ANALYTICAL STUDIES OF SOME BUILDING MATERIALS

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IN FOND MEMORY OF MY FATHER, CHIA AKOSO, MY GUARDIAN, ITYOVENDA AKOSO, AND TO MY MOTHER, NYIKU CHIA, MY WIFE M.N. CHIA, AND MY DAUGHTERS, NGODOO AND NGUEMO.

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G.A. Chia

A3STRACT

',:: o analytical Studies of some Building Materials such as soils fro.?. Birinin Kebbi, Zaria and Makurdi; clay from Tsambe, Scioto, Ogbcl'iri.! Itak Ikot p.nd Durumi; Limestcns from Ifon; and marble from Jakuru, have been carried out to study their chemical composition* The analysis of the samples included the determination of loss on ignition and the determination of SiO , $Al_o0^$, FGCV, CaO, MgO, KO, Na,0, Li_o0, Ti^O, $P_o0_$ and MnO^ (or $Mn,.O_o$ in case of cement samples). In addition, the insoluble residue and sulphur trioxide* SO , were determined in case of the cement Samples, Loss on ignition, insoluble residue, sulphur trioxide, and th© main silica were determined gravimetrically; Al_o0 , CaO and MgO titrimetricallyj rec? dual silica, Fe_2O_3 . Ti^O, P_o0 and $IIn0_o$ (or IJi 0) spectrophotometrically; v/hile the alkali oxides ucro determined flame photometrically.

j?ho sa;. lo solutions used for the determination of all the oi'-idos [except for the sulphur trioxide and the alkali oxides), ./ore prepared by tv/o decomposition methods, viz: the alkali fusion (l'_oC0 /u^CO) followed by dissolution of the melt in :.y:".roc':Ioric acid for soils, clays, limestones and marble; and acid decomposition (HC1) for cements.

**ie sample solutions used for the determination of alkali oxides ($i:_o0$, Na 0, Li_o0) were separately prepared by the acid decomposition methods: nitric acid/sulphuric acid/hydrofluoric

acid mixture for soils, clays, limestones and marble; and hydrochloric acid for cement samples.

The analytical results obtained for the various samples are summarised hereunder:

Soils

The major component was found to be silica (76.07 - 83.42%). Other components occured in relatively lower concentrations: loss on ignition 3.25 - 5.23%; alumina 4.06 - 9.21%; ferric oxide 1.65 - 6.00%; magnesia 0.10 - 0.22%; potassium oxide 0.28-3.2%; sodium oxide 0.18 - 58%; lithium oxide 0.12 - 0.56%, manganese oxide 0.02 - 0.07% and phosphorous pentoxide 0.20 - 0.70%. Lime was found to be completely absent in all the samples.

Clays

The predominant components were silica (44.88 - 66.56%), alumina (0.13 - 30.73%) and loss on ignition (4.86 - 13.88%). The concentrations of other components were comparatively low: ferric oxide 0.65 - 6.60%, magnesia 0 - 0.1%, potassium oxide 0.16 - 1.20%, sodium oxide 0.18 - 3.30%, lithium oxide 0.12 - 0.80%, titania 0.60 - 1.93%, phosphorous pentoxide 0.16 - 0.53% and magnese oxide 0.03 - 0.05. The concentration of lime was zero for all the samples except the Ogbakiri clay (0.57%).

Limestones and Marble

Loss on ignition (24.47 - 43.51%), and lime (17.67 - 53.96%) were the major components. Other components occured in concentrations less than 10%: alumina 0 - 3.16%, ferric oxide 0.15 - 3.43% except for sample GL 62598 (9.10%), magnesia 0.80 - 10.56%, potassium oxide 0.09 - 0.48%, sodium oxide 0.32 - 0.92% lithium oxide 0.10 - 0.16%, titania 0.08 - 0.50%, manganese oxide 0.03 - 0.46%, and phosphorous pentoxide 0.23 - 4.20%.

Cements

Lime (40.28 - 62.84%) and silica (19.89 - 28%) formed the major components. The concentrations of alumina (3.24 - 7.30%) ferric oxide (1.93 - 4.95%), magnesia (1.13 - 5.48%) sulphur trioxide (0.91 - 3.35%), loss on ignition (1.40 - 4.71%), and insoluble residue (0.38 - 3.98%) except Unicem 325 19.83%), were fairly high. The concentrations of other components were less than 3%: titania 0.27 - 0.56%, potassium oxide 0.16 - 2.88%, sodium oxide 0.12 - 2.04%, lithium oxide 0.12 - 0.22%, manganic oxide 0.06 - 0.56% and phosphorous pentoxide 0.08 - 1.68%.

These results show that there is complete lack of lime in the soil samples. Since lime is responsible for the cementing qualities of Building Materials, the inability of mud-huts to withstand adverse conditions as against structures constructed using cements may be attributed to the absence of lime in the

soils used for their contructions and suggests that soils used for constructing mud-huts should normally be supplimented with additional lime. The results also indicate that some of the cements imported into this country do not have sufficient lime content, and suggest that the poor quality of some of the building and engineering works constructed using cements could be due to the lack of sufficient amount of lime in some of these cements.

CHAPTER I

INTRODUCTION

The term "Building Material"[1,2] includes stones, clays, soils, cements, paints, plasters, bitumen, felt, metals, etc. etc. The present work is, however, concerned with only three types of those building materials, namely, soils, clays and cements. A brief explanation of each of these Building Materials in the content of the present work is given hereunder.

1-1 Soils:

The word soil is used in several different senses. To the agriculturist soil[3] refers to the superficial layer of the terrestrial globe capable of producing plant crops, whereas to the pedologist, it is a layer in which chemical and physical changes have taken place. To the civil engineer, earth or soil[4,5] is any unconsolidated material composed of discrete solid particles with gases or liquid between. It is the unaggregated or uncemented deposits of mineral and/or organic particles or fragments covering large portions of the earth's crust. Soils vary very widely in particle size. The maximum size[4] that qualifies soil is defined by the function involved; it may extend from only a fraction of a micron in diameter up to many feet in diameter.

Soils include a wide variety of material[5,6] such as the gravel sand and clay mixtures deposited by glaciers, the alluvial sands and silts and clays of the flood plains of rivers, the soft marine clays and beach sands of the coast, a mixture of the fine particles erroded from rocks of the locality and various plant and animal matter, both dead and living, and even cinders, bedsprings, tin cans, and ashes of the city dump. Soil can be a well-defined mixture of a few specific minerals or a chaotic mixture of almost anything. It forms a layer only a foot or two thick, sometimes shallower, sometimes deeper, on the surface of the underlaying rocks.

-f Clays:

Clay[7,8,9] is regarded as the active mineral portion of the soil composed of particles less than 2 microns effective diameter and has a specific mineral composition, and forms a coherent stichy mass when mixed with water; when wet this mass is readily mouldable but if dried it becomes hard and brittle and retains its shape. Moreover, when fired, it is converted to a rock-like mass which is no longer susceptible to the action of water.

Geologically, clays are considered to be a type of sedimentary rock formed by weathering and sedimentation of the igneous rocks. The chemical reactions[10,11] giving rise to the formation of clays are exemplified by the decomposi-

tion of the alkali felspar present in plutonic rocks such as syenite and granite:-

$$K_2O.Al_2O_3.6SiO_2 + 3H_2O + CO_2 \longrightarrow Al_2O_3.2SiO_2.2H_2O + 4SiO_2 + K_2CO_3$$

Orthoclase felspar — derived from percolating water — Clay — Removed in SOhr by running water

$$CaO.Al_2O_3.2SiO_2 + 3H_2O + 2CO_2 \longrightarrow Al_2O_3.2SiO_2.2H_2O + Ca(HCO_3)_2$$

Plagioclase felspar anorthite in granite — Clay

Thus clay is chemically an alluminosilicate. Different types of clays have been described in literature[11,12,13]. These clays differ enormously in composition and properties.

1-3 Cements:

Cement[14] may be defined as any plastic material employed to produce adhesion between stones, bricks, etc. in the construction of building and engineering works.

Cement plays a very vital role in modern construction. A brief history of its manufacture, an outline of the present production process, and the different types of cements available today are hereby discussed.

1-3.1 History[14] of Cement:

The Egyptians were the first people to use the present day system of uniting blocks and slabs of stones with a mortar made of a mixture of sand with a cementitious material which was obtained by burning impure gypsum. The mixture obtained had irregular setting properties as the gypsum was not properly burnt. As limestone required higher temperature for calcination, and fuel was scarce, the Egyptians never used it. It was first used by the Greeks and Romans in making mortar. The mortar was prepared by slaking lime and mixing with sand, gravel, crushed stone and broken tile or brick. This gave birth to the first concrete.

The remarkable hardness of these mortars stimulated interest in the study of factors responsible for the cementing properties of limestone. It was noticed that some sands were of greater value than others, especially for producing mortars that would be resistant to the action of water for a long time. Furthermore, both Greeks and the Romans found that certain volcanic deposits, if pulverized and mixed with lime, yielded a mortar which had superior strength and resistance to the action of water. The Greeks employed the volcanic tuff of the island of Thera (now Santorin), the Santorin earth. The Romans used a mixture of lime and a

reddish volcanic tuff found around the Bay of Naples and called pozzolana as it was found in the neighbourhood of Pozzoli or Pozzuoli. This gave birth to a class of mortars called pozzolanic cements.

The use of volcanic earth spread and in England the Rhenish tuff, Trass, was used.

The extraordinary durability of the structures constructed with the Roman mortars - the Roman Pantheon, the Colosseum, the Basilica of Constantine, etc - led some workers to believe that the Romans possessed some secret of mixing or fabrication which had since been lost, for in the Middle Ages the quality of workmanship and longevity were much inferior. It was left to later workers like Rondelet[15] to prove that "the excellence of the Roman mortars depended not on any secret in slaking or composition of the lime but on the thoroughness of mixing and ramming".

In 1756, John Smeaton[16,17,18] an English builder, who had undertaken to re-erect the Eddystone Rock Lighthouse which had been destroyed by fire, discovered during his search for water-resistant mortars that the limestones which yielded the best water-resistant mortars contained a considerable proportion of of clay matter. He thus

recognized for the first time what is now called hydraulic lime. This hydraulic lime was not extensively used as the pozzolanic cements continued to be used in preference.

The search for raw materials continued to yield fruitful results and in 1796, James Parker[19] discovered that hydraulic cements could be made by calcining modules of an argillaceous limstone, septaria, found in the tertiary strata. This was named Roman Cement. Because of its quick-setting property, it received popularity which was, however, shortlived as it was soon superseeded by the Portland Cement.

The invention of the Portland Cement is usually accredited to Joseph Aspdin[20], a Leed's builder, though notable contributions were made by other contemporary workers such as John Vicat and James Frost[21]. In 1824 Joseph Aspdin calcined crushed limestone and mixed the lime with clay, grinding to a fine slurry with water and evaporating the mixture in the sun or by heating over fire or steam pipes. The mixture was then broken into suitable lumps and calcined in the furnace, cooled pulverized, and used as cement.

Aspdin kept his process secret- proportions of limestone and clay in the mixture and the calcination temperature were not revealed. However in 1845, Isaac Charles

Johnson[21] found that overburnt lumps found in the kilns, although low-setting when ground, yielded a cement of superior hardness and colour. By further experiments he established the proportions of clay and chalk in the mixture as well as the calcination temperature. This appears to be the birth of the Portland Cement Industry.

Most of the early works were on the Thames and Medway, Chalk and Thames' mud being used as raw materials but the manufacture later became world wide.

1-3.2 Manufacture of Cement:

Cement is manufactured[22] from two major raw materials[23], calcareous (lime) and argillaceous (clayey) materials. The calcareous material contains calcium carbonate or lime whilst the argillaceous material contains alluminosilicate. The principal calcareous materials are limestones, cement rock, chalk, marl, marine shells and alkali waste (precipitated $CaCO_3$ obtained as byproduct from manufacture of caustic soda by the Le Blanc Process); while the principal argillaceous materials are clay, shale and slates which are of about the same composition but of different geologic ages; blastfurnace slag, and cement rock. The latter is a limestone which contains such a quantity of argillaceous material that little or no additional

argillaceous material has to be added.

During the manufacturing process, correctly proportioned mixture of good quality calcareous and argillaceous materials is ground to a fine powder. If the mixing and grinding are performed in the dry condition the process is called Dry Process; if performed in water the process is called Wet Process. The resulting mixture is then fed into a rotary kiln and heated slowly to sintering temperature. Water and carbon dioxide are expelled and the mixture enters the clinkering zone where chemical reactions occur between the compounds resulting in the formation of new compounds. The clinker[24] is then cooled, mixed with a small quantity of gypsum (Ca 2-3 per cent) to prevent "flash" set which would occur if water were added to the untreated cement, and ground to a fine powder to form the Portland Cement. The ground cement is stored in silos until tested for composition, fineness, strength etc and shipped.

1-3.3 Types of Cement:

Technological advancement in the production process and special requirements of satisfactory cements for specific uses in the building and engineering works, have

resulted in the production of different types of cements. Some of these cements are discussed hereunder.

A. Portland Cement

Portland Cement is defined in the standard specification of the American Society for Testing Materials[25] as "the product obtained by pulverizing clinker consisting essentially of hydraulic calcium silicates to which no additions have been made subsequent to calcination other than water and/or untreated calcium sulphate except that additions not to exceed 1.0 per cent of other materials may be interground with the clinker at the option of the manufacturer, provided such materials in the amount indicated have been shown not to be harmful by tests carried out or reviewed by Committee C-1 on Cement.

Portland Cement as defined above is also called the ordinary Portland Cement and forms the bulk of all Cements produced and is the type commonly used for building and road construction. Lea and Desch[26] have described different varieties of Portland Cement some of which are discussed hereunder.

(i) Rapid-hardening Portland Cement[27]

Rapid-hardening Portland Cement is similar to the ordinary Portland Cement but contains a higher percentage of tricalcium silicates and is more finely ground. These two factors result in higher strength at early ages. It is commonly used for road repair work where it is necessary to open the road to traffic with minimum delay.

(ii) Quick-setting Portland Cement

The composition of this cement is similar to the Portland cement but has less setting time due to its higher percentage of tricalcium aluminate ($3CaO.Al_2O_3$).

(iii) White Portland Cement[28]

White Portland Cement is the Portland cement made by limiting the iron oxide content to such a low value that it is practically white. It is therefore manufactured using limestone and white china clay of exceptional purity. It is of special importance in architectural concrete where pure white is required or where brilliant colours are sought by addition of pigments or coloured aggregates.

(iv) Water-Proofed Portland Cements[29]

These are ordinary Portland Cements containing approximately 0.1 to 0.2 per cent water-repelling agents, and/or finely ground powders such as calcium stearate, sodium and potassium oleate and stearate, or non-saponifiable oils. These water repelling agents make the concrete impermeable to water.

(v) Low-heat Portland Cement[29]

The chemical composition of this cement is so adjusted as to reduce heat of hydration - it has low tricalcium silicate and tricalcium aluminate content. It is used for mass concrete, for construction of bridge abutments, massive retaining walls, etc., where high temperature during hydration might induce cracking. Its rate of strength development is lower than that of the normal Portland Cement but the ultimate strength is the same.

(vi) Sulphate-resisting Portland Cement[29]

Sulphate-resisting Portland Cement is manufactured to resist attack from sulphate bearing waters or soils containing sulphur trioxide.

(vii) Kuhl Cement[26]

This is a Portland Cement of low-silica and high alumina and iron content.

(viii) Ferrari Cement[26]

This is a Portland Cement with an alumina/iron oxide ratio of approximately one and having improved resistance to chemical attack.

(ix) Expanding Cement[39,31,32]

These cements expand slightly on hardening. They are made by intergrinding 70 per cent of Portland clinker with 20 per cent granulated blastfurnace slag and 10 per cent of calcium sulphoaluminate cement. It is used in bridges and water and oil storage tanks.

(x) Air-entraining Cements

These are Portland or Portland blastfurnace cement to which a small amount of air-entraining agent such as alkali salts of wood resins, calcium lingosulphate, alkali or triethanolamine salts of fatty acids etc., has been added during grinding.

(xi) Coloured-Cements[33]

Coloured-cements are obtained by adding mineral pigments to the rapid-hardening Portland cement or white Portland cement; carbon black used for black, or dark cement, chromium oxide for green, ultramrine for blue and magnese oxide for black or brown cements. These pigments reduce the strength sometimes to as little as two thirds of the normal concrete strength.

D. High-alumina Cement[34,35]

High alumina, or aluminous, cement is made by heating until molten a mixture of limestone and bauxite, the product being cooled and ground. It has a high rate of strength development at early ages, about 75 per cent of the ultimate strength being attained in 24 hours. It also has high rate of heat development during hydration but is very resistant to chemical attack. It tends to produce a brittle concrete which bleeds easily. It is seriously affected by presence of even small amounts. of Portland cement, setting times being seriously reduced and "flash" (sudden) set occuring. Concretes made of high-alumina cement deteriorates at temperatures in excess of $45^{o}C$.

C. Granulated blastfurnace slag Cements[36]

This group of cements is made by mixing finely ground blastfurnace slag with lime or Portland cement.

In combination with Portland cement clinker or lime, granulated slag hardens rapidly and contributes its own hydraulic action to that of other constituents of the mixture. Slag cements composed with Portland cements have lower early strength and correspondingly a lower development of heat which made them acceptable for mass structures but more sensitive to low temperatures. They have been successfully used in structures exposed to sea and sulphate waters.

Two types of this group of cements are described hereunder:

(i) Portland blastfurnace cement[34]

This is made by intergrinding Portland cement clinker and granulated blastfurnace slag such that the content of the granulated slag is not more than 65 per cent. It has similar properties to the normal Portland cement except that its resistance to chemical deterioration is rather higher and its rate of hardening falls more rapidly as the temperature increases.

(ii) Supersulphated or Sursulphated Cement[30]

This is made by intergrinding 15 per cent gypsum, 5 per cent Portland cement clinker and 80 per cent slag. Because of its low heat development, it is used in producing mass construction, and especially for structures exposed to sea and sulphate waters.

D. Pozzolanic Cement[35]

Pozzolanic cements are made by intergrinding either Portland clinker or a hydrated lime and pozzolana. These cements have low rate of strength development low rate of heat evolution and high inherent resistance to chemical deterioration.

E. Oil-well Cements[38]

The very unusual demands made upon the cement to be used for sealing oil and gas wells have necessitated the production of special oil-well cements. These cements are made by adding to the coarsely ground Portland or slow-setting Portland cement, special retarders such as starches, sugars or organic hydroxy acids.

F. Masonry Cements[39]

The preponderant constitution of masonry cements today is a finely interground mixture of Portland cement and limestone, given a high degree of plasticity and water retention by the interground addition of an air-entraining agent and regulated in setting time by gypsum. They are used for mortars.

G. Magnesium Oxychloride or Sorel Cement[33]

This is always freshly prepared from a solution of magnesium chloride in water (20% w/v) and magnesium oxide obtained by calcining magnesite at 750 - 950°C. The magnesium oxide reacts with the magnesium chloride to form a solid mass of magnesium oxychloride, $3\ MgO.MgCl_2.11H_2O$.

Sorel cement is mainly used in magnesite flooring[41] but it is attacked by water and has to be kept dry.

H. Gypsum Plasters[42]

Gypsum plasters are obtained by the partial or complete dehydration of gypsum, $CaSO_4.2H_2O$, some retarders being added to effect slow-setting.

Other cements include iron-ore cement, Keene's cement, gaize cement, silicate cement, sulfur cement, and cements containing calcium chloride.

1-4 Motivation of The Project

The properties of building and concrete structures such as resistance to chemical attack, setting time, resistance to cracking, rate of strength development and drying shrinkage result from the chemical composition of the cements used. Thus to have cements to be used for different building and engineering works, these cements have to meet the engineers' specifications which become increasingly restrictive as his demands for different cements for different uses increases. This has led to different engineers from different countries having different[2] standard specifications for cements. These specifications include those of the American Society for Testing and Materials, Philadelphia (ASTM), the British Standard Institution, London (B.S.S.), Association Francaise de Normalisation, Paris (AFNOR), the Deutscher Normenausschuss, Berlin (DIN); the International Organisation for Standardization, Geneva (ISO); the South African Bureau of Standards, Pretoria (SABS) and the Standards Association of Australia, Sydney (SAA). Whatever specification is adopted, it is fundamentally required that particular types of cements should have specific chemical composition in order to be used for specific building and engineering work.

During the last decade, millions of tons of cements have been imported into this country from various manufacturing countries in order to execute the various building and construction projects throughout the country. Some of these projects executed with these cements do not seem to be durable - buildings crack; roads develop potholes quickly etc. Apart from such factors as cement/aggregate ratio, and cement/water ratio, the poor quality of these structures could be due to the intrinsic chemical constitution of the cement. It is this view that motivated the analytical studies of some of these Building Materials. In this work, therefore, an attempt has been made:

(i) to study the chemical composition of the imported cements available on the Nigerian Markets and classify them according to one internationally accepted standard specifications; namely, the American Society for Testing and Materials, ASTM.,

(ii) to compare the chemical composition of the Nigerian made cements to those imported, and

(iii) to compare the chemical composition of the local Building Materials (Soils) with that of cements.

1-5 The Scope Of The Project

The Building Materials analysed were soils, clays and cements. Clays, limestones, marble and shale were also studied as raw materials of cement.

The analyses of soils included the determination of loss on ignition and the following oxides: SiO_2, Fe_2O_3, Fe_2O_3, CaO, MgO, SO_3, Na_2O, K_2O, Li_2O, P_2O_5 and Mn_2O_3. The soil samples analysed included ordinary soil as defined on page 1, the "mud-balls" used by local builders and soils from dilapidating walls of the mud huts or of ancient city.

The analyses of cement involved determination of loss on ignition, insoluble residue, sulfur trioxide and other oxides as determined in the case of soil samples.

The determination of loss on ignition, insoluble residue, sulfur trioxide and gravimetric silica were carried out gravimetrically while Al_2O_3, CaO, and MgO were determined titrimetrically using ethylenediamine tetraacetic acid, EDTA. The alkali oxides, Na_2O, K_2O, and Li_2O were determined flame photometrically while the remaining oxides were determined spectrophotometrically.

It was originally planned to compliment the chemical analysis by differential thermal analysis (DTA) and X-ray diffractometric methods but due to instrumental breakdown this was not possible.

CHAPTER II

ANALYSIS OF SOILS, CLAYS, LIMESTONES AND MARBLE

The different samples of soils, clays, limestones and the marble were obtained from different locations as described in section II-1.

Since the successful analysis of complex and heterogeneous materials such as soils, rocks and similar materials depends on proper sampling, this technique is discussed in section II-2.

The analysis performed included the determination of loss on ignition at 1000°C, and the following oxides: SiO_2, Al_2O_3, Fe_2O_3, MgO, CaO, Na_2O, K_2O, Li_2O, TiO_2, P_2O_5 and MnO. The analytical techniques employed included gravimetry (loss on ignition and SiO_2) complexometric titrimetry (Al_2O_3, CaO and MgO), spectrophotometry (Fe_2O_3, TiO_2, P_2O_5 and MnO_2) and flame photometry (Na_2O, K_2O, and Li_2O). The various experimental procedures followed in the various determinations are detailed in section 2-3.

2-1 Location And Collection Of Samples

The soil samples and the Tsambe Clay were collected at different places as described below. The remaining clay

samples, limestones and the marble were supplied by the Geological Survey of Nigeria, Kaduna; Directorate of Federal Ministry of Mines and Power. These samples were collected by this directorate during their routine mineral prospecting. The location of the different samples are also described hereunder.

(i) Birinin Kebbi Mud-brick: This sample was obtained from Birinin Kebbi headquarter of the Birinin Kebbi Local Government Council of Sokoto State. The mud-bricks are made by intimately mixing soil, hay and water to produce a workable plastic material which is then moulded into "mud-balls" or mud-bricks. The mud-bricks are sun-dried and used for building, using a freshly prepared workable mix as a cementing material between the bricks.

(ii) Birinin Kebbi Falling Wall: This sample was "chopped" from the wall of a dilapidating mud-hut in Birinin Kebbi town. The mud-hut had been built with the type of mud-bricks discussed above.

(iii) Samaru Mud-brick: Samaru is a village on the north-eastern outskirts of Ahmadu Bello University, Zaria. The natives of the village construct their mud-huts in the same manner as those of Birinin Kebbi. The mud-bricks are thus

prepared in the same way as those described above (section II-1(i)).

(iv) Samaru Falling Wall: This sample was obtained from an old falling wall in Samaru village. It was estimated that the wall had been standing for seven years.

(v) Zaria City Wall: The historic Zaria City wall in Zaria Local Government Council of Kaduna State was constructed in 1536[43,44]. Samples were taken at three points of about 200 metres apart along the Zaria-Kaduna road and then combined into a composite sample.

(vi) Makurdi Soil: Makurdi is the capital of Benue State of Nigeria. The town is located on the southern bank of the River Benue. The soil sample was taken at the eastern side of the town at a depth of about 0.60 metres.

(vii) Tsambe Clay: Tsambe is a district in Vandeikya Local Government Council of Benue State. The clay has been used for local pottery industry for years.

(viii) Sokoto Aluminous Clay: Sokoto is the capital of Sokoto State on the north-western part of Nigeria. The clay

samples were taken by the Geological Survey of Nigeria, Kaduna, from a number of pits outside Sokoto town. The two samples analysed in this work were those from Pit 3 and Pit 5 as labelled by Geological Survey of Nigeria, Kaduna.

(ix) Ogbakiri Clay: Ogbakiri is in Ikwere Local Government Area of Rivers State of Nigeria. The sample was supplied by the Geological Survey of Nigeria, Kaduna.

(x) Itak Ikot Clay: This sample was obtained from Itak Ikot, in Obio Ishe, Ikono North Development Area, in Enyong Division of Cross River State by the Geological Survey of Nigeria, Kaduna.

(xi) Durumi Clay: This sample was collected at Major Arnas house at Durumi near Liberty Dam, on the Jos Plateau by the Geological Survey.

(xii) Ifan Limestones: These limestone samples were obtained from Ifan within the clay-shale group between Ogtesso and Uhomora by the Geological Survey, Kaduna. The seven samples were labelled GL 62592 - GL 62598.

(xiii) Jakura Marble: This sample was collected from Jakura. It was supplied by the Geological Survey of Nigeria, Kaduna.

Sampling

Sampling[45] is the process of extracting from a large quantity of material, a small portion which is truly representative of the composition of the whole material.

The importance of sampling in rock analysis has been pointed out by Grout[46]; the different methods for sampling soils have been discussed by Cline[47], and Petersen and Calvin[48]; and those for rocks and minerals by Maxwell[49], Groves[50], and Hillner[51] and will not be delved into here. Suffice it to state that the author found it convenient to take soil samples of any given location at three spots of about a metre apart and to combine these samples to form one composite sample of that location, thus simulating Grout's[46] method.

Procedure

The composite samples, about 2 - 3 kg, were air-dried and crushed with a wooden mallet to smaller particle sizes suitable for grinding and then sampled by coning and quartering as follows:

The sample was spread on a large piece of paper and rolled from one corner of the paper to the opposite corner by raising one corner and causing the sample to tumble upon itself. This process was repeated raising each corner until the entire sample was throughly mixed. The sample was gathered in the centre of the paper as a flat cone and, using a glass rod, divided into four quarters and the opposite quarters removed. The mixing, quartering and removal of opposite quarters were repeated until a sample of about 20g was obtained. This then formed the "representative portion" of the bulk sample and was further subjected to sample preparation and sample decomposition which are discussed hereunder.

.. Sample Preparation

Sample preparation[49], which includes crushing, splitting, grinding, mixing and drying, is an important step in analytical work. There are many ways of preparing samples and it is necessary to choose the best procedure for the job at hand.

Contermination of the sample during sample preparation is an ever-present and unavoidable danger. It is impossible to prepare a sample of a complex material like soil and rock without changing its composition in some respect, either

through foreign material, the preferential loss of material, or the oxidation of constituents. The analyst aims at minimizing these undesirable effects, either by preventing their ready occurence or by employing the procedure that will favour a type of contermination that is least harmful. Contermination is very often introduced by the equipment at various stages of sample preparation particularly grinding and sieving[52]. Ways of minimizing contermination as discussed by Thiers[53] in respect of biological materials apply equally to soil and rock material. In the present work, samples were ground in an agate mill and sieved through brass sieves (- 120 mesh BS).

The finely ground sample (- 120 mesh BS) was thoroughly mixed by rolling the powder from one side to the other on a sheet of glazed paper so that the sample tumbled over itself. The powder was then placed in labelled sample bottle with a cap and stored until required to be used.

B. Sample Decomposition

In analysing complex materials like soils and rocks which are not completely soluble in water, one of the most crucial decision of the analyst is that of method of decomposing the sample as this sets the course of subsequent analytical work and can save unnecessary steps. The various

methods of decomposing a sample fall into four categories: acid digestion, acid fusion, alkaline fusion and ammonium salt attack. The analyst has to choose the method that, taking everything into consideration, is best adapted to the material to be analysed. No general rule can be applied regarding the advantages to be gained by employing any particular method as this is determined by the nature of the material and the subsequent analytical procedures. Many factors[55], however, have to be considered: Does the process attack the vessel in which it is conducted? How effective is it? Will the reagents interfere in any analysis? Will the excess reagents be removed, if necessary? Will any loss of material be involved?

The various methods of decomposing soils, silicates and rocks have been extensively treated by Hillebrand et al[56] Jackson[57], and Williard and Rulfs[55]. Furthermore Sulcek et al[58] have reviewed the problems associated with decomposition of inorganic materials and these would not be delved into here. Suffice it to say that the alkali fusion (Na_2CO_3/K_2CO_3) followed by acid dissolution (HCl) was employed for preparing solutions to be used for determination of all oxides except those of alkalis, not because it was better than any other methods but because it was convenient for the course of analytical procedure followed. The solutions used

for determination of alkali oxides were prepared by the acid decomposition method (nitric acid, sulphuric acid, and hydrofluoric acid mixture).

-3 Analytical Studies of Soils, Clays, Limestone and Marble

Analytical studies performed on the various samples of soils, clays, limestones and marble included the determination of loss on ignition, silica, alumina, lime, magnesia, ferric oxide, titania, manganese oxide, phosphorous pentoxide, and the alkali oxides (Li_2O, K_2O, Na_2O). The various analytical methods employed for these determinations are detailed in the appropriate sections below.

EXPERIMENTAL

Apparatus

Platinum Crucibles:	20, 30, and 50-cm^3 capacity
Desiccator:	Containing silica gel as desiccant
Oven:	Gallenkamp, temperature range 0-300°C
Muffle furnace:	Carbolyte, temperature range, 0-1200°C
Hot plate:	Gallenkamp, temperature range, 0-650°C

Reagents

All reagents used were of analytical grade unless stated otherwise.

Fusion Mixture: An equimolecular mixture of anhydrous potassium and sodium carbonates.

Boric acid

Sodium Carbonate

Ethanol (95%)

Hydrochloric acid (d = 1.18)

Dilute hydrochloric (50% $^{v}/_{v}$)

Dilute hydrochloric (5% $^{v}/_{v}$)

Sulphuric acid (d = 1.84)

Dilute sulphuric acid (50% $^{v}/_{v}$)

Ammonia Solution (d = 0.88)

Diluted ammonia (50% $^{v}/_{v}$)

Hydrofluoric acid (40% $^{w}/_{w}$)

2-3.1 Determination of Loss on Ignition

Loss on ignition[59] is conventionally taken as the equilibrium weight loss on heating at 1000°C. This weight loss consist of bound or chemically adsorbed water, water formed by dehydroxylation of initially hydrous or hydroxylated silicate structure (particularly applicable to clays), carbon dioxide and sulfur trioxide from decomposition of carbonates and sulphates respectively.

Loss on ignition is determined gravimetrically.

Procedure

1.000g of the finely, ground and dried (10 5-110^{o}C) soil, clay, limestone or marble sample was weighed in a clean constant weight platinum crucible (20-cm^{3}). The latter was partially covered with the lid and placed in the muffle furnace. The temperature of the muffle furnace was slowly raised to 1000 $\pm$ 20^{o}C and the sample ignited at this temperature for 30 min. The crucible was then removed from the furnace, completely covered with the lid, cooled in the disiccator and weighed.

Loss on ignition was then calculated as follows:-

Weight of crucible + sample ... ... = a

Weight of crucible + residue after ignition = b

Loss in weight of sample ... ... = a-b

$\therefore$ Loss on ignition at 1000^{o}C (%) = (a-b)x100

The results are given in Table II-1

2-3.2 Decomposition of the Soil, Clay, Limestone and Marble Samples

The decomposition method employed for all these samples was the alkaline fusion (K_2CO_3/Na_2CO_3) followed by the dissolution of the cake in hydrochloric acid.

Procedure

1.000g of the finely ground dried (at 105-110°C sample was weighed in a platinum crucible (50-cm^3). 3g of fusion mixture and 0.4g of boric acid were added and the mixture thoroughly mixed to form a charge at the bottom of the crucible. The crucible was covered with the lid and heated over the Bunsen flame, gently at first and then gradually raising the temperature to the full heat for about 10min. The crucible was then transferred to a muffle furnace at 1200°C and the contents fused for 15min. After cooling, if the fusion appeared blue or blue-green, indicating the presence of manganese, 2cm^3 of ethanol(95%) were added to it before dissolution.

15cm^3 of hydrochloric acid (d = 1.18), 1cm^3 of sulphuric acid (50% $^{v}/_{v}$) and 10cm^3 of water were added and the crucible transferred to a steam bath to facilitate dissolution of the melt. If the solution gelled before dissolution was completed, the gel was stirred with glass rod. After dissolution was complete the lid was removed and any spray adhering to it washed into the crucible with minimum amount of water.

2-3.3 Determination of Gravimetric Silica

Silica, or silicon dioxide, SiO_2, is best determined by gravimetric, colorimetric, and spectrographic methods[60]. In the present work gravimetric and calorimetric methods were used. The main silica was determined gravimetrically (hence "gravimetric silica") while the residual or soluble silica was determined colorimetrically. The values obtained by the two methods were summed up to obtain the total silica content of the samples studied (see sections 2-3.5 & 2-3.6).

Reagents

Whatman accelerator tablet.

Polyethylene oxide: 0.5g of polyethylene oxide were added to 200cm^3 of water slowly and with stiring until dissolved. The solution was discarded after 2 weeks.

Procedure

The platinum crucible (50-cm^3) with its contents from the decomposition of the sample (Section 2-3.2) was digested over the steam until a stiff gel formed or for 30 min where there was no gel formation (ie for samples having less than 20% silica). Any loss of hydrochloric

acid during the digestion was replaced by adding appropriate amount of diluted hydrochloric acid (50% $^{v}/_{v}$).

After the gel had formed or after 30min. the crucible was removed from the steam bath and a Whatman accelerator tablet mixed into the gel until the mixture was homogeneous, breaking any gel adhering to the sides of the crucible. $5cm^3$ of polyethylene oxide coagulant solution ($2.5g/cm^3$) were slowly added with stirring, ensuring that any gel adhering to the sides of the crucible was brought into contact with the coagulant. $10cm^3$ of water were added and the mixture allowed to stand for 5min.

The precipitate was filtered using Whatman No.541 filter paper, transferring the precipitated silica to the filter paper with hot dilute hydrochloric acid (5% $^{v}/_{v}$), and scrubbing the crucible with a rubber-tipped glass rod. The precipitate was washed four times with hot dilute hydrochloric acid (5% $^{v}/v$) and then with hot water until practically free from chlorides. The precipitate and washings were reserved. The filter paper containing the precipitate was transferred to a constant weight platinum crucible ($30-cm^3$), charred over the Bunsen flame until free from carbonaceous matter, and then ignited in a muffle furnace at $1200^{o}C$ for 30min. After cooling in a disiccator, the crucible was weighed. This gave the weight of silica and impurities.

The contents of the crucible were moistened with water, 5 drops of diluted sulphuric acid (50% $^{v}/_{v}$) and 10cm^3 of hydrofluoric acid (40% $^{w}/_{w}$) added in turn, and the mixture evaporated over a low-temperature hot plate in a fume cupboard.

The crucible with the residue was cautiously heated over the gas flame and then finally ignited in a muffle furnace at 1000^{o}C for 5min. After cooling, the crucible was weighed to obtain the weight of impurities. The difference between the two weights represented the "gravimetric silica".

Weight of crucible + silica and impurities = c

Weight of crucible + impurities ... = d

$\therefore$ Weight of silica ... ... = c-d

weight of gravimetric silica (%) ... = (c-d)x 100

The results are added to the values for the residual silica (section 2-3.5) to obtain the total silica content for the sample (section 2-3.6).

2-3.4 Preparation of the Solution for the Determination of Residual Silica, Alumina, Lime, Magnesia, Ferric Oxide, Titania, Manganese Oxide, and Phosphorous Pentoxide

Procedure

The residue from hydrofluoric acid treatment was fused with 1g sodium carbonate and 0.2g boric acid and the melt dissolved in the main filtrate from the determination of gravimetric silica

(Section 2-3.3). After cooling, the solution was diluted to 500cm^3 with water in a volumetric flask to form the "stock solution".

2-3.5 Determination of Residual Silica

Residual or soluble silica is the silica still left in the solution after the main silica has been precipitated. Residual silica was determined calorimetrically using the molybdenum blue[61] procedure.

Apparatus

Spectrophotometer: SP6 - 200, Pye Unicam with 10mm cuvettes.

Reagents

2, 4-Dinitrophenol indicator: 0.1g of 2, 4-dinitrophenol was dissolved in 100cm^3 of water, cooled and filtered.

Ammonium molybdate (80g/dm^3): 80g of ammonium molybdate were dissolved in 1dm^3 of water, filtered and stored in a polythene bottle. The solution was discarded after 4 weeks.

Stannous chloride (10g/dm^3): 1g of stannous chloride was dissolved by warming in 1.5cm^3 of hydrochloric acid (d = 1.18). After cooling the solution was diluted to 100cm^3 with water.

This solution was discarded after 24 hours.

Standard Silica Solution (0.5mg SiO_2/cm^3): 0.5000g of specpure silica was fused with 5g of anhydrous sodium carbonate in a platinum crucible (50-cm^3), cooled and dissolved in water in a polythene beaker. The resulting solution was quantitatively transferred to a 1-dm^3 volumetric flask and diluted to volume. This solution was stored in a polythene bottle.

Diluted Standard Silica Solution (0.020mg SiO_2/cm^3): 20.0cm^3 of the standard silica solution (0.50mg SiO_2/cm^3) were diluted to 500cm^3 in a volumetric flask when this solution was required.

Procedure

0, 2, 4, 6, 8 and 10cm^3 aliquots of the dilute silica standard solution (0.020mg SiO_2/cm^3) were pipetted into 100-cm^3 volumetric flasks and each diluted to 20cm^3 with water. 5cm^3 of dilute hydrochloric acid (20% $^{v}/_{v}$) and 6cm^3 of ammonium molybdate solution (80g/dm^3) were added in turn with swirling and the solution left to stand at room temperature for 10min. 45cm^3 of diluted hydrochloric acid (50% $^{v}/_{v}$) were added with swirling and again left to stand for 10min. Finally 10cm^3 of stannous chloride (10g/dm^3) were added and the solution in each flask diluted to mark and thoroughly mixed.

The absorbance of each solution was measured using the solution in the "0-flask" as the blank in 10mm cells at 800nm; the colour being stable between 5 and 30min after the addition of stannous chloride ($10g/dm^3$).

A plot of absorbance against concentration of silica gave the calibration curve, Fig.1.

$5.0cm^3$ aliquot of the stock solution was transferred to a $100-cm^3$ volumetric flask A; and $15cm^3$ of water and 2 drops of 2, 4-dinitrophenol indicator added. Diluted ammonia (50% $^{v}/_{v}$) was added dropwise until the indicator turned yellow. The amount of ammonia added was noted and $5cm^3$ of dilute hydrochloric acid (20% $^{v}/_{v}$) added.

$20cm^3$ of water were added to another flask B followed by the same amount of ammonia 50% $^{v}/_{v}$) as was added in flask A. Two drops of 2, 4-dinitrophenol were added followed by dilute hydrochloric (20% $^{v}/_{v}$) until the solution was neutral and then $5cm^3$ in excess. The colours of the solution were developed as above.

The absorbance of the solution in flask A was measured against the solution in flask B as in the case of standards.

The silica content of the solution was then determined with reference to the calibration curve.

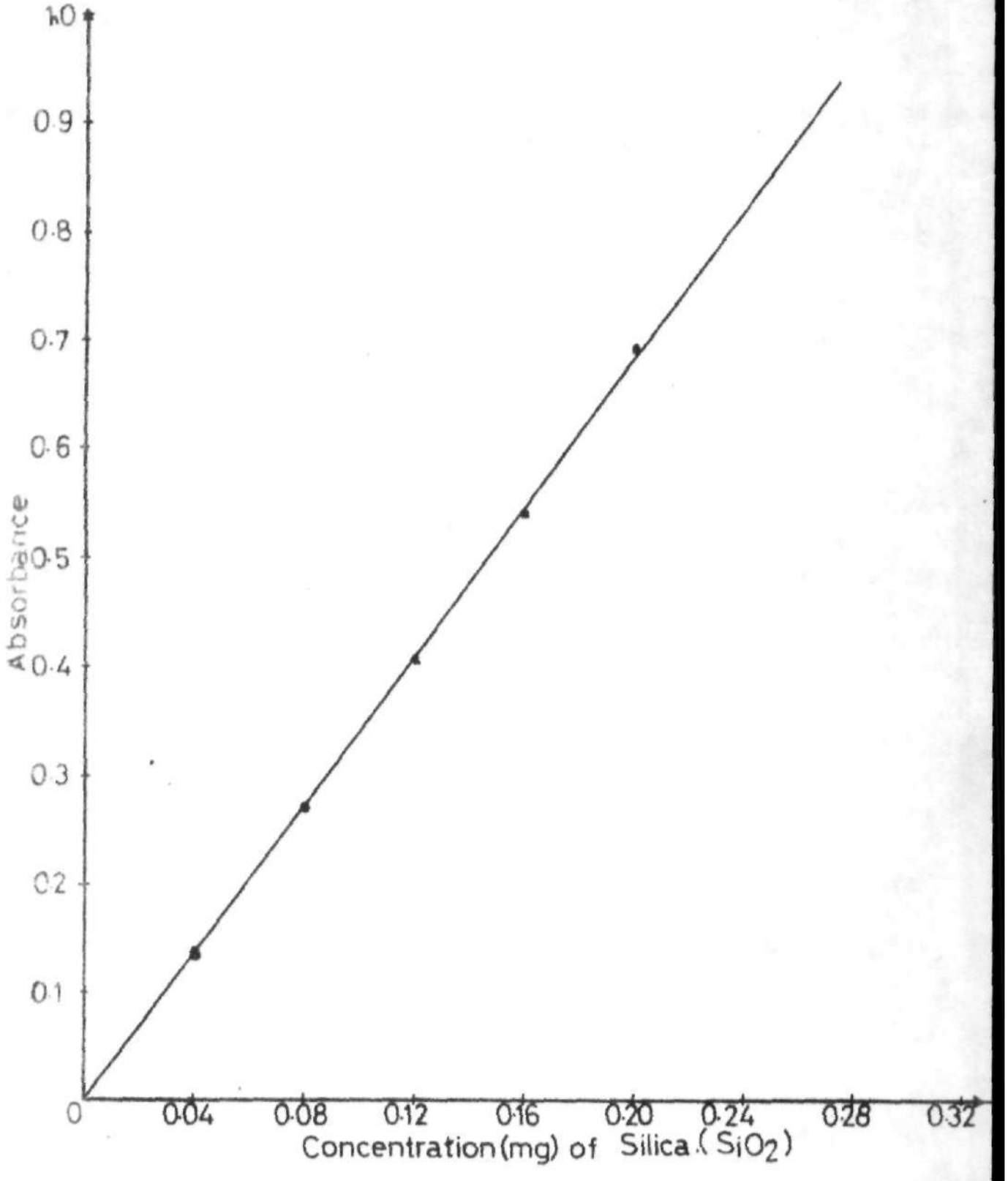


FIG 1 CALIBRATION CURVE FOR DETERMINATION OF RESIDUAL SILICA

The results were added to the appropriate value for gravimetric silica to obtain the total silica content of the sample (Section 2-3.6).

2-3.6 Calculation of Total Silica, SiO_2

The values for the gravimetric silica (Section 2-3.3) and residual silica (Section 2-3.5) are summed up to obtain the total silica content of the sample.

The results are given in Table IV-1

2-3.7 Determination of Alumina, Lime, and Magnesia

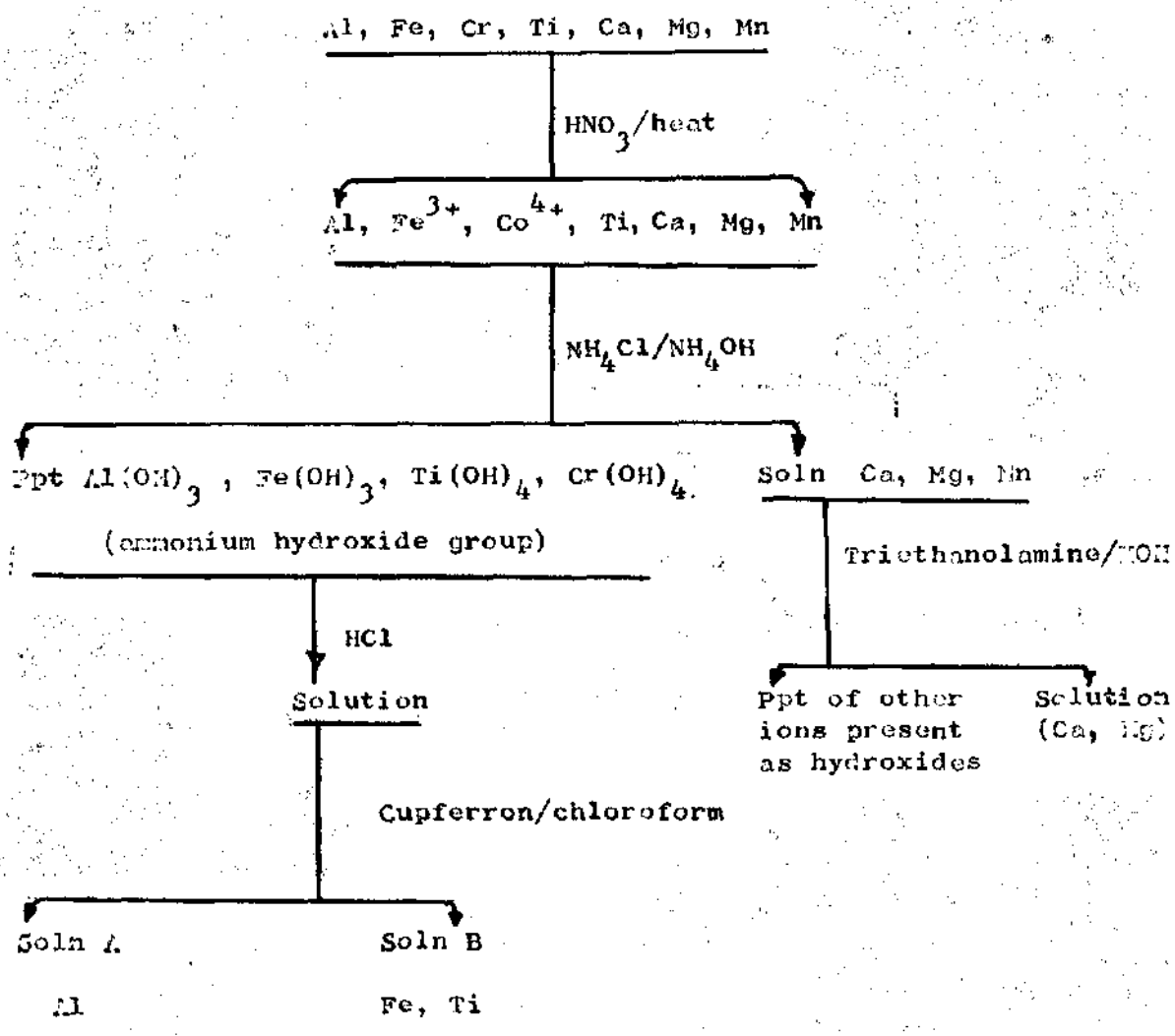
These three oxides, alumina (Al_2O_3), lime (CaO), and magnesia (MgO), were determined titrimetrically using ethylenediaminetetraacetic acid, EDTA.

In the absence of interfering substances aluminium[62] can be accurately determined by many different methods. But in the presence of other ions some of which are present in soils, and clays, the exact determination of aluminium is difficult. Thus the main requirement for satisfactory analysis is either to separate the interfering substances from the aluminium or to mask them as soluble complexes. Furthermore EDTA[63] itself is non-selective in its action with metal ions. Hence, to determine either aluminium, calcium or magnesium, the interfering metals must be removed or their effect masked.

The influence of some of the interferring ions may be overcome by adding complexing agents[64] such as cyanide ions which form stable complexes with copper, zinc, nickel, iron, cobalt, silver and the platinum. Alternately the interfering ions can be precipitated and removed from the solution. In the method used, aluminium is separated from other metals by first precipitating it together with some of the metals in form of their hydroxides, R_2O_3 (where R = Al, Fe, or Cr). Both the precipitate and filtrate are reserved.

The precipitate is dissolved in hot hydrochloric acid and aluminium separated from the other metals by extracting the latter as cupferrates in chloroform. The filtrate containing calcium and magnesium is used for the determination of lime and magnesia. Any ions which might interfere in the analysis are effectively masked with triethanolamine.

The separation of aluminium, calcium and magnesium and the interfering ions may be summarized schematically as follows:-



4. Removal of interfering ions

The method adapted for removing the interfering ions is similar to that of Bennett and Reed[65], and McLean[62] with some modifications.

Reagents

Sulphurous acid: 200cm^3 of water saturated with sulphur dioxide.

Nitric Acid (d = 1.42).

Bromophenolblue indicator: 0.1g of bromophenol blue ground with 1.5cm^3 of sodium hydroxide solution (Ca 0.1M) and diluted to 100cm^3 with water.

Ammonical ammonium nitrate (10g/dm^3): 10cm^3 of nitric acid (d = 1.42) were diluted to 200cm^3 with water. Ammonia solution (50% $^{v}/_{v}$) was added until the solution was just alkaline to bromophenol blue. After cooling the solution was diluted to 1dm^3.

Chloroform

Cupferron solution (6% $^{w}/_{v}$): 1.5g of cupferrom (ammonium salt of N-nitroso-N-phenylhydroxylamine) were dissolved in 25cm^3 of water and filtered.

(i) Removal of Calcium, Magnesium, and Manganese

Procedure

100cm^3 of the stock solution were pipetted into a 500-cm^3 beaker. 10cm^3 of sulphurous acid were added and the excess sulphur dioxide boiled off. This action reduced Cr^{4+} which interferes quantitatively with aluminium to Cr^{3+}.

The solution was colled slightly, 5cm^3 of nitric acid (d = 1.42) added and, the solution boiled again for 15 min to oxidize any Fe^{2+} to Fe^{3+}. After cooling to about 80^{o}C, 5g of ammonium chloride were added followed by ammonia solution (50% $^{v}/_{v}$) with stirring until the solution was just alkaline to bromophenol blue. This action precipitated aluminium, iron, chromium, and titanium as their hydroxides, R_2O_3. The excess ammonia was boiled off, the precipitate allowed to settle for 5min and quantitatively transferred to a Whatman No.541 filter paper and thoroughly washed with hot ammonical ammonium nitrate (10g/dm^3).

The filtrate and washing were transferred to a 250-cm^3 volumetric flask diluted to the mark with water and reserved for the determination of lime (CaO) and magnesia (MgO) (Section 2-3.7C).

(ii) Removal of Chromium, Iron, and Titanium

Procedure

The precipitate containing aluminium, iron, chromium and titanium was dissolved with 20cm^3 of hot hydrochloric acid (50% $^{v}/_{v}$) and the paper washed thoroughly with hot water. After cooling the solution was transferred

quantitatively to a separatory funnel rinsing the beaker with hot water. 20cm^3 of chloroform and 10cm^3 of cupferron solution (6% $^{w}/_{v}$) were added. After shaking vigorously, iron, chromium and titanium were extracted as cupferrates in the chloroform layer and the latter drained off. Complete extraction was ensured when addition of a few drops of the cupferron solution (6% $^{w}/_{v}$) did not produce any coloured precipitate.

The extraction was repeated with 10cm^3 aliquots of chloroform until the chloroform layer was colourless. The chloroform extracts containing iron, chromium, titanium and copper (if any) were discarded while the aqueous portion containing aluminium was transferred to a 250-cm^3 volumetric flask and made to volume with water.

D. Determination of Alumina, Al_2O_3

Of the various titrimetric[66] methods available for the determination of aluminium, the back titration of EDTA by zinc using dithizone indicator was adapted. This method was first used by Wanninen and Kingbom[66] and has since found application in the determination of aluminium in soils, cements[67], silicates and rocks[68,69], acid water and other materials.

The method is highly accurate and reproducible, the best working pH range being pH4.4-5.0.

Reagents

Naphthol Green B(1g/dm^3)

Dithizone indicator: 0.0125g of diphenyl thiocarbazone (dithizone), $C_6H_5N{=}N.CS.NH.NH.C_6H_5$, was dissolved in 50$cm^3$ of ethanol (95%). The solution was discarded after 1 week.

Standard Zinc Solution (0.05M): Zinc pellets were washed in dilute hydrochloric acid (2M) to remove any oxide film and then with water alcohol and ether in turn. 3.285g of the oxide free metal were dissolved 10cm^3 of hydrochloric acid (d = 1.18) and 50cm^3 of water added. After cooling the solution was diluted to 1dm^3 in a volumetric flask. 1cm^3 of 0.05M Zinc soln ≡ 0.55mg Al_2O_3.

Standard EDTA Solution (0.05M): 18.6125g of ethylenediaminotetraacetic acid (disodium salt) was dissolved in warm water, filtered cooled and diluted to 1dm^3 in a volumetric flask and stored in a polythene bottle. The solution was standardised[70] against standard zinc solution (0.05M) (1cm^3 of 0.05M EDTA ≡ 0.55mg Al_2O_3).

Ammonium acetate buffer: 120cm^3 of acetic acid (glacial) were added to 500cm^3 of water followed by 74cm^3 of ammonia solution (d = 0.88). After mixing and cooling, the solution was diluted to 1dm^3.

Procedure

50cm^3 aliquot of the aluminium solution was pipetted into a 500-cm^3 conical flask. A few drops of bromophenol blue indicator were added followed by ammonia solution (d = 0.88) dropwisely until the solution was just alkaline to bromophenol blue. The solution was quickly reacidified with hydrochloric acid (d = 1.18), adding 5 drops in excess. 10.0cm^3 of EDTA solution (0.05M) were added and then ammonium acetate buffer added until the indicator turned blue followed by 10cm^3 in excess.

The solution was boiled for 10min, cooled rapidly under tap water and a volume of ethanol (95%) equal to the total volume of the solution added. 2cm^3 of dithizone indicator were added followed by a few drops of naphthol Green B solution (1g/dm^3) to screen out any reddish or pinkish tinge and the solution titrated with the standard zinc solution (0.05M) from a semi-microburette (10-cm^3) from blue/green to the first appearance of a permanent pink colour.

The alumina content of the sample was then calculated thus:

$$Al_2O_3 = 2.5E\ (V-v)$$

where E = Al_2O_3 equivalent of standard zinc solution (0.05M) in mg.

V = volume of EDTA (0.05M) added

v = volume of standard zinc solution (0.05M) used in the back titration

The results are given in Table IV-1

C. Determination of Lime (CaO) and Magnesia (MgO)

Schwarzenbach and Co-workers[71-75] suggested the use of EDTA as a complexing agent for the alkaline earths and other metals as a titrant for the sum of calcium and magnesium in water using the Eriochrome Schwarz T (Indicator F 241) as indicator. The method has been modified using different metal indicators such as the Eriochrome Black T, Solochrome Black, murexide, etc. and is amply employed in the determination of water hardness[76,77] determination of alkaline earths in rocks[78], cements[79], soils, biological materials[81], etc.

In the procedure described hereunder the total calcium and magnesium is determined on an aliquot by adding triethanolamine and titrating with EDTA using Solochrome Black 6B indicator. Calcium is determined on another aliquot

by titrating with EDTA using the HHSNNA indicator. The calcium equivalent is then substracted from the total calcium and magnesium to obtain the amount of magnesium present in the sample.

Reagents

Triethanolamine (20% $^{v}/_{v}$)

Hydroxylammonium chloride (10%)

Monoethanolamine (redistilled)

Potassium hydroxide (8M, aqueous)

HHSNNA, or Patton and Reeder's, indicator: 0.50g of the solid dyestuff, 2-hydroxy-1-(2-hydroxy-4-sulpho-1-naphthylazo)-3-naphthoic acid, were titrated with 50g anhydrous sodium sulphate in a glass mortar until the dye was evenly distributed and stored in a well-stoppered amber-coloured bottle.

Solochrome Black 6B indicator: 0.2g of the dye sodium-(1-hydroxy-2-naphthylazo)-2-naphthol-4-sulphonate ground in 50g of potassium chloride.

Magnesium chloride solution (0.01M): 0.6162g of magnesium sulphate heptahydrate $MgSO_4.7H_2O$, were dissolved in water and diluted to 250-cm^3 in a volumetric flask.

Hydroxylamine (10% $^{w}/_{v}$)

Calcium Standard Solution (0.01M): 2.000g of oven-dried (100 - 110°C) Calcium carbonate were dissolved in 100cm^3 of dilute hydrochloric acid (5% $^{v}/_{v}$) and warmed to expel carbon dioxide. After cooling the solution was diluted to 2dm^3 in a volumetric flask.

Standard EDTA Solution (0.01M): This solution was standardised against the standard calcium solution (0.01M) using the procedure outlined below and stored in a polythene bottle.

Buffer Solution (pH = 10): 55cm^3 of concentrated hydrochloric acid (d = 1.18) were added to 400cm^3 of distilled water and thoroughly mixed. 310cm^3 of redistilled monoethanolamine were slowly poured into the mixture with stirring. After cooling to room temperature 50.0cm^3 of the stand magnesium solution (0.01M) were titrated with the EDTA solution (0.01M) using 1cm^3 of the monoethanolamine-hydrochloric acid solution as buffer and solochrome Black 6B as indicator. The volume of EDTA (0.01M) obtained was mixed with 50.0cm^3 of magnesium chloride solution (0.01M) and poured into the monoethanolamine-hydrochloric acid solution, thoroughly mixed and the solution diluted to 1dm^3.

(i) Determination of Lime (CaO)

25.0cm^3 aliquots of the filtrate from the precipitation of aluminium, iron, chromium and titanium (section 2-3.7.(3)) were pipetted into two 250-cm^3 conical flasks. After diluting the volume to 50cm^3 with water, 5cm^3 of hydroxylammonium chloride (10%) and 10cm^3 of triethanolamine solution (20% $^{v/v}$) were added in turn with swirling. 10cm^3 of aqueous potassium hydroxide solution (8M) were added to only one of the flasks to which, after further stirring for about 3min, 0.2g of the HHSNNA indicator were added and the solution titrated with standard EDTA (0.01M) until the colour changed from wine-red to blue. This gave the approximate value of the titre for the calcium present.

To the second flask, the volume of the standard EDTA (0.01M) equivalent to about 95 per cent of the calcium present as determined above was added followed by 10cm^3 of potassium hydroxide solution (8M) and the titration completed as above. This gave the accurate titre for calcium.

The percentage of lime in the original sample was calculated from the formula:

$$CaO(\%) = 5\ V_1F_1$$

where V_1 = volume of EDTA solution (0.01M) used in titration of sample soln. in cm^3

F_1 = mg of CaO equivalent to $1cm^3$ of standard EDTA solution (0.01M).

$1cm^3$ of 0.01M EDTA ≡ 0.5608mg CaO

The results are given in Table IV-1

(ii) Determination of Magnesia (MgO)

Procedure

$25.0cm^3$ of the filtrate from the precipitation of aluminium, iron, chromium and titanium were transferred to a $250-cm^3$ connical flask and diluted to $50cm^3$ with water. With swirling, $5cm^3$ of hydroxylammonium chloride solution (10%), $10cm^3$ of triethanolamine solution (20% $^{v}/_{v}$), $20cm^3$ of buffer solution, a volume of standard EDTA solution (0.01M) equal to that required for the titration of calcium oxide, V_1, and 0.2g of Solochrome Black 6B indicator were added in turn. The solution was titrated with the standard EDTA solution (0.01M) to a pure blue end point.

The magnesia content of the original sample was calculated using the formula:

$$MgO(\%) = 5\ (V_2 - V_1)\ F_2$$

where V_2 = volume of standard EDTA solution (0.01M) required for titration of sample solution in cm^3

V_1 = volume of standard EDTA solution (0.01M) required for titration of the sample solution in the determination of CaO.

F_2 = MgO equivalent of $1cm^3$ of standard EDTA solution (0.01M)

[$1cm^3$ of 0.01M EDTA ≡ 0.4032mg MgO]

The results are given in Table IV-1

Where the lime and magnesia contents were very small, the aliquot volumes were increased to $100cm^3$ and the volumes of the reagents also increased accordingly to maintain the solution at about pH 10.

4-3.3 Determination of Ferric Oxide, Fe_2O_3

Iron[82] in soils or other geological materials may exist in both the ferrous and ferric states. Therefore, to determine the iron content of such samples, the analyst has to employ a method which ensures that the iron in the two states is quantitatively determined. The various methods for determination of total iron content of silicates have been reviewed by Melnick[83] and Chalmers[84], and the spectrophotometric methods for the determination of trace quantities of iron have also been described by Sandell[85] and would not be considered here. In the colorimetric procedure described below, hydroxylamine (as the hydrochloride salt) is added to sample solution

to reduce any Fe^{3+} to Fe^{2+}. The latter is then complexed with 1, 10-phenanthroline reagent giving a strongly coloured reddish-orange complex[86] tris (1, 10-phenanthroline) iron(II).

$$4Fe^{3+} + 2NH_2OH = 4Fe^{2+} + N_2O + 4H^+ + H_2O$$

$$Fe^{2+} + 3C_{12}H_8N_2 = \left[Fe(C_{12}H_8N_2)_3\right]^{2+}$$

tris (1, 10-phenanthroline) iron(II)

This complex is quite stable and conforms to Beer's law, its colour intensity being constant in weakly acidic, neutral or weakly alkaline medium (pH = 2-9), and having maximum absorbance at 510nm.

Reagents

Hydrogen peroxide (6% $^{w}/_{v}$)

Ammonium Acetate (10%): $140cm^3$ of glacial acetic acid were diluted $2000cm^3$ with water and $140cm^3$ of ammonia solution (d = 0.88) carefully added. The solution was mixed and the pH adjusted to 6 using either acetic acid or ammonia solution.

1, 10-phenanthroline (0.1%): 100mg of the 1,10-phenanthroline monohydrate were dissolved in $2cm^3$ of acetic acid (glacial) and diluted to $100cm^3$ with water.

Standard iron(II) Solution (0.1mg Fe_2O_3/cm^3): 0.4911g of ferrous ammonium sulphate, $Fe(NH_4)_2.(SO_4)_2.6H_2O$, were dissolved in water and $2.5cm^3$ of sulphuric acid (d = 1.84) and $5cm^3$ of hydrogen peroxide (6%) added in turn. After boiling for 15min and cooling the solution was diluted $1dm^3$ in a volumetric flask.

Diluted standard iron(II) solution (0.01mg/cm^3): $50.0cm^3$ of the standard iron(II) solution (0.1mg Fe_2O_3/cm^3) were diluted to $500cm^3$ in a volumetric flask when required.

Procedure

0, 10, 20, 25, 40 and 50-cm^3 aliquot of the diluted standard iron(II) solution (0.01mg Fe_2O_3/cm^3) were pipetted into 100-cm^3 volumetric flasks. $2cm^3$ of hydroxylammonium chloride (10%), $5cm^3$ of 1,10-phenanthroline solution (0.1% $^{w}/_{v}$) and $2cm^3$ of ammonium acetate solution (10% $^{w}/_{v}$) were added in turn. After standing for 15min the solution in each flask was diluted to volume with distilled water.

The absorbance of the solutions were measured against the reagent blank in a 10mm cell at 510nm using Pye Unicam SP6-200 spectrophotometer. A plot of absorbance against the concentration of iron oxide in each flask yielded the calibration curve, Fig.2.

5.0cm^3 aliquots of the stock solutions were transferred to 100-cm^3 volumetric flasks. The colour and the absorbance were developed and measured respectively as outlined above. The ferric oxide content of the solution was then determined by reference to the calibration curve.

The results are given in table IV-1.

2-3.9 Determination of Titania, TiO_2

Weller's[87,88] method depending on formation of intensely yellow peritanic acid when hydrogen peroxide is added to the acidified solution of titanium sulphate is widely used for the determination of titanium. This is a fast and reliable calorimetric method.[89] The procedure followed is that described by Bennet and Reed[90].

Reagents

Phosphoric acid (40% $^{v}/_{v}$)

Standard titanium solution (1.0mg TiO_2/cm^3): 0.5000g of titanium oxide were mixed with 16g ammonium sulphate and 40cm^3 of concentrated sulphuric acid (d = 1.84) and heated until the mixtured dissolved. After cooling, about 90cm^3 of water were added and the solution quantitatively transferred to a 500-cm^3 volumetric flask and diluted to volume.

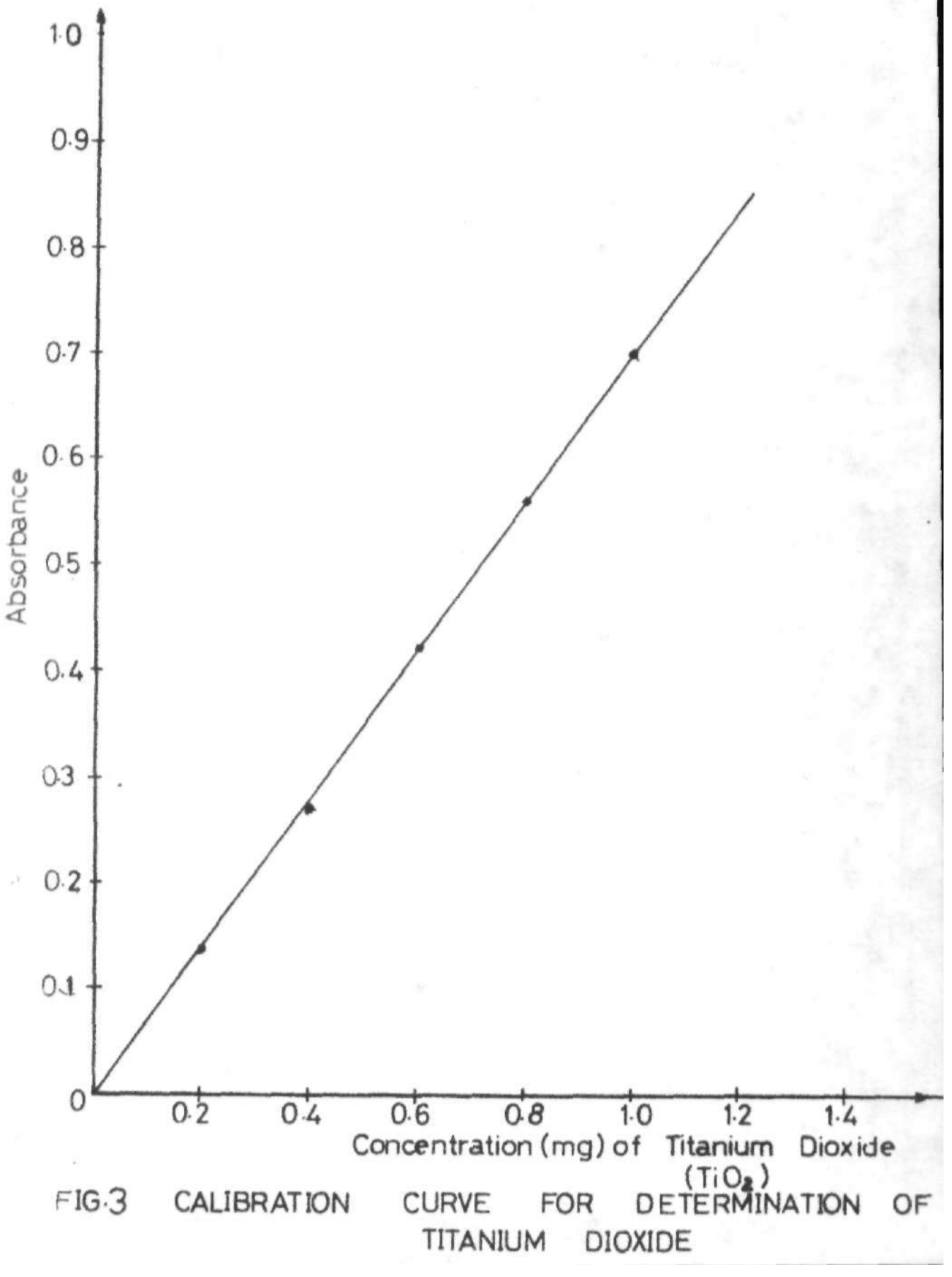
Diluted standard titanium solution (0.04mg TiO_2/cm^3): $20cm^3$ of the standard titanium solution (1.0mg TiO_2/cm^3) were diluted to $500cm^3$ in a volumetric flask when this solution was required.

Procedure[90]

Duplicate aliquots of 0, 5, 10, 15, 20 and $25cm^3$ respectively of the diluted standard titanium solution (0.04mg TiO_2/cm^3) were transferred to $50cm^3$ volumetric flasks. To each, $10cm^3$ of phosphoric acid (40% $^{v}/_{v}$) were were added and to one of each pair only 10 cm^3 of hydrogen peroxide solution (6% $^{w}/_{v}$) were added. The solution in each flask was diluted to volume and thoroughly mixed.

The absorbance of the peritanic acid was measured against the appropriate control solution in a 40mm cell at 390nm using Pye Unican SP6-200 spectrophotometer; the colour of the solution being stable for 24 hours. The calibration curve was obtained by plotting absorbance against concentration of TiO_2, Fig.3.

$20.0cm^3$ aliquots of the stock solution were transferred to each of the two $50-cm^3$ volumetric flasks, A and B. $10cm^3$ phosphoric acid (40% $^{v}/_{v}$) were added to both flasks while $10cm^3$ of hydrogen peroxide (6% $^{v}/_{v}$) were added to only flask A. Each solution was then diluted to $50cm^3$ and thoroughly mixed.



FIG·3 CALIBRATION CURVE FOR DETERMINATION OF TITANIUM DIOXIDE

The absorbance of solution A was measured against that of B as above. and the titania content of the original sample calculated by reference to the calibration curve.

The results are given in table IV-1

3-3.10 Determination of Manganese Oxide, MnO_2

A rapid and reliable colorimetric method for determination of small amounts of manganese is that developed by Williard and Greathouse[91]. It is based on the oxidation of Mn^{2+} to MnO_4^- by potassium or sodium metaperiodate in a strongly acidic solution, the reaction equation being:

$$2Mn^{2+} + 5IO_4^- + 3H_2O = 2MnO_4^- + 5IO_3^- + 6H^+$$

The reaction proceeds smoothly over a wide range of manganese concentrations. The few interferences encountered are usually readily eliminated.

Reagents

Potassium periodate:

Standard Manganese solution (0.1mg MnO/cm^3): 70.50cm^3 of standardized potassium per-manganate (0.1N) were diluted to 1dm^3 in a volumetric flask.

Diluted standard manganese solution (0.01mg MnO/cm^3): $50cm^3$ of the standard manganese solution (0.1mg Mno/cm^3) were diluted to $500cm^3$ in a volumetric flask when this solution was required.

Procedure

0, 10, 20, 25, 40, and $50cm^3$ aliquots of the dilute manganese solution were transferred to 100-cm^3 volumetric flasks and diluted to volume with water.

The absorbance of each solution was measured in 40mm cells at 524nm against water as blank using the Pye Unican SP6-200 spectrophotometer. The absorbance of each solution was plotted against the concentration of manganese to obtain the calibration curve, Figure 4.

$50.0cm^3$ aliquot of the stock solution was transferred to a 250-cm^3 beaker. $10cm^3$ of diluted sulphuric acid (50% $^{v}/_{v}$) and $5cm^3$ of nittric acid (d = 1.42) and the solution evaporated to strong fumes to expel chlorides. The solution was then cooled, $20cm^3$ nitric acid (d = 1.42), $10cm^3$ of dilute phosphoric acid (10% $^{v}/_{v}$) and $50cm^3$ of water were added in turn and the solution boiled to dissolve the salts and to expel nitrous fumes. After cooling slightly, 0.2g of potassium periodate were added, the solution boiled for 2min and then transferred to a steam bath and kept hot for 10min. After

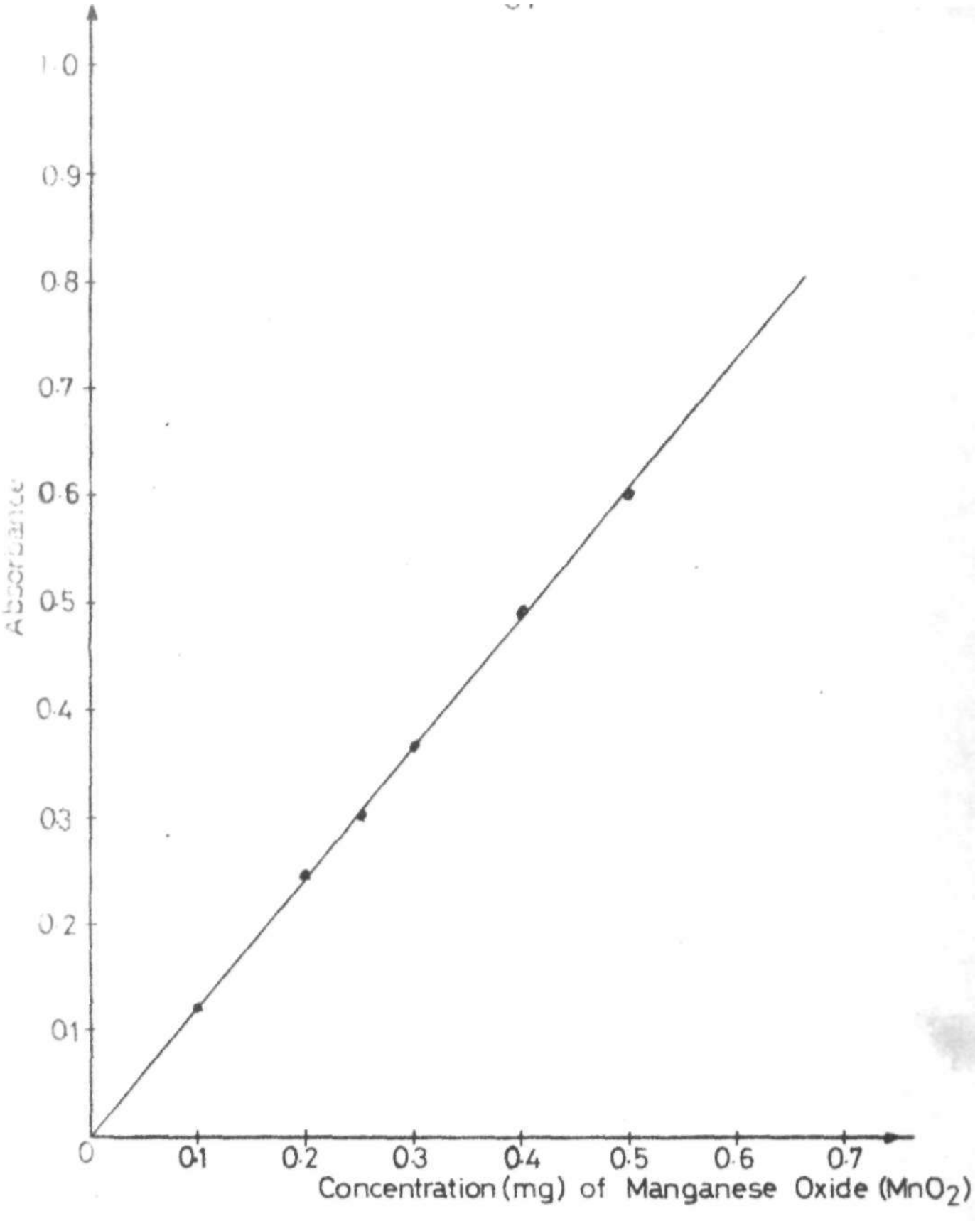


FIG. 4 CALIBRATION CURVE FOR DETERMINATION OF MANGANESE OXIDE

cooling, the solution was quantitatively transferred to a 100-cm^3 volumetric flask and diluted to volume.

The absorbance of the solution was measured as outlined above and the manganese oxide content determined by reference to the calibration curve.

5-3.11 Determination of Phosphorous Pentoxide, P_2O_5

The most sensitive methods for the colorimetric determination of phosphorous is the "molybdenum blue"[92] method. The phosphorous is reacted with ammonium molybdate to form ammonium phosphomolybdate which is selectively reduced with mild reductants to the "molybdenum blue", a molybdenum(v) species of uncertain composition:

$$7PO_4^{3-} + 12\left[(NH_4)_6Mo_7O_{24}\right] + 3H_2O \longrightarrow \left[(NH_4)_3PO_4 \cdot 12MoO_3\right] + 51NH_4^+ + 72OH^-$$

$$(NH_4)_3PO_4 \cdot 12\ MoO_4 + \text{Reductant} \longrightarrow \text{Mo(v) species}$$

"Molybdenum blue".

The blue colour of the solution is measured spectroscopically at 725nm.

Reagents

Hydrochloric acid (6.5M): 540cm^3 of concentrated hydrolic acid (1.42) were diluted to 1dm^3 with water.

Sulphuric acid (5.3M): 300cm^3 of concentrated sulphuric acid (d = 1.84) were cautiously added to about 600cm^3 of ice-cooled distilled water in a 1-dm^3 volumetric flask with swirling. After cooling to room temperature, the solution was diluted to volume with water.

Ammonium molybdate solution (25g/dm^3): 25g of ammonium molybdate, $(NH_4)_6Mo_7O_{24}.4H_2O$, were dissolved in about 250cm^3 of water and poured into a 1-dm^3 flask containing 500cm^3 of sulphuric acid (5.3M). After cooling the solution was diluted to volume with distilled water.

Ascorbic acid (0.1% $^{w}/_{v}$)

This solution was always freshly prepared.

Standard phosphorous solution (0.1mg P_2O_5/cm^3): 0.1917g of oven-dried (105-110°C) potassium dihydrogen phosphate were dissolved in water and diluted to 1dm^3 in a volumetric flask.

Procedure[93]

0, 2, 4, 6, 8 and 10cm^3 of the standard phosphorous solution (0.1mg P_2O_5/cm^3) were pipetted into 250-cm^3 tall form beakers. 35cm^3 of hydrochloric acid (6.5M), 5cm^3 of ammonium molybdate solution (25g/dm^3) and 1cm^3 of ascorbic acid (0.1% $^{w}/_{v}$) were added to each beaker in turn. The solutions were heated to

vigorous boiling and then boiled for 2min. After cooling the solutions were transferred quantitatively to 100-cm^3 volumetric flasks and diluted to volume with water.

The absorbance of each solution was measured against water at 725nm in 10mn cuvettes on the SP6-200 spectrophotometer. The calibration curve was obtained by plotting the absorbance of each solution against the concentration of phosphorous pentoxide, Fig. 5.

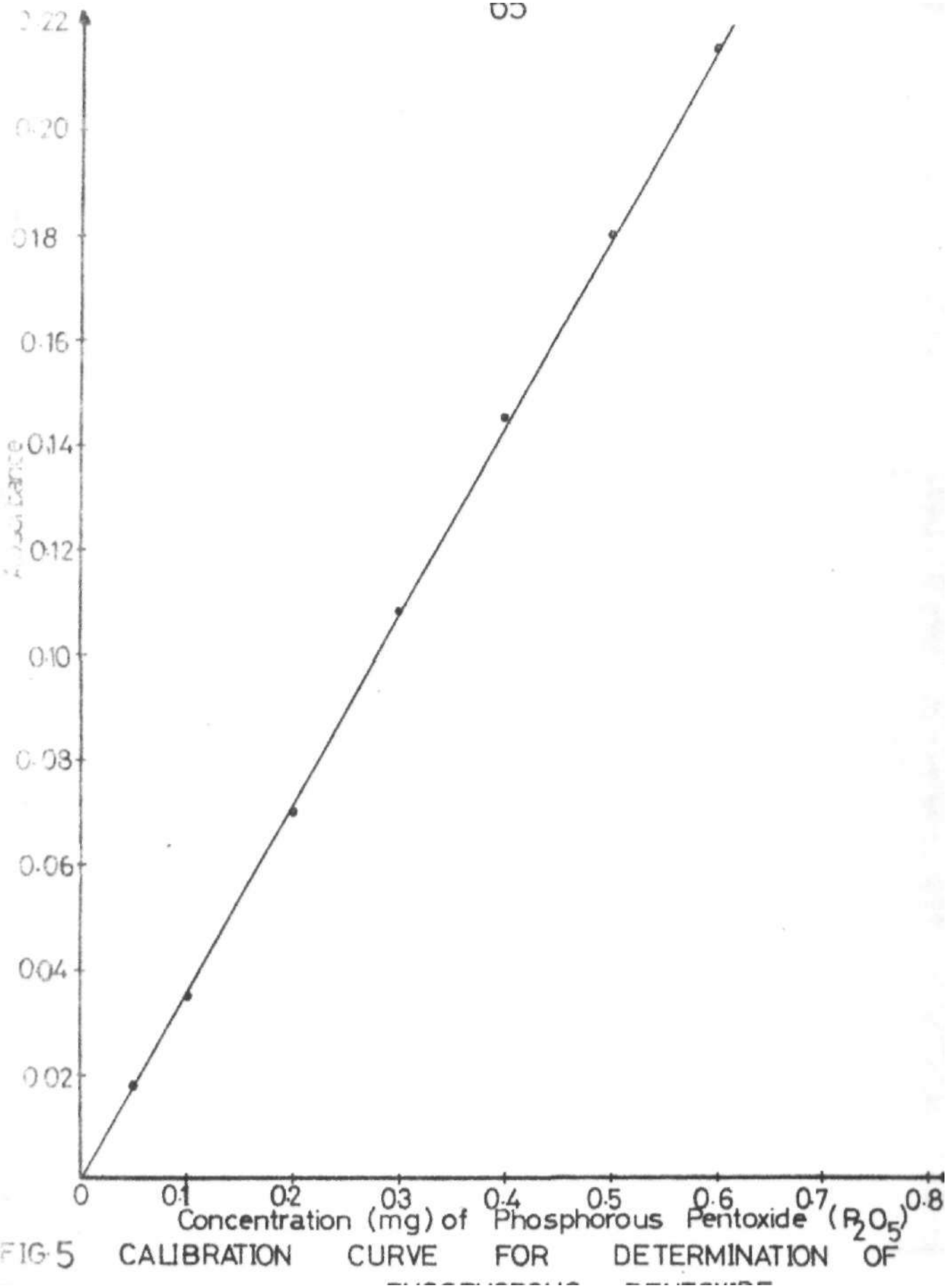
50.0cm^3 aliquots of the stock solutions were pipetted into 250-cm^3 tall form beakers. 5 cm^3 of ammonium molybdate solution (25g/dm^3) and 1cm^3 of ascorbic acid solution (0.1% $^{w}/_{v}$) were added in turn and the colour and absorbance of the solutions were respectively developed and measured as above. The net absorbance of each solution was obtained by subtracting the absorbance of the reagent blank prepared by diluting 10cm^3 of hydrochloric acid (d = 1.42) to 100cm^3 in a volumetric flask.

The concentration of phosphorous pentoxide in the original sample was determined by reference to the calibration curve.

The results are given in table IV-1

3-3.12 Determination of Alkali Oxides: Li_2O, K_2O, and Na_2O

The alkali oxides - Li_2O, K_2O and Na_2O - were determined by flame photometric method. Since the stock



FIG·5 CALIBRATION CURVE FOR DETERMINATION OF

solution used for analysis described hitherto was prepared by fusion with the fusion mixture (K_2CO_3/Na_2CO_3) these solution could not be used for determination of the alkali oxides. The solutionsused for this purpose were prepared by acid attack.

A. Decomposition of soil, clay, limestone and marble Samples for determination of alkali Oxides

The samples were decomposed by a mixture of acids - sulphuric acid, nitric acid and hydrofluoric acid.

Reagent

Sulphuric acid - nitric acid mixture: $50cm^3$ of sulphuric acid (d = 1.84) were cautiously added to $700cm^3$ of water with stirring followed by $250cm^3$ of nitric acid (d = 1.42).

Procedure

0.25g of the finely ground dried (at 100-110°C) sample of soil, clay, limestone, or marble were weighed in a platinum crucible (30 or 50-cm^3) and ignited gently for 10 min to remove the organic matter.

To the cool crucible, $10cm^3$ of each of sulphuric acid-nitric acid mixture and hydrofluoric acid (40% $^{w}/_{w}$) were added. The crucible was transferred to a low-

temperature hot plate and allowed to react with the lid on for 15 min and then evaporated to dryness. To the cool residue, 10cm^3 of sulphuric acid-nitric acid mixture were added, rinsing down the sides of the crucible with water. The solution was again evaporated to dryness.

The cool dry residue was dissolved by warming with 20cm^3 of dilute nitric acid (5% $^{w}/_{v}$). After cooling and filtering, if necessary, the solution was diluted to 250cm^3 in a volumetric flask to form the "stock solution A".

3. Flame Photometric determination of the alkali oxides

Flame photometry is branch of spectroscopy in which the flame is the source of excitation energy. Dvoracek[94] et al attribute the first quantitative application of radiation emitted by a flame to Lundegardh who is regarded as the true founder of the method. He introduced a solution of the sample into the flame in the form of aerosol and detected the radiation using a photographic plate. Though the plant physiologist Hiendergardh[94] had developed this method to study the distribution of some elements in plants only, this method was found to be of great significance in all analytical chemistry. This method has been widely investigated and today finds application not only in industrial control laboratories but in many other aspects

of human activity ranging from medical laboratories to criminal investigation.

The detailed treatment of the principle of flame photometry is given in general texts[94-95] on the subject and will be only briefly considered here. When compounds of some elements are introduced into the non-luminous flame of the Bunsen burner, they give characteristic colours: sodium salts yellow, lithium salts red etc. This colour is due to the emission of radiation by atoms or molecules. The radiation forms the spectrum of the atom or molecule, the spectrum being unique for that atom or molecule. Atoms give line spectra while molecules give band spectra.

The character of the emitted radiation is temperature dependent. When an ordinary gas flame is used as a source of excitation energy, only those elements such as lithium, potassium, and sodium that have low energy electronic levels are excited. With hotter flames (above 3200°C), other elements also give emission lines. Because the lines are relatively few in a typical line spectrum, a rather simple instrument is used to achieve satisfactory separation of the lines for analysis. One such instrument is the flame photometer which differs from the ordinary photometer or spectrophotometer in that the light source of the photometer is replaced by the atomiser and burner.

The intensity of the lines at a specific temperature is directly proportional to the concentration of the element. This offers a method of determining the concentration of a given element in the sample.

Apparatus

Flame photometer: Corning-Eel; with lithium, potassium and sodium filters.

Reagents

Aluminium sulphate (10mg Al_2O_3/cm^3): Pure aluminium metal was cleaned with hydrochloric (50% $^{v}/_{v}$), ethanol (95%), and ether. To 10.58g of the clean dry metal, $40cm^3$ of sulphuric acid (d = 1.84) $120cm^3$ of nitric acid (d = 1.42) and approximately $50cm^3$ of water were added. After reacting in the cold, the mixture was gently heated until the metal dissolved and the nitric oxides were expelled and the sulphuric acid fumed strongly. The solution was cooled and the crystalline melt dissolved in water and diluted to $2dm^3$.

Aluminium sulphate A (2000ppm Al_2O_3): $400cm^3$ of the aluminium sulphate solution (10mg Al_2O_3/cm^3 were diluted to $2dm^3$.

Lithium concentrated solution (400ppm Li_2O): Lithium sulphate monohydrate was dehydrated by drying at 150°C for 24 hours.

1.4717g of the anhydrous salt was dissolved in water and diluted to $1dm^3$ in a volumetric flask and stored in a polythene bottle.

Lithium standard solution B (40ppm Li_2O): $50cm^3$ of the concentrated lithium solution A were diluted to $500cm^3$ in a volumetric flask and mixed.

Potassium/Sodium concentrated standard solution A (400ppm K_2O, 100ppm Na_2O): 0.6331g of potassium chloride and 0.1886g of sodium chloride, both salts dried at 150^oC, were dissolved in water and diluted to $1dm^3$ in a volumetric flask.

Potassium/Sodium standard solution B (40ppm K_2O, 10ppm Na_2O): $50.0cm^3$ of the concentrated potassium/sodium standard solution A were diluted to $500cm^3$ in a volumetric flask.

Lithium top standard (20ppm Li_2O): $25.0cm^3$ of the lithium concentrated standard solution and $40cm^3$ of nitric acid (5% $^{v}/_{v}$) were diluted to $500cm^3$ in a volumetric flask and mixed.

Potassium/sodium top standard (20ppm K_2O, 5ppm Na_2O): $50.0cm^3$ of potassium/sodium concentrated standard solution, $40cm^3$ of dilute nitric acid (5% $^{v}/_{v}$) and $30cm^3$ of aluminium sulphate solution (10mg Al_2O_3/cm^3) were transferred to $1-dm^3$ volumetric flask, diluted to volume with water and mixed.

Potassium/Sodium zero standard (and diluted for alkalis in excess of 4% K_2O, 1% Na_2O): $40cm^3$ of dilute nitric acid (5% $^{v}/_{v}$) and $30cm^3$ of aluminium sulphate solution 10mg Al_2O_3/cm^3) were transferred to $1dm^3$ volumetric flask, diluted to volume and mixed.

Intermediate Calibration Standards:

Lithium: 10, 20, 30 and $40cm^3$ aliquots of the lithium top standards were transferred to $50cm^3$ volumetric flasks containing $4cm^3$ of dilute nitric acid (5% $^{v}/_{v}$) and diluted to $50cm^3$ with water and mixed. These concentrations were equivalent to 4, 8, 12, and 16ppm Li_2O or 0.4, 0.8, 1.2 and 1.6% Li_2O.

Potassium/Sodium: 2.5, 5, 10, 20, 25, 30 and $40cm^3$ aliquot respectively of the potassium/sodium standard solution B were transferred to $100-cm^3$ volumetric flasks containing $4cm^3$ dilute nitric acid (5% $^{v}/_{v}$) and $3cm^3$ of aluminium sulphate solution 10mg Al_2O_3/cm^3) and diluted to volume. This gave 2, 4, 8, 10, 12 and 16ppm K_2O and 0.25, 0.5, 1, 2, 2.5, 3 and 4ppm Na_2O respectively or 0.2, 0.4, 0.8, 1.6, 2.0, 2.4 and 3.2% K_2O and 0.05, 0.1, 0.2, 0.4, 0.5, 0.6 and 0.8% Na_2O.

Procedure

The flame photometer was lit and air turned on and adjusted to $10lb/in^2$. Water was sprayed and the gas flow adjusted to

give well-defined blue cones. The appropriate filter was fitted.

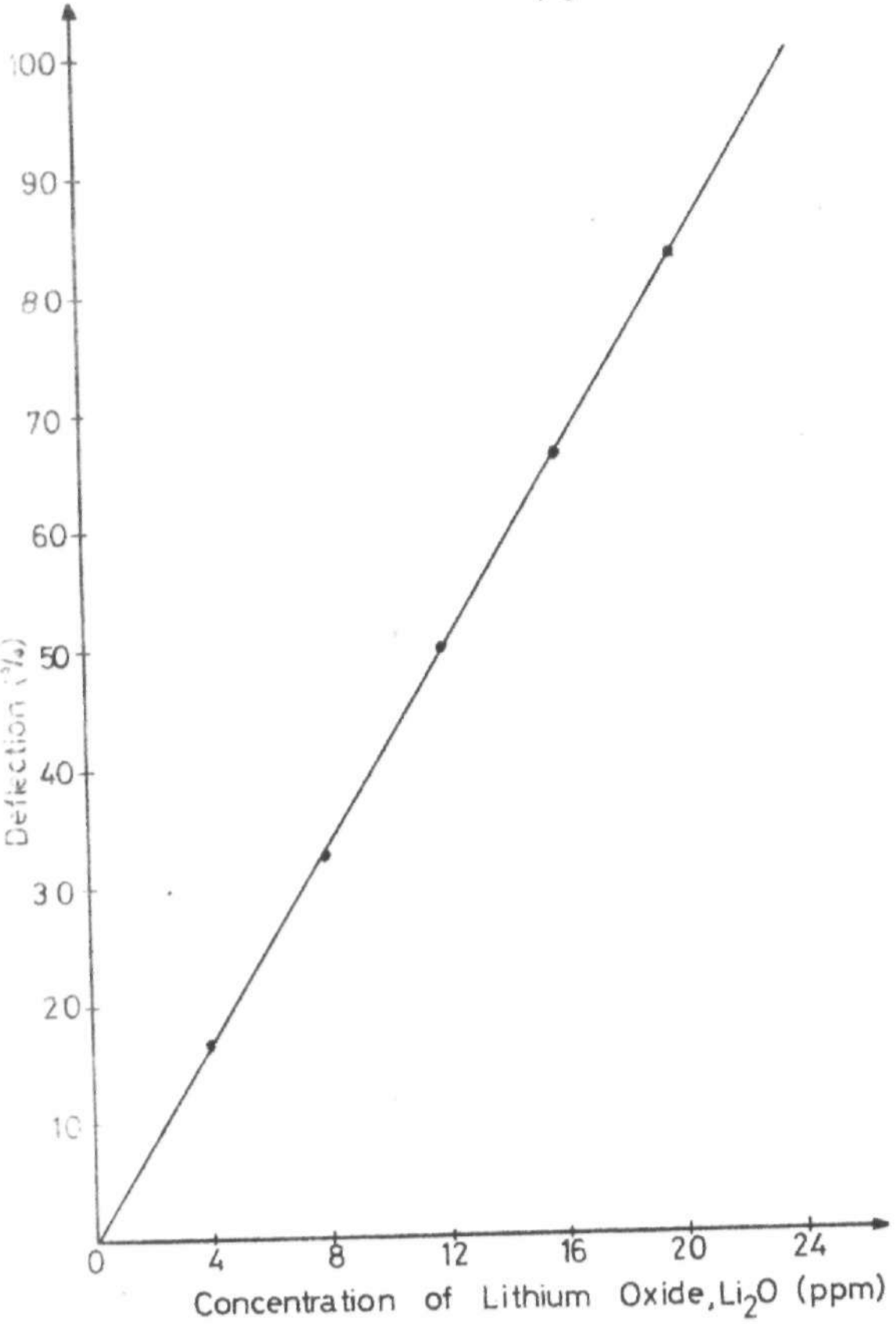
For lithium the full scale was set with 20ppm Li_2O top standard and zero with distilled water. The intermediate calibration standards were then sprayed, noting the readings and checking the full scale and zero frequently. From the readings a calibration curve was prepared, Fig. 6.

The sample solutions A were similarly sprayed, the readings noted and the concentration of lithium in the original sample calculated by reference to the calibration curve.

For potassium and sodium, the full scale was set with the potassium/sodium top standard (20ppm K_2O, 5ppm Na_2O), and zero on potassium/sodium zero standard. The intermediate standards were again sprayed as above and calibration curves similarly obtained, Figs. 7 & 8.

25.0cm^3 of the stock solutions A were transferred to 50-cm^3 volumetric flasks containing 5cm^3 of aluminium sulphate (2000/ppm Al_2O_3) and diluted to mark with water to give solution B. These solutions were sprayed as above, the readings noted and the concentrations of potassium and sodium in the original samples calculated by reference to the appropriate calibration curve.

The results are given in table IV-1.



FIG·6 CALIBRATION CURVE FOR DETERMINATION OF LITHIUM OXIDE

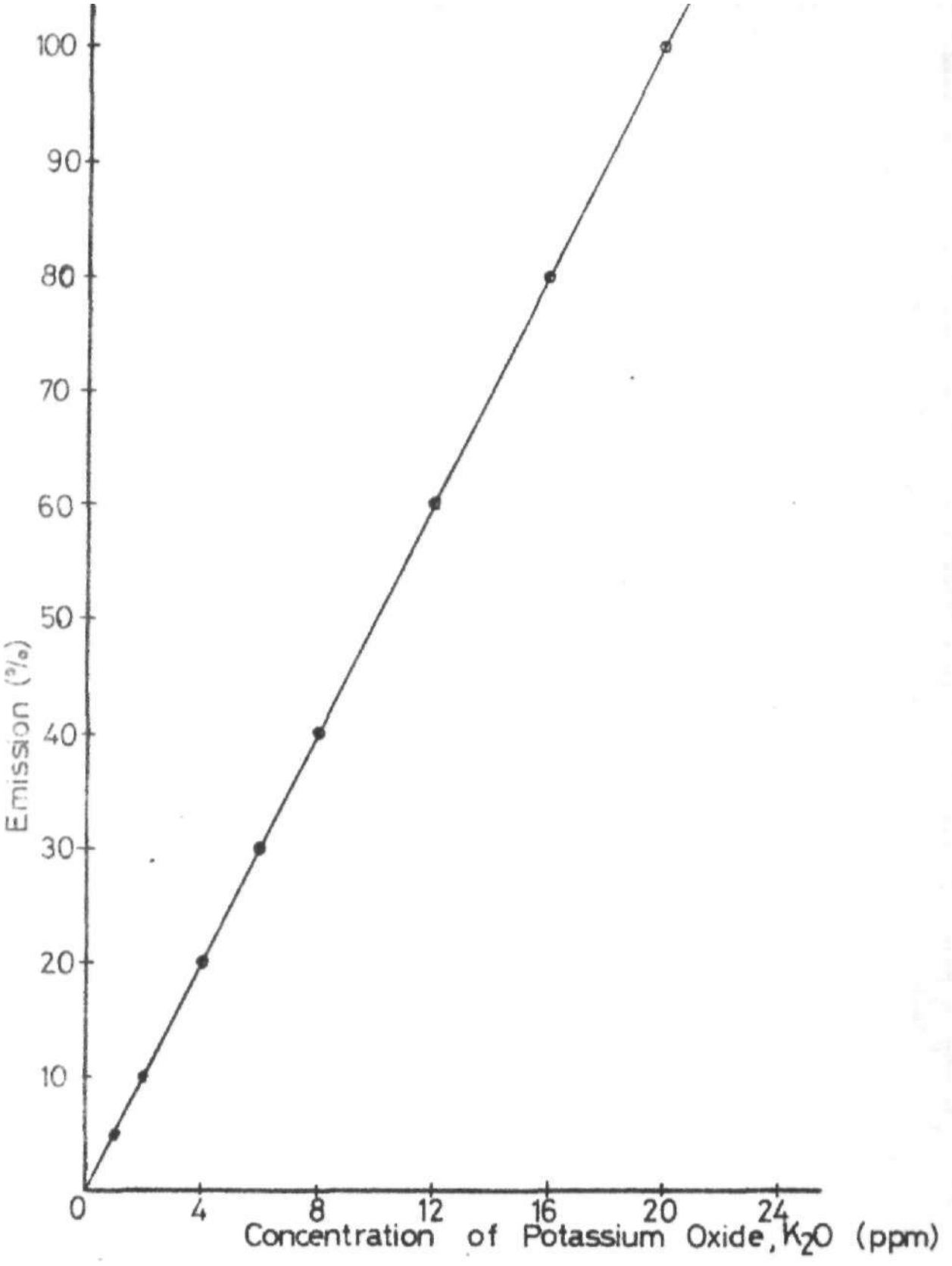


FIG. 7 CALIBRATION CURVE FOR DETERMINATION OF POTASSIUM OXIDE

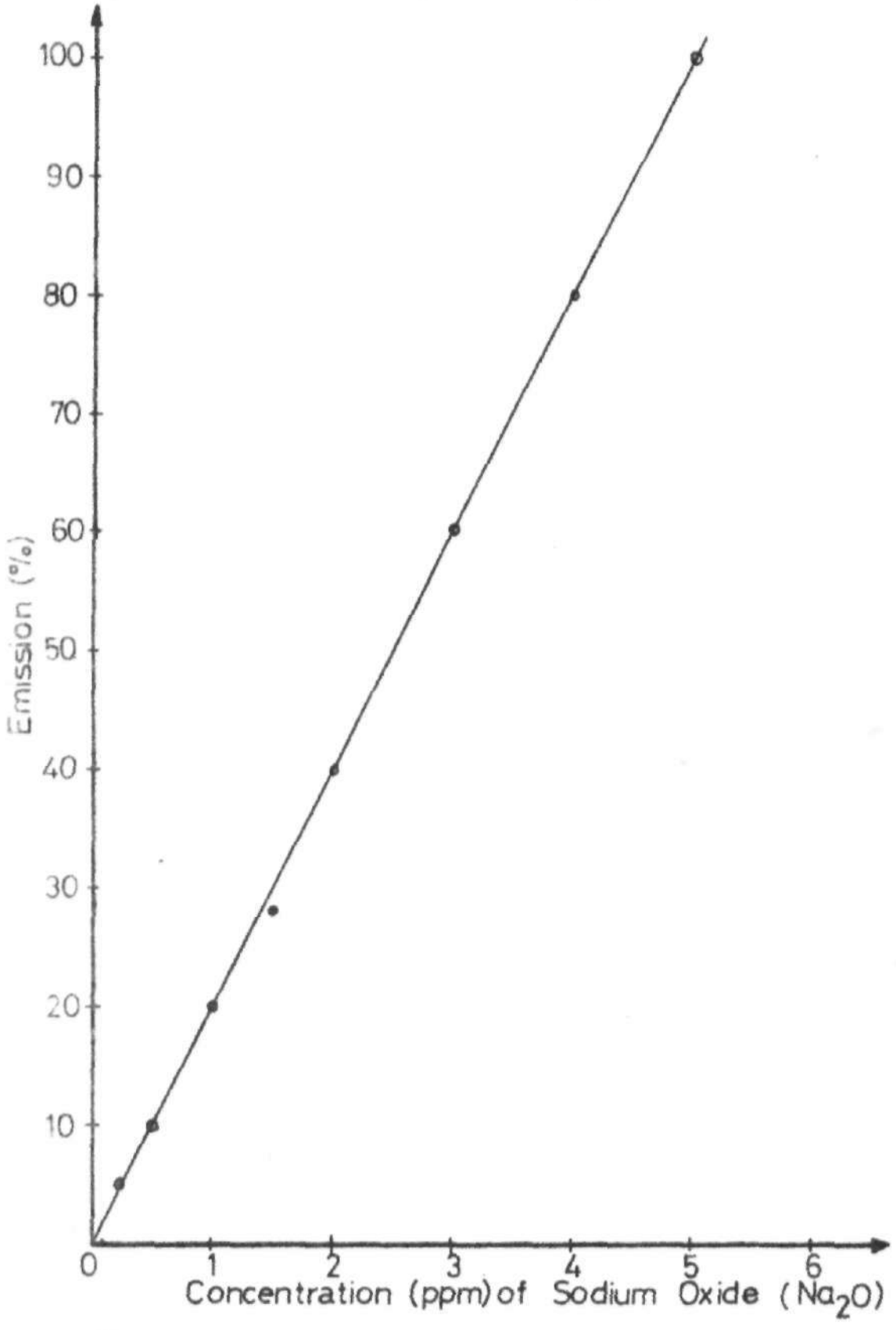


FIG. 8 CALIBRATION CURVE FOR DETERMINATION OF SODIUM OXIDE

CHAPTER III

ANALYSIS OF CEMENT

The analysis of the cement samples included the determination of loss on ignition, insoluble residue, SO_3, Al_2O_3, Fe_2O_3 CaO, MgO, Na_2O, K_2O, Li_2O, P_2O_5 and Mn_2O_3.

The various brands of cement studied, comprising mostly of those imported from different producing countries in the world, are given in Section 3-1 below.

3-1 Collection Of Samples

The cement samples were collected on building sites on and around the Ahmadu Bello University Campus, mostly from the Senate Building. The samples were taken from freshly opened bags of cements, put in polythene bags and tightly notched. All relevant information regarding the brand and producer were noted. The samples collected were:-

(i) CEMENTO PIRINED: Portland Cement, Made in Spain.

(ii) TITAN: Hellenic Portland Cement, Titan Cement Co., strength equivalent, BS12/58-71, Made in Greece.

(iii) POLCEM: Poland Cement, Polcem Brands, BS:12:1958, Made in Poland.

(iv) FOUR FLAG: Hellenic Portland Cement, Strength Requirement according to BS:12/71, BS:12/1958. Heracles General Cement, Athens, Greece.

(v) JAGUAR: Gran Canaria, Cementos Especiales, S.A. Arguinegun, Equivante en resistance at BSS 12/1958 Puz-1-350, Made in Italy.

(vi) ZEMON: Zekom Portland Cement, Pz 450, veb Zemon Kombinat, Gute Uberwacht, Nach DIN 1164 ASMW DAR, Made in Germany.

(vii) CCIPANHI.. DE CIMENTO: Secil Sore, Portland Normal, [illegible]

(viii) ZEMON: Veb Zement werke Ruders Dorf Betriebsteil 4, Zemon Pz 45, Made in Germany.

(ix) UNICEM 325: Cemento Pozzolanico, Stabilimento di Guildoma Physically, Sacchificio Turderasda Varesi, Equivante al BSS/12/1958 Made in Italy.

(x) ALBA CEMENT: Export Cement, Cemento, Made in Italy.

(xi) BURHAM: Portland Cement, Burham Cement Co. Ltd., London, Packed in Nigeria for Nigerian National Supply Co., NNSC.

(xii) ELEPHANT: Portland Cement, Made in Nigeria

(xiii) SIMENTIR: Cement, Esportazione, Made in Italy.

EXPERIMENTAL

Apparatus

Platinum Crucible: 20 and 30-cm^3 capacity

Muffle furnace: Carbolyte, temperature range 0-1200°C

Spectrophotometer: Pye Unican SP6-200 with 10mm and 40mm cuvettes

Reagents

All reagents used were of analytical grade unless stated otherwise.

Hydrochloric acid (d = 1.18)

Hydrochloric acid (5% $^{v}/_{v}$)

Sodium hydroxide solution (10% $^{w}/_{v}$)

Ammonium chloride solution (20g/dm^3)

Methyl red indicator:

1g of the free acid dissolved in 1dm^3 of hot water.

Barium chloride solution (100g/dm^3)

Polyethylene oxide solution (2.5g/dm^3)

Sulphuric acid (50% $^{v}/_{v}$)

Sodium carbonate

Boric acid

3-2 Preparation Of Cement Samples

Since all the cement samples collected were in the finely pulverized state, no grinding was necessary. No pre-treatment was performed on the samples before analysis. These samples were therefore analysed as collected.

Samples decomposition was by the acid decomposition method using hydrochloric acid as given in Section

3-3 Analytical Studies Of Cement Samples

The analytical studies carried out on the cement samples were the determinations of loss on ignition, insoluble residue, SO_3, Al_2O_3, Fe_2O_3, CaO, MgO, Na_2O, K_2O, Li_2O, P_2O_5 and Mn_2O_3.

The analytical techniques employed in these determinations are outlined in the appropriate sections below.

3-3.1 Determination of Loss on Ignition

The loss[97] in weight on ignition of cement at 1000°C is primary due to loss of water and carbon dioxide. However, oxidizable matter may also give rise to loss (organic matter) or gain (sulphide sulphur), and the loss may also be affected by other components[98] present in the sample.

Procedure[99]

1.000g of the dry cement sample was weighed in a constant weight platinum crucible. The latter was almost completely covered with the lid and ignited in a muffle furnace at 1000 $\pm$ 20°C for 30min. The crucible was then removed from the furnace, completely covered with the lid, cooled in a desiccator and reweighed. The percentage loss on ignition was calculated thus:-

Weight of platinum crucible + cement = x

Weight of platinum crucible + residue = y

Loss on ignition ... ... = x-y

∴ Loss on ignition ... = (x-y) x 100

The results are given in table IV-2.

3.3 Determination of Insoluble Residue

The insoluble residue[100] in cement comes about generally from clay and slag which are used in the manufacture of cement as already discussed (Chapter I).

Procedure[99,101]

1.000g of the cement sample was accurately weighed and transferred to a 250-cm^3 beaker and covered with a clock glass. About 25cm^3 of water were added through the lip of

beaker and the cement dispersed in the water. While swirling, $5cm^3$ of hydrochloric acid (d = 1.18) were added. The mixture was gently warmed over a hot plate, breaking any lumps with the flattened end of a glass rod until the decomposition was complete as indicated by ceasation of effervescence.

The solution was diluted to $50cm^3$ with water, heated quickly to boiling and then, with the cover still on, digested over the steam bath for 15min.

The solution was filtered using a Whatman No. 41 filter paper, rinsing the beaker and the residue thoroughly with hot water. The filtrate was reserved for the determination of sulphur trioxide.

The filter paper with its contents was transferred to the origional beaker and digested just below the boiling point with $100cm^3$ of sodium hydroxide solution (10% $^{w}/_{v}$) for 15min, stirring the mixture occasionally to macerate the filter paper.

The solution was acidified with hydrochloric acid (d = 1.18) using methyl red as indicator and adding 4-5 drops of the acid in excess. The solution was filtered and the filter paper and residue washed 14 times with hot ammonium chloride solution ($20g/dm^3$). The filter paper with its contents was then ignited in a constant weight crucible at $1000^{o}C$ for 30min, cooled in a desiccator and weighed.

A blank determination, following the same procedure and using the same amounts of reagents, was performed and the results obtained in the analysis corrected accordingly.

3-3.3 Determination of Sulphur Trioxide

Sulphur trioxide is determined by turbidimetric[102], conductometric[103], and gravimetric[104] methods. The classical gravimetric method was used in this work.

Procedure[104]

The filtrate from the determination of insoluble residue was diluted to about 250cm^3 in a 500-cm^3 beaker with distilled water. The solution was heated to near boiling and 10cm^3 of hot barium chloride solution (100g/dm^3) added slowly and dropwisely from a pipette. The solution was digested near the boiling point for 12hr. maintaining the volume of the solution between 225 and 260cm^3.

The precipitate was filtered and washed thoroughly with hot water. The filter paper containing the precipitate was transferred to a constant weight crucible, charred, and then ignited at 900^{o}C in a muffle furnace.

After cooling in a desiccator it was weighed as barium sulphate, $BaSO_4$.

A reagent blank determination was performed following the same procedure and using the same amounts of reagents.

The results of the analysis was then corrected accordingly.

The percentage of sulphur trioxide was calculated using the formula:-

$$SO_3(\%) = 34.30W$$

where 34.30 = gravimetric factor (0.3430) multiplied by 100

W = Weight (g) of $BaSO_4$

The results are given in Table IV-2.

3-3.4 Determination of SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, TiO_2, P_2O_5 and Mn_2O_3

These oxides were determined on aliquots of the stock solution prepared by hydrochloric acid decomposition of the cement samples using the various analytical procedures given the appropriate sections below.

A. Decomposition of the cement samples

Procedure

1.000g of the dried (105-110°C) sample was transferred to a 250-cm^3 beaker. 10cm^3 of water and 25cm^3 of hydrochloric acid (d = 1.18) were added. The

beaker was covered with a clockglass and boiled over a low temperature hot plate for 30 min.

3. Determination of main silica

The main silica was determined gravimetrically.

Procedure

The beaker and contents from the decomposition of sample were allowed to cool and the clockglass rinsed with water into the solution. A Whatman accelerator tablet was added and the solution stirred to break the pulp. 5cm^3 of polyethylene oxide solution (2.5g/dm^3) were added with stirring and allowed to stand for 5min.

The precipitate was filtered using a Whatman No. 541 filter paper, transferring the precipitated silica with hot dilute hydrochloric acid (5% $^{v}/_{v}$) and scrubbing the beaker with a rubber-tipped glass rod. The precipitate was washed 6 times with hot dilute hydrochloric acid and then with hot water until free from chlorides. The filtrate and washings were reserved.

The filter paper containing the precipitate was transferred to a constant weight platinum crucible, charred over the gas flame to remove carbonaceous matter and finally

ignited in a muffle furnace at 1200°C for 20min, cooled in a desiccator and weighed.

The residue was moistened with water, 5 drops of diluted sulphuric acid (50% $^{v}/_{v}$) and 10cm^3 of hydrofluoric acid (40% $^{w}/_{w}$), and the solution evaporated to dryness over a low temperature hot plate in a fume cupboard. The crucible with residue was heated cautiously at first over the gas flame, and finally ignited for 5min at 1200°C, cooled and weighed.

Where the residue weighed more than 30mg the sulphuric acid/hydrofluoric acid treatment was repeated.

The difference between the two weights represented the main or "gravimetric silica".

C. Preparation of solution for determination of residual silica, Al_2O_3, Fe_2O_3, CaO, MgO, TiO_2, P_2O_5, and Mn_2O_3

Procedure

The residue from the hydrofluoric acid treatment of the "gravimetric silica" was fused with 2g of sodium carbonate and 0.4g of boric acid. The melt was dissolved in the main filtrate the determination of the "gravimetric silica", cooled and diluted to 500cm^3 in a volumetric flask to give the stock solution the aliquots of which were used for the determination of the above mentioned oxides.

D. Determination of residual silica

The amount of soluble or residual silica present in the stock solution was determined spectrophtometrically as described before, Section 2-3.5.

E. Calculation of total silica content

The values for the gravimetric and residual silica respectively were summed up to obtain the total silica content of the sample.

The results are given in Table IV-2.

F. Determination of Al_2O_3, Fe_2O_3, CaO, MgO, TiO_2, and P_2O_5

The procedures employed for the determinations of these oxides were exactly the same as those described in Chapter II. The results are given in Table IV-2.

G. Determination of magnanic oxide, Mn_2O_3

The same procedure as used for the determination of MnO_2 in Chapter II (Section 2-3.10) was used. The values of MnO_2 obtained, were multiplied by 1.113 to obtain Mn_2O_3.

The results are given in Table IV-2.

3-3.5 Determination of Alkali Oxides

Because the solution used for the determinations outlined hitherto was prepared by fusing the residue from the hydrofluoric acid treatment with sodium carbonate this solution could not be used for alkali determination particularly Na_2O. A fresh portion of the cement sample was therefore decomposed using hydrochloric acid for the determination of the alkali oxides.

A. Decomposition of Cement Samples for determination of Akali Oxides (Li_2O K_2O, Na_2O)

Procedure

0.1000g of the cement sample was weighed and transferred to a 250-cm^3 beaker and dispersed with 10cm^3 of water and 5cm^3 of hydrochloric acid (d = 1.18) added with swirling. Any lumps of cement remaining was broken up with the flattened end of the glass rod. The solution was digested over the steam bath for 15min and filtered using Whatman No.41 filter paper into a 100-cm^3 volumetric flask, washing the beaker thoroughly with water. After cooling to room temperature the solution was diluted to 100cm^3 and mixed thoroughly. This solution was used, for the determination of the alkali oxides.

B. Flame Photometric determination of Alkali Oxides

This was performed as described in Chapter II, Section 2-3.12B.

The results are given in Table IV-2.

CHAPTER IV

RESULTS AND DISCUSSION

In this chapter the results of the analyses of the Building Materials are presented. Table IV-1 summarizes the analytical data on the soil, clay, limestone and marble samples, while Table IV-2 is a compilation of the analytical results obtained on the cement analysis.

Based on the analytical data, the cement samples are classified, where possible, according to the American Society for Testing and Materials Specification (ASTM); comparison between the Nigerian made cement and the imported cement is made and the analytical data on the cement samples compared with those on the local Building Material, soil. Finally, conclusions and suggestions for further work are made.

Results of the analyses and their discussion follow below.

4-1 Results

All the analytical results are shown in Tables IV-1, IV-2 below.

4-2 Discussion Of Results Of Analysis, Of Soils, Clays, Limestones And Marble

The results of the analyses of these materials are as shown in Table IV-1. The analytical results for each of these materials are considered hereunder.

TABLE IV-1 CONTD

MgO	CaO	Na_2O	K_2O	LOI	TiO_2	P_2O_5	MnO_2	Li_2O
0.10	0	0.21	0.32	4.17	0.73	0.70	0.02	0.12
0.10	0	0.18	0.28	5.23	0.95	0.50	0.03	0.12
0.22	0	0.50	2.64	4.25	0.83	0.34	0.04	0.56
0.20	0	0.42	3.20	4.25	0.85	0.29	0.07	0.56
0.22	0	0.23	2.40	4.59	0.50	0.31	0.02	0.54
0.10	0	0.25	0.40	3.55	0.26	0.20	0.02	0.12
0.82	0	0.46	1.63	5.45	0.70	0.41	0.06	0.36
0.1	0	3.30	0.16	11.75	1.93	0.23	0.03	0.12
0.1	0	2.20	0.14	13.37	1.05	0.21	0.03	0.12
0	0.57	0.48	0.72	4.86	0.60	0.21	0.04	0.20
0	0	0.26	1.28	10.26	1.56	0.53	0.05	0.20
0	0	0.10	0.16	13.88	0.60	0.16	0.03	0.12
2.00	48.60	0.06	0.20	42.76	0.08	1.10	0.18	0.12
0.84	48.34	0.02	0.28	38.91	0.10	4.20	0.16	0.12
1.79	49.76	0.92	0.24	42.20	0.15	1.95	0.15	0.16
1.00	47.21	0.30	0.32	40.18	0.18	0.23	0.22	0.20
6.37	17.67	0.76	0.48	24.47	0.50	2.95	0.46	0.14
3.27	44.90	0.61	0.30	42.46	0.09	1.10	0.10	0.12
10.56	30.51	0.38	0.20	41.18	0.10	1.70	0.30	0.36
0.80	53.96	0.42	0.09	43.51	0.08	0.38	0.30	0.16

TABLE IV-2 CONTD

SO_3	LOI	Na_2O	K_2O	Li_2O	TiO_2	P_2O_5	Mn_2O_3	IR
3.09	3.34	0.19	0.80	0.20	0.36	0.59	0.06	3.34
3.83	3.03	0.24	0.56	0.16	0.32	0.08	0.13	1.32
3.37	1.36	0.12	0.68	0.27	0.28	0.56	0.24	0.93
3.70	4.15	0.20	0.74	0.20	0.28	0.84	0.11	3.27
3.37	3.85	0.20	0.68	0.18	0.34	0.67	0.58	3.93
3.24	1.40	0.15	1.14	0.22	0.34	0.36	0.16	1.56
3.19	3.53	0.21	0.76	0.12	0.30	0.58	0.11	3.78
3.35	1.40	0.20	1.14	0.14	0.37	0.36	0.11	1.21
1.60	4.71	2.04	2.88	0.16	0.56	1.68	0.29	19.83
3.33	1.55	0.21	0.82	0.21	0.32	0.56	0.06	3.13
3.07	1.65	0.16	0.36	0.12	0.34	1.04	0.16	0.45
0.91	1.65	0.12	0.26	0.18	0.28	1.68	0.13	0.38
3.59	3.38	0.15	0.76	0.20	0.32	0.45	0.04	1.63

4.2.1 Soils

From the data on the soils, silica, SiO_2, appears to be the predominant component of the soil. The value obtained ranged from 64.40 to 83.42%. It is followed by alumina, Al_2O_3, whose value ranges from 4.6 to 9.21%.

The amount of the iron oxide is also fairly high, 1.65 - 6.00%, and may be responsible for the reddish/brown colour of some of these soils (Birinin Kebbi Falling Wall, Samaru Falling Wall and Zaria City Wall).

The fairly high concentration of alkali oxides in the Samaru Mud-brick (3.78%), Samaru Falling Wall (4.18%) and Zaria City Wall (3.17%) may be due to the fact that these soils, were, as it is usually done, mixed with hay, ashes, and animal droppings.

The lime content of these soil samples is practically zero. This is due to the fact that calcium[105] which exist in soils as $CaCO_3$ and $CaSO_4$ is easily washed away by rain water.

The other oxides, MgO, TiO_2, P_2O_5 and MnO_2 occur in relatively low concentrations, the respective concentrations for these oxides being less than 1% in all the samples.

These analytical results are in fair agreement with those obtained on some soils by Akanya[106]. The silica content however, appears to be much higher than the average

value obtained by this author (45.86%). This may be due to the fact that the soil used for making the mud-brick is usually the loomy soil which consists mostly of sand whereas this author obtained his samples at some depth in the ground.

4-2.5 Clays

The predominant component here again is silica with the value ranging from 44.88 to 78.83. It is followed by alumina, Al_2O_3, with which it is usually combined forming aluminosilicates. The concentration of alumina ranges from 0.13 to 30.73%. The concentration of iron oxide, Fe_2O_3, ranges from 0.65 to 6.60%. Apart from these oxides, the concentration of other oxides remain generally low.

Apart from the Ogbakiri Clay, other clay samples show zero lime content. The occurence of lime in the Ogbakiri Clay sample may be due to its riverine location.

Titania, TiO_2, shows a wide range in its concentration, 0.08 - 1.93%. The alkali oxides occur in concentrations ranging from 0.12 to 0.92%. Na_2O appears generally in higher concentrations than Li_2O and K_2O. Li_2O has a fairly constant concentration (0.12%) in all the samples.

Phosphorous pentoxide, P_2O_5, occurs in values ranging from 0.21 to 0.53%. The amount of MnO_2 is generally very low in all the samples (0.03 - 0.06%).

The loss on ignition, which is due to loss of water, sulphur trioxide and carbon dioxide, has a range of value from 4.86 to 13.88.

The analytical data obtained for the clay samples analysed compare quite favourably with the specimen analysis quoted by Grimshaw[10.7], Mitchel et al[10.8] and Worall[10.9], Appendix A.

8.3 Limestones and Marble

The major components of limestones and marble is lime, CaO, with a range of concentration from 30.51 to 53.96%. The concentration of silica is generally low except for one sample (GL 62596) which has a high silica content (34.28%).

Alumina, Al_2O_3, iron oxide, Fe_2O_3, and magnesia, MgO, occur in low concentrations generally. The sample GL 62598, however, has fairly high iron oxide (9.10%) and magnesia (10.56%) contents.

The concentrations of other oxides - titania, alkali oxides, manganese oxide and phosphorous pentoxide are generally very low.

The value for loss on ignition is quite high. The loss in weight of limestones and marble on being ignited at 1000°C is due to the loss of water, and, in main carbon dioxide.

These results are compared with those of Bennett and Reed[110], Appendix B.

4-3 Discussion Of Results Of Cement Analysis

In cement chemistry, it is conventional to use shortened notations instead of the chemical notations. When first appearing, the compounds are shown in the ordinary chemical notations, but subsequently the shortened notation is used. Some of the shortened formulae which will be encountered in this discussion include the following:-

$A = Al_2O_3$

$C = CaC$

$F = Fe_2O_3$

$S = SiO_2$

$C_3S = 3CaO.SiO_2$

$C_2S = 2CaO.SiO_2$

$C_3A = 3CaO.Al_2O_3$

C_5A_3 = $5CaO.3Al_2O_3$

$C_{12}A_7$ = $12CaO.7Al_2O_3$

C_4AF = $4CaO.Al_2O_3.Fe_2O_3$

$KC_{23}S_{12}$ = $K_2O.23CaO.2SiO_2$

NC_8A_3 = $Na_2O.8CaO.3Al_2O_3$

The analytical data on the cement samples are presented in Table IV-2. These data are considered below.

The main oxides of the cement samples analysed is the lime, the value of which ranges from 39.96 to 64.45%. Lime is an essential component of all cements, being derived from the decomposition of calcium carbonate, $CaCO_3$ mainly, and sometimes being added in the form of gypsum to control the setting of cement. The $CaCO_3$ is fed in the kiln in the form of the raw materials, namely the calcareous materials - limestone, cement rock, chalk, marl marine shells and alkali waste.

Lime occurs in cement combined with three other principal constituents of cement - silica, alumina, and iron - to form four principal compounds[22]:-

(i) tricalcium silicate, $3CaO.SiO_2$

(ii) tricalcium aluminate, $3CaO.Al_2O_3$

(iii) dicalcium silicate, $2CaO.SiO_2$

(iv) tetracalcium aluminoferrite, $4CaO.Al_2O_3.Fe_2O_3$

These compounds are responsible for the properties of cements such as setting rate, early strength, resistance to chemical attack etc. Theoretically the difference[22] in strength from one stock to another stock of cement can be attributed to the difference in the proportion of C_3S and C_2S present in the cement, which compounds are mainly responsible for the development of the strength. C_3A controls the setting time while C_4AF increases resistance to sulphate attach. Other lime compounds include calcium aluminate, CA, C_5A which are very important in high alumina cements.

Silica, SiO_2, the next principal component of cement, which is usually present in the state of combination, is derived from argillaceous (clayey) materials - clay, shale, slate, blast-furnace slag, ashes, cement rock - of the raw mix. As stated above, it combines with lime to form calcium silicates which are responsible for the strength of the cement. In the present work the silica cement, as shown in Table IV-2, ranges from 19.55 to 28.0%.

The third major component, alumina, Al_2O_3, has value of 3.24 - 7.30%. It also occurs combined with silica in clays. Alumina is present in Portland cement principally as C_3A. It makes little contribution to the hardening of Portland cement. Its main use in cement manufacture is that it acts as a flux,

reducing the clinkering temperature. Cements of high C_3A content have lowered resistance to sea-water.

The last principal component is iron oxide, Fe_2O_3, whose concentration varies from 1.93 to 4.95%. Iron is derived mainly from clay or shale but as seen from the analysis of limestones, some iron is also introduced into the cement clinker by use of limestone. Iron is an important component of high-alumina cement where it is derived from bauxite.

Apart from these major components, minor components in commercial raw materials also enter, to a limited extent, into solid solutions in the major compounds, or form modified compounds. These minor components include MgO, SO_3, TiO_2, P_2O_5, Mn_2O_3 and the alkali oxides. The presence of these minor components affects both the compound composition and properties of the cement.

Magnesia, MgO, is derived from limestone in the form of dolomite, $CaCO_3.MgCO_3$, or to a small extent from clay or shale. It associates with all other components of the clinker as well as occuring in free state in Portland Cement. Its presence in cement clinker leads to long-term unsoundness of resultant cement because of expansion which accompanies slow hydration. It has some value as a flux. In the cement samples analysed its content ranges from 1.25 to 5.68%.

The sulphur trioxide content ranges from 0.91 to 3.35%. Sulphur compounds are present in clay or shale in small proportion in form of pyrites, sulphates or more rarely, in the form of organo-sulphur compounds. Sulphur may also be introduced into the cement clinker by the fuel used.

The sulphur compounds are oxidized to sulphur trioxide, SO_3, which is absorbed by raw mix. At higher temperature down the kiln, $CaSO_4$ decomposes. Considerable proportion of the sulphur is finally lost in the form of fuel dust.

The amount of sulphur trioxide present in cement is of considerable importance to the compound composition as well as physical and chemical properties of the cement. It reacts with alkali oxides, Na_2O and K_2O, to form alkali sulphate. This reaction reduces the amounts of Na_2O and K_2O available to form $KC_{23}S_{12}$ or NC_8A_8 so that the effect on the potential compound composition[112] of the cement clinker is similar to that produced by lowering the alkali content of the clinker. The influence of SO_3 content of Portland cement on the creep and other physical properties of concrete has been investigated by Alexander *et al*[113]. These authors found that the creep of concrete is very sensitive to the SO_3 content of cement; the creep doubles when SO_3 content is reduced from 3.7 to 1.6%

The cement samples analysed generally have SO_3 content less than the limit of 3.0% specified by ASTM.

Titania, TiO_2, occurs in small extent in all the cement samples analysed, the concentration ranging from 0.27 to 0.56%. It is derived from clay or shale. It is more important in high-alumina cement where it is derived from bauxite.

Phosphorous pentoxide, P_2O_5, is found to be present in cement and is introduced into it by the raw materials used for the manufacture of cement. P_2O_5, when present, decomposes C_3S in favour of C_2S solid solution containing P_2O_5 and excess CaO. This remarked reduction in the C_3S by P_2O_5 explains the pronounced effect of P_2O_5 in depressing the rate of hardening and early strength[114-116] of cements. Further, if large amounts of P_2O_5 are present, free lime[117] is formed.

The percentage content of P_2O_5 found in the present work ranges from 0.08 - 1.68%.

The manganic oxide, Mn_2O_3, is a constituent of all cement clinkers produced by burning raw mixes of blast furnace slag with limestone but is present only in very small amounts when clay or shale and limestones are used as raw materials. Mn_2O_3 imparts a brown colour to cement but otherwise appears as a substitute for Fe_2O_3 and to have little effect on the properties of cement. It is thought to be present in Portland cement in form of a solid solution[118], $4CaO.Al_2O_3.Mn_2O_3$. The

values obtained for Mn_2O_3 in this work range from 0.06 - 0.58%.

The last oxides determined in this work were the alkali oxides. The alkali oxides usually discussed in cement chemistry are potassium and sodium oxides. In this work, lithium oxide, Li_2O, was also determined. The concentration of K_2O is generally higher than the other alkali oxides. The concentration of Li_2O is the least. The total alkali concentration for the samples analysed is generally not much higher than 1% except for one sample whose total alkali concentration is 5.08%.

The alkali concentration has to be controlled due to the various deleterious effects it has on the cement clinker and the concrete. They may have significant effect on the potential compound composition[112] of the clinker: they may combine with the major component of the clinker to form new compounds in which the percentage of the alkali oxides is low such as $KC_{23}S_{12}$ and NC_8A_7. The reaction of alkali with sulphur trioxide has already been discussed.

Alkali have been found to cause deterioration of concrete due to alkali-aggregate[110,121] reaction. Premature breakdown of concrete, some expansion of concrete in overground building, bridge construction and hydraulic structures are all due to the alkali-silica reaction[122-124]. Finally, alkali[125] have also been found to affect the strength of Portland cement: addition of alkali decreases the compressive strength.

The loss[97] on ignition which is due to loss of water and carbon dioxide, has values ranging from 1.40 to 4.71%. Apart from three samples - Four Flag, Jaguar and Unicem 325 - the value for loss on ignition lies within the ASTM Specification limit for the Portland cements (3.0%).

Finally the insoluble residue[100] which is mainly due to the clay raw material ranges from 0.45 to 3.93%. For Portland cements the ASTM specification for the maximum insoluble residue content is 0.75%. Thus apart from the Durham and Elephant cement samples, all the other cements studied had insoluble residue content higher than the specified maximum limit.

The chemical requirements - maximum limits of the various components - as required by the ASTM specification are shown in Appenxi C.

The analytical data of other workers are also included in Appendices.

4.4 Classification Of Cement Samples

Of the various specification or classification schemes for cements already mentioned, the American Society for Testing and Materials (ASTM) Specification was chosen as it could readily be obtained from literature.

To classify or specify cements, approximate compound composition of the cement are calculated by use of equation[126,127] developed from equilibrium data. The analytical data and the calculated potential compound composition of each cement sample are then compared with those for various types of cement as given by the ASTM Specification to determine the type of cement.

A. Calculation of Potential Compound Composition

The potential compound composition of Portland cement was calculated from the chemical analysis using the following equations[127,126].

$\% C_3S = 4.07\ C - 7.60S - 6.72A - 1.43F - 2.85\ SO_3$

$\% C_2S = 2.87\ S - 0.754\ C_3S$

$\% C_3A = 2.65A - 1.69F$

$\% C_4AF = 3.04F$

The results are given in Table IV-3 below.

CEMENT SAMPLE	POTENTIAL COMPOUND COMPOSITION (%)			
	C_3S	C_2S	C_3A	C_4AF
Cemento Pirineo	33	37	2	15
Titan	55	15	11	7
Polcem	49	26	8	7
Four Flag	n.c.	nc.	9	10
Jaguar	22	46	11	9
Zoton	50	20	8	6
Compañia de Cimento	29	39	10	6
Lemon	29	35	7	6
Unicem 325	n.c	n.c	11	15
Alba	39	32	7	6
Durham	54	22	2	11
Elephant	63	11	6	10
Snowtir	42	29	9	9

n.c. = not calculatable using analytical results obtained.

D. Classification of the Cement Samples

The ASTM Specification C150 - 63 has classified Portland Cement into four types:-

Type I: Used in general concrete construction when no special properties are specified.

Type II: Used in general concrete construction exposed to moderate sulphate action, or where moderate heat of hydration is required.

Type III: Used when a high early strength is required.

Type IV: Used when a low heat of hydration is required.

The chemical composition of these cement types are shown in Appendices C - E.

By comparing the analytical results and the calculated potential compound composition of the cement samples analysed with those specified for different types of cement by the ASTM Specification, Appendices C-E, the cement type was determined. The resultant classification of the cement samples follow below, Table IV-4.

TABLE IV-4: Classification of the Cement Sample:

CEMENT SAMPLE	TYPE	COMMENTS
Cemento Pirinod	IV	Chemical composition roughly corresponds to Portland Type IV appendices C - F
Titan	III	Both chemical composition and calculated potential compound composition roughly corresponds to Portland Type III
Polcem	I	Chemical composition is quite similar to that given for Portland type I. Appendices C-E
Four Flag	-	Both the analytical results and the calculated potential compound composition do not show any similarity to available data.
Jaguar	IV	The chemical composition is fairly similar to Portland type IV. Appendices C - E.
Zolom	-	Chemical and calculated potential compound compositions do not show any similarity to the available data.

TABLE IV-4 CONTD

CEMENT SAMPLE	TYPE	COMMENTS
Companhia de Cimento	-	Cannot be classified using the ASTM data.
Unicom 325	Pozzolana	Chemical and calculated compound composition do not correspond to ASTM cement type but indicate that it is a Pozzolanic cement Appendix D.
Alba	IV	Chemical composition fairly similar to Portland type IV. Appendices C, E
Burham	I	Chemical and calculated potential compound compositions correspond fairly well with Portland type I Appendix
Elephant	I	Chemical composition fairly similar to Portland type I. Appendice C - E.
Snentir	II	Both chemical and calculated potential compound composition fall within the range of Portland type II appendices D, E.

Some of the cement samples could not be classified by the ASTM Specification. It is observed that the lime content of such cements was less than the minimum amount of lime specified for Portland cements, i.e. 60%, though the labels on the bags classified them as Portland cements. Further, the insoluble residue content of such cements samples was found to be much higher than the maximum limit specified by the ASTM Specification. Since the lime content is critical for the good quality of any cement, those cement samples whose lime content (and other chemical components) do not meet the required specifications should normally be rejected. However, according to the ASTM Specification [128], "cement shall not be rejected for failure to conform to a chemical requirement unless all determinations of the constituents involved and separations prior to determinations of any one constituent are made entirely by the prescribed referee methods". Almost all of these methods are classical gravimetric or titrimetric methods, most of which are tedious. Though the author limited the use of the classical methods to the determinations of loss on ignition, SiO_2, Al_2O_3, CaO and MgO, the results obtained by using the methods described in Chapter III, showed good reproducibility and the variations for duplicate analyses were all within the limits specified by this ASTM specification [128], Appendix G. Moreover, spectrophtometric methods are generally more accurate than the classical methods. Hence the

analytical procedures adapted in this work should be as good as, if not better than, the classical methods. Therefore, other things being equal, these cement samples failing to satisfy the chemical requirements should be rejected.

Since these cements are used in building and engineering construction works in Nigeria, the poor quality of some of these structures could be attributed to the chemical shortcomings of these cements - particularly lack of sufficient lime content.

4-5 Comparision Of Nigerian Cements And Imported Cements

The Nigerian made cement studied was the Elephant Portland cement. The Burham cement is only packed in Nigeria; it is produced by the Burham Cement Company of London.

These cements show satisfactory chemical requirements for good quality Portland cement as specified by the ASTM Specification. The present trend in the composition of Portland cements puts emphasis on the steady rise in the lime content while a fall in the silica content. This view is supported by the recent works of Bennett and Reed[129], Smith and Halliwell[130], and Giles and Poisack[131] whose results are shown in Appendix H. The Nigerian Cement has fairly high lime content and low contents of those minor components which usually have deleterious effects as already discussed. The Elephant Cement belongs to the Portland cement type I of the ASTM specification which is suitable for use in

general concrete construction. It compares well with other imported cements of the same type as is seen from its chemical composition (Table IV-2).

4-6 Comparision of Chemical Composition of Soils and Cements

Comparision of the analytical data on both soils and cement samples (Tables IV-1, IV-2) reveals some stricking differences in the chemical composition of these Building Materials. The soil samples have practically no lime whereas the cement samples have high lime content. The MgO content of soils is fairly constant (0.1 - 0.2%) whereas that of the cement samples varies from 2.02 to 5.59%. On the other hand the silica, SiO_2, alumina, Al_2O_3, and titania, TiO_2, contents in the soils are generally much higher than those in the cement samples. The amounts of other components are generally similar for both types of Building Materials.

Since lime is responsible for most of the cementing properties, its absence in the mud-brick used for constructing the mudhuts is responsible for the inability of these mud-huts to withstand such adverse conditions such as changes in temperature, heavy rains, chemical action, winds, stress, strain, etc. as against structures built with cement.

4-7 Conclusions

From the chemical analysis of soils, clays, limestones, marble and cements, the following conclusions can be made.

(i) The clays, limestones and marbles present in Nigeria could, by proper proportioning, be used for cement manufacture.

(ii) Some of the cements imported into the country have lime content less than 60%, the minimum requirement for Portland cement which is used for general construction work. The poor chemical quality of these cements may be responsible for the rapid deterioration of some building and engineering works constructed using these cements.

(iii) The few Nigerian made cements analysed have quality of good Portland cement Type I which is used for general concrete construction.

(iv) The lack of cementing qualities in mud-bricks and the consequent inability of the mud-huts to withstand adverse conditions such as rain, stress, strain, etc is due to the lack of lime in the soil. This suggests that mud-bricks, when used, should be supplemented with additional lime.

4-3 Recommendations For Further Work

Some aspects of analytical studies of these Building Materials deserve further work:

1. Some elements such as the halogens, chromium, cobalt, copper, lead, vanadium, zinc, and zirconium have not been determined. Recent investigations[132] indicate that some of these elements, though only present in trace quantities in cement, may have important effects out of proportion to their concentration. Thus fluorine[116,133] is able to increase the strength gain of cement remarkably while its maximum concentration is only about 1%. It would therefore be worthwhile determining the concentrations of these trace elements in cements.

2. Only a few samples of cements made in Nigeria have been studied. It would be worthwhile making a comprehensive analytical study of all the cement samples with the view of evolving a National Scheme for Specification of Cements made in Nigeria. Such work would include the study of the physical or engineering properties such as fineness, soundness, setting time, compressive strength, etc.

3. A broader survey of the country's clay and limestone deposits would provide raw materials for local cement factories. Furthermore, from the analysis of some clays, it is clear that some have very high silica content. Additional study

in this field would be invaluable in determining the potentiality of glass industries in the country.

4. Finally analytical study on these Building Materials using both the classical methods and the rapid instrumental methods - atomic absorption, spectrophotometry and flame photometry - would offer a comparision between the results obtained using these two methods.

APPENDICES

The chemical compositions of soils, clays, limestones, marble and cements obtained on the analysis of these samples have been presented in chapter IV. In this section the results obtained by other workers on a few similar samples as well as the chemical requirements of cements as specified by the American Society for Testing and Materials (ASTM) are presented in the appropriate appendices.

APPENDIX A

Composition Obtained on Analysis of Typical Clays (% by weight)

Oxide	Red-Brown Clay*	Grey Clay*	China Clay**	Brick-Making Clay***
SiO_2	43.72	45.64	46.29	63.2
Al_2O_3	23.82	25.77	38.38	18.2
Fe_2O_3	8.10	4.60	0.30	4.1
MgO	4.06	3.49	0.59	0.8
CaO	0.65	0.62	0.61	0.7
Na_2O	0.27	0.21	0.15	1.1
K_2O	3.72	4.36	0.51	3.3
LOI	7.22	7.63	13.59	6.4
TiO_2	1.47	1.72	0.02	0.7
P_2O_5	-	-	-	-
MnO_2	0	0	-	-
Li_2O	-	-	-	-

Sources:

* Mitchell *et al*[108]

** Worall[109]

*** Grimshaw[107]

APPENDIX B

Specimen Analysis of Limestones (% by weight)

Oxide	I	II
SiO_2	9.62	0.59
Al_2O_3	1.65	0.38
Fe_2O_3	1.44	0.12
MgO	0.98	0.20
CaO	47.44	54.75
Na_2O	0.12	0.03
K_2O	n.d.	n.d.
LOSS	37.87	43.45
TiO_2	0.18	0.01
P_2O_5	n.d.	n.d.
MnO_2	n.d.	n.d.
LiO_2	n.d.	n.d.

n.d. = not determined
Source: Bennett, & Reed[110]

APPENDIX C

Principal Chemical Requirements for Portland Cement, ASTM C 150-65

	Type I	Type II	Type III	Type IV	Type V
Silicon dioxide, %, min		21.0			
Aluminium oxide, %, max		6.0			a
Ferric oxide, %, max		6.0		6.5	a
Magnesium oxide, %, max	5.0	5.0	5.0	5.0	4.0
Sulfur trioxide, %, max when C_3A is 8% or less	2.5	2.5	3.0	2.3	2.3
when C_3A is more than 8%	3.0		4.0		
Loss on ignition, %, max	3.0	3.0	3.0	2.5	3.0
Insoluble residue, %, max	0.75	0.75	0.75	0.75	0.75
C_3S, %, max				35	
C_2S, %, min				40	
C_3A, %, max		8	15[b]	7	5

a. The C_3A shall not exceed 5%, and the C_4AF plus twice amount of C_3A shall not exceed 20%.

b. When moderate sulfate resistance is required for type III cement, C_3A may be limited to 8%.

When high sulfate resistance is required, the C_3A may be limited to 5%.

APPENDIX D

Typical Composition of Various Cements

CEMENT TYPE	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	LOSS	InsO
Portland Type I	21.3	6.3	2.7	63.2	2.9	1.8	1.3	0.2
Portland Type II	22.3	4.7	4.3	63.1	2.5	1.7	0.8	0.1
Portland Type III	20.4	5.9	3.1	64.3	2.0	2.3	1.2	0.2
Portland Type IV	24.3	4.3	4.1	62.3	1.8	1.9	0.9	0.2
Portland White	25.5	5.9	0.6	65.0	1.1	0.1	n.d.	n.d.
Natural	27.8	5.5	4.3	35.6	21.2	0.5	4.1	n.d.
Aluminous	5.3	39.8	14.6	33.5	1.3	0.1	-	4.8
Pozzolane	26.0	6.9	3.6	52.3	4.2	1.8	4.8	9.4
Trass 30/50	22.3	8.3	2.5	46.8	1.9	1.8	3.4	9.5
Trass 50/50	25.1	8.9	3.3	35.3	1.2	1.1	5.8	15.9
Gaize	26.5	7.0	3.0	43.0	1.0	1.0	2.0	16.5
Eisenportland	23.5	8.5	1.7	57.2	3.3	2.0	n.d.	n.d.
Hochofen	31.3	R_2O_3 =	13.5	47.2	2.2	0.7	n.d.	n.d.
Metallurgi de fer	26.0	8.0	3.0	58.0	2.5	1.0	1.5	n.d.
Metallurgic de Laitier	29.0	15.5	1.5	48.0	2.5	2.0	0.5	n.d.
Ferarrari	22.9	3.5	5.5	63.8	1.3	2.1	-	n.d.

n.d. = Not determined

Source: Bogue[134]

Composition of Some American Portland Cements (% by weight)

ASTM TYPE	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	TiO_2	C_3S	C_2S	C_3A	C_4AF
I	20.7	5.6	2.4	63.8	3.7	1.6	0.21	0.51	0.23	50	22	12	7
	22.1	4.7	3.0	63.1	2.5	1.7	0.06	1.30	0.21	42	32	8	9
	22.2	4.7	2.1	65.8	1.1	1.6	0.04	0.19	0.31	50	26	10	7
	21.1	6.7	2.5	62.8	1.7	1.8	0.95	0.51	0.39	33	36	14	8
II	20.8	4.8	4.8	61.4	3.1	1.8	0.06	1.30	0.21	44	29	5	15
	24.0	4.0	2.1	64.9	1.9	1.7	0.23	0.55	0.23	41	38	7	6
III	20.0	5.2	2.5	65.6	1.4	2.3	0.21	0.44	0.27	60	13	10	8
	20.3	5.1	2.0	63.6	4.3	2.5	0.19	0.28	0.21	52	19	10	6
IV	22.9	4.6	5.0	59.6	3.0	1.3	0.06	1.19	0.23	20	51	5	15
	25.2	3.7	3.1	63.6	1.1	1.9	0.33	0.01	0.19	29	52	5	9
V	24.4	3.1	3.3	64.3	1.7	1.4	0.08	0.22	0.19	41	39	4	10
	26.1	1.9	1.3	64.2	2.5	2.0	0.10	0.15	0.12	36	48	3	4

Source: Lea, & Desch[135]

APPENDIX F

Average Potential Compound Composition of Type Cements(% by weights)

ASTM Type	C_3S	C_2S	C_3A	C_4AF
Type I	45	27	11	8
Type II	44	31	5	13
Type III	53	19	11	9
Type IV	28	49	4	12
Type V	38	43	4	9

Source: Bogue[134]

APPENDIX G

Maximum Permissible Variations in Results of Cement Analysis: ASTM (C114-58)

COMPONENT	BETWEEN TWO RESULTS	BETWEEN THE EXTREME VALUES IN THREE RESULTS
Silicon dioxide, SiO_2	0.16	0.24
Aluminium Oxide, Al_2O_3	0.20	0.30
Ferric Oxide, Fe_2O_3	0.10	0.15
Calcium Oxide, CaO	0.20	0.30
Magnesium Oxide, MgO	0.16	0.24
Sulphur Trioxide, SO_3	0.10	0.15
Loss on ignition	0.10	0.15
Sodium Oxide, Na_2O	0.03	0.05
Potassium Oxide, K_2O	0.03	0.05
Water-Soluble Alkali	0.05	0.08
Phosphorous pentoxide, P_2O_5	0.03	0.05
Magnic Oxide, Mn_2O_3	0.03	0.05
Insoluble residue	0.10	0.15

APPENDIX H

Recent Analysis of Some Cement Samples (% by weight)

OXIDE	I *	OPC M798**	OPC M236**	OPC M240**	ENG ***	Tvl $_{***}^{1}$	Tvl $_{***}^{2}$
SiO_2	20.46	20.96	19.32	23.40	20.8	24.0	24.1
Al_2O_3	4.79	5.80	6.17	3.59	6.2	4.0	3.7
Fe_2O_3	3.25	2.40	3.54	1.46	2.3	2.4	2.4
CaO	64.86	64.04	62.78	65.80	67.2	66.4	67.0
MgO	1.51	1.24	2.36	0.77	0.9	2.2	1.7
SO_3	2.47	2.52	2.91	2.32	1.3	n.d	n.d
LOI	1.33	1.71	1.48	1.67	n.d	n.d	n.d
Na_2O	0.56	0.25	0.10	0.09	0.2	n.d	n.d
K_2O	n.d	0.01	0.71	0.62	0.7	n.d	n.d
LiO_2	0.05	n.d	n.d	n.d	n.d	n.d	n.d
TiO_2	0.39	0.42	0.35	0.30	n.d	n.d	n.d
P_2O_5	n.d	0.20	0.07	n.d	n.d	n.d	n.d
Mn_2O_3	1.00	0.07	0.11	0.08	n.d	n.d	n.d
PCC							
C_3S		48.8	45.1	49.2			
C_2S		23.5	21.6	30.2			
C_3A		11.3	10.4	7.0			
C_4AF		7.3	10.8	4.4			

LOI = Loss on ignition, n.d = not determined
PCC = Potential Compound Composition
Sources: *Bennett[129] **Smith, M.A., and Halliwell [130]
***Gilles, I.S., and Peisach [131]

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