TABLE 4.2: Method of Standard Addition

µg OF Mg	ABSORBANCE READINGS					
	1	2	3	4	5	6
0	10.0	10.2	10.2	9.5	10.0	9.5
10	14.5	15.0	15.0	14.0	15.0	14.0
20	19.0	19.0	20.0	19.0	19.5	18.5
30	23.5	24.0	24.0	23.0	24.0	23.0
40	28.0	28.0	28.5	27.5	28.5	27.5
50	32.5	33.0	33.5	32.5	32.5	32.0
SAMPLE (µg)	22.0	22.5	22.0	21.5	22.0	21.5
% $MgCO_3$	3.63	3.71	3.63	3.55	3.63	3.55

The percentage of magnesium carbonate by the Direct Calibration method was found to be 3.58% with a standard deviation of 0.11. By the method of Standard Addition it was found to be 3.62% with a standard deviation of 0.06. Both results show good comparison to the result found by Chilanga Factory Laboratory (3.61%)

FIGURE 4·1

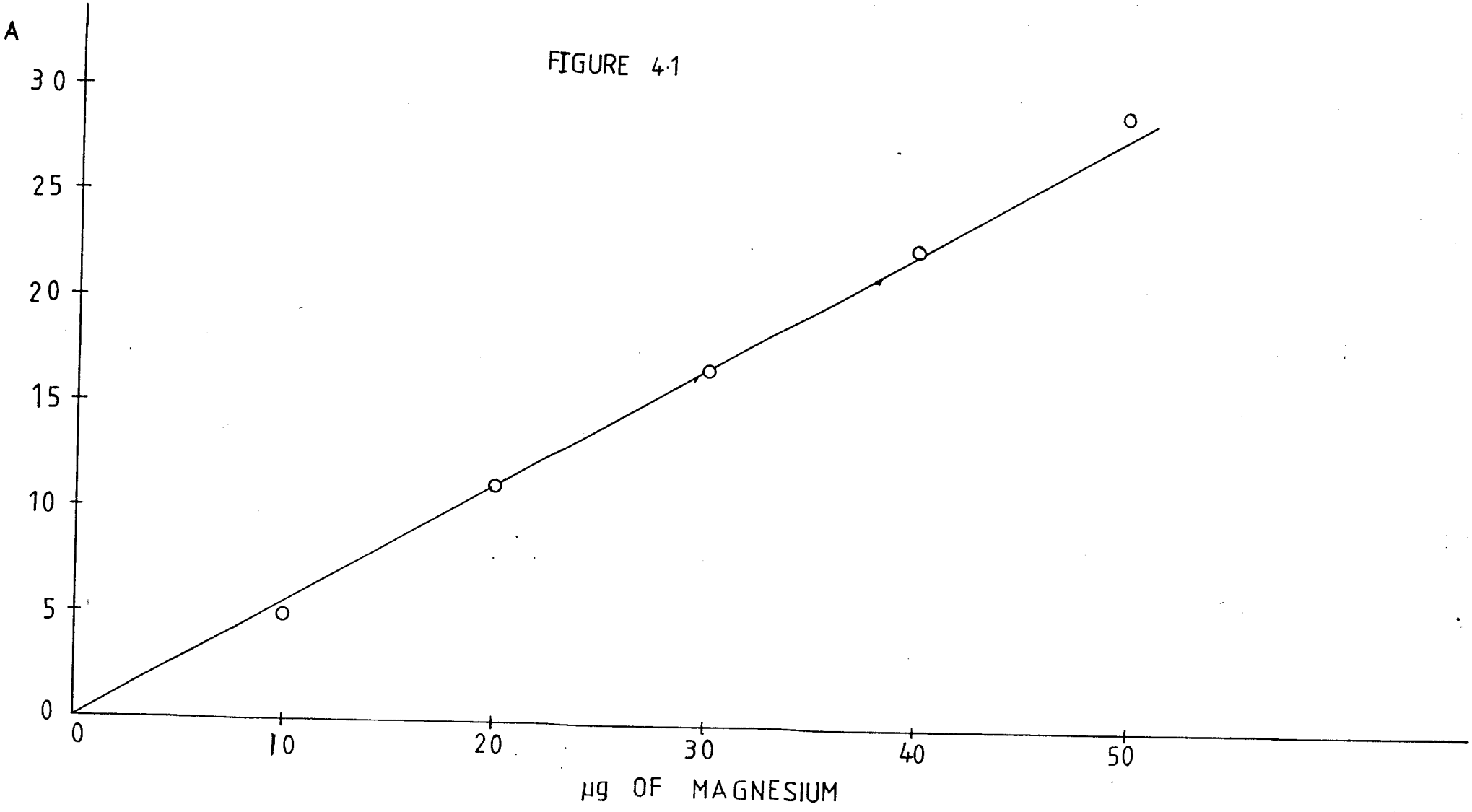
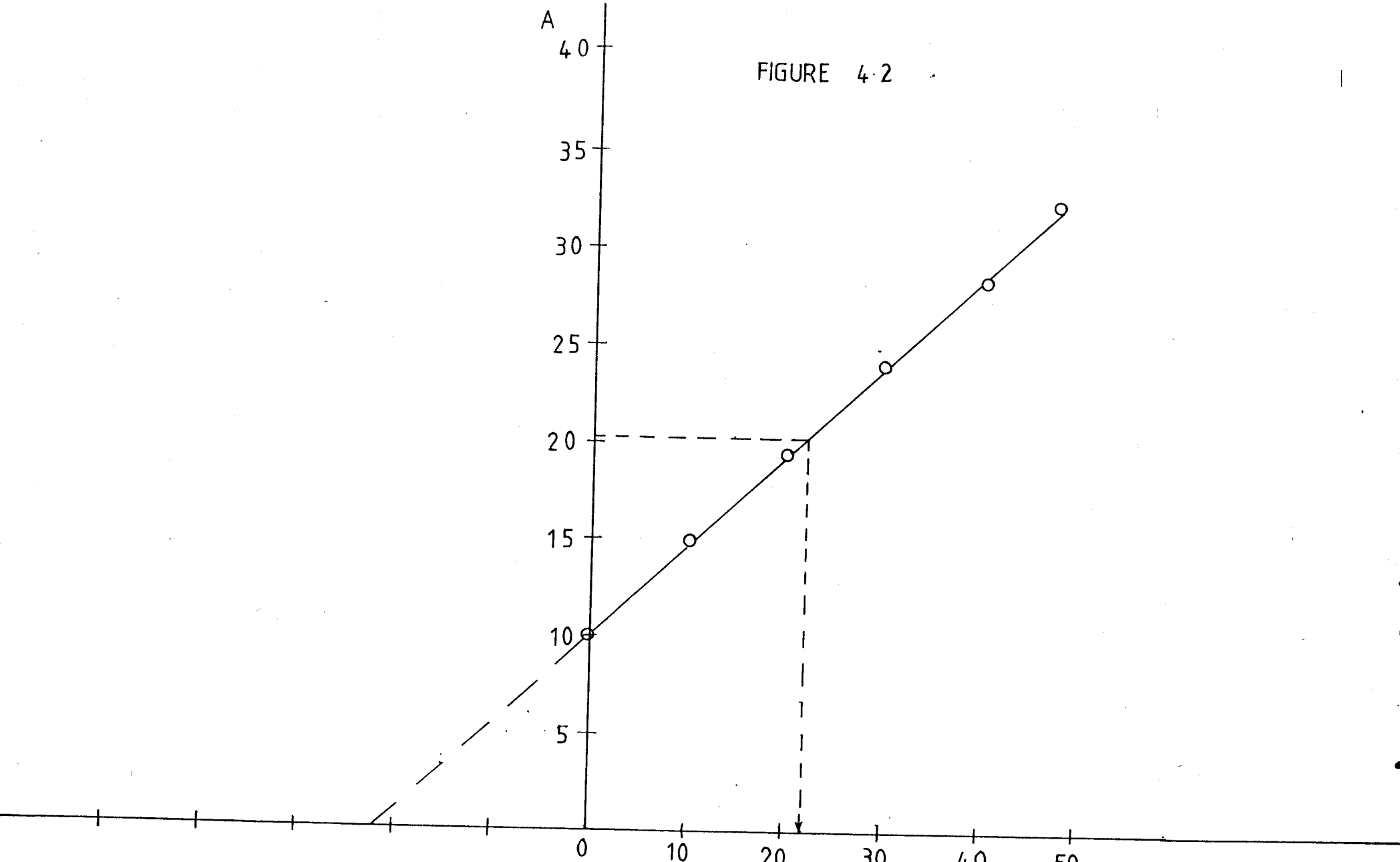


FIGURE 4·2



On comparing the two results found by the two techniques, one does not see any significant difference except that the values found by the Direct Calibration method show more scatter as shown by the standard deviation. In fact, taking the value found by the Standard Addition method as a "true" value and applying the t-test at 95% level of confidence, it turns out that there is no determinate error in the Direct Calibration method. Applying the same test at the same level of confidence on the standard addition method against the Direct Calibration method leads to the same conclusion.

To explain the difference in the two results and why the values found by the Direct Calibration method show more scatter, it is better to look more closely at the possible interferences. All the forms of spectral interference, except when more than one absorbing line is in the spectral bandpass (case i), affect all the samples in the same manner. This means that these interferences are not an adequate explanation for the observed discrepancy. When more than one absorbance line is in the spectral bandpass, a straight line calibration curve cannot be obtained. Since this was not the case in the present work it is not far fetched to assume that this form of interference was insignificant.

Chemical interferences were expected to come mainly from the silicate, aluminate, phosphate and sulphate oxyacids. The effect

of the oxyacids is normally appreciable only when the anion is in a chemical excess over the element under analysis. The aluminium interference, however, is so adverse that if aluminium is present in concentrations comparable to magnesium the bulk of it, or if possible all of it, must be removed from the sample[35]. The interference of the oxyacids when they are in excess suggest that an equilibrium is being set up between the species M-Cl, or M-O if the rock is dissolved in perchloric acid, and M-O-X, where -O-X is the oxyacid.

$$M\text{-}O\text{-}X \xrightarrow[\text{excess oxyacid}]{\text{heat}} M\text{-}Cl \xrightarrow[\text{low flame temperature}]{\text{heat}} M + Cl \quad \text{.....(1)}$$

In the presence of excess -O-X the equilibrium of equation (1) will move to the left preventing the formation of free M. Low flame temperatures and/or excess of the oxyacid thus favour the persistence of the stable oxy-salt. It is clear from the equation that the use of a hotter flame such as a nitrous oxide-acetylene flame will shift the equilibrium to the right. But the use of a hotter flame also increases ionization which is undesirable. For example calcium which does not ionize significantly in an air-acetylene flame is almost 50% ionized in a nitrous oxide-acetylene flame[4]. However, ionization can be reduced by introducing a second metal with a lower ionization potential to act as an ionization buffer. *Lithium, with an ionization potential of 520KJ/mole has*

been used for this purpose for most metals which include calcium and magnesium whose ionization potentials are 489 kJ/mole, and 733 kJ/mole respectively. Lanthanum, with an ionization potential (541 kJ/mole) comparable to that of lithium can also be used as an ionization buffer.

Another way, which was used in this work, of shifting the equilibrium in equation (1) to the right is to employ a releasing reagent (R)

$$M\text{-}O\text{-}X \xrightarrow{\text{excess R}} R\text{-}O\text{-}X + M \quad \ldots\ldots\ldots(2)$$

If R is a metal which forms a similarly stable compound with the oxyacid, and it is present in excess, then mass action dictates that the reaction (2) must proceed to the right, producing a higher proportion of free atoms of M. Good releasing reagents are therefore those metals which themselves form stable oxy-salts. Slavin and Trent[8] found that lanthanum removes interferences by silicate, aluminate, phosphate and sulphate. Another metal that has been used for the same purpose is strontium[36]. It was also found that lanthanum is a better reagent than strontium[36]. Lanthanum is certainly a better reagent because it also suppresses ionization. It is for the above reason that lanthanum was preferred to strontium in this work. Nickel has also been found to block interference from silicon and aluminium when the ratio of nickel to silicon and

aluminium is 500:1[37]. The ratio of nickel to magnesium is not important as it does not interfere with the magnesium absorption. The aluminium interference can also be overcome with 8-hydroxy-quinoline[38]. The oxine, however, does not eliminate the interference from silicon, phosphate and sulphate. The oxine overcomes the interference by forming co-ordinate complexes with aluminium while at the same time effecting what is commonly known as "organic enhancement". Calcium has also been found to offer considerable protection for magnesium against silicate. It affords little protection against phosphate but none at all against aluminium.

With the above discussion in mind it is concluded that the addition of lanthanum effectively eliminated, or at least minimized, the chemical interferences. This conclusion is further supported by the fact that, if there was any chemical interference, it would have affected the results by the two methods in the same manner as the same reagents were used for both methods.

Of the physical causes of interference scatter effects and background absorption are the easiest to detect. Ideally calibration curves should pass through the origin. If this is not the case then either there is a reagent blank in the standards or there is background absorption and scatter or both. These interferences can easily be corrected for by setting the instrument to read zero absorbance using a blank solution, which was done in the present work.

Incomplete volatilization is another physical cause of interference. This means that, at the temperature of the flame being used, the droplets produced by the nebulizer have given rise to solid particles which are not completely converted to vapour. This may be due to the speed with which the droplets pass through the flame or because they have a high vaporization temperature. This leads to a lower degree of atomization than expected. To reduce incomplete volatilization hotter flames could be employed. Alternatively, the flow rate could be reduced by using ultrasonic nebulizers. For example, Stupar and Dawson[39] showed that interference effects from silicon and aluminium on magnesium, previously thought to be entirely chemical in nature, could be drastically reduced when an ultrasonic nebulizer with flow rate less than 0.1 cm^3 per minute, providing a more uniform smaller droplet size, was employed. Large droplets are usually incompletely vaporized unless hot flames, such as a nitrous oxide-acetylene flame is used. In the present work to make sure that incomplete volatilization, if there was any, affected the absorbance readings in the same proportion, the same nebulizer was used throughout. Furthermore, all the readings were taken under the same flame conditions.

The other physical cause of interference are matrix effects. These influence the number of atoms actually entering the radiation beam. They usually arise from differences in the physical properties of samples and the matching standards. A difference in

acid concentration, for example, causes a difference in viscosity or surface tension. The viscosity affects the rate of uptake of the sample solution by a nebulizer and the surface tension affects the size distribution of the droplets forred and hence nebulizer efficiency. It is recommended that matching of standards and samples is necessary in respect of corponents found in the sample, or at least those components whose concentration is greater than 1% in the final solution[4]. It is for this reason that a calcium compensating solution was used in the case of the Direct Calibration method. The calcium compensating solution and the sample were all prepared in the same amount of acid so that there would not be much difference in acid concentration in the final solutions. However, it is clear, from the way the standard and sample solutions were prepared, that the solutions for the method of Standard Addition had a more uniform composition in as far as the components of the solutions are concerned. The sulphate concentration was, however, different throughout for both methods due to the different volumes of the magnesium stock solution added. The above discussion means that matrix effects would be more pronounced in the Direct calibration method. This is in agreement with standard deviations found for the two methods.

Another factor which could have contributed to the differences in the results and their standard deviations is the way they were computed. In the case of the method of Standard Addition, a

calibration curve was first plotted and the concentration of magnesium read off from it. Unless the points of the curve are in a perfectly straight line, an ideal case, a line of best fit has to be drawn. This goes to affect the results since the positioning of the line will depend on the analyst. The results for the Direct Calibration method were calculated theoretically by the method of least squares.

One source of error in this method lies in the numerous measurements that have to be made. Since the method is very sensitive small fluctuations in the exact volume transferred can be detected. Small fluctuations in the volumes may result in the values showing more scatter, more especially if concentrated solutions are used. Errors from this source can be minimized by working with as dilute solutions as possible. Another source of error lies in the sample solution preparation, and this has been discussed in the preceeding chapter. The absorbance readings also have uncertainities which contribute to the error.

4.3. CONCLUSION

Atomic absorption spectrometry is one of the best methods available for the determination of magnesium, and indeed for many other metals. It has quite a number of advantages which makes it quite attractive. The method is very sensitive. The detection

limit for magnesium is as low as 0.0001 mg/l at 285.2 nm[4] in an air-acetylene flame. It is highly specific. Interferences such as oxyacids of aluminium, phosphorus, silicon, titanium, etc, interfere in an air-acetylene flame but their interference is overcome by addition of 0.1% of lanthanum or strontium chloride. The method requires no waiting time as in colour development for many spectrophotometric methods, drying of precipitates in gravimetric methods, etc. High specificity makes a typical atomic absorption procedure simple and economical since prior separations are minimized and often avoided altogether. These facts, combined with the ease of handling an atomic absorption spectrometer, make it possible for routine analysis to be carried out quickly.

C H A P T E R 5

ABSORPTION SPECTROPHOTOMETRY

5.1. INTRODUCTION

Methods based on the absorption of radiation are useful tools in analytical chemistry. In the visible region, spectrophotometric methods are widely used for the quantitative determination of many substances, especially inorganic elements; the ultraviolet region is mainly used for qualitative and quantitative determination of organic compounds. The basic principle of quantitative analysis lies in comparing the amount of radiation absorbed by the sample with that of a set of standards at a selected wavelength[40].

When filter photometers are used, a suitable filter is selected in preparing an analytical curve for the unknown substance. These devices are suitable for many routine methods that do not involve complex spectra. With a spectrophotometer, the spectrum of the absorbing compound is determined and a suitable working wavelength, usually the wavelength of maximum absorption, is chosen. The chosen wavelength, however, should not fall in a region where the absorbance changes appreciably with a small change in wavelength. In some cases the wavelength of maximum absorption cannot be used as a working wavelength because the colour forming reagent also absorbs significantly at or near this wavelength. For systems that are sensitive to pH and for which an isosbestic point, i.e., a wavelength at which two absorbing compounds in equilibrium have a common value of molar absorptivity, can be located, measurements

at the latter wavelength are preferred if the pH cannot be readily controlled.

For many cases, the sample compound does not absorb radiation appreciably in the wavelength region provided on a spectrophotometer. It then becomes necessary to form an absorbing compound by reacting the element to be measured with other reagents. The reagents used should be selective in their reactions and should not form interfering absorbing compounds with other elements likely to be present in the sample. Their reaction with the element to be measured must quantitatively go to completion. In choosing these reagents such factors as the time it takes for the colour to develop, the stability of the formed absorbing compound and the pH of the solution must also be taken into consideration[40].

For a large number of elements there are usually more than one reagent that can be used for their spectrophotometric determination. For magnesium several reagents have been used. One of the earliest reagents to find general application is Titan yellow also known commercially as Titan yellow 2GS, Clayton yellow, thiazole yellow, brilliant yellow and acridingelb 5G[2]. It is a water soluble triazole dye which forms a red coloured lake with freshly formed colloidal magnesium hydroxide. The colloid is protected from precipitating by adding other colloids such as starch, glycerol and polyvinyl alcohol. It has been shown[41] that the best colloid

protector is polyvinyl alcohol at a concentration of 0.01% in the final solution. However, when polyvinyl alcohol is used a higher wavelength has to be used to prevent interference from the polyvinyl alcohol-Titan yellow complex which has maximum absorption very close to the wavelength of maximum absorption of the magnesium complex.

King and Pruden[42], however, showed that the commercial dyes differ considerably in their reactivity towards magnesium. They went on to separate an acetone-soluble material from a commercial dye which, it was claimed, was the most active component and in a later paper[43] published a synthesis procedure for the material.

When Titan yellow is used interferences are expected to come mainly from calcium and the ammonia group elements, aluminium, iron, phosphorus and titanium. Calcium can be removed from the test solution as an oxalate[2] and the ammonia group elements can be precipitated with ammonia[2, 44]. Alternatively, the ammonia group elements can be precipitated with sodium succinate[45] at pH 6. Calcium is not removed but its interference is blocked by adding sucrose.

Other reagents that have been used are phenazo (3, 3'-dinitrilo-4, 4'-bis-(p-hydroxyphenylazo)-diphenyl) and magneson II (2-p-nitrophenylazo)-1-naphthol)[46]. The spectrophotometric

characteristics of these reagents were also compared to those of Titan yellow. From the differences of the absorption spectrum maxima, it was found that of the three Titan yellow was the most sensitive. But Kuznetsov et al[47] preferred phenazo to Titan yellow. They found that among other characteristics, its solutions are more stable, the alkalinity is not critical and silicate interferences are reduced. Phenazo, an azo dye, is insoluble in water and acids. It gives a red solution in alkaline solutions and a yellow solution in chloroform, benzene, acetone and ethanol. It is absorbed on magnesium hydroxide to give a blue violet solution.

Another reagent that has been used often is magon[48, 49]. It is usually used as the sodium salt, sodium-1-azo-2-hydroxy-3-(2, 4-dimethylcarboxanilido)-naphthalene-1'-(2-hydroxybenzene-5-sulphonate). It is a brilliant red solid soluble in water and ethanol. In the pH range 8-11, magnesium causes a colour change from blue-violet to pink. The complex has a wavelength of maximum absorption at 540 nm while that for the complex is at 555 nm. If the solutions are in 95% ethanol the colour of the reagent is blue and that of the complex is salmon-pink. The wavelength of maximum absorption shifts to 615 nm for the reagent while the complex now has two peaks at 540 nm and 510 nm. This also shows that the choice of solvent is important in absorption spectrophotometry.

The other reagent that has been used quite often is Erio T[5]. Several methods have been reported[5, 50-54] that are very similar to each other except for the masking reagents employed and the pH at which the determination is done. The method described by Young et al[54] is for the simultaneous determination of calcium and magnesium. The reagent forms a pink coloured complex with the cations.

Other reagents that have been used, though not quite often are SPADNS[55] and 8-hydroxyquinoline[5, 56, 57]. SPADNS, 3-(4-sulphophenylazo) chromotropic acid, can be used for both magnesium and calcium. The reagent forms a crimson coloured complex at pH 8. The absorbance readings are taken at 570 nm. Calcium is determined at pH 10.6 where it forms a blue-violet complex with the reagent.

Most methods that use 8-hydroxyquinoline involve extraction of magnesium as oxinate into chloroform. The extraction is done in the presence of n-butylamine and potassium tartarate. Calcium is not extracted by the oxine either in presence or absence of butylamine. The magnesium is extracted as the ion-association system $(n\text{-}C_4H_9NH_3)^+ \ (Mg(OX)_3)^-$; OX = anion of oxine. In the absence of butylamine the normal magnesium oxinate, $Mg(OX)_2.2H_2O$, which is sparingly soluble in neutral solvents that are immiscible with water, cannot be extracted into chloroform. A preliminary extraction with oxine and chloroform in the absence of butylamine

serves to remove other metals, such as iron, that would interfere with the magnesium extraction.

An indirect method with 8-hydroxyquinoline was described by McAllister[58]. The magnesium is precipitated from ammoniacal solution with the oxine. The precipitate is then redissolved in dilute acid. The oxine is determined colorimetrically by means of the orange-red colour that it gives when it is reacted with 4-aminophenazone and the complex oxidized with potassium ferrocyanide in alkali solution.

Another indirect method involves precipitation of magnesium as magnesium ammonium phosphate ($MgNH_4PO_4$). The precipitate is then dissolved in acid and the concentration of phosphorus in the solution, which is proportional to the magnesium concentration, is determined by any one of the methods for phosphorus[59]. It has been found[60, 61] that this method is reliable, accurate and can be applied to a wide range of materials but it requires more time than the direct methods.

5.2. EXPERIMENTAL

The procedure used here was adapted from that given by Malat Miroslav[5].

REAGENTS

Hydrochloric acid: concentrated, Sp. Gr. 1.18.

Magnesium stock solution: The heptahydrate magnesium sulphate (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).

Magnesium working solution: A 10.00 cm^3 aliquot of the stock solution was pipetted into a 100 cm^3 flask and diluted to volume with water (1 cm^3 ≡ 10 µg Mg).

Eriochrome black T solution (0.05% w/v): The reagent (0.0500g) was dissolved in 100 cm^3 of 95% ethanol in a 100 cm^3 volumetric flask.

Buffer solution (NH_4Cl - NH_4OH, pH 10): Ammonium chloride (70.00 g) was dissolved in 300 cm^3 of water then 570 cm^3 of ammonia solution (Sp. Gr. 0.910) was added. The mixture was diluted to volume in a 1000 cm^3 volumetric flask.

Pctassium cyanide (KCN) solution (0.100M): The reagent (6.5110 g) was dissolved in water and diluted to volume in a 1000 cm^3 volumetric flask.

Sodium hydroxide (NaOH) solution (0.10 M): The reagent (0.40 g)

was dissolved in water and diluted to volume in a 100 cm^3 volumetric flask.

Calcium compensating solution: Calcium carbonate (0.0375 g) was dissolved in 5 cm^3 of concentrated hydrochloric acid. The solution was neutralized to the methyl red endpoint (pH 6) and then diluted to volume in a 100 cm^3 volumetric flask (1 cm^3 = 150 µg Ca).

INSTRUMENTS

Coleman Spectrophotometer 295 E with matching cuvettes.

PROCEDURE

The finely ground rock (2 g) was dried in a electric oven at 280 K for one hour and left to cool in a desiccator. A 0.1027g sample was then weighed out and quantitatively transferred to a 250 cm^3 beaker. The sample was moistened with a small volume of water and then dissolved in hydrochloric acid (5 cm^3). The inside of the beaker was rinsed with water; more water was then added to bring the volume to about 50 cm^3. The beaker was put on a hotplate and the solution boiled gently for three minutes. The beaker was removed from the hotplate and left to cool. The cocl solution was neutralized to the methyl red endpoint (pH 6) with sodium hydroxide. The neutral solution was then filtered through a Whatman No. 41 filter paper into a 250 cm^3 volumetric

flask. After washing the residue with water the flask was filled up to the mark.

SELECTION OF WORKING WAVELENGTH

An aliquot (0.5 cm^3) of the standard magnesium working solution was pipetted into a 25 cm^3 volumetric flask. This was followed by the addition of 5 cm^3 of the buffer solution and 2.5 cm^3 of the potassium cyanide solution. Then 0.5 cm^3 of the calcium compensating solution and 1 cm^3 of Erio T were pipetted into the flask. The flask was then filled to the mark with water. The absorbance of the resulting solution was measured from 500 nm to 560 nm at 5 nm intervals (table 5.1). A blank solution, containing all the other components except magnesium was prepared and its absorbance measured over the same range (table 5.1). The plots of absorbance against wavelength (FIGURE 5.1) were made and the working wavelength (530 nm) selected.

DIRECT CALIBRATION METHOD

An aliquot of the sample solution (0.2 cm^3) was pipetted into a 25 cm^3 volumetric flask. This was followed by the addition of 5 cm^3 of the buffer solution and 2.5 cm^3 of the potassium hydroxide solution. Finally 1 cm^3 of Eric T was pipetted into the flask and the flask filled to the mark with water. A set of standards containing 1, 2, 3, 4 and 5 µg of magnesium were prepared as above but with the inclusion of 0.2 cm^3 of the calcium compensating

solution. A blank solution containing all the other reagents except magnesium was also prepared. Using the blank to set zero absorbance reading the absorbances of the solutions were measured at 530 nm (table 5.2.). A plot of absorbance against concentration of magnesium was made (FIGURE 5.2). The procedure was repeated five more times. The concentration of magnesium in the sample was calculated by the method of least squares.

METHOD OF STANDARD ADDITION

An aliquot of the sample solution (0.2 cm^3) was pipetted into six 25 cm^3 volumetric flasks. Then 0.0, 0.1, 0.2, 0.3, 0.4 and 0.5 cm^3 of the standard magnesium working solution were pipetted into the flasks. The buffer solution (5 cm^3) and potassium cyanide solution (2.5 cm^3) were then added. Erio T (1 cm^3) was then pipetted into the flask and the flask filled to the mark with water. A blank solution was also prepared as in the Direct Calibration method. Using the blank to set zero absorbance reading, the absorbances of the solutions were measured at 530 nm (table 5.3). A plot of absorbance against concentration of magnesium was made (FIGURE 5.3). The concentration of magnesium in the sample was read from this graph. This procedure was repeated five more times.

5.3. RESULTS AND DISCUSSION

Table 5.1: Selection of working wavelength

λ (nm)		500	505	510	515	520	525	530	535	540	545	550	555	560
ABSORBANCE	Mg COMPLEX	0.040	0.075	0.105	0.145	0.170	0.190	0.200	0.195	0.175	0.150	0.120	0.110	0.100
	ERIO T	0.010	0.010	0.010	0.012	0.015	0.018	0.025	0.032	0.040	0.048	0.060	0.072	0.088

Table 5.2: Results of Direct Calibration method

µg OF Mg	ABSORBANCE READINGS					
	1	2	3	4	5	6
0	0.000	0.000	0.000	0.000	0.000	0.000
1	0.025	0.026	0.030	0.030	0.030	0.028
2	0.050	0.058	0.060	0.060	0.060	0.060
3	0.075	0.090	0.090	0.090	0.088	0.088
4	0.098	0.110	0.120	0.120	0.122	0.115
5	0.130	0.140	0.150	0.150	0.150	0.142
SAMPLE	0.022	0.025	0.025	0.026	0.025	0.026
$\%MgCO_3$	3.74	3.62	3.52	3.66	3.53	3.64

Table 5.3: Results for the Method of Standard Addition

µg OF Mg IN STANDARD	ABSORBANCE READINGS					
	1	2	3	4	5	6
0	0.025	0.025	0.025	0.026	0.024	0.025
1	0.055	0.055	0.054	0.055	0.054	0.054
2	0.086	0.086	0.085	0.086	0.085	0.086
3	0.112	0.114	0.115	0.115	0.112	0.115
4	0.145	0.144	0.144	0.145	0.142	0.144
5	0.175	0.176	0.178	0.178	0.172	0.178
SAMPLE	0.800	0.850	0.850	0.875	0.800	0.838
% $MgCO_3$	3.59	3.59	3.59	3.70	3.38	3.54

Table 5.4: Results for the comparison of the Titan yellow and Erio T methods.

% $MgCO_3$	
TITAN YELLOW	ERIO T
3.66	3.74
3.60	3.55
3.75	3.65
3.75	3.59
3.67	3.60

The percentage of magnesium carbonate in the sample by the Direct Calibration method was found to be 3.62% with a standard deviation of 0.09. By the method of Standard Addition it was found to be 3.57% with a standard deviation of 0.10. Both results compare well with the result found by Chilanga Factory laboratory (3.61%). Unlike in atomic absorption spectrometry, the two methods have comparable standard deviations. The standard deviations are so close to each other that a statistical comparison is not

FIGURE 5·1

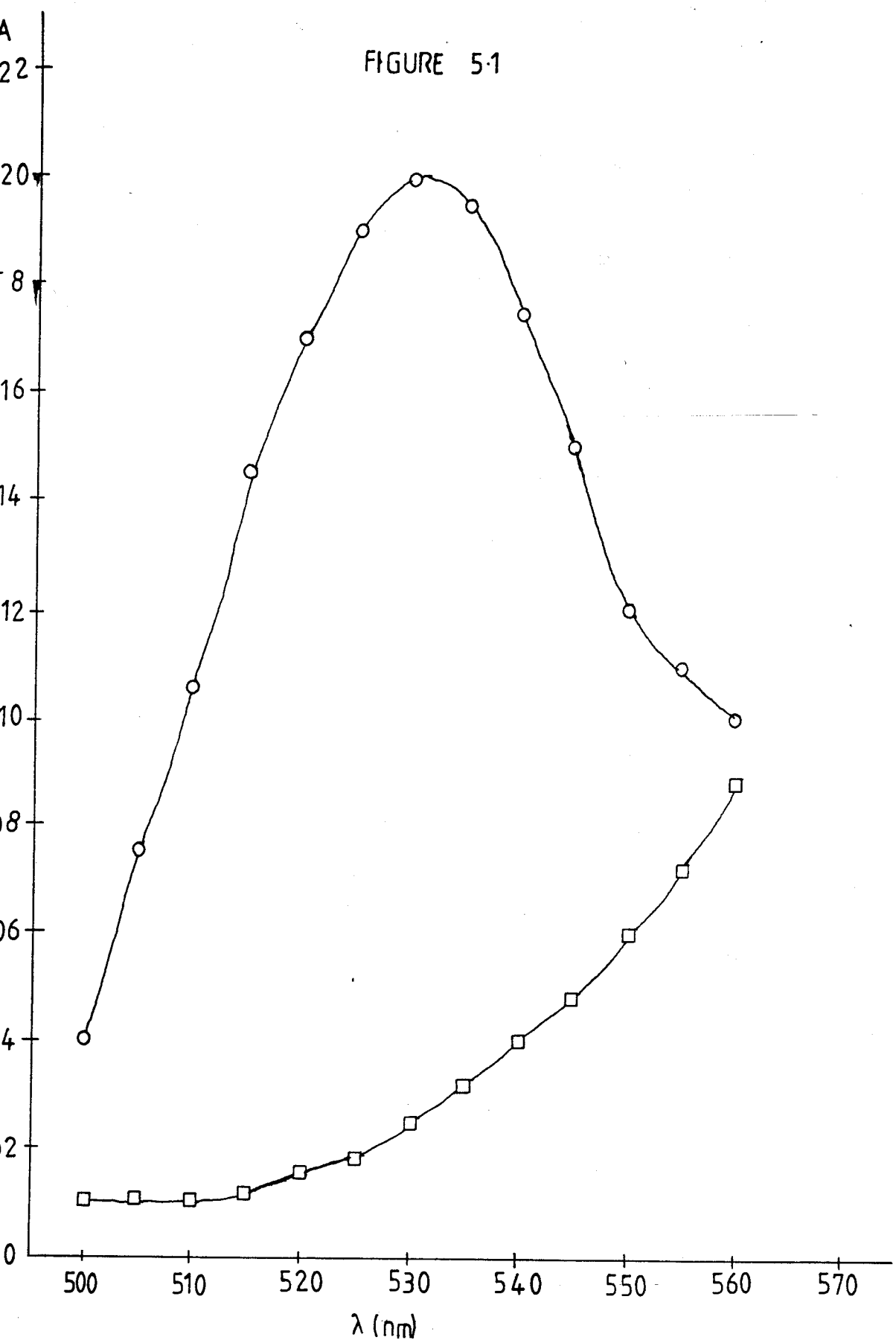

A
22
20
8
16
14
12
10
8
06
4
2
0
500
510
520
530
540
550
560
570
λ (nm)
Magnesium - Eriochrome Black T Complex
Eriochrome Black T

FIGURE 5·2

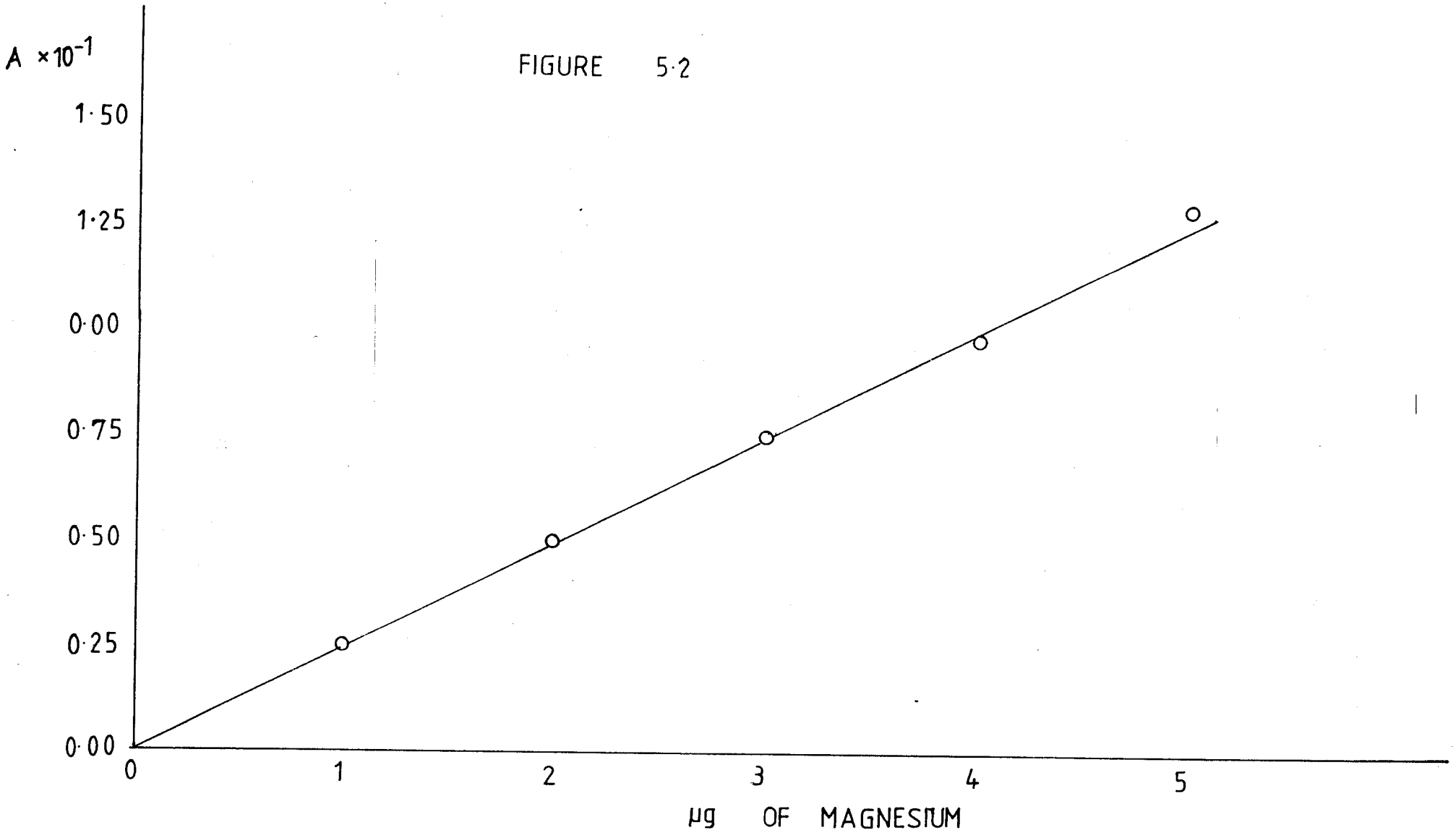
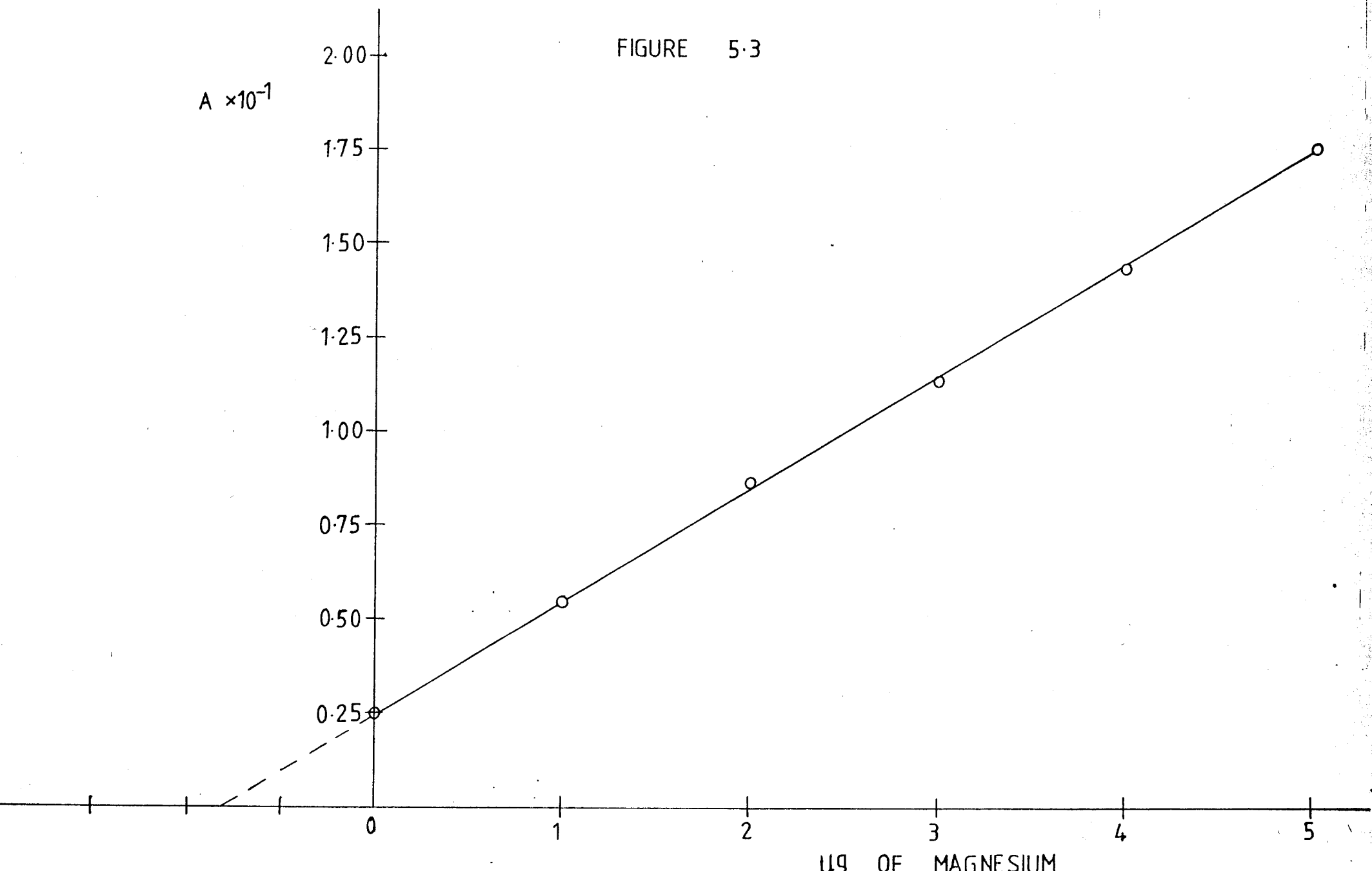


FIGURE 5·3



necessary. Also in contrast to atomic absorption is the observation that the Standard Addition method has a slightly higher standard deviation.

There are several sources of error in this method. Some of them, such as sample preparation and the uncertainty in the absorbance readings have already been discussed in the preceding chapters. The other source lies in the interference from the other elements. It is because of excessive interference from other elements that absorption spectrophotometry has not found general application for the determination of magnesium as is the case with atomic absorption spectrometry. As an example, when magon[48] is used as the complexing reagent, interferences are expected from not less than thirty elements. With such a large number of interfering elements it becomes difficult to choose a suitable masking reagent. For some reagents, such as Titan yellow and Erio T, interferences mainly come from the elements of the ammonia group and calcium[5, 45]. For the Titan yellow procedure the ammonia group elements are removed as succinates at pH 6 and the calcium interference is blocked by adding sucrose. In the Erio T procedure the ammonia group elements are masked with cyanide. In this work the Titan yellow procedure was compared to that of Erio T using the Direct Calibration method. The results are shown in table 5.4. These results were statistically compared using the Student's t-test at 95% level of confidence and found to be the same. The Erio T procedure was then chosen as it required less time (less than 30 minutes). The Titan yellow method takes

more than one hour. From the same results it was concluded that removal of the ammonia group elements was not necessary.

When Erio T is used the major interference, after masking the ammonia group and other heavy elements, thus comes from calcium. Calcium also forms a complex with the reagent that absorbs strongly at the wavelength of maximum absorption for the magnesium complex. So far no masking reagent for calcium has been reported that does not affect the absorption of the magnesium complex. In view of this a calcium compensating solution had to be employed for the direct calibration method. This solution was added to all the standard solutions including the blank. In this way the absorption due to the calcium complex was corrected for. Alternatively, calcium can be removed from the test solution either gravimetrically or by ion-exchange[2]. The ion-exchange procedure, however, requires at least 24 hours and would thus make the overall procedure too long for routine quality control in a production factory such as Chilanga Factory. The gravimetric method, besides, making the procedure long, increases the error due to co-precipitation of magnesium and also due to the amount of solution handling required.

It is also worth mentioning here that the instrument that was used in this work is not the best available. However, at the time of analysis it was the only one available. It is recommended[40] that the absorbance readings should fall within the range

0.2 - 0.7. This is due to the fact that small errors in measuring the absorbance cause large relative errors in the calculated concentration at low and high absorbances. However, with the instrument used, this was not possible because of the way the scale is graduated.

CONCLUSION

Quantitative absorption spectrophotometric methods have been employed for the determination of a large number of compounds and elements. The major requirement is that the compound to be determined should absorb radiation, especially ultraviolet and visible light. It should also obey Beer's law, the basis of quantitative analysis. If the compound of interest does not absorb visible light then, in most cases, a reagent can be found that forms a coloured complex with it. With most transition metals, such a problem does not arise as most of their complexes are coloured. The major problem, however, is finding a reagent that is specific for a particular element or compound. Indirect methods are also important and have been used quite often, especially when a lot of interferences are expected with the direct method.

Absorption spectrophotometric methods have advantages over such methods as gravimetry and classical titrations as they can be used for concentrations as low as parts per million. However,

it is at a disadvantage in this respect when compared to atomic absorption spectrometry. It is not advisable to use concentrations as low as those used in atomic absorption, unless the compound has a large molar absorptivity, as this would give low absorbances, the consequences of which have been discussed in the preceding section. The other disadvantage of this method is that prior separation of the element under analysis from the interfering elements is often required; in most cases such a separation would not be required if atomic absorption was to be used. When applied to magnesium using Erio T the method required quite a number of reagents for an instrumental method.

APPENDIX A: The Method of Least Squares.

The analyst is frequently confronted with plotting data which fall on a straight line, as in an analytical curve. This is usually done by simply "eyeballing" the best straight line by placing a ruler through the points, which invariably have some scatter. A better approach is to apply statistics to define the most probable straight line fit of the data. If a straight line is assumed, then the data fit the equation.

$$y = mx + b$$

where m is the slope of the line and b is the intercept on the ordinate (Y-axis). y is usually the measured variable, which is plotted as a function of changing x. Statistically, the best straight line through a series of experimental points is that line for which the sum of squares of the deviations of the points from the line is a minimum. This definition is known as the method of least squares. With the definition put in mathematical form and differential calculus applied it has been shown that

$$m = \frac{\Sigma x_i y_i - (\Sigma x_i \Sigma y_i)/n}{\Sigma x_i^2 - (\Sigma x_i)^2/n}$$

$$b = \bar{y} - m\bar{x}$$

where n is the number of experimental data:

Example: Data from table 4.1.

µg Mg x_i	absorbance y_i	x_i^2	$x_i y_i$
0.0	0.0	0	0
10.0	5.0	100	50
20.0	10.0	400	200
30.0	15.5	900	465
40.0	21.0	1600	840
50.0	26.0	2500	1325
Σ150.0	78.0	5500	2880
$\bar{x}$ =25.0	$\bar{y}$ =13.0		

$$m = \frac{2880 - (150)(78)/6}{5500 - (150)^2/6}$$

$$= \frac{2880 - 1950}{5500 - 3750}$$

$$= 0.53$$

$$b = \bar{y} - m\bar{x}$$

$$= 13.0 - 0.53 \times 25.0$$

$$= -0.250$$

Absorbance of the sample = 11.5

The sample concentration is

$$11.5 = 0.53\,x - 0.250$$

$$x = 22.2\ \mu g\ Mg.$$

Therefore 5.00 cm^3 of the sample solution contains 22.2 µg Mg. The total volume of the sample solution is 250 cm^3. Therefore the total amount of magnesium is

$$= \frac{22.2 \times 250}{5}$$

$$= 1.11 \times 10^{-3}\ g\ Mg.$$

This is equivalent to

$$= \frac{1.11 \times 10^{-3} \times 84.313}{24.305}$$

$$= 3.85 \times 10^{-3}\ g\ MgCO_3$$

Mass of the sample taken = 0.1051 g

% $MgCO_3$ in the sample is

$$= \frac{3.85 \times 10^{-3} \times 100}{0.1051}$$

$$= 3.66\%$$

This procedure was followed for all the results shown in tables 4.1 and 5.2.

APPENDIX B: Confidence limits of the results at 95% level of confidence.

Statistical theory allows the estimation of the range within which the true value might fall, within a given probability (or confidence level), defined by the experimental mean and standard deviation. The range is called the confidence interval, and the limits of this range are called the confidence limit. Mathematically

$$\text{Confidence limit} = \bar{x} \pm \frac{t.s}{\sqrt{n}}$$

where $\bar{x}$ is the mean result, s is the estimated standard deviation of the experimental data, n is the number of data and t is a statistical factor (obtained from Statistical Tables) that depends on the number of degrees of freedom and the confidence level required. For 5 degrees of freedom and 95% level of confidence t is equal to 2.571.

Example: The classical titration method (table 2.3)

$$\bar{x} = 3.74\%, s = 0.12, n = 6 \text{ and } t = 2.571$$

$$\text{Confidence limit} = 3.74 \pm \frac{2.571 \times 0.12}{\sqrt{6}}$$

$$= (3.74 \pm 0.13)\%$$

Following the same procedure for the other methods the following confidence limits were obtained.

METHOD	CONFIDENCE LIMIT
Classical titration	3.74 ± 0.13%
Complexometric titration	3.62 ± 0.19%
Atomic absorption (direct calibration)	3.58 ± 0.12%
Atomic absorption (standard addition)	3.62 ± 0.06%
Absorption spectrophotometry (direct calibration)	3.62 ± 0.09%
Absorption spectrophotometry (standard addition)	3.57 ± 0.10%

APPENDIX C: Statistical comparison of the methods using the Student's t-test at 95% level of confidence

The Student's t-test is used when an analyst wishes to decide whether there is a statistical difference between the results obtained using two different procedures, that is whether they both measure the same thing. A statistical t value is calculated and compared with a tabulated value for the given number of tests at the desired confidence level. If the calculated t value exceeds the tabulated value, then there is a significant difference between the results by the two methods at that confidence level. If the calculated value does not exceed the tabulated value, then it can be predicted that there is no significant difference between the methods.

Example: A comparison between the classical and complexometric titrations.

Classical titration ($\bar{x}$ = 3.74)

x_i	$x_i - \bar{x}$	$(x_i - \bar{x})^2$
3.92%	0.18	0.0324
3.65%	-0.09	0.0081
3.61%	-0.13	0.0169
3.68%	-0.06	0.0036
3.76%	0.02	0.0004
3.85%	0.11	0.0121

Σ = 0.0735

$$\text{variance } S_1^2 = \frac{\Sigma (x_i - \bar{x})^2}{n_1 - 1}$$

where n_1 is the number of data.

$$S_1^2 = \frac{0.0735}{6 - 1} = 0.0147$$

Complexometric titration ($\bar{y}$ = 3.62%).

y_i	$y_i - \bar{y}$	$(y_i - \bar{y})^2$
3.59%	-0.03	0.0009
3.89%	0.27	0.0729
3.69%	0.07	0.0049
3.39%	-0.23	0.0529
3.69%	0.07	0.0049
3.49%	-0.13	0.0169

Σ = 0.1534

$$\text{variance } S_2^2 = \frac{0.1534}{6 - 1} = 0.03068$$

$$F = \frac{Sx^2}{S_y^2} \quad \text{where } S_x^2 > S_y^2$$

Therefore

$$F = \frac{0.03068}{0.0147} = 2.087$$

For 5,5 degrees of freedom at 95% level of confidence, the tabulated value of F is 5.05 which is greater than the calculated value (2.087). This means the two methods have comparable variances and thus the Paired t-test can be applied.

$$\pm t = \frac{\bar{x} - \bar{y}}{Sp} \sqrt{\frac{n_1 n_2}{n_1 + n_2}}$$

and

$$Sp = \left(\frac{\Sigma (x_i - \bar{x})^2 + \Sigma (y_i - \bar{y})}{n_1 + n_2 - 2} \right)^{\frac{1}{2}}$$

Sp is the pooled standard deviation

$$Sp = \left(\frac{0.0735 + 0.1534}{6 + 6 - 2} \right)^{\frac{1}{2}} = 0.1506$$

then

$$\pm t = \frac{3.74 - 3.62}{0.1506} \sqrt{\frac{(6)(6)}{6 + 6}} = 1.380$$

For 10 degrees of freedom the tabulated t value at 95% level of confidence is 2.228. This value is greater than the calculated value (1.380) and, therefore, this means that there is no statistical difference in the results by the two methods.

Following the same procedure for the other methods, the calculated t values at 95% level of confidence were found to be less than the tabulated value except for two methods namely Atomic Absorption - Direct calibration (2.379) and Absorption spectrophotometry - Standard addition (2.596). This means that there is no statistical difference in the results by the methods except between the classical titration and the two methods mentioned above. However, the calculated t values of the two methods that failed the t-test are close to the tabulated value and this prompted the use of another test, the correlation coefficient, to ascertain whether the methods were used on samples

that have a truly different magnesium content.

APPENDIX D: Correlation coefficient

The correlation coefficient (r) is used as a measure of the correlation between two variables which are not functionally related, that is, are not directly dependent upon one another. As a general rule, $0.90 < r < 0.95$ indicates a fair correlation, $0.95 < r < 0.99$ a good correlation, and $r > 0.99$ indicates a very good correlation. It should be mentioned that it is possible to have a high degree of correlation between two methods (r near unit) but to have statistically significant different between the results of each according to the t-test. This would occur, for example, if there were a constant determinate error in one method. Mathematically the correlation coefficient is given as:

$$r = \frac{n \Sigma x_i y_i - \Sigma x_i \Sigma y_i}{\{ (n \Sigma x_i^2 - (\Sigma x_i)^2 (n \Sigma y_i^2 - (\Sigma y_i)^2) \}^{\frac{1}{2}}}$$

where xi, yi are the two variables and n is the number of data.

Example: Correlation between the classical and atomic absorption-direct calibration with x denoting results by the classical titration method and if by atomic absorption.

x_i	y_i	x_i^2	y_i^2	$x_i y_i$
3.61	3.52	13.0321	12.3904	12.7072
3.65	3.52	13.3225	12.3904	12.8480
3.68	3.62	13.5424	13.1044	13.3216
3.75	3.64	14.1376	13.2496	13.6864
3.85	3.66	14.8225	13.3956	14.0910
3.92	3.74	15.3664	13.9876	14.6608
Σ = 22.47	21.70	84.2235	78.5180	81.3150

$$(\Sigma x_i)^2 = (22.47)^2 = 504.9009$$

$$(\Sigma y_i)^2 = (21.70)^2 = 470.8900$$

Correlation coefficient

$$r = \frac{(6)(81\text{-}3150) - (22.47)(21.70)}{\{((6)(84.2235) - 504.9009)((6)(78.5180) - 470.8900)\}^{\frac{1}{2}}}$$

$$= \frac{487.890 - 487.599}{((0.4401)(0.2180))^{\frac{1}{2}}}$$

$$r = 0.93_9$$

Using the same formula the correlation coefficient between the classical titration and Absorption Spectrophotometry-Standard Addition methods was found to be 0.82_4. From the r value (0.93_9) there is a fair correlation between the classical titration and the atomic absorption methods. This could mean that there was a

constant determinate error in one of the methods as the t-test showed that there is a significant statistical difference in the results by the two methods. The correlation between the classical titration and absorption spectrophotometry is not good ($r = 0.82_4$). This could mean that the methods were used on samples that had different magnesium contents altogether or the sample dissolution was incomplete in the case of absorption spectrophotometry. However most of the results lie around 3.60% (cf 3.57% for the absorption spectrophotometry and 3.74% for the classical titration) which rules out incomplete dissolution. When all the results are compared at the same time, and taking into consideration the difficulties encountered with the endpoint for the classical titration (discussed in chapter 2, section 3), it seems that magnesium was over estimated with the classical titration method.

The correlation coefficient formula used above was also used to examine the linearity of the calibration curves used in chapters 4 and 5. The coefficients were all found to be greater than 0.99 indicating very good linearity.

REFERENCES

1. G.E. Troxwell, H.E. Davis and J.W. Kelly; "Composition and Properties of Concrete," Pg 10-29, 46-54, McGraw-Hill Book Company, New York, 1968.
2. P.G. Jeffery; "Chemical Methods of Rock Analysis," Pg 307-324, Pergamon Press, Oxford, 1975.
3. G. Schwarzenbach and H. Flaschka; "Complexometric Titrations," Pg 27-30, 159-162, 170-179, Methuen and Company Ltd., London, 1969.
4. W.J. Price; "Spectrochemical Analysis by Atomic Absorption," Pg 112-142, 319, Heyden and Son Ltd., London, 1979.
5. M. Malat, "Absorption Inorganic Photometry," Pg 222-230, Academia, Prague, 1973, (In Czeck).
6. Chilanga Cement Factory Manual.
7. S. Sprague; Atomic Absorption Newsletter, Aug. 1963, 43.
8. W. Slavin and D. Trent; Atomic Absorption Newsletter, March 1964, 17.
9. W.T. Elwell and J.A.F. Gidley; "Atomic Absorption Spectroscopy," Pergamon Press, Oxford, 1966.
10. R.K. Hansen and R.H. Hall; Anal. Chim. Acta, 1977, 92 (2), 307.
11. M. Leiritie and B. Mattsson; Analt. Lett., 1970, 3 (6), 315.
12. T.S. West, "Complexometry with EDTA and related reagents," Pg 31-33, 191-193, BDH Chemicals Ltd., Poole, 1969.

13. D.A. Skoog and D.M. West; "Fundamentals of Analytical Chemistry," Pg 352-357, Holt, Rinehart and Winston Inc. New York, 1963.

14. A. Ringbom; "Complexation in Analytical Chemistry," Pg 82-93, 148-149, 361-364, Wiley and Sons (Interscience Publishers), New York, 1963.

15. D.N. Sahai; Technology Sindri, 1974, 11 (4), 420.

16. S. Rahut, S. Gosh and K.C. Seal; J. Inst. Chem. (India), 1978, 50 (5), 219.

17. B.W. Budesinsky; Mikrochem. J., 1975, 20 (1), 17.

18. H. Khalifa and I.A. Ismail; Egypt J. Chem., 1973 (1974), 16 (4), 307.

19. M.D. Alvarez - Jimenez, J.A. Perez - Bustamante and F. Burriel - Marti; Anal. Chem., 1975, 47, (3), 512.

20. V.V. Abramov, S.M. Chesnokova and P.A. Andreev; Analit. Khim., 1975, 30 (11), 2250.

21. J.E. Allan; Analyst, 1958, 83, 466.

22. M. Renard and P. BLane; C. r. hebd, Seanc. Acad. Sci., Paris, D.; 1972, 274 (5), 632.

23. G. Schwarzenback; "Complexometric Titrations," Pg 62-65, Methuen and Company Ltd., London, 1957.

24. J. Banks; Analyst, 1952, 77 484.

25. M. Derderian; Anal. Chem., 1961, 33, 1796.

26. H.A. Flaschka, A.J. Barnard Jr. and P.E. Sturrock; "Quantitative Analytical Chemistry: Vol. I", Pg 232, Barnes and Noble Inc./ Harper and Row, Publishers Inc., New York, 1969.

27. H. Diehl and J.L. Ellingboe; Anal. Chem., 1956, 28, 882.

28. A.D. Kenny and V.H. Cohn; Anal. Chem., 1958, 30, 1366.

29. C.A. Baugh, K.H. Decker and J.W. Palmer; Anal. Chem., 1961 33, 1804.

30. J. Kotek and J. Dolezal; Anal. Chim. Acta, 1980, 120, 93.

31. C.W. Frank, W.G. Schrenk and C.E. Meloan; Anal. Chem., 1966, 38, 1005.

32. J.D. Morris and P.B. West; Anal. Chem., 1974, 46, 1423.

33. R.A. Newstead, W.J. Price and P.J. Whiteside; Progress in Analytical Atomic Spectroscopy (Background correction in Atomic Absorption), 1978, 1, 276.

34. D.J. David; Analyst, 1960, 85, 495.

35. J.E. Allan; Analyst, 1958, 83, 466.

36. J.B. Willis; Anal. Chem., 1961, 33, 556.

37. T.R. Andrew and P.N.R. Nichols; Analyst, 1962, 87, 25.

38. F.J. Wallace; Analyst, 1963, 88, 259.

39. J. Stupar and J.B. Dawson; Appl. Opt., 1968, 7, 1351.

40. H.H. Bauer, G.P. Christian and J.E. O'Reilly; Instrumental Analysis," Pg 154-177, Allyn and Bacon Inc., Boston, 1968.

41. E.G. Bradfield; Anal. Chim. Acta, 1962, 27, (3), 262.

42. H.C.C. King and G. Pruden; Analyst, 1967, 92, 83.

43. H.C.C. King, G. Pruden and N.F. Janes; Analyst, 1967, 92, 306.

44. A.I. Cherkeson and Yu V. Pushinov; Zav. Lab., 1964, 30, (9), 1053.

45. W.H. Evans; Analyst, 1968, 93, 306.

46. A.K. Babko and N.V. Lutokhina; Zhur Anal. Khim., 1962, 17 (4), 416.

47. V.I. Kuznetsov, L.M. Budanova and L.A. Nenasheva; Zav. Lab., 1958, 24 (9), 1053.

48. C.K. Mann and J.H. Yoe; Anal. Chem., 1956, 28, 202.

49. C.K. Mann and J.H. Yoe; Anal. Chim. Acta, 1957, 16, 155.

50. A.E. Harvey Jr. J.M. Komarmy and G.M. Wyatt; Anal. Chem., 1953, 25, 498.

51. J.K.R. Casser; Analyst, 1955, 80, 482.

52. A.J. Smith; Biochem. J., 1955, 60, 522.

53. V.P. Madhava Menon and M. Sankar Das; Analyst, 1958, 83, 434.

54. A. Young, T.S. Sweet and B.B. Baker; Anal. Chem., 1955, 27, 356.

55. G. Banerjee, S.K. Kanjii and S. Mandal; Z. Analyt. Chem., 1976, 282 (1), 47.

56. V.T. Athavale, R.L. Bhasin and B.L. Jangida; Analyst, 1962, 87, 217.

57. E.J. Newman and C.A. Watson; Analyst, 1963, 88, 506.

58. R.A. McAllister; Analyst, 1954, 79, 522.

59. L.C. Thomas and G.J. Chamberlin; "Colorimetric Chemical Analystical Methods," Pg 308-330, 424, The Tintometer Ltd., Salisbury, England, 1980.

60. F.W. Heaton; J. Clin. Path., 1960, 13, 358.

61. E.J. Butler, D.H.S. Forbes, C.S. Munro and J.C. Russell; Anal. Chim. Acta, 1964, 30 (6), 524.