. Then 0.1051 g was weighed out and quantitatively transferred to a 250 cm^3 beaker with the aid of a jet of water. Concentrated hydrochloric acid was slowly added until effervescence ceased, then an excess of 1 cm^3 added. The inside of the beaker was washed with water; more water was added to bring the volume to about 50 cm^3. The beaker was placed on a hotplate and the solution gently boiled for five minutes and then left to cool. The cool solution was filtered through a Whatman No. 41 filter paper into a 250 cm^3 volumetric flask. The residue was washed with water and then the flask filled to the mark with water.

Two 20.00 cm^3 aliquots of the sample solution were pipetted into two 250 cm^3 erlenmeyer flasks. Two drops of methyl red indicator were added to each flask. Sodium hydroxide was added dropwise until the solutions turned yellow (pH ≈ 6.0).

Into the first flask was added 2 cm^3 of the buffer solution and 5 cm^3 each of triethanolamine and hydroxylamine hydrochloride. Four drops of Erio T were added and the solution titrated against EDTA until the solution turned a clear blue. The volume of EDTA used was recorded (table 3.1). The titration was performed six times.

Into the second flask was added 5 cm^3 each of triethanolamine and hydroxylamine hydrochloride followed by 5 cm^3 of sodium hydroxide. Enough murexide indicator (1 cm^3, the amount of indicator to be added depends on the concentration of calcium) was then added. The solution was titrated against EDTA until it turned blue. The volume of EDTA used was recorded (table 3.1). This titration was also performed six times.

3.3: RESULTS AND DISCUSSION

The average value of the percentage of magnesium carbonate in the sample was found to be 3.62% with a standard deviation of 0.18. The confidence limit at 95% level of confidence is ±0.19%. This value compares well with that which was found at Chilanga Cement Factory Laboratory (3.61%).

This method, as mentioned earlier, was done in two parts, one part for the determination of total carbonates, and the other part for the determination of calcium carbonate. The determination of total carbonates does not present as many problems as that of calcium carbonate. The titration is performed at pH 10 where both magnesium and calcium form stable complexes with EDTA. During the titration calcium, which has a higher metal-EDTA stability constant (5.0×10^{10}) compared to that for the magnesium-EDTA complex (4.9×10^{8}), is complexed first[3, 23]. This difference in stability constants is made use of in choosing the indicator for the titration. Since magnesium is the last one to remain in solution in appreciable concentration, indicators that give sharp endpoints for magnesium are normally employed.

TABLE 3.1.

RUN NO.		VOLUME OF EDTA (0.01022 M) (cm^3)			VOLUME OF SAMPLE SOLUTION (cm^3)	% TOTAL CARBONATE	% $CaCO_3$	% $MgCO_3$
		INITIAL	FINAL	USED				
1	a	0.80	7.60	6.80	20.00	82.73		3.59
	b	7.60	14.05	6.45	20.00		78.47	
2	a	14.50	21.32	6.82	20.00	82.97		3.89
	b	22.00	28.44	6.44	20.00		78.35	
3	a	30.00	36.80	6.80	20.00	82.73		3.69
	b	37.00	43.44	6.44	20.00		78.35	
4	a	0.50	7.28	6.78	20.00	82.49		3.39
	b	8.00	14.45	6.45	20.00		78.47	
5	a	14.50	21.28	6.78	20.00	82.49		3.69
	b	22.00	28.42	6.42	20.00		78.11	
6	a	29.00	35.80	6.80	20.00	82.73		3.49
	b	36.00	42.46	6.46	20.00		78.59	

a) = determination of total carbonate

b) = determination of calcium carbonate

There are several advantages associated with the choice of magnesium indicators. At pH 10 most metallochromic indicators tend to form unstable complexes with calcium which start dissociating before the endpoint is reached. This makes the endpoint sluggish and rather difficult to detect. This, however, is not the case with magnesium which forms stable metal-indicator complexes with such indicators as Erio T. The formed complexes do not dissociate appreciably until the endpoint is reached. Another advantage is that by using magnesium indicators, we are sure of titrating all the magnesium and calcium present in solution. This is due to the fact that all the calcium present will be complexed with EDTA, since the calcium-EDTA complex has a larger stability constant than the magnesium-EDTA complex, before all the magnesium is complexed. Furthermore, at the endpoint, the change in pMg is sharper than the change in pCa^3 thus making the endpoint sharper. Yet another advantage for using magnesium indicators is the fact that the sharpness of the endpoints is not affected by the magnesium to calcium ratio.

There are several sources of error in this part of the procedure. The major one is interference from other elements especially iron, aluminium and manganese. Apart from reacting with EDTA, these elements all react irreversibly with indicators recommended. If the elements are present in trace amounts, they can be masked by complexing them with triethanolamine. If they are in more than trace amounts, the bulk of them must be removed from the test solution.

In the present work two experiments were performed to determine whether the elements mentioned above had to be removed from solution. In one experiment the titration was performed without prior removal of the cations, but masking them with triethanolamine. In the second experiment iron and manganese were extracted with chloroform as complexes with diethyldithiocarbamate. Aluminium, which is not extracted under these conditions, was masked with triethanolamine. The results are shown in table 3.2.

Table 3.2.

% TOTAL CARBONATES

BEFORE EXTRACTION	AFTER EXTRACTION
82.55	82.60
82.64	82.85
82.40	83.00
82.83	83.05
82.62	82.74
Standard deviation: 0.16	0.19

Applying the t-test at 95% level of confidence showed that there is no statistical difference in the results. With this in mind, it was concluded that there was no need to carry out a prior removal of the cations from the test solutions.

If it becomes necessary to remove iron and manganese from the test solution, two other methods have been found satisfactory. One method employs ammoniacal salts, e.g., ammonium chloride[24]. However, it was found that an excess of the ammonium salt affected the colour of the indicators. This is because the ammonium cation hydrolyses and therefore a correct pH cannot be attained. Another method employs quadrivalent salts of zirconium at pH 5.5 - 6.5[25]. This method has an added advantage in that zirconium can also remove orthophosphates if present in the solution, which, otherwise, would also interfere with the titration.

It has also been shown[3] that Erio T indicator is sensitive to the presence of oxidants in the test solution. In view of this, hydroxylamine hydrochloride was added to all test solutions to reduce any oxidants present. It was for this same reason that nitric acid was not used for sample dissolution due to its oxidative nature.

It is also important to note that when Erio T is used as the indicator, the titration can only be successfully carried out in the pH range 9.3 - 10.5, with pH 10 being the optimum value[3]. At pH values less than 9 the free indicator is pink, the same

colour as that of the metal-indicator complexes. This means that the endpoint cannot be detected as it is shown by a change in colour brought about by the free indicator. Above pH 10.5 the magnesium starts precipitating as hydroxide. The precipitated magnesium will then not react with EDTA thus lowering the total carbonate content. Furthermore the indicator starts decomposing above pH 11.0[26].

The titration of calcium is carried out at pH values above 12, the exact value depending on the indicator employed. Indicators such as calcein[27] and palladiazo[19] can be used at any value above 12 whereas for murexide[28], the pH has to be controlled at pH 12.4-12.6. This titration cannot be carried out below pH 12 as magnesium will not be completely precipitated and will compete with calcium for EDTA[28].

With this part of the procedure difficulties arise mainly due to interference from magnesium, the other interfering cations having been complexed with cyanide and triethanolamine. Magnesium interferes in two ways mainly, firstly by carrying down the calcium as it precipitates out as magnesium hydroxide and secondly the magnesium hydroxide interferes with the indicator colour. The major interference is the coprecipitation of calcium especially for rocks with a high magnesium content.

The magnesium interference in the determination of calcium was studied by Kenny and Cohn[28]. It was found that for moderately

concentrated solutions with respect to calcium, magnesium interferes significantly when the ratio of magnesium to calcium is three or more. They also found that using dilute solutions with respect to calcium reduced the interference. However, the latter observation is in constrast with the observations made in this work. In the present work titrations were performed on solutions that had calcium to magnesium ratios of 1:10, 1:1 and 10:1. The 1:10 solution gave calcium recoveries as low as 95% whereas the 1:1 solution gave recoveries of 97%. The 10:1 solution gave calcium recoveries of not less than 98%.

Several ways of reducing this interference have been suggested. One way is to let the solution stand for sometime, after precipitation of magnesium to allow the coprecipitated calcium to come back into solution. This method is quite effective for rocks that have a low magnesium content. It is this method that was followed in the present work.

The other way, probably the best for rocks that are moderately high in magnesium content, is by back-titration[3]. A known volume of the rock solution is placed in a volumetric flask. Excess EDTA is added to the flask. Masking reagents, if necessary, are added and the solution neutralized. The solution is made alkaline by adding sodium hydroxide and then the flask is filled to the mark with water. The flask is left to stand for at least thirty minutes. Then aliquots are withdrawn and the slight excess of EDTA titrated against a standard calcium solution. This

procedure was performed in the present work. The results are in table 3.3.

Table 3.3.

% $CaCO_3$

BACK-TITRATION	DIRECT TITRATION
78.25	78.40
78.30	78.33
78.23	78.41
78.27	78.20
78.34	78.28

On comparing the two sets of results using the t-test at 95% level of confidence showed that they are statistically the same. The direct titration was preferred to the back-titration mainly because it requires less chemicals and time (approximately 15 minutes).

Some authors[2] tried to suppress the magnesium interference by adding such reagents as sucrose, gelatin, polyvinyl alcohol and carboxy-methyl-cellulose. The reagents were added to try and suppress the adsorption of calcium on magnesium hydroxide. Other

authors[29] tried to minimize the interference by slow precipitation of magnesium using a buffer solution of sodium hydroxide-potassium cyanine-hydroxylammonium chloride. Although the interference was not completely eliminated, there was a general improvement in the results.

It has also been found[3] that if there is only very little magnesium, the magnesium hydroxide does not precipitate out immediately so that there is sufficient enough time to titrate the supersaturated solution. Correct amounts of calcium are found but show more scatter than in the absence of magnesium.

An alternative reagent for EDTA, ethylenebis (oxyethylene-nitrilo)-tetraacetate (EGTA) was employed by Kotek and Dolezal[30]. The method proved satisfactory mainly because the stability constants of the metal complexes are sufficiently different, that of calcium being higher. The main difficulty lay in the lack of a suitable indicator. This was overcome by potentiometrically titrating calcium using a calcium ion-selective electrode.

The other magnesium interference, i.e., the interference with indicator colours is not a very serious one. The magnesium forms complexes with the indicator thus making the endpoint rather drawn out. This interference is overcome by adding more indicator. This is in agreement with the observations of Kenny and Cohn[28] who observed that increasing the amount of indicator reduced the magnesium interference. What happens can, probably,

be explained as follows: when very little indicator is added, both calcium and magnesium compete for it. Calcium, being free, i.e., in solution, complexes most of it. As the indicator is displaced from calcium by the EDTA during the titration, it is taken up by the magnesium. Therefore at the endpoint there is very little free indicator to show the endpoint. Furthermore, the blue colour of the free indicator at the endpoint is tinted with the pink colour of the magnesium-indicator complex. When more indicator is added there is enough of it for both metals.

For rocks with a high magnesium content, alternative indicators are available that can be used to avoid adding too large a volume of the murexide indicator. For instance, Diehl and Ellingboe[27] successfully titrated calcium in solutions with magnesium to calcium ratios of 30 and above using calcein indicator. This indicator is independent of the magnesium content of the solution as it does not form a complex with magnesium.

3.4. CONCLUSION

This method has certain attractive features of which one of the most attractive is the amount of sample that is required. With only one weighing of the rock sample, it is possible to carry out several determinations of the three quantities: total carbonates, calcium carbonate and magnesium carbonate; the magnesium carbonate being found by difference.

The fact that only one weighing is required for several determinations has an added advantage for sample preparation. In case the rock sample needs to be fused, with for example sodium carbonate, for complete dissolution, then the fusion need only be done once. This is unlike the Chilanga Factory procedure where fusion would have to be done for each single determination. However, there is also a disadvantage that goes with this single weighing of the sample. To get truly representative results the sample must first be made homogeneous, which is not so easy for solid samples.

The other good feature of the method is the simplicity of the equipment employed. They are probably one of the simplest and easiest to handle equipment that can be found in an analytical laboratory.

The main disadvantage of this method, when compared to the Chilanga Factory procedure, is the number of reagents required. The preparation of the reagents also requires particular attention more so for the buffer solution, EDTA and though to a lesser extent sodium hydroxide. In case of sodium hydroxide, it does not require very particular attention in its preparation since a pH meter can be employed to check that a correct pH is attained. The drying of EDTA should be done at 370-380 K as drying it at higher temperatures, especially above 390 K, would also remove some water of crytallisation in which case the formula weight will be difficult if not impossible to determine. Preparation of the

required reagents has been discussed in detail[23].

The error in a result found by this method can arise from a number of sources. The first source lies in the weighing if the balance is not properly aligned. Errors arising from this source, especially with modern balances, are minimal and usually insignificant. The errors are further minimized by the fact that the weights of the samples are found by difference. The second source lies in the transferring of the sample from the weighing bottle to the beaker for dissolution. Unless one is careful with this step it can turn out to be a major contributor to the final error. This step could be avoided by weighing directly into a beaker but it was found that, with the balance used (Torbal, Model EA 1), weighing a small amount of the sample in a 250 cm^3 beaker was usually inaccurate. The third source of error lies in the endpoint detection in the determination of calcium. The colour change is not sharp and it is difficult to tell whether one has over titrated as the intensity of the colour does not change even when excess EDTA is added. In fact the analyst has to carry out several titrations with synthetic solutions to acquaint himself with the endpoint.. The fourth source is due to the interference discussed in the preceding section. It should also not be forgotten that the reading of weights and volumes also have an uncertainity in them which contribute to the final error.

C H A P T E R 4

ATOMIC ABSORPTION SPECTROSCOPY

4.1. INTRODUCTION

Atomic absorption spectrometry, in its analytical context, may be defined as a method for determining the concentration of an element in a sample by measuring the amount of radiation absorbed by atoms produced from the sample at a wavelength that is specific and characteristic of the element under consideration. It is used for the determination of the majority of metallic elements and metalloids in mainly trace concentrations[4,9]. The form of the original sample is not important provided that it can be brought into solution. Atomic absorption methods combine the high specificity of other atomic spectral methods with the adaptability of wet methods. High specificity means that elements can be determined in the presence of each other. Separations, which are necessary with almost all other forms of wet analysis, are reduced to a minimum and often avoided altogether.

In atomic absorption spectrometry there are two main causes of interference, namely spectral and chemical. In addition, minor interferences are caused by various physical phenomena such as incomplete volatilization of the solid particles of the sample formed in the flame, variations in the physical properties of the solutions (matrix effects) and scatter and background absorption. Absorption measurements are, however, free from those interferences which arise from interactions between excited atoms. Any effect

which increases the number of free atoms in the flame, be it chemical or physical, is also favourable.

Spectral interferences can take any of the following forms:

(i) more than one absorbing line in spectral bandpass; This is a situation whereby a line of lower absorbance occurs within the bandpass.

(ii) non-absorbed line emitted by the excitation source; This is normally referred to as a bandpass effect. The line profiles of the resonance and offending non-absorbed line are sufficiently close to pass through the exit slit of an atomic absorption monochromator. This interference can be removed by using higher resolution monochromators.

(iii) spectral overlap in the atom source;
This suggests that the interfering line is sufficiently close to the wavelength of the analysis actually to absorb some of the radiation from the emission line. This would lead to an erroneously high reading for the element under consideration. The problem can only be overcome by removing the interfering element from the sample, or better, if possible, by using another absorption line for the analysis. Such an interference would occur in the determination of magnesium if iron[31] or mercury[32]

were present in the sample solution in appreciable quantities with respect to the concentration of magnesium.

(iv) continuum or broad band absorption and scatter; This is a situation whereby the actual readings obtained are increased. The sensitivity is not improved but a false absorption is added to the true value. The causes of false absorption signals, their effect and instrumental methods of correction have been critically reviewed[33].

Interferences which influence the proportion of atoms in the flame available to absorb radiation arise largely from chemical effect which originate either in the flame itself or in the sample solution. Such interferences are caused by the formation of stable compounds or by ionization. These interferences either enhance or depress the absorbance readings. In all cases, however, the presence of substances which produce an improved sensitivity for a given element actually do so by reducing an existing depressive interference.

Stable compound formation is the best known depressive interference. It arises because compounds or radicals containing the element being measured are not broken down into individual atoms at the temperature of the flame being used; stable compounds may even be formed in the flame. The presence of silicate, aluminate, phosphate and sulphate have been shown to lower the

absorbance of alkaline earth metals when using an air-acetylene flame[4, 34, 35].

To get a good and correct response from the spectrometer, instrumental parameters should be properly adjusted. For example, if the lamp current is not properly set it causes the calibration curve to deviate from linearity. Allan[35] briefly discussed the theoretical aspects of atomic absorption with particular emphasis to magnesium, i.e., the effect of changing lamp current on the intensity of emission and the width of the emitted line. It was found that the intensity of the magnesium line increases more rapidly than the current, and, to keep the intensity of the magnesium line at 285.2 nm to within ±1% the current should be controlled to within ±0.1 mA. The broadening of the magnesium line at 285.2 nm has adverse effects on the calibration curve.

4.2. EXPERIMENTAL

The procedure given below was adapted from the methods given by Jeffery[2], Sprague[7] and Price[4] taking into consideration the instrumental parameters and flame conditions as given by Elwell and Gidley[9].

Reagents

Hydrochloric acid (HCl); concentrated, specific gravity 1.18

Magnesium standard solution; magnesium sulphate heptahydrate, $MgSO_4.7H_2O$ (1.0187 g) was dissolved in water and diluted to the mark in a 1000 cm^3 volumetric flask (1 cm^3 ≡ 100 µg Mg).

Lanthanum chloride ($LaCl_3$) solution; the spectroscopic buffer reagent (10% w/v La) was diluted in a 1:1 ratio with water (1 cm^3 ≡ 50, 000 µg La).

Calcium compensating solution; calcium carbonate, $CaCO_3$ (0.3750 g) was dissolved in concentrated hydrochloric acid (10 cm^3) and diluted to the mark with water in a 1000 cm^3 volumetric flask (1 cm^3 ≡ 150 µg Ca).

Instruments

Atomic absorption spectrometer, Varian Techtron Model 1000.

Magnesium Hollow cathode lamp.

PROCEDURE

The finely ground rock sample (2.0 g) was dried in an electric oven at 380 K for one hour and cooled in a desiccator. Then 0.1051 g was weighed out and quantitatively transferred

to a 250 cm^3 beaker. The sample was moistened with a little water. Concentrated hydrochloric acid (10 cm^3) was then slowly added down the side of the beaker. The inside of the beaker was washed with water; more water was added to bring the volume to about 50 cm^3. The beaker was placed on a hotplate and the solution boiled for five minutes and then left to cool. The cool solution was filtered through a Whatman No. 41 filter paper into a 250 cm^3 volumetric flask. The residue was washed with water adding the washings to the main filtrate. The flask was then filled to the mark.

DIRECT CALIBRATION METHOD

An aliquot of the sample solution (5.00 cm^3) was pipetted into a 100 cm^3 volumetric flask. Lanthanum chloride (20.00 cm^3) was then added and the flask filled to the mark with water. A set of standard solutions containing 10, 20, 30, 40 and 50 µg of magnesium were also prepared as above but with the inclusion of 5.00 cm^3 of the calcium compensating solution to each flask. A blank solution containing all the constituents including calcium but without magnesium was also prepared. The spectrometer wavelength and monochromator slit width were set at 285.2 nm and 0.2 nm respectively. Checking that the instrument is zeroed before each reading with the blank solution, the absorbances of the standard and sample solutions were taken. A plot of absorbance against

concentration of the standards(FIGURE 4.1) was made to check if the calibration curve was linear, calculating the concentration of magnesium in the sample by the method of least squares. The procedure was repeated five more times. The results are shown in table 4.1.

METHOD OF STANDARD ADDITION

A set of standard solutions were prepared by pipetting 1.00, 2.00, 3.00, 4.00 and 5.00 cm^3 of a 10 mg/l Mg solution (prepared from the 100 mg/l Mg solution) into 100 cm^3 volumetric flasks. This was followed by adding 5.00 cm^3 of the sample solution to each flask. Lanthanum chloride (20.00 cm^3) was then added and the flasks filled to the mark with water. A blank solution was prepared which consisted of lanthanum chloride and water only. With the spectrometer set as in the Direct calibration method, using the blank solution to adjust to zero absorbance reading, the absorbances of the solutions were read. A plot of absorbance against concentration of magnesium (FIGURE 4.2) was made. The magnesium concentration in the sample was then read from the graph (see graph 4.2). The procedure was repeated five more times. The results are shown in table 4.2.

4.3. RESULTS AND DISCUSSION

TABLE 4.1: Direct Calibration Method.

µg OF Mg	ABSORBANCE READINGS					
	1	2	3	4	5	6
0	0.0	0.0.	0.0.	0.0.	0.0.	0.0
10	5.0	5.0	5.0	5.0	5.5	5.0
20	10.0	10.5	10.0	11.3	11.0	10.5
30	15.5	15.0	15.0	17.0.	17.0	16.0
40	21.0	20.5	20.0	23.0	22.5	21.0
50	26.5	26.0	25.0	29.5	27.5	26.5
SAMPLE	11.5	11.5	10.5	12.5	11.5	11.5
% $MgCO_3$	3.66	3.71	3.47	3.61	3.42	3.60