ANALYTICAL STUDIES

OF

IRON ORE AND PHOSPHATE ROCKS

A Thesis Presented to the

AHMADU BELLO UNIVERSITY

IN PARTIAL FULFILMENT FOR THE DEGREE OF

MASTER OF SCIENCE

IN ANALYTICAL CHEMISTRY

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October 1980

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For Turai, Maryama and Zainab.

A C K N O W L E D G E M E N T S

I can find no words to fully express my appreciation and gratitude to my supervisor, Dr. K. Singh without whose advise, guidance and encouragement, this work could not have been possible. I'm also grateful to professor U. D. Gomwalk, the Head of Department of Chemistry for providing the necessary facilities to carry out this work.

I thank the Director, Nigerian Institute of Geological Survey, Kaduna for providing me with the indigenous phosphate rock sample from Sokoto state, and the General Manager of the Federal Super Phosphate Fertilizer Company, Limited, Kaduna for providing me with the phosphate rock samples from Togo, Senegal (Thiers) and Niger Republic.

Finally, I'm grateful to my brother and friend, Mal. Abu Aminu Yar'adua for making me to realise what post-graduate research work is all about.

A B S T R A C T

The analytical study of iron ore sample of the Agbaja plateau in Kwara state and phosphate rock samples from Togo, Senegal, Niger Republic and an indigenous rock from Sokoto state was carried out with a view to evaluating the grade of the iron ore sample for the manufacture of steel, and the suitability of the phosphate rock samples for the manufacture of phosphatic fertilizers, with particular reference to the wet process phosphoric acid production.

The analysis of the iron ore sample included the estimation of SiO_2, Fe_2O_3, AL_20_3, P_2O_5 and S. The estimation was carried out in two parts: a systematic gravimetric and photometric determination involving the use of ion-exchange separations, and individual determinations of other elements by specific methods on separate portions of the sample.

In the systematic portion of the analysis, $Si0_2$, Fe_2O_3 and Al_2O_3 were estimated in one and the same portion of the sample. The sample solution was prepared by fusion with Na_2O_2. The melt was taken up rith HC1 and the silica determined by the double dehydration method. The filtrate from the separation and determination of silica was subjected to anion exchange

separation. Two fractions wore /collected for iron and aluminium: the total iron in the sample was determined gravimetrically by precipitation with ammonia and alumina was estimated colorimetrically by measuring the colour of the oxinate in chloroform.

In the non-systematic portion of the analysis, P_3O_5 and S were estimated on separate portions of the sample. For the estimation of P_2O_5, the iron ore sample was decomposed by digestion with HNO_3 and HF, and then fusing the insoluble residue with Na_2CO_3,. The P_2O_5 was then determined colorimetrically by the molybdovanadophosphoric acid method. In the determination of sulphur, the sample solution was prepared by fusion of the sample with a mixture of Na_2CO_3, and Na_2O_2 and the sulphur precipitated and weighed as $BaSO_4$.

The results obtained reveal that the ore is rich in iron (72% Fe_2O_3 , with tolerable amounts of silica (6.32% SiO_2) , P_2O_5 (2.77%) and S (0.13%) for steel manufacture. It is however found to be high in alumina (7.60% Al_2O_3).

The analysis of the phosphate rock samples involved the determination of moisture, total P_2O_5, SiO_2, Fe_2O_3, Al_2O_3, F^- and CaO.

Moisture and P_2O_5 were estimated in one and the same portion of the sample. The moisture was estimated by loss on ignition at 110^0C, after which the dried sample was decomposed by

digestion with nitric acid. The P_2O_5 was estimated gravimetrically with quimociac reagent and colorimetrically by the molybdovanadophosphoric acid method.

In another portion of the dried sample, SiO_2, Fe_2O_3 and Al_2O_3, were determined. Silica was determined gravimetrically by employing the Hoffman and Lundell roLification of the Berzelius method. The residue after the estimation of silica was fused with a mixture of Na_2CO_3, and Na_2O_2 and the resulting solution added to the combined filtrates from the silica determination. The resulting solution was then passsed through an anion exchange column in the Cl^- form . Two fractions were collected for iron and aluminium. Iron was estimated colorimetrically by the 1,10-phenanthroline method, and alumina estimated colorimetrically by the 8-hydroxyquinoline method. The fluoride content was determined on a separate portion of the sample. The dried sample powder was steam distilled with perchloric acid and the F^- determined by titration with a standard solution of thirium nitrate. Lime (CaO) was estimated on a separate portion of the sample. The sample solutions were prepared by fusion with a mixture of Na_2CO_3 and Na_2O_2 and the melts taken up in de-ionized water. The CaO was then estimated by flame photometry.

The results obtained for the various phosphate rock samples studied are summarized below:

Indigenous (FSA 1) rock from Sokoto state:

The results obtained reveals that this rock is high in P_2O_5 (36.25%), low in SiO_2 (3.44%), low in Fe_2O_3 (1.30%), low in $A1_2O_3$ (1.50%), low in I" (3.85%), low in moisture (0.76%) and high in CaO (52.30%).

The rock is of the calcium type and is a high ferade rock for the manufacture of phosphatic fertilizers.

Togo rock;

The Togo rock is also of the calcium type and high grade for the manufacture of phosphatic fertilizers. The rock is rich in P_2O_5 (36.60%) and CaO (52.20%). It is low in moisture (0.84-%), $A1_2O$ (2.10%), Fe_2O_3 (1.20%) and F^- (4.61%).

Senegal (Thiers)_ rock:

The P_2O_5 content of the rock is high (34%). The lime, moisture, alumina and iron content are within the specified limits of a high grade rock, being, 46.10%, 0.68%, 2.39% and 1.20% respectively. The rock is however high in silicious matter (8.19% $Si0_2$) and high in F^- (6.44%).

Niger Republic rock:

This rock is a difficult phosphate rock and of low grade. It is low in P_2O_5 (2?.40%), high in F" (6.23%), high in $A1_2O_3$ (3.00%), high in Fe_2O_3, (3.70%). The lime content is 47.70% and the moisture content is 0.75%. This rock is not suitable for the manufacture of phosphatic fertilizers unless

it is blended with an appropriate high grade phosphate rock in the proportion that would bring the constituents within the required specified limits.

C H A P T E R 1

INTRODUCTION

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C H A P T E R 1

INTRODUCTION.

1 - 1 Iron:

Iron (Fe) has had a profound effect upon the development of the human race. It has become such a distinctive feature of civilisation that it gives its name to one of the ages in archeological chronology. As a major constituent or in trace amounts, it is found in almost every material in the earth crust, of which it constitutes 5.1%. It ranks fourth in abundance after oxygen, silicon and aluminium. The red and yellow colour of soils is due principally to iron compounds. The most abundant forms of the element in nature are the divalent and trivalent states, combined as ferrous and ferric compounds. It also occurs (rarely) in the uncombined, metallic state in meteorites.

Besides the earth's crust, there is a possibility that the centre of the earth may be iron. Indirect evidence based on the study of earthquake waves and tidal action indicate that the core of the earth is liquid and has a density corresponding to that of liquid iron at high pressure.

The element is an essential component of the human body. It occurs in blood, in the form of haemoglobin and in storage

compounds, ferritin and heamosiderin.

Commercially, iron has an industrial importance which at present exceeds that of any other element. Although it finds other applications, (as in combating iron deficiency anemia) by far the most important use of iron is in the manufacture of steel.

1 - 1.2 Iron ore:

The list of iron-containing minerals is extremely long[1] but only a few are of industrial importance as a source of the metal or its compounds. These are:

magnetite, Fe_3O_4; heamatite, Fe_2O_3; limonite, $Fe_2O_3 \cdot nH_2O$; siderite, $FeCO_3$ and pyrite, FeS_2.

The ore may be defined as "a beneficiated mineral aggregate, (natural mineral aggregate) that occurs in sufficient quantity to be a sustained supply of raw material to industry, and from which iron can be satisfactorily recovered under existing economic conditions or which may be usable in anticipated economic circumstances."[2]

Commercially important iron ore are found all over the world. Ore deposits are usually associated with plutonic, basic igneous and granite rocks. Deposits associated with plutonic rocks consist of layered, disseminated, interstitial and injected magnetite with minor heamatite and ilmenite. Iron, magnesium and manganese are generally most abundant in ultramafic rocks and decrease in abundance as rocks become more silicic.

In Nigeria, two known iron ore deposits having quality and situation which makes them possible sources of iron ore, are, the Enugu Ironstone, situated 7 miles west of Enugu in Anambra State with an estimated reserve of 16 million tons[3], and the over 260 million tons deposit of the Agbaja Plateau in Kwara State.[4,5] Another ore deposit is known to exist to the south of Birnin Kebbi in Sokoto State.[6]

The iron ore sample studied came from the Agbaja Plateau deposits in Kwara State. The Agbaja Plateau is a table-land stretching from Jenata southwards along the west bank of the Niger river to within 4 miles of Lokoja. It covers an area of about 40 square miles and is a typical example of the steep-sided, flat-topped, laterite-capped hills which border the Niger river from Baro down-stream to Ajaokuta.

The ironstone crust capping the Plateau consist of an irregular mantle of cellular and concretionary laterite which overlies a bed of oolitic and pisolitic ironstone of variable thickness.[7]

1 - 1.3 Characteristic features of commercially prefered iron ores for the manufacture of steel:

The history of the iron and steel industry which forms the backborn of modern technology probably dates back to about 1300 B.C., although iron objects dating from the third millinium B.C. have been found.[8] The prototype of the modern blast furnace was developed in the fourteenth centuary A.D.

The raw materials for the production of steel are, iron ore, limestone and coke. The overall reaction giving rise to the crude product of the blast furnace, called pig iron, which contains about 4% carbon, 2% silicon, a trace of sulphur and other impurities is:

$$Fe_2O_{3(s)} + 3CO_{(g)} = 2Fe_{(l)} + 3CO_{2(g)}$$

The limestone decomposes to give lime (CaO) which reacts with silica to give a lava-like slag.

The pig iron is subjected to refining operations which are technical and of great variety. Basically however, the refining operations are designed to produce steel, which is an alloy of iron with small and carefully controlled amounts of carbon plus many other elements depending on the required specifications. In the refining operations, limestone is added to provide CaO for converting oxidation products such as P_2O_5 into slag.

The fundamental requirement for a commercially useful iron mineral is the iron content. For an iron ore to be considered as a raw material for the iron and steel industry, it should have an iron content of about 37.2% Fe_2O_3 (or 26% Fe) and above. A high grade iron ore should have, among other things an iron content of between 85.8% to 97.2% Fe_2O_3 (or 60 - 68% Fe). Once the ore meets the requirement as regards the iron content, then other features become important in determining the economic feasibility of utilising it as a raw material for

making steel. The whole thing is a question of cost; wheather the cost of capital investment, other raw materials and labour justifies the use of the ore in the manufacturing process. Thus, the effects of other minor constituents in the ore, namely, phosphorus, sulphur, manganese, silica and alumina in the manufacturing process become important.

Silica gives an acid reaction in the blast furnace and is removed by fluxing with lime or magnesia. A high silica content therefore requires more coke and limestone which raises the production cost.

Alumina is also a slag forming constituent, and like silica, a high alumina content raises production cost.

In the case of phosphorus, only limited amounts are acceptable in ores for smelting and steel manufacture. It is reduced when the ore is smelted, and practically all remains with the pig iron and must be removed when pig iron is converted into steel. Much phosphorus in steel causes brittleness, e.t.c.

Sulphur is an undesirable impurity. It causes objectionable properties in steel similar to that of phosphorus. Since it is hard to remove in refining operations, an ore containing more than 0.1% sulphur is usually not acceptable for use in blast furnace.

Titonium gives an acid reaction in the furnace, and when fluxed it tends to make the slag highly viscous and difficult to

control. It may also form accretions in the furnace that are not melted at ordinary operating temperatures. It is therefore an undesirable constituent, and an ore having a titanium content of more than 0.1% is ussually unacceptable.
The desired specifications of a high grade iron ore is given in Appendix II (page 133).

1 - 2 Phosphorus:

Phosphorus is widely distributed over the earth in both igneous and sedimentary rocks. It ranks twelveth in abundance, constituting approximately 0.13% of the lithosphere. The most abundant forms of the element in nature are the salts of orthophosphoric acid.

It is a universal constituent of protoplasm, and is required for growth, health and reproduction in all forms of animals and plants. It occurs as orthophosphates, various polyphosphates and esters, phosphoproteins and complex nucleoproteins. In animals, the element is found in highest concentration in bone and teeth, and at lower levels it is vital to many other biological processes.

Commercially, white phosphorus is employed in chemical warfare as an antipersonel, and a smoke generator, and as an igniter for gelled-gasoline incendiary bombs.[9] Red phosphorus is used for wood and paper safety matches, being an ingredient of the abrasive surface on which match is scratched. But by far, the most important commercial application of phosphorus is in the manufacture of phosphate fertiliser.

1 - 2.2 Phosphate rock:

Commercially, phosphorus is obtained from minerals collectively known as apatites of general formula, $Ca_5X(PO_4)_3$, where X may be fluorine, carbonate or hydroxyl. The fluorapatites are the most insoluble, and hence the phosphate

ore has a composition close to it. This ore is known as 'Phosphate rock'.

Extensive deposits of the rock occur all over the world. These include apatite deposits of igneous origin, marine phosphorites, residual phosphorites, river-pebble detossils, phosphatized rock and guano.[10] These deposits are thought to originate from the pellet phosphorites, the characteristic ore of sedimentary type which is deposited under favourable marine conditions.[11]

In Nigeria, a phosphate rock deposit has been found in Sokoto State. Another deposit is known to exist in Oyo State, varying from the aluminium type rock phosphate in Kajola and Papa Alanto to the calcium type rock deposit near Abeokuta.[12]

1 - 2.3 Specification and use of phosphate rock in the manufacture of phosphatic fertilizers:

The use of bones and guano for plant nuitrition has been known for a very long time, but the history of the fertilizer industry dates back to about 1842.[13] The chief ore of the rock, calcium fluorapatite is insoluble and the phosphorus is therefore not available to plant life. The ore has to be treated with acid or heated to elevated temperatures for them to release their phosphorus.

The principal phosphate fertilizer products in commercial use in the world today, in the approximate order of their P_2O_5 volume, are:

1. Phosphoric acid and its derivatives:
   a. ammonium phosphates
   b. triple superphosphates
2. Single superphosphates (SSP).
3. Nitrophosphates.
4. Basic slag.
5. Ground phosphate rock for direct application.
   a. raw apatitic rock
   b. calcined aluminium phosphate ore
6. Sintered alkali-rock phosphate materials (mainly Rhenania phosphate).
7. Fused calcium magnesium phosphate.
8. Defluorinated phosphate rock.
9. Dicalcium phosphate.

Phosphoric acid and its derivatives occupy a preeminent place in fertilizer technology and discussion would be limited to the wet phosphoric acid process. As is well known, this process implies a reaction of rock phosphate with sulphuric acid, the resulting calcium sulphate being separated by filtration. Depending on the reaction temperature and the phosphoric acid concentration, the calcium sulphate is precipitated as dihydrate, hemihydrate or anhydrite.
In the wet process production of single superphosphate (SSP), the process consist basically of causing sulphuric acid to react with the phosphate rock, and then curing the product to

obtain a porous material which is the superphosphate. Hence, normal superphosphate (SSP), is essentially monocalcium phosphate monohydrate, $Ca(H_2PO_4)_2 \cdot H_2O$ and calcium sulphate hemihydrate, $CaSO_4 \cdot \frac{1}{2} H_2O$, with some impurities originally contained in the rock. The P_2O_5 content of the superphosphate fertilizer varies between 16 - 24%, depending on the grade of the rock, degree of dryness of product and the ratio of rock to acid employed in the manufacturing process.

The first fundamental requirement for a phosphate rock to be of any value as raw material for the production of phosphatic fertilizers (SSP in particular) is that it must have a high P_2O_5 content for fixing water soluble P_2O_5. A lower P_2O_5 content means that more tonnage of the rock has to be handled.

A high grade phosphate rock is one that has, among other things, a P_2O_5 content equal or greater than 32%. Once the P_2O_5 content of a rock is considered sufficient to justify its use as a raw material for the manufacture of phosphatic fertilizers, then other features of the rock become important. These are the effects of other constituents of the rock on the manufacturing process. Rocks high in silicious matter have been classified among the common type of difficult ores.[14] High silicious matter

in rocks leads to problems in grinding and aloso slow down the acid reaction. However, if the silica is present in an unreactive form, it will not normally cause any special problem in the phosphoric acid production process if the plant is designed with sufficient filtration and washing capacity to remove the silica with the calcium sulphate filter cake.[15] Nitrophosphate processes can however accept high silica ores by providing a simple silica removal step following the nitric acid digestion step.

Rocks high in iron and aluminium are normally regarded as unusable in wet-process phosphoric acid manufacture. When the R_2O_3 (Fe_2O_3 + Al_2O_3) content exceeds a certain proportion, which is usually placed at 3 - 5%. A low R_2O_3 content is required to avoid reversion. Such difficult ores, high in R_2O_3 cannot satisfactorily be beneficiated. The problem also results from the mineralogical forms in which the iron and aluminium are present, for example, as phosphates, silicates, oxides or other minerals. Hence, ores high in aluminium/iron phosphates and those high in non-phosphatic iron/aluminium minerals are also classified as difficult ores.

Another requirement of a good grade phosphate rock is that it should have a low fluoride content. Normally, the

maximum fluoride content that can be tolerated is put at about 4%. Serious corrosion of the plant material results from the treatment of a high fluoride ore due to release of free hydrofluoric or fluorosilicic acid.
The carbonate content of a phosphate rock is an important feature in wet process phosphoric acid manufacture. High carbonate aids reactivity and give rise to high evolution of carbon dioxide, giving rise to a porous product which is easier to bag, while low carbonate and low reactivity leads to stichness of product (SSP).
On the other hand, ores containing a high percentage of carbonates, particularly calcite and/or dolomite may be uneconomical to process because of the high consumption of sulphuric acid.
The optimum carbonate in a high grade ore has been put at a maximum of 3%.
Organic matter in phophate rock can cause difficulty in wet - process phosphoric acid production by giving rise to foaming and by forming a sludge which interferes with filtration. A good grade ore should have a low content of organic matter.
Low moisture is also preferable in phosphate rocks due to consequent grinding problems.
The desired specification for a high grade phosphate rock is given in Appendix IV (page 135).

1 - 3 The Scope of The Project:

The present work has been carried out with the following objectives in view:

i) To characterize the iron ore sample from the Agbaja Plateau in Kwara State of Nigeria. Specifically, an analysis was carried out to determine the total iron, silica, alumina, phosphorus and sulphur content of the ore.

ii) To characterize the phosphate rock sample from Sokoto State of Nigeria (designated FSA 1 sample) in particular and other phosphate rock samples obtained from Togo, Senegal (Thiers) and Niger Republic.
Specifically, an analysis was carried out to determine the following constituents in the phosphate rock samples, thus:
moisture, silica, P_2O_5, Fe_2O_3, alumina, fluoride and lime (CaO).

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C H A P T E R II

ANALYSIS OF IRON ORE.

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C H A P T E R II

ANALYSIS OF IRON ORE.

The iron ore sample studied was obtained from the Agbaja Plateau deposit in Kwara State.
As is generally the case in mineral analysis, the analyst is not often involved in sampling and preparation of sample other than in the griding and subsequent sieving operations.
The analysis performed included gravimetry (determination of silica, total iron and total sulphur) and sphectrophotometry (determination of Al_2O_3 and P_2O_5).

2 - 1 Sampling:

Sampling and sample preparation procedures have been extensively treated.[1,2,3] It is generally agreed that an analysis is no better than the sample it represents. A sample taken for analysis must accurately represent the whole quantity of material under consideration.
Generally, sampling may be divided into three parts, thus;

a. obtaining the grose sample,
b. taking the laboratory sample,
c. preparing the laboratory sample for analysis.

The laboratory sample as obtained from the minerologist must be homogenous and truely representative of the gross sample.
In the present work, the laboratory sample was obtained in the form of small lumps .

2 - 2 Sample preparation:

Sample preparation includes such operations as crushing, splitting, grinding, mixing and drying, and is an important step

in analytical work. There are various ways of preparing a laboratory sample for analysis and it is necessary to choose the best procedure for the task at hand.

Contermination of a sample during preparation is an ever-present danger and it is almost impossible to prepare a sample of a complex material, like rock, mineral or soil samples without changing its composition in some respects, either through foreign material, loss of material or the oxidation of the constituents. Hence during preparation, care must be taken to avoid contaminating the sample, or where this is not possible, to opt for a procedure that will favour a type of contermination that is least harmful.

In the present work, the laboratory sample was air-dried and crushed using a porcelain mortar and pestle to smaller particle sizes suitable for grinding and then sampled by coning and quartering. For ease of attack and complete dissolution, the sample was grinded into a fine powder using a porcelain mortar and pestle. The final sample for analysis was obtained by sieving the finely ground sample through a Twente wire sieve of 120 mesh size.

The finely ground sample was then throughly mixed by rolling the powder (- 120 mesh size) 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 a labelled sample bottle with a cap and stored until required for use.

2 - 3 Sample decomposition:

The methods for opening up iron-containing minerals are numerous, and the choice of any decomposition procedure depends on the nature of the material and the purpose of the analysis. A few iron bearing minerals are soluble in water. Many of the oxidized minerals yield to attack by hydrochloric or nitric acid or aqua regia, often when ground extremely fine

and subjected to prolonged attack. Many minerals that do not yield to attack by acids can be opened up by employing fusion procedures. Decomposition by the use of fluxes have been adequately treated by Hillebrand et al[4] and by Maxwell.[5]

With the exception of boric oxide, the common fluxes are compounds of alkali metals; carbonates, peroxides, hydroxides and borates on the alkaline side; bisulphates, pyrosulphates and acid fluorides on the acid side.

Several factors must be considered in choosing the appropriate fusion procedure.[6] These may be summarized, thus:-

a. the method choosen must effectively decompose the sample,
b. introduction of large quantities of material which may be troublesome in subsequent stages of the analysis must be avoided. In this respect the use of acids have a definate advantage over the use of a flux because of the ease of removal of the excess acid and the fact that fluxes are not so readily obtained in as pure a form as are acids.
c. if a flux is used, then a crucible medium that will best resist attack by the flux should be employed: platinum is commonly employed with carbonate, pyrosulphate and borate, while nickel is employed for peroxide fusion,
d. the method of decomposition used should not result in loss of constituents by volatilization. In this respect alkaline fluxes have an advantage over acids and acid fluxes.

Snell[7] has outlined a summary of the general methods used for opening up iron ores.

In the present work, a basic flux was used for opening up the iron ore sample. The choice of a basic flux was considered advantageous due to less tendency for losses to occur by

volatilisation. Ajiboye[8] reported a lower percentage of iron when a phosphoric and perchloric acid mixture is used for decomposing iron ore samples as compared to the use of a basic flux.
Also, the choice of a flux ensures that the small amount of material introduced during fusion did not interfere with the subsequent stages of the analysis.

2 - 4 Analytical approach:

In rock and mineral analysis, the separation and determination of silica is usually the first step in a succession of operations that lead to the determination in one and the same sample of many other elements. These may be, after first separating silica, first, elements precipitable by hydrogen sulphide, then those precipitable by ammonium hydroxide, followed by the alkaline earths, and finally magnesium. The general procedure usually followed has been fully developed,[9] and various forms of this procedure has been schematized.[10] Variations in the general procedure may be called for in some cases, and not all the elements in a group are necessarily determined in the group precipitate. Some of the elements to be estimated may require separate portions of the sample.
After the separation and determination of siiica, and the precipitation of the hydrogen sulphide group, if this was considered desirable, the next step is to ensure that iron exists in the trivalent state. The analysis can now follow any one of several courses, depending on the end in view.
In the usual case, iron, aluminium, vanadium, phosphorus and others, collectively known as "R_2O_3" group, are determined in the ammonia precipitate. The precipitation is usually carried out with aqueous ammonia at a pH just below seven. Under these conditions, manganese remain in solution. The filtrate from the

precipitation of the "R_2O_3" group now contains the alkaline earths (Ca, Sr, Ba), magnesium, manganese, a relatively large amounts of sodium salts and small amounts of a number of elements which have for some reasons escaped separation.
Next follows the separation of manganese, zinc and nickel by precipitation with ammonium sulphide, after which calcium is determined by precipitation with oxalate, followed by the determination of magnesium as the phosphate.
In the present work, the aim of the iron ore analysis as previously mentioned (section 1 - 3) is to determine the amount of total iron, alumina, silica, phosphorus (P_2O_5) and sulphur in the sample, and this has determined the analytical procedure employed. Accordingly, the classical scheme of analysis was modified, and modern analytical techniqes included to produce a scheme of analysis divided into two main sections, thus;

i) a systematic gravimetric and sphectrophotometric analysis involving the use of ion exchange separations, and
ii) individual determinations of other elements by specific methods on separate portions of the sample.

In the systematic analysis, silica, total iron and aluminium were determined in one portion of the sample: after the separation and determination of silica by the double dehydration method, the filtrate was subjected to ion-exchange separation. Two fractions were collected for iron and aluminium: iron was estimated gravimetrically and aluminium was determined by a sphectrophotometric method.
In the non-systematic part of the analysis, phosphorus and total sulphur were determined on separate portions of the sample by specific methods for the elements.

2 - 5 Systematic analysis:

As mentioned in the preceding section, this part of the analysis involves the determination of silica, total iron and alumina in one and the same portion of the sample. The various analytical methods employed for these determinations are detailed in the appropriate sections below.

2 -5.1 Decomposition of the iron ore sample:

A basic flux was used for the decomposition of the sample for reasons outlined in section 2 - 3 (page 17). The flux choosen for the fusion of the sample was sodium peroxide. This is because it is a very powerful disintegrator and oxidant. One of the chief difficulty of the use of sodium peroxide as a flux is that of finding a vessel in which the fusion can be carried out and still not seriously contaminate the analysis.[11] Also due to its hygroscopic nature, it is difficult to handle as compared with other fluxes. Fusion generally takes place at 600 - 700^{0}C and platinum is seriously attacked at this temperature. If however the inside of the platinum crucible is coated with a thin layer of fused sodium carbonate and then with a thin layer of fused sodium peroxide and the fusion carried out at the lowest possible temperature and not unduly prolonged, then a platinum crucible can be employed.[12] Silver, gold and zirconium crucibles resist attack by the fused peroxide. In the usual case, however, the fusion is made in crucibles of nickel or iron, with accompanying contermination of the fusion by the constituents of the crucible. The fusion procedure is hence used in analysis for which the conterminating substances are not to be determined. Thus in the present work, the crucible employed is a nickel crusible. The crucible material used in peroxide fusion generally has a short life time. Muehlberg[13] recommended a procedure for sodium peroxide fusions that results in little or no attack on nickel crucibles.

E X P E R I M E N T A L

Reagents

All reagents were of analytical grade unless stated otherwise.

Sodium peroxide

Hydrochloric acid (d = 1.18)

Procedure

A mixture of 1 g and 4 g of the iron ore sample and sodium peroxide respectively was carefully fused in a nickel crucible using a bunsen burner. In order to avoid froathing, the mixture was heated gently at first with constant swirling until a melt was obtained. The mixture was then strongly heated until a clear homogenous liquid phase was obtained.

$$Na_2O_2 + Fe\ (mineral) = FeO_4^{2-} + Na^+$$

After cooling, the sample cake was transfered to a 1 litre porcelain dish. The dish was covered with a watchglass. To the dried and cooled mass, 15 ml of hydrochloric acid conc was continously added, and then after about one minute, 100 ml of hot water was also added. The cover was rinsed with water and the dish transfered to a steam bath with constant stirring until a clear solution was obtained.

2 - 5.2 Gravimetric determination of silica:

Numerous methods for the determination of silica have been developed. Modern instrumental techniques, direct and indirect, for the determination of heteropoly acids (silicon, phosphorus and arsenic) provide rapid and accurate methods for the estimation of silica. The techniques generally depend on the formation of molybdosilicic acid. The silicon can then be estimated spectrophotometrically,[14] or indirectly by atomic absorption spectroscopy.[15]

Hurford and Boltz[16] have reported a method for the indirect simultaneous determination of silicon and phosphorus by ultra-violet spectroscopy.

The most common analytical tool employed in the determination of silica is the gravimetric method described by Maxwell[17] and Hillebrand et al.[18] This is usually due to the desirability of the removal of silica which would otherwise seriously interfere with the determination of other major constituents if not first removed. In the gravimetric determination, the sample solution which was either directly decomposed by acid or rendered into an acid-decomposable form by fusion with a flux is evaporated. The solution becomes supersaturated with respect to silica present as silicic acid, $Si(OH)_4$, which coagulates into high molecular weight aggregates. On further evaporation, the hydrated silica loses water and is rendered

insoluble in a form which shows only a slight tendency to revert to a colloidal form when treated with dilute acid. A single dehydration usually separates 97 - 99% of the silica; a second dehydration leaves less than 1 mg of the silica in solution which is coprecipitated with the ammonia precipitate in the classical scheme of analysis and is estimated colorimetrically in very accurate work.

The precipitated silica, which is impure is ignited at 1200^{0}C to constant weight after purification with HF and H_2SO_4 and the silica content obtained by loss of weight as it volatilises as hydrofluosilicic acid.

The most serious interference arise due to the presence of boron and fluorine in significant amounts. Boron will in part accompany the silica and be volatilised with it as BF_3, thus resulting in high results for silica. Fluorine interferes by forming SiF_4 in strong acid solution and is lost when the temperature is raised above 100^{0}C and causes low results for silica.

E X P E R I M E N T A L

Apparatus

Platinum crucible:	25-ml capacity
Desiccator:	containing silica gel as desiccant
Oven:	Gallenkamp, temperature range, 0-200^{o}C
Muffle furnace:	Carbolyte, temperature range, 0-1200^{o}C

Reagents

All reagents used were of analytical grade unless stated otherwise.

Dilute hydrochloric acid (50% V/V)
Dilute hydrochloric acid (5% V/V)
Dilute hydrochloric acid (1% V/V)
Dilute sulphuric acid (25% V/V)
Hydrofluoric acid (48% V/V)

Procedure

The solution of the iron ore sample prepared in section 2 - 5.1 (page 22) was evaporated to dryness in the porcelain dish on a steam bath. Heating was continued overnight so that the separated silica was sufficiently dehydrated. The residue was taken up with 30 ml of hot dilute HCl (50% V/V) and filtered

through a Whatman No. 40 filter paper which was previously washed with warm dilute HCl (5% V/V), catching the filtrate in a litre porcelain dish. The silica and the filter paper were washed with hot dilute HCl (5% V/V) until the yellowish colour of iron was completely removed from the paper. The residue was then washed ten times with hot water and the filter paper sucked dry at the pump. The residue and filter paper were kept and the filtrate and washings evapourated to dryness on a steam bath. Heating was continued overnight to dehydrate the silica. The dish was heated in an oven at 110°C for about one hour. It was then covered and the residue taken up with 20 ml hot dilute HCl (50% V/V) and heated on the water bath for ten minutes. Filtration followed immediately on a new and smaller filter paper, catching the filtrate in a 400 ml beaker. The residue and paper were washed with cooled dilute HCl (1% V/V), and finally with hot water. The filtrate and washings were reserved for the determination of iron and aluminium.

The combined filter papers containing the separated silica were placed in a platinum crucible and moistened with a few drops of dilute H_2SO_4. In order to avoid mechanical loss, the silica was carefully heated over a low bunsen flame until it slowly dried and the filter paper charred without inflaming. The crucible was partly covered and the heat slowly increased until the carbon was throughly burnt. The crucible was then tightly covered and

heated in an electric muffle furnace at 1200^{o}C for half an hour. It was cooled in a desiccator and weighed. The ignition was repeated at 15 minutes intervals until constant weight was obtained. After the weight has become constant, the impure silica was moistened with water, followed by the addition of 5 ml HF and a few drops of dilute H_2SO_4. The contents of the crucible were cautiously evaporated to dryness. The crucible and contents were then ignited at 1200^{o}C for 1 minute, cooled in the desiccator and weighed. The ignition, cooling and weighing operation was repeated until constant weight was obtained. The crucible and content were kept for the next stage of the analysis.
The determination was repeated for a 0.8g and 0.9g sample weight respectively.

Calculation of percent silica

The weight lost during the hydrofluoric acid treatment equals the weight of silica.

Weight of crucible + silica and impurities = a

Weight of crucible + impurities .. .. = b

∴ Weight of silica .. .. = a - b

Percent silica in sample .. .. .. $\frac{a - b}{w} \times 100$

The results obtained are given in table I.

T A B L E I

RESULTS FOR THE GRAVIMETRIC DETERMINATION OF SILICA IN IRON ORE SAMPLE

Sample No.	Weight of sample (g)	Weight of silica (g)	Percent silica	Mean percent silica
I	1.0	0.0620	6.20	
II	0.9	0.0576	6.40	6.32
III	0.8	0.0508	6.35	

2 - 5.3 Preparation of the solution and ion-exchange separation for the determination of total iron and alumina.

After the separation and determination of silica, the next stage in the systematic analysis is the estimation of total iron and alumina. Consequently, both iron and alumina have to be brought into favourable environments free from interferences. This calls for analytical separations designed to;

a. separate iron from aluminium and other interfering substances, and

b. separate aluminium from substances that might interfere with its determination.

There are several established procedures for the separation of iron (III) from aluminium and other elements. Precipitation methods for this purpose have been extensively dealt with by Hillebrand[19] and Maxwell.[20] Peterson[21] has reported a method for the separation of iron prior to its determination by cupferron precipitation and extraction with chloroform. Iron (III) can also be separated from aluminium and other elements by extraction with ether from hydrochloric acid solution.[22] Ion-exchange techniques are often employed in the separation of iron (III) from aluminium and other elements. Cation exchangers can be used in the separation of iron (III) by elution with 12M HCl.[23] Anionic exchangers can also be employed for the same purpose. Kurt and Kraus[24] have reported the

behaviour of divalent transition elements including iron (III) in hydrochloric acid solution on an anion exchange resin. In 10M HCl, aluminium is not absorbed on an anion exchanger, while iron (III) is retained by the resin.[25]

In the present work, aluminium and other constituents of the ore were separated from iron (III) by carrying out anion exchange separation by eluting with 10M HCl. The separation depends on the formation of chlorocomplexes of iron (III) in strong hydrochloric acid solution whereby the hexaquoiron (III) cationic complex interact with the chloride ions to form chlorocomplexes.[26] The formation of the chlorocomplexes follow the pattern indicated.

$$Fe(H_2O)_6^{3+} + 4HCl \longrightarrow Fe(H_2O)_2Cl_4^- + 4H_3O^+ \quad .....(i)$$

$$Fe(H_2O)_2Cl_4^- + 2H^+ \longrightarrow FeCl_4^- + 2H_3O^+ \quad .....(ii)$$

Both chlorocomplexes shown in equations (i) and (ii) above are known to exist in hydrochloric acid solution of iron (III) compounds.[27] On an anion exchange resin in 10M HCl, aluminium and phosphorus (in the form of orthophosphate) are not adsorbed and are collected in the effluent, while the iron (III) is retained by the resin and can be eluted with water.

After the ion-exchange separation, the iron (III) fraction is analysed for total iron and the effluent is subjected to futher separation in order to separate aluminium from phosphorus and other interfering substances.

One of the chief difficulties in the determination of aluminium is that of effecting a sharp separation from interfering substances. This is the reason why in the classical scheme of analysis, aluminium is obtained by difference after the determination of all the other members of the "R_2O_3" group in the ammonia precipitate. However, various gravimetric procedures have been treated by Hillebrand[28] and Maxwell[29] for its separation from other elements. The only gravimetric method cited in the literature capable of producing, in one operation, a good separation of aluminium from other elements is that in which it is precipitated as the hydrated chloride, $AlCl_3 . 6H_2O$, by passing gaseous hydrochloric acid into a cold, concentrated solution of aluminium chloride in a mixture of hydrochloric acid and ether.

Solvent extraction techniques for the separation of aluminium prior to its determination have been developed.[30] The extraction method using 8-hydroxyquinoline is not very sensitive, but is highly selective provided appropriate masking agents are used. Between pH 4.5 and 10, 8-hydroxyquinoline forms the chelate, $Al(C_9H_6ON)_3$, which is sparingly soluble in water but readily dissolve in chloroform. Although 8-hydroxyquinoline is a group reagent, and reacts with many other metal ions, the use of appropriate masking agents makes the method specific for aluminiu In the present work, aluminium in the effluent was separated from other constituents of the ore by extracting it with 8-hydroxyquinoline into chloroform (see sec 2 -5.5).

E X P E R I M E N T A L

Apparatus

Platinum crucible: 25-ml capacity

Hot Plate: Gallenkamp, temperature range, 0 - 250°C

Ion-exchange column:

Reagents

All reagents used were of analytical grade unless stated otherwise.

Dilute hydrochloric acid (50% V/V)

Anhydrous sodium carbonate

Sodium peroxide

Concentrated hydrochloric acid (10M)

Amberlite resin IRA 400 (Cl^- form)

Preparation of ion-exchange column

The anion exchange resin, Amberlite IRA 400, supplied in the chloride form was air dried for about 24 hours. 5.0g of the air dried resin was taken and washed with water by soaking and decantation until all suspended particles were eliminated. The resin was then soaked in 10M hydrochloric acid and uniformly packed into the column making sure that no air bubbles were trapped so as to avoid channeling. Finally

the column was washed twice with 25-ml portions of 10M HCl, maintaining the flow rate at 2 ml per minute.

Preparation of solution for the ion-exchange separation

The residue from the volatilisation of silica was mixed with 2g and 0.5g of sodium carbonate and sodium peroxide respectively in the platinum crucible. The mixture was carefully fused, the melt allowed to cool and then taken up with 15 ml of hot dilute HCl (50% v/v). This was heated on a hot plate until a clear solution was obtained. The solution was added to the combined filtrates and washings from the silica determination in the 400 ml beaker. The fusion treatments (sec 2 -5.1 and sec 2 -5.3) have ensured that all the iron in the sample is present in the sample solution as iron (III).
The solution was concentrated to about 200 ml on a steam bath, transferred to a 250 ml volumetric flask and made upto the mark with distilled water. A 50 ml aliquot portion of this solution was taken for the ion-exchange separation.

Procedure

The 50 ml aliquot portion of the solution in a 250 ml beaker was concentrated to about 10 ml on a hot plate. 30 ml of 10M hydrochloric acid was added and the solution passed through the ion-exchange column at a flow rate of 2 ml per minute. The column was washed four times with 50 ml portions of 10M HCl, with the same flow rate and the effluent caught in a 400 ml

beaker. This fraction was kept for the determination of aluminium.

To remove the iron from the column, 200 ml of water was passed through the column. The breakthrough for iron was shown by the appearance of a yellow effluent solution through the column. The iron fraction was collected in a 400 ml beaker and kept for the determination of iron.

2 - 5.4 Determination of total iron

The conventional techniques for the analysis of iron minerals are many and include gravimetry, titrimetry, spectrometry and electrometry.[31, 32] Gravimetry is the method employed in this study and it is often used when the concentration of iron in the sample lies within the range of 10 - 100%. The method is selective, often requiring complete separation of the metal or compound of interest. It is time consuming and tedious but cheap, requiring no complicated equipment and capable of yielding a reasonable degree of accuracy with precision better than 1 part in 1000.

Conventionally, iron (III) is determined gravimetrically by precipitating it as the hydrous oxide by addition of hydroxyl ions from ammonia.

$$Fe^{3+} + 3OH^- \longrightarrow Fe(OH)_3 \downarrow$$

Strictly speaking, hydrous oxide has no definate stoichiometry. It is represented by the formula, $Fe_2O_3 \cdot xH_2O$. The precipitate is typically amorphous and readily forms colloidal solutions. In washing the precipitate, an electrolyte is used to prevent peptisation and production of slimy material. Ammonium nitrate is most suitable for this because on ignition it volatilises, and does assist somewhat in the subsequent ignition of the precipitate. Ammonium chloride is not suitable for washing because ferric chloride which is volatile is formed during the

ignition, thus:-

$$Fe_2O_3 + 6NH_4Cl \longrightarrow 2FeCl_3 + 6NH_3 + 3H_2O$$

Ignition must be carried out in the presence of an oxidizing agent (air), otherwise partial reduction to Fe_3O_4 or even to the metal may occur. Of the major and minor constituents of the ore, aluminium, phosphorus, titanium, vanadium and manganese would be expected to interfere with the determination. Of these, only manganese may not have been separated during the ion-exchange separation. Manganese can be completely separated by careful neutralisation of the solution with ammonia during the precipitation.

E X P E R I M E N T A L

Apparatus

Porcelain crucible:	30-ml capacity
Desiccator:	Containing silica gel as desiccant
Oven:	Gallenkamp, temperature range, 0 - 200°C
Muffle furnace:	Carbolyte, temperature range, 0 - 1200°C

Reagents

All reagents were of analytical grade unless stated otherwise.

Dilute ammonia solution (50% v/v)

Dilute hydrochloric acid (50% v/v)

Ammonium nitrate solution (1% m/v)

Methyl red indicator: Prepared by dissolving 0.02 g of the free acid in 100 ml of hot water, allowing the solution to cool and then filtering through a Whatman No. 40 filter paper.

Procedure

To the iron solution in the 400 ml beaker was added four drops of methyl red indicator and heated just to boiling. Dilute ammonia (50% v/v) was added dropwise until the colour of the solution changed to a distinct yellow. The solution was then boiled for two minutes, more ammonia being added if the colour of the solution changed to orange or red. After digestion of the reddish-brown precipitate, the solution was filtered at once through an ashless Whatman No. 40 filter paper. The precipitate was washed three times with 50 ml portions of hot 1% ammonium nitrate until no positive test for chloride was obtained from the washings. The precipitate was dissolved in warm dilute HCl and the precipitation and washings repeated. The filter paper was throughly drained after the second precipitation and washings. It was then carefully folded over the edges and transferred to a weighed porcelain crucible

which had previously been ignited at 700^{0}C in an electric muffle furnace and weighed to constant weight. The crucible was heated over a low bunsen flame until the filter paper was charred without inflaming. The heat was increased until the carbon was throughly burnt off. The crucible was then placed in the furnace with the cover displaced to one side and the door of the furnace opened slightly to allow access to air in order to avoid reduction of the Fe_2O_3. The crucible was then heated at 700^{0}C for 1 hour. Heating at a temperature greater than 700^{0}C was avoided as it would result in the reduction of iron (III) oxide to iron (II) oxide by the reaction;

$$2Fe_2O_3 \longrightarrow 4FeO + O_2$$

The crucible and content were cooled in a desiccator and weighed. The ignition, cooling and weighing of the precipitate as Fe_2O_3 were repeated to constant weight.

The determination was repeated for the 0.8 g and 0.9 g sample weight respectively.

Calculation of percent iron (III) oxide.

The percentage of total iron as Fe_2O_3 in the iron ore sample was calculated as follows:-

Wt of crucible + Fe_2O_3 in 50 ml aliquot .. .. = x g

Wt of crucible .. .. = y g

∴ Wt of Fe_2O_3 in 50 ml aliquot .. .. = x-y g

Hence Wt of Fe_2O_3 in 250 ml of sample solution = 5 x (x-y) g

Wt of sample taken for analysis .. .. .. = w g

∴ % Fe_2O_3 in sample .. .. = $\frac{500 \times (x-y)}{w}$

The results obtained are given in table II.

T A B L E II

RESULTS FOR THE GRAVIMETRIC DETERMINATION OF TOTAL IRON AS Fe_2O_3.

Sample No.	Weight of sample (g)	Weight of Fe_2O_3 (g)	Percent Fe_2O_3	Mean percent Fe_2O_3
I	1.0	0.1448	72.4	
II	0.9	0.1269	70.5	72.0
III	0.8	0.1170	73.1	

2 - 5.5 Determination of alumina

In the classical scheme of analysis, aluminium (as Al_2O_3), is usually determined by difference in the "R_2O_3" precipitate. Methods for the direct determination of aluminium include gravimetry,[33, 34] atomic absorption and fluorescence spectroscopy,[35] colorimetry[36] and other techniques.

In the present work, aluminium (as Al_2O_3) was determined spectrophotometrically by measuring the yellow colour of the oxinate of aluminium in chloroform.

Full accounts of spectroscopy as an analytical tool have been treated in detail by Donbrow[37] and Dyer.[38] Atoms and molecules are capable of undergoing energy transitions by absorption or emission of quanta of the appropriate electromagnetic radiant energy, given by Plank's equation;

$$E = h\nu .$$

where,

h = Plank's constant, and

ν = frequency of electromagnetic radiation.

The value of ν depends on the type of transition and the species involved. For instance, electronic transitions result in emission or absorption of energy in the ultraviolet - visible region of the electromagnetic spectrum. Quantitative analytical aspect of molecular absorption spectroscopy are

based on Beer - Lambert's law, often represented by,

$$A = Ecl,$$

where,

c = concentration of absorbing species in mol l^{-1}

A = absorbance of the solution

l = thickness of sample solution in cm

E = absorption coefficient for the sample in $mol^{-1}\ cm^{-1}$ at a particular wavelength.

Aluminium oxinate is yellow when dissolved in chloroform, carbon tetrachloride or benzene. The colouration is not very appreciable to the eye, but the absorption is high in violet and ultraviolet light with a sensitivity of;

E = 6,700 at 390 nm and 80,000 at 260 nm.

Separation from other elements, in particular other constituents of the ore such as phosphorus, manganese, sulphur, vanadium, chromium and other interfering metal ions was achieved by extracting the oxinate into chloroform in an ammoniacal medium at pH 9 in the presence of tartrate, cyanide and hydrogen peroxide, as masking agents. Also, the presence of tartrate keeps aluminium in solution at pH values at which it normally hydrolyses.

EXPERIMENTAL

Apparatus

pH meter

Spectrometer: spectronic - 20 instrument.

Reagents

All reagents used were of analytical grade unless stated otherwise.

8-hydroxyquinoline (oxine, 2% m/v): 2 g of 8-hydroxyquinoline was dissolved in 100 ml of spectroscopic grade chloroform.

Potassium cyanide (13% m/v)

Sodium sulphite (20% m/v)

Tartaric acid (10% m/v)

Hydrogen peroxide (10% v/v)

Dilute sulphuric acid (0.01 N)

Ammonium nitrate.

Standard aluminium solution (1 mg/ml): 17.59 g of aluminium potassium sulphate, $KAl(SO_4)_2 \cdot 12\ H_2O$ was dissolved in water containing 5 ml of concentrated sulphuric acid. The solution was quantitatively transferred to a 1 litre volumetric flask and made upto the mark with water.

Preparation of calibration curve:

Aliquots of the standard aluminium solution were pipetted into labelled 100 ml volumetric flasks and diluted to the mark with 0.01 N H_2SO_4 to give solutions of 0.10, 0.15, 0.20, 0.25, 0.30, 0.35, 0.40, 0.45 and 0.50 mg per 100 ml. 25 ml of the standard solutions were pipetted into labelled 150 ml beakers. 2 ml of tartaric acid and 1 ml of hydrogen peroxide were added and the solutions allowed to stand for five minutes. 5 ml of sodium sulphite were added and after allowing to stand for three minutes, 10 ml of the potassium cyanide solution were added. The solutions were heated to about 70°C and then cooled to about 25°C. 2 g of ammonium nitrate were added and the pH of the solutions adjusted to 8.9 ± 0.3 with ammonia or HCl using a pH meter. The solutions were transferred to labelled 250 ml separatory funnels. 5 ml of oxine were added and the funnels shaken for two minutes. After allowing to settle, the organic phase was collected in a 50 ml volumetric flask. The extraction was repeated three times and the solutions were made upto the mark with chloroform. The absorbance of the solutions was measured at 389 nm against a reagent blank using spectronic - 20.

A calibration curve was obtained (Fig 1) by plotting absorbance against concentration.

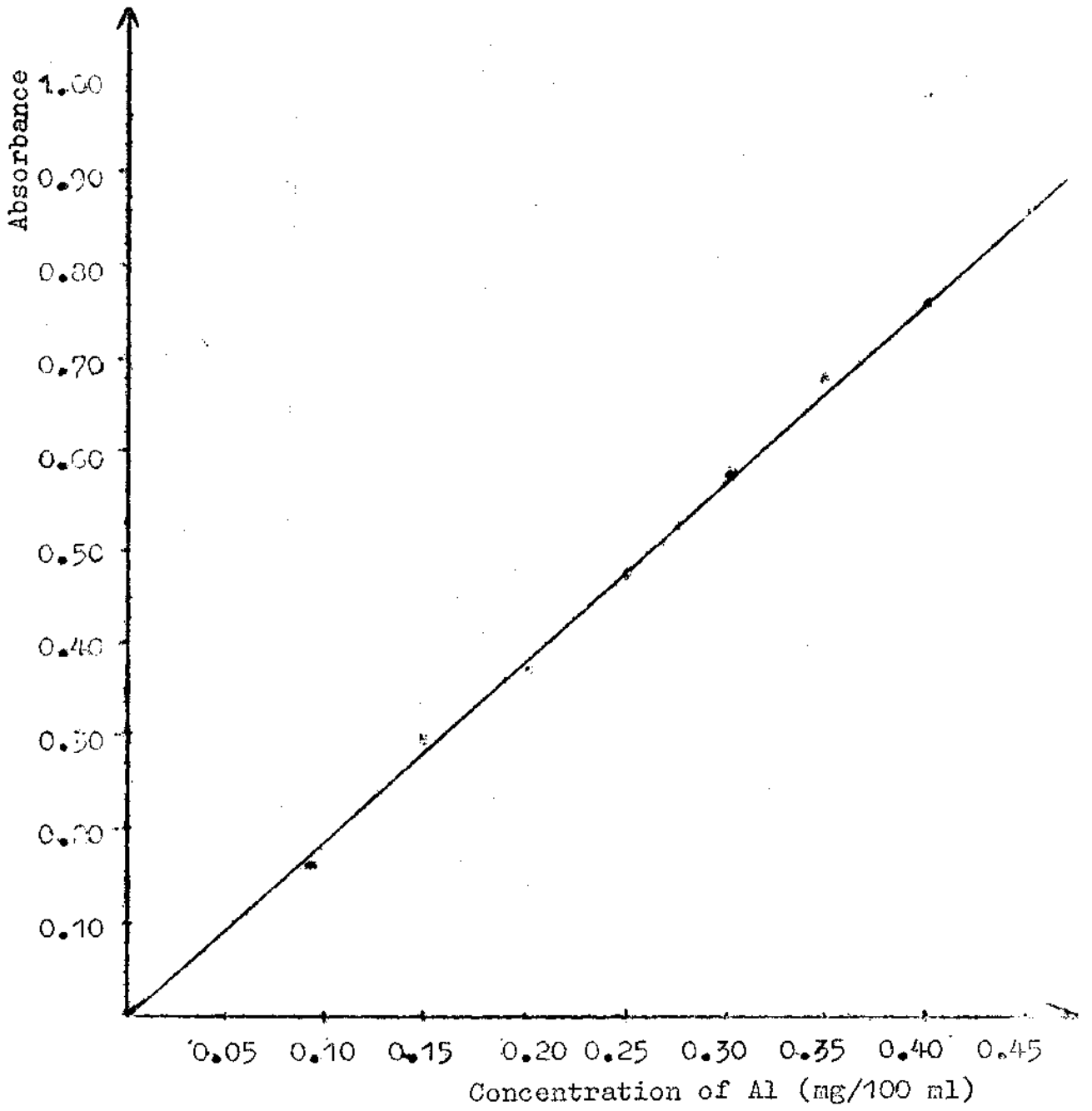


FIG. 1: CALIBRATION CURVE FOR THE DETERMINATION OF Al_2O_3.

Procedure for the determination of alumina:

The aluminium fraction from the ion-exchange separation (section 2 - 5.3) was concentrated to about 20 ml on a steam bath and ammonia solution added until faintly acidic. The solution was transferred to a 1 litre volumetric flask and made upto the mark with water. 25 ml of this solution was pipetted into a 100 ml volumetric flask and made upto the mark with water. 25 ml of this final solution was taken, the oxinate prepared and extracted into chloroform as previously described. The absorbance was measured at 389 nm and the concentration of aluminium in the solution obtained from the calibration curve (Fig. 1).

Calculation of percent alumina:

Let the concentration of solution as obtained from the calibration curve in ng per 100 ml = a

Since the 100 ml of final solution was obtained by diluting 25 ml of solution with water, then the number of ng in this 25 ml = a

But the 25 ml was an aliquot from 1 litre of the diluted solution after ion-exchange separation,

∴ the number of ng in 1000 ml of solution = a x 40

But 50 ml was taken for ion-exchange separation out of 250 ml of sample solution,

∴ number of ng of aluminium in sample solution = a x 200

Hence, number of mg of Al_2O_3 in sample = a x 200 x 1.8899,

where 1.8899 is the conversion factor.

$\therefore$ % Al_2O_3 in sample = $\frac{a \times 200}{w} \times 1.8899 \times 100$

where, 'w' is the weight of sample in mg.

The results obtained are given in table III.

T A B L E III

RESULTS FOR THE SPECTROPHOTOMETRIC DETERMINATION OF ALUMINIUM BY THE 8-HYDROXYQUINOLINE METHOD.

Sample No.	Weight of sample (g)	Absorbance	% Al_2O_3	Mean % Al_2O_3
I	1.0	0.39	7.6	
II	0.9	0.35	7.6	7.6
III	0.8	0.32	7.6	

2 - 6 Non-systematic analysis:

In this part of the analysis, the phosphorus and sulphur content of the iron ore sample are determined on separate portions of the solid powder as prepared in section 2 - 2 (page 16). The analytical techniques employed in the determinations are detailed in the appropriate sections below.

2 - 6.1 Determination of phosphorus

The determination of phosphorus in the proportions in which it occurs in silicate rocks and minerals is ussually carried out on a separate portion of the sample. The various methods for the separation and determination of phosphorus have been fully treated (see chapter III, section 3-4.2). Suffice it to say here that the estimation was carried out by measuring the colour of the yellow molybdovanadophosphoric acid complex. The method is considered to be most specific for phosphorus. Elements such as silicon, arsenic and germenium, which like phosphorus form coloured heteropoly acid complexes interfere with the determination and must be removed. Removal of silica can be easily accompolished by decomposing the sample with a mixture of nitric and hydrofluoric acids. Fluoride ion interferes with the development of the colour and can be expelled by evapouration with nitric

acid to dryness after decomposition of the sample and baking at temperatures not greater than 250°C. A higher temperature can result in loss of phosphorus by volatilisation. Elements which form coloured compounds such as iron, nickel and copper interfere with the method and must either be removed by preliminary separation of the phosphorus or the absorbance be corrected for that due to the coloured substances. This is particularly important for iron (III) due to the nature of the sample. The optimum concentration range is 5 - 40 ppm and the absorbance is measured at 400 - 460 nm.

E X P E R I M E N T A L

Apparatus

Platinum dish: Capacity - 30 ml.

Spectrometer: spectronic - 20 instrument.

Reagents

All reagents used were of analytical grade unless stated otherwise.

Nitric acid (Conc.)

Nitric acid (50% v/v)

Hydrofluoric acid (48% v/v)

Boric acid (5% m/v)

Sodium carbonate (anhydrous)

Ammonium molybdate (5% m/v): 50g of ammonium molybdate $(NH_4)_6Mo_7O_{24}.4H_2O$ was dissolved in about 500 ml of warm water. The solution was allowed to stand for several hours, filtered through a Whatman No. 42 filter paper, diluted to the mark in a litre volumetric flask, mixed well and stored in a polyethylene bottle.

Ammonium metavanadate (0.25% m/v): 2.5g of ammonium metavanadate (NH_4VO_3) was dissolved in about 500 ml of hot water and then cooled. 20 ml of concentrated nitric acid was added and the solution allowed to stand for several hours. The clear solution was diluted to 1 litre with distilled water and stored in a glass bottle.

Standard phosphate solution (1mg P/ml): 3.7137g of ammonium orthophosphate, $NH_4H_2PO_4$ (re-crystallised and dried at 100°C), was dissolved in water and diluted to 1 litre. The solution was stored in a tightly capped polyethylene bottle.

Preparation of calibration curve:

To a series of 100 ml volumetric flasks, aliquots of the standard phosphate solution were pipetted to give solutions of 0.00, 1.00, 1.50, 2.00, 2.50, 3.00, 3.50

Hydrofluoric acid (48% v/v)

Boric acid (5% m/v)

Sodium carbonate (anhydrous)

Ammonium molybdate (5% m/v): 50g of ammonium molybdate $(NH_4)_6Mo_7O_{24}.4H_2O$ was dissolved in about 500 ml of warm water. The solution was allowed to stand for several hours, filtered through a Whatman No. 42 filter paper, diluted to the mark in a litre volumetric flask, mixed well and stored in a polyethylene bottle.

Ammonium metavanadate (0.25% m/v): 2.5g of ammonium metavanadate (NH_4VO_3) was dissolved in about 500 ml of hot water and then cooled. 20 ml of concentrated nitric acid was added and the solution allowed to stand for several hours. The clear solution was diluted to 1 litre with distilled water and stored in a glass bottle.

Standard phosphate solution (1mg P/ml): 3.7137g of ammonium orthophosphate, $NH_4H_2PO_4$ (re-crystallised and dried at 100°C), was dissolved in water and diluted to 1 litre. The solution was stored in a tightly capped polyethylene bottle.

Preparation of calibration curve:

To a series of 100 ml volumetric flasks, aliquots of the standard phosphate solution were pipetted to give solutions of 0.00, 1.00, 1.50, 2.00, 2.50, 3.00, 3.50

and 4.00 ng P/100 ml.

5 ml of concentrated nitric acid were added and the solutions diluted to about 50ml with water. 10 ml of ammonium vanadate solution was added, followed by 20 ml of the ammonium molybdate solution. The solutions were diluted to volume with water, throughly mixed and allowed to stand for 30 minutes at room temperature. Finally, the absorbance of the yellow complex was measured at 460 nm against a reagent blank using spectronic - 20 spectrometer.

A calibration curve was obtained (Fig. 2) by plotting absorbance against concentration.

Procedure for the determination of phosphorus:

0.3g of the iron ore sample was placed in a 30 ml platinum dish, moistened with water and stirred with a stiff platinum wire. The dish was covered and 10 ml conc. HNO_3 was added. After effervescence has ceased, the cover was removed, rinsed with water and 10 ml of HF was added. The dish was placed on a sand bath and the contents slowly evapourated to near dryness with occasional stirring. After cooling the contents of the dish were moistened with water followed by the addition of 5 ml HNO_3 and 5ml HF respectively. The mixture was stirred and evapourated to dryness on a sand bath. The solid mass was allowed to cool, 20 ml

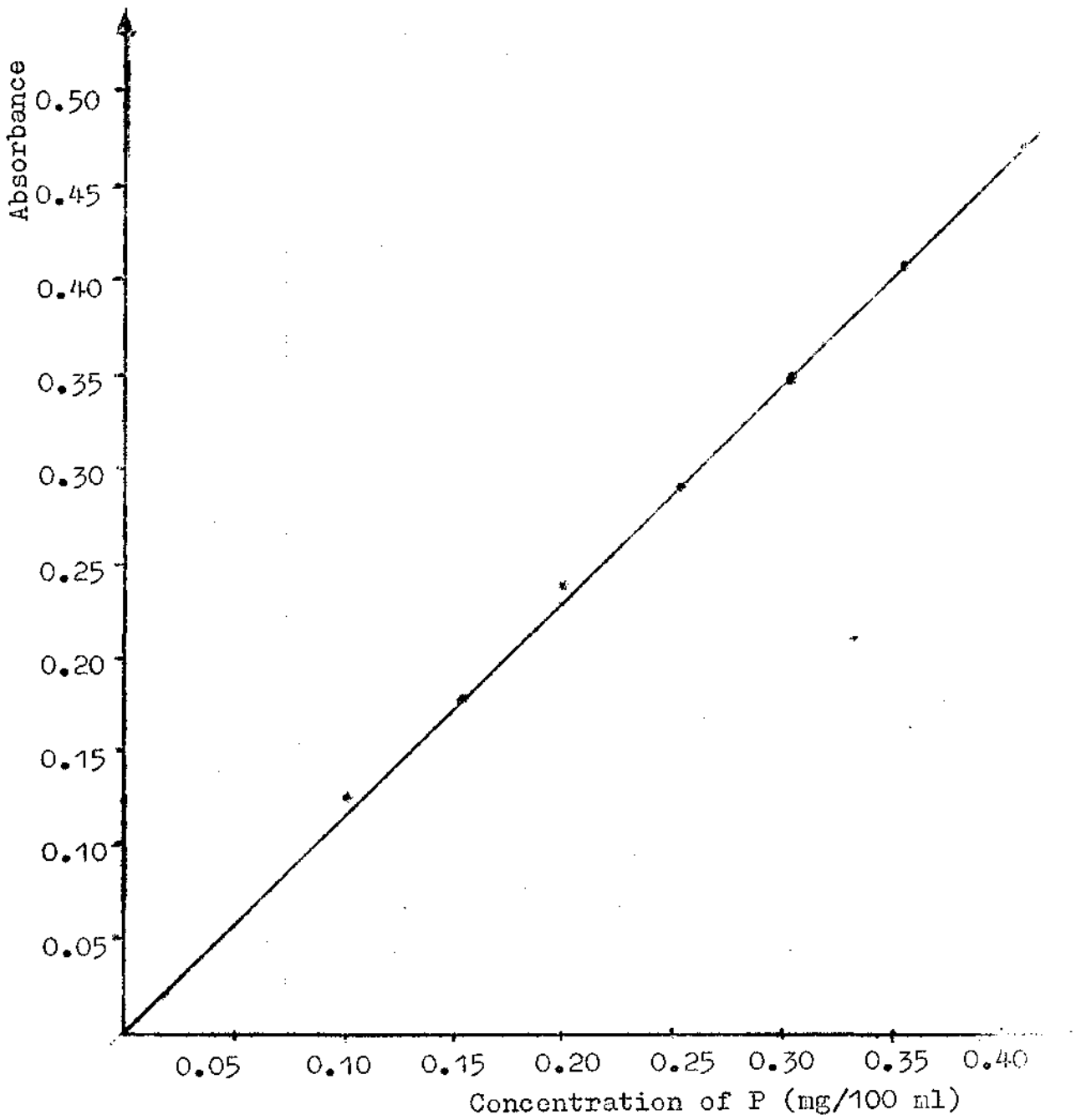


FIG. 2: CALIBRATION CURVE FOR THE DETERMINATION OF P_2O_5.

of HNO_3 (50% V/V) added and again evapourated to dryness and the solid mass heated for about 30 minutes. After cooling, 20 ml of HNO_3 (50% V/V, previously boiled and cooled to remove oxides of nitrogen) and 10 ml of boric acid were added and the residue broken up with a platinum rod. The dish was covered with a plastic cover and the contents digested on a water bath for 2 hours. The solution was filtered through a Whatman No. 40 filter paper into a 100 ml volumetric flask. The dish was throughly policed with water containing a few drops of HNO_3. The dish and the paper were washed several times with this wash solution.

The residue and the filter paper were ignited in a platinum crucible over a low flame until the filter chars without inflaming. The carbon was burnt off, the residue ignited and fused with 1g Na_2CO_3. After cooling, the cake was leached with water, filtered, the filtrate made acid with HNO_3 and added to the solution in the volumetric flask. Finally, the solution was diluted to the mark with water and throughly mixed.

50 ml of the solution was pipetted into a 100 ml volumetric flask. 5 ml of conc. HNO_3 was added and the determination carried out as described previously.

To correct the absorbance due to presence of iron (III), the remaining 50 ml of the sample solution was diluted

to 100 ml with water, and the absorbance of the solution measured at 460 nm against distilled water as blank. The absorbance was subtracted from that of the yellow complex to obtain the corrected absorbance reading. The concentration of phosphorus in the solution was obtained from the calibration curve (Fig. 2)

Calculation of percent P_2O_5:

Let the concentration of phosphorus in the solution as obtained from the calibration curve for the 50 ml aliquot be a mg/100 ml.

∴ for 100 ml of sample solution, the concentration of phosphorus in mg/100 ml = ... 2 x a

∴ the number of mg of P_2O_5 in sample solution = 2 x a x 2.2912, where the figure 2.2912 is the conversion factor.

$$\% P_2O_5 = \frac{2 \times a \times 2.2912}{w}$$

where, 'w' is the weight of sample in mg.

The results obtained for the three sample weights are shown in table IV.

T A B L E IV

RESULTS FOR THE SPECTROPHOTOMETRIC DETERMINATION OF PHOSPHORUS AS P_2O_5 BY THE MOLYBDOVANADOPHOSPHORIC ACID METHOD.

Sample No.	Weight of sample (g)	Absorbance	% P_2O_5	Mean % P_2O_5
I	0.3000	0.18	2.67	
II	0. 4034	0.30	2.84	2.77
III	0.3273	0.24	2.80	

2 - 6.2 Determination of total sulphur

In silicate rocks and minerals, sulphur usually occurs in the form of a sulphide such as pyrite (FeS_2), pyrrhotite (Fe_7S_8), or troilite (FeS).
The analytical problems encountered in the determination of sulphur arise when it is associated with elements such as barium, lead, strontium or large amounts of calcium with which it forms insoluble sulphates. In the case of the first three elements, and in particular with barium, an insoluble sulphate is formed and caught with silica, thus causing problems in the determination of the main portion constituents in a complete analysis.
The sample taken for the determination of sulphur must not be too finely grinded so as to avoid loss of sulphur as the dioxide due to oxidation . Care must also be taken in the decomposition of the sample in order to avoid contamination by sulphur compounds in the atmosphere and in particular by ignition or fusion over flames that are fed by gases containing sulphur. Such contamination can be avoided by means of an asbestos shield.[39] In general, the sample is decomposed under oxidising conditions to render the sulphur into the form of a soluble sulphate.
Various methods for the separation and determination of

sulphur have been extensively treated[40]. Iron and other elements that are precipitable by ammonia without formation of basic sulphates can be separated from the sulphate ion by double precipitation. Electrolysis with a mercury cathode in dilute acid solution can separate bases such as iron, chromium, nickel and molybdenum. Magnesium and the alkaline earths can be separated prior to the precipitation of barium sulphate by fusing the sample with sodium carbonate, extracting the melt with water and washing the residue with hot 1% solution of sodium carbonate. The analytical techniques often employed in the determination of sulphur include titrimetry, photometry, turbidimetry and gravimetry.

In the present work, sulphur was estimated gravimetrically as total sulphur in a separate portion of the sample. Fusion with sodium carbonate and extraction with water ensures separation from the alkaline earths. Ferric ion can be reduced to the ferrous state by addition of aluminium powder. The precipitation of barium sulphate must be carried out under well defined conditions due to the solubility of the precipitate in acid medium, occlusion and co-precipitation. In general the sample solution should contain only a small excess of hydrochloric acid because the

solubility of barium sulphate increases with increasing acid concentration. The volume of the sample solution should be large to minimise the tendency of barium sulphate to adsorb other ions and to prevent the precipitation of silica. Precipitation is carried out at boiling point to minimise the tendency of barium sulphate to super saturate. The precipitate and solution should be allowed to stand preferably overnight so as to minimise coprecipitation.

As barium sulphate is easily reduced by carbon, ignition of the precipitate should be carried out at a low temperature (below 600°C) and under good oxidising conditions. The ignited residue is treated with HF and H_2SO_4 and then re-weighed so as to remove any silica that might have gone down with the barium sulphate.

E X P E R I M E N T A L

Apparatus

Platinum crucible:	25-ml capacity
Desiccator:	containing silica gel as desiccant
Oven:	Gallenkamp, temperature range, 0 - 200°C

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

Reagents

All reagents used were of analytical grade unless stated otherwise.

Hydrochloric acid (12 N)

Sulphuric acid (Conc.)

Hydrofluoric acid (48% V/V)

Hydrochloric acid (50% V/V)

Ammonia solution

Saturated bromine water (Freshly prepared)

Ethyl alcohol

Barium chloride (5% m/V)

Sodium carbonate (1% m/V)

Sodium carbonate (Anhydrous)

Sodium peroxide

Aluminium powder

Procedure

About 1.0000g of the sample (100 mesh size) was dried in an oven at 110°C and transferred to a 25 ml platinum crucible. 3 g of anhydrous sodium carbonate and 0.5 g of Na_2O_2 were added and mixed throughly with

a glass rod which was wiped free of particles by rubbing it in 1 g Na_2CO_3 on a filter paper and the flux used to cover the mixture in the crucible. The crucible was then placed on an asbestos boat over a bunsen flame and heated until a melt was obtained. After cooling, the cake was loosened with a few mls of water and a stirring rod and transferred to a 250 ml beaker. The inside of the crucible and cover were policed with a rubber policeman and the rinsings transferred into the beaker. The contents were diluted to 50 mls with water. About 3 mls of ethyl alcohol and 1 g powdered aluminium were added and digested on an electrically heated water bath with constant stirring for about ten minutes.

The solution was filtered into a 600 ml beaker through a Whatman No. 40 filter paper. The residue and beaker were washed several times with cold 1% solution of Na_2CO_3 and the rinsings poured through the filter paper. The paper and contents were washed five times with 5 mls portions of the wash solution. 5 mls of saturated bromine water was added to the filtrate and the volume diluted to 300 mls with water. The beaker was covered with a watchglass and HCl (50% V/V) added dropwise until the solution was acidic.

The solution was heated to boiling to expel carbon dioxide and bromine, cooled, neutralized with ammonia solution and acidified by adding 2 mls of 12 N HCl. It was then heated to boiling and 25 mls of hot 5% solution of $BaCl_2$ added dropwise with vigorous stirring. The solution and precipitate were digested on a water bath for 1 hour and allowed to stand overnight. The solution was filtered through a Whatman No. 42 filter paper by first decanting as much of the supernatent liquid as possible, keeping most of the precipitate in the beaker, and the filtrate discarded. The precipitate was then transferred onto the filter paper with a stream of hot water. The paper was folded around the precipitate and placed in a weighed platinum crucible previously ignited at 900°C and cooled in a desiccator before weighing. The crucible cover was placed loosely to allow access to air and the crucible heated over a low bunsen flame. Without allowing the crucible to become red the paper was charred without inflaming. The cover was displaced to one side and the temperature raised until the carbon was completely burnt off. The residue was ignited at 900°C in an electric muffle furnace and cooled in a desiccator. One drop of conc. H_2SO_4 and 2 mls of hydrofluoric acid were added, evaporated to dryness,

and reignited at 900°C to constant weight.

Calculation of percent sulphur

Since the precipitate was weighed as $BaSO_4$, the percentage of total sulphur in the iron ore sample was computed from the relation:

$$\% S = \frac{\text{Wt of } BaSO_4 \times 0.1374 \times 100}{\text{Wt of sample}}$$

where, 0.1374 is the gravimetric factor.
The results obtained for all the three sample weights taken are given in table V.

T A B L E V

RESULTS FOR THE GRAVIMETRIC DETERMINATION OF TOTAL SULPHUR BY PRECIPITATION AS BARIUM SULPHATE.

Sample No.	Weight of sample (g)	Weight of $BaSO_4$ (g)	% S	Mean % S
I	1.0000	0.0095	0.13	
II	0.8000	0.0088	0.15	0.13
III	0.6975	0.0057	0.11	

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C H A P T E R III

ANALYSIS OF PHOSPHATE ROCK

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C H A P T E R III

ANALYSIS OF PHOSPHATE ROCK

Four phosphate rock samples were studied, namely;

a. FSA I phosphate rock sample located in Sokoto state of Nigeria. This sample was obtained from the Institute of Geological Survey, Kaduna.

b. Togo phosphate rock, located in Togo .

c. Senegal phosphate rock, located in Thies, Senegal.

d. Niger phosphate rock, located in Niger Republic.

All the phosphate rock samples, b - d, were obtained from the Federal Super Phosphate Fertilizer, Kaduna.

The analysis of the phosphate rock samples was carried out to determine the following constituents, thus:

moisture, silica, P_2O_5, Fe_2O_3, alumina, fluoride and lime.

The analytical techniques employed include, gravimetry (determination of moisture, P_2O_5 and silica);colorimetry (determination of P_2O_5, Fe_2O_3, Al_2O_3); titrimetry (determination of fluoride) and flame photometry (CaO).

3 - 1 Sampling and sample preparation

Sampling and sample preparation procedures have been fully discussed in chapter two (sections 2-1 and 2-2, page 16). Suffice it to say here that all the four phosphate rock samples were obtained in the finely powdered form, hence making the laboratory treatment of the sample unnecessary. However, all the finely powdered samples were sieved through a Twente wire sieve of 120 mesh size.

3 - 2 Sample decomposition

Procedures for decomposing phosphate rock samples have been fully developed.[1,2] Acid decomposition or fusion procedures can be employed, the choice of method being governed by the nature of the constituents to be determined and the analytical techniques envisaged. Digestion with hot strong acid is most commonly employed. The use of sulphuric acid is not recommended due to volatilisation of phosphorus when the solution is strongly fumed. Nitric acid is preferrable and is most commonly used. Hydrofluoric acid may be required to decompose the silica, however, when used, the excess acid should be removed by repeated evapouration to dryness.

Fusion with sodium carbonate or sodium peroxide followed

by extracting the melt with water can be used for opening up phosphate rock samples. Fusion with pyrosulphate in open crucibles or at very high temperatures results in loss of phosphorus and should be avoided.
The criteria for the choice of an appropriate decomposition procedure have been discussed in chapter two (section 2-2, page 16).

3 - 3 Analytical approach

The scheme for the systematic analysis of rocks and minerals have been outlined in chapter two (section 2-4, page 19). The chief difficulty in the analysis of phosphate rock lies in the systematic analysis, as the separation of minor amounts of group-3 metals from the predominant alkaline earths by the ammonia precipitation is vitiated by the prescence of large amounts of phosphate.
Another difficulty often encountered is in the determination of silica in the prescence of fluoride and vice-versa. In strong acid solution, SiF_6^{2-} complex ion is formed and decomposes to the volatile SiF_4 on heating at a temperature above $100^{o}C$, thus giving low results for both silica and fluoride.
Various procedures have been devised to overcome the

problem of chemical separations in the prescence of phosphate, and in the determination of silica in the prescence of fluoride. Wilson[3] devised a scheme for analysing phosphate rocks where group-3 metals are separated by a double precipitation as benzoates and calcium is separated by a double precipitation as oxalate. Gravimetric finishes are then employed for the determination of aluminium, calcium and magnesia. Methods for the estimation of silica in the prescence of fluoride have treated by Hillebrand[4] and Maxwell.[5] The determination of fluoride is problematic in phosphate rock analysis due to the prescence of not only silica but also large amounts of phosphate and calcium. So numerous are the problems of chemical separations in the analysis of phosphate rocks that Hoffman and Lundell[6] avoided systematic analysis and determined each element separately.

In the present work, moisture and P_2O_5 were determined in a separate portion of the sample. In another portion of the sample, silica, iron as Fe_2O_3 and alumina were determined. Fluoride was estimated separately in one portion of the sample by titration with a standard solution of thorium nitrate. Calcium was also separately determined by flame photometry.

3-4 Determination of moisture and total phosphorus

As mentioned in section 3-3, moisture and total phosphorus as P_2O_5 were determined in one and the same portion of the sample. The moisture content of the sample was determined by loss of weight on heating at a temperature of 110°C. Phosphorus was estimated gravimetrically with quinociac reagent and colometrically by the molybdovanado phosphoric acid method. The experimental procedures are detailed in the appropriate sections below.

3-4.1 Determination of moisture

Moisture (H_2O^-), or non-essential water is generally regarded as water held by surface forces such as adsorption and capillary action. It excludes the possible prescence of H_2O as water of crystallization. The moisture content of a sample is related more to the physical properties and sample treatment than to composition. The fineness of the powder governs the amount of surface area exposed and has a great effect on the initial amount of adsorbed moisture, but later variations in moisture content are mainly caused by changes in humidity. It is important that the moisture content of the sample remain constant during the period of the analysis.

Generally, heating at 100 - 110°C drives off most of the moisture and the amount of moisture is thus determined

indirectly by loss of weight on the assumption that the loss of weight on heating at the stated temperature range is due to moisture alone. Crucibles of platinum, porcelain, nickel or even a glass weighing bottle can serve for the determination.

E X P E R I M E N T A L

Apparatus

Porcelain crucible:	25-ml capacity
Desiccator:	containing silica gel as desiccant
Oven:	Gallenkamp, temperature range, 0 - 200°C

Procedure

A clean porcelain crucible and cover was placed in an oven and heated at 110°C for 1 hour, cooled in a desiccator and weighed. The heating, cooling and weighing was repeated to constant weight.
About 1 g of the powdered phosphate rock sample was placed in the crucible and weighed, thus obtaining the weight of the sample by difference. The crucible cover was removed and the crucible and contents placed in the oven and covered with a 10 cm diameter filter paper.

The crucible and content was heated at 110°C for 1 hour, cooled in a desiccator for half an hour and weighed with the cover on. The heating cooling and weighing operations were repeated to constant weight.

Calculation of percent moisture

The loss in weight of the sample on heating at 110°C equals the weight of moisture.

Weight of crucible and sample before heating = a

Weight of crucible and sample after heating = b

Weight of ignited crucible .. .. = c

∴ Weight of sample .. .. .. = a - c

and Weight of moisture .. .. .. = a - b

Hence, % moisture in sample .. .. $= \frac{a - b}{a - c} \times 100$

The results obtain are given in table VI.

T A B L E VI

RESULTS FOR THE DETERMINATION OF MOISTURE IN PHOSPHATE ROCK SAMPLES

Sample No.	Weight of sample (g)	Weight of moisture (g)	Percent moisture
F S A 1	0.8520	0.0065	0.76
Togo rock	1. 0230	0.0086	0.84
Senegal (Thiers)	0.9600	0.0065	0.68
Niger Rep. rock	0.7321	0.0055	0.75

3-4.2 Determination of total phosphorus

There are several methods for the estimation of phosphorus in minerals, roks and ores, e.t.c.[7,8] All methods for the determination of phosphorus calls for its prescence as orthophosphate. Meta or pyrophosphates must be converted to the orthophosphate by appropriate treatments such as alkali fusion or digestion with strong acids. Phosphate rock samples are often brought into solution by digestion with strong acids. The use of sulphuric acid is not desirable for this purpose due to loss of phosphorus by volatilisation on fuming. Nitric acid is generally employed and preferrably alone. Most methods for the determination of phosphorus involve its precipitation as ammonium phosphomolybdate and subsequent treatment of the precipitate. In general, the methods for the treatment of the phosphomolybdate precipitate can be classified into two -- those requiring a reasonably pure precipitate of any composition and those based on a pure precipitate of definate composition. With regards to the first type, the most common procedure employed is that calling for final weighing of the precipitate as magnesium pyrophosphate. In the second case, the methods employed include weighing of the dried or ignited precipitate, the reduction of the molybdenum

and subsequent titration with a standard permanganate solution, or the titration of the precipitate with a standard alkali solution. Addition of citric acid and the use of an excess of magnesia mixture can be employed for the precipitation of phosphorus directly as magnesium ammonium phosphate in the prescence of elements such as calcium, iron, aluminium, titanium, vanadium and is often employed in the determination of total phosphorus in phosphate rock samples. However, the gravimetric procedure involving precipitation with quimociac reagent has been developed specifically for the determination of phosphorus in phosphate rock samples.[9,10]

Colorimetric procedures are among the common methods used in the estimation of phosphorus in phosphate rock samples. These depend on the measurement of the intensity of the yellow coloured complex formed by orthophosphate,vanadate and molybdate, or of the blue colour formed by the selective reduction of the orthophosphatemolybdate complex. Elements that form similar heteropoly acid complexes, such as silicates, arsenates and molybdate interfere and must be removed. In phosphate rock samples, it is only necessary to remove silicate by volatilisation of the silicon with hydrofluoric acid.

Indirect spectrometric methods for the determination of

of phosphorus have been developed. These depend on the formation of molybdophosphoric acid in an acid solution by addition of excess molybdate. The molybdophosphoric acid is then extracted with diethyl ether and the extract subjected to acidic washings to remove excess molybdate. The molybdophosphoric acid is then decomposed by contacting the extract with a basic buffer solution and the resulting molybdate determined either by measuring the absorbance of the solution at 230 nm using an ultraviolet spectrometer or by measuring the absorbance of the solution at 313.3 nm resonance line of molybdenum using an atomic absorption spectrometer.[11]
In the present work, total phosphorus was estimated gravimetrically by precipitation with quimociac reagent and colometrically by measuring the yellow colour of molybdovanadophosphoric acid complex.

3-4.2.1 Gravimetric determination of total phosphorus as P_2O_5 with Quimociac reagent

The gravimetric determination of phosphorus in phosphate rock samples with quimociac reagent is very specific. The prescence of citric acid prevents interfence from elements that do occur with phosphorus in the rock. The precipitate is weighed as quinoline phosphomolybdate $(C_9H_7N)_3 \cdot H_3PO_4 \cdot 12MoO_3$.

E X P E R I M E N T A L

Apparatus

Desiccator: containing silica gel as desiccant

Oven: Gallenkamp, range, 0 - 200°C

Sintered glass crucible: G_3

Reagents

All reagents used are of analytical grade unless stated otherwise.

Sodium molybdate dihydrate

Citric acid monohydrate

Synthetic quinoline

Acetone

Nitric acid (Conc.)

Hydrochloric acid (Conc.)

Quimociac reagent: 70g of sodium molybdate dihydrate was dissolved in 150 ml of water. 60g of citric acid monohydrate was dissolved separately in 150 ml of water to which 85 ml of Conc. HNO_3 was added. The solution was allowed to cool and then molybdate solution was mixed to it with stirring. To this was added 5 ml synthetic quinoline mixed with 100 ml of water and 35 ml Conc. HNO_3 dropwise with stirring. The resulting solution was allowed to stand overnight before filtering through a Whatman No 40 filter paper. The solution was then mixed with 280 ml

acetone and diluted to 1 litre with water to get the reagent ready for use. The reagent was stored in a polythene bottle.

Preparation of sample solution

About 1g of the dried (moisture free) sample was accurately weighed and placed in a 250 ml beaker. To this was added 20 ml digestion acid (four parts 1;1 HNO_3 to one part HCl) causing effervescence followed by liberation of light brown fumes. The beaker was covered with a watchglass and heated to moderate boiling on a hot plate until the brown fumes ceased to evolve. The mixture was cooled to room temperature, diluted with water and then filtered. The solution was transferred to a 250 ml volumetric flask and the volume adjusted to the mark.

Procedure

25 ml of sample solution was taken in a 500 ml conical flask, diluted to about 100 mls with water and added 50 mls quimociac reagent by means of a pipette. The flask was placed on a hot plate, the contents boiled for 1 minute and allowed to cool to room temperature by constant shaking. The yellow precipitate was filtered through a sintered glass crucible, G3, using suction. The precipitate was washed five times with 20 mls portions of water while

allowing it to suck dry between the washings. The crucible was dried at 200°C for 1 hour in an oven and then allowed to cool in a desiccator. The precipitate was weighed as quinoline phosphomolybdate to constant weight.

Calculation of percent P_2O_5 in sample

Weight of precipitate, $(C_9H_7N)_3.H_3PO_4.12MoO_3$, in the 25 ml aliquot portion of the solution = b, then the weight of P_2O_5 in the same aliquot portion of the sample solution is obtained by multiplying the weight of the precipitate by a factor of 0.03273,

∴ Weight of P_2O_5 in 25 ml aliquot portion of the sample solution .. .. .. = b x 0.03273

and, weight of P_2O_5 in 250 ml of sample solution .. .. = b x 0.3273

If the weight of sample taken .. .. = a

then, percent P_2O_5 .. .. = $\frac{b \times 32.73}{a}$

The results obtained are given in table VII.

T A B L E VII

RESULTS FOR THE GRAVIMETRIC DETERMINATION OF TOTAL PHOSPHORUS AS P_2O_5 BY PRECIPITATION WITH QUIMOCIAC REAGENT

Sample No.	Weight of sample (g)	Weight of P_2O_5 (g)	% P_2O_5
Togo rock	1.0005	0.0365	36.50
FSA 1	1.0038	0.0361	35.94
Senegal (Thiers)	0.8367	0.0287	33.80
Niger Republic.	1.0453	0.0287	27.43

3-4.2.2 Colorimetric determination of total phosphorus by the molybdovanadophosphoric acid method.

The colorimetric determination of phosphorus by measuring the colour of the molybdovanadophosphoric acid complex has been discussed in detail in chapter two, section 2-6.1 (page 47). Suffice it to mention here that the sample solutions prepared in the previous section were used for the determination. Silica was removed by boiling the solution with concentrated perchloric acid. This operation also eliminates interference from iron (III).[12]
Because rock phosphates contain considerable amounts of phosphorus the method entails extreme dilution of the sample solution to bring it into the proper concentration range for colorimetric measurement.

E X P E R I M E N T A L

Apparatus

Spectrometer: Spectronic - 20 instrument.

Reagents

All reagents used were of analytical grade unless stated otherwise.

Nitric acid (Conc.)

Perchloric acid

Ammonium molybdate (5% $^{m}/_{V}$): Prepared as in chapter 1, section 2-6.1

Ammonium vanadate (0.25% $^{m}/_{V}$): Prepared as in chapter 1, section 2-6.1

Procedure

5 ml of the sample solutions prepared in section 3-4.2.1 (FSA 1, Togo and Senegal rock samples only) was pipetted into a 100 ml beaker. About 5 mls of perchloric acid were added, boiled, cooled, transferred to a 100 ml volumetric flask and made upto the mark with water. 25 ml of this solution was pipetted into a 50 ml volumetric flask and made upto the mark with water.

5 ml of the Niger Republic phosphate rock solution (prepared in the previous section) was pipetted into a 100 ml beaker. 5 ml of perchloric acid was added and the mixture boiled to fumes of perchloric acid, cooled, transferred to a 100 ml volumetric flask and made upto the mark with water.

25 ml of these diluted solutions were taken, neutralized with acqueous ammonia and transferred to 100 ml volumetric flasks. 5 ml of Conc. HNO_3 was added to each flask and the

determinations
/carried out as previously described (see chapter two, section 2-6.1, page 47).

The concentration of phosphorus was obtained from the calibration curve (Fig. 2, page 51).

Calculation of percent P_2O_5

Let the amount of phosphorus per 100 ml of the 25 ml aliquot solution as obtained from the calibration curve .. .. = b mg

Then the amount of phosphorus in the FSA 1, Togo and Senegal rock samples = 100 x b mg

and the amount of P_2O_5 in these samples (see sec. 2-6.1, page 53) = 100 x b x 2.2912 mg

and the percentage of P_2O_5 in these samples .. .. = $\frac{100 \times b \times 2.2912}{a} \times 100$

where a is the sample weight in mg.

Similarly, the percentage of P_2O_5 in the Niger Republic rock sample = $\frac{100 \times 50 \times b \times 2.291}{a}$

The results obtained are given in table VIII.

T A B L E VIII

RESULTS FOR THE COLORIMETRIC DETERMINATION OF PHOSPHORUS AS P_2O_5 BY THE MOLYBDOVANADO-PHOSPHORIC ACID METHOD.

Sample No.	Weight of sample (g)	Absorbance	% P_2O_5
FSA 1	1.0038	0.19	36.6
Togo rock	1.0005	0.19	36.7
Senegal (Thiers)	0.8367	0.15	34.2
Niger Republic	1. 0453	0.30	27.4

3 - 5 Determination of silica, total iron and alumina

As mentioned in section 3-3, silica, total iron as Fe_2O_3, and alumina were determined in one and the same portion of the sample.

Silica was estimated first. After the separation and estimation of silica, the filtrate was subjected to ion-exchange separation. Two fractions were collected for iron and aluminium. Iron was estimated colorimetrically by the ortho-phenanthroline method and aluminium was determined colorimetrically by measuring the absorbance of the oxinate in chloroform. The details of the analytical techniques employed are discussed in the appropriate sections below.

3-5.1 Determination of silica

Methods for the determination of silica in rocks and minerals have been discussed in chapter two, section 2-5.2 (page 23). The main problem encountered in the determination of silica in phosphate rock samples arises due to the prescence of fluoride. When a solution containing silica and fluoride is made strongly acid, a strong complex, SiF_6^{2-} is formed. On raising the temperature of the solution to above 100°C the complex decomposes to form silicon tetrafluoride (SiF_4) which is volatilized.

Consequently, low results would be obtained if either silica or fluoride is being determined.

Numerous methods have been developed for the determination of silica in the prescence of fluoride. Fusing the sample with boric oxide or sodium tetraborate provides boron which ties up the fluorine as boron trifluoride (BF_3) and minimises loss of silica by volatilisation.

Berzelius achieved a separation of silica from fluoride by precipitating the silica in a variety of ways in alkaline solution. Some insoluble silicates are formed during the leaching of the alkaline fusion cake and are removed by filtration. Some soluble silica is separated by precipitation with ammonium carbonate and the rest with ammoniacal ZnO.

Hoffman and Lundell modified the Berzelius method by substituting the use of ammonium carbonate with Zn (II) and introducing the use of Al (III) in the final recovery of soluble silica.

Shell and Craig[13] recommended fusion with a mixture of ZnO and Na_2CO_3 and the estimation of the residual silica spectrophotometrically. Shell[14] reported that silica can be estimated without separating fluorine in the prescence of large amounts of Al(III).

Czech et al[15] recommended fusion with Na_2CO_3, $Na_2B_4O_7$ and

Al_2O_3 for the determination of silica in the prescence of much phosphate and fluorine.

In the present work, silica was determined by employing the Hoffman and Lundell modification of the Berzelius method.

E X P E R I M E N T A L

Apparatus

Platinum crucible:	25-ml capacity
Porcelain dish:	250-ml capacity
Desiccator:	Containing silica gel as desiccant
Oven:	Gallenkamp, temperature range, 0 - 200°C
Muffle furnace:	Carbolyte, temperature range, 0 - 1200°C

Reagents

All reagents used were of analytical grade unless stated otherwise.

Sodium carbonate (anhydrous)

Sodium carbonate (2% m/v)

Zinc Oxide

Dilute nitric acid (50% v/v)

Dilute nitric acid (10% v/v)

Dilute hydrochloric acid (5% V/V)

Concentrated hydrochloric acid (12 N)

Concentrated sulphuric acid (18 N)

Hydrofluoric acid (48% V/V)

Ammonium carbonate

Ammonium hydroxide

Methyl red indicator: dissolved 0.02 g of the free acid in 100 ml of hot water, allowed to cool and filtered.

Procedure

About 0.5g of the powdered phosphate rock sample which has been previously dried at 110°C was accurately weighed into an ignited and weighed platinum crucible. It was thouroughly mixed with 5g Na_2CO_3 and fused over a Mecker burner. The cake was cooled, transferred with water to a 250 ml porcelain dish and heated on a water bath until disintegration is complete. The platinum crucible was ignited, weighed and reserved for later use.

The contents of the porcelain dish were filtered through a Whatman No. 41 filter paper into a 600 ml beaker keeping the bulk of insoluble material in the dish. The residue was transferred back to the dish with a jet of water. 50 mls of Na_2CO_3 (2% m/V) was added and the contents boiled for a few minutes. The solution was

filtered through the same paper and the dish and residue throughly washed with hot water. The filtrate and washings were combined with the first filtrate and the residue (A) reserved for the determination of silica.

To the combined filtrates was added a solution of 1g ZnO in 20 mls dilute HNO_3 (10% V/V), boiled for 1 minute and filtered through a Whatman No. 41 filter paper. The residue (B) was throughly washed with hot water and reserved for silica determination.

To the combined filtrate and washings was added a few drops of methyl red indicator, nearly neutralized with HNO_3 and evapourated to about 200 mls on a hot plate making sure that the solution remained alkaline during the evapouration. After cooling, dilute HNO_3 (50% V/V) was added dropwise until a pink colour just appeared. A solution of 1g ZnO in 20 mls of water containing 2g $(NH_4)_2CO_3$ and 2 mls NH_4OH was added and boiled in a covered porcelain dish until ammonia gas ceased to evolve. The solution was diluted by adding 50 mls of warm water, stirred, allowed to settle for a few minutes and filtered through a Whatman No. 40 filter paper. The residue and dish were throughly washed with cold water. The filtrate was reserved for the estimation of iron and aluminium and the residue (C) reserved for silica determination.

The residues A, B and C were washed with a jet of dilute HCl (5% V/V) into a 250 ml porcelain dish. The filter papers were ignited in the platinum crucible and the residue obtained added to the contents of the dish. 25 mls of conc. HCl were added and the silica separated by a double dehydration as previously described in chapter two section 2-5.2 (page 25). However, 10 mls H_2SO_4 (18 N) were added to the filtrate from the first dehydration and evapourated to fumes of sulphur trioxide. This was due to the prescence of considerable $ZnCl_2$ which is dried only with difficulty in the abscence of considerable amounts of silica. The filtrate was reserved for the determination of iron and aluminium.

The separated silica was ignited in the platinum crucible and treated with H_2SO_4 and HF and the amount of silica obtained by loss of weight as descibed in chapter two section 2-5.2.

Calculation of percent silica

The weight lost during the hydrofluoric acid treatment equals the weight of silica.

Percent silica in sample was calculated from the relation,

$$\% SiO_2 = \frac{a - b}{w} x\ 100$$ (see page 27).

The results obtained are given in table IX.

T A B L E IX

RESULTS FOR THE GRAVIMETRIC DETERMINATION OF SILICA BY THE METHOD OF HOFFMAN AND LUNDELL.

Sample No.	Weight of sample (g)	Weight of silica (g)	% SiO_2
FSA 1	0.4416	0.0152	3.44
Togo rock	0.5000	0.0163	3.25
Senegal (Thiers)	0.6213	0.0509	8.19
Niger Republic	0.4122	0.0166	4.02

3 - 5.2 Preparation of the solution and ion-exchange separation for the determination of total iron and alumina

After the separation and determination of silica, the course followed by the analysis is the estimation of total iron and alumina. The problem of chemical separations to bring iron and aluminium into favourable environments free from interference for their estimation have been fully dealt with in chapter two, section 2-5.3 (see page 29). Suffice it to say here that anion exchange separation, the theory of which has been previously dealt with, was employed for the separation. On passing the sample solution in 10M HCl through an anion exchange column, phosphorus as orthophosphate and aluminium are not adsorbed by the resin, but iron(III) is retained by the resin. The iron(III) fraction can then be eluted with water and the aluminium separated from the phosphorus and other interfering elements by extracting the oxinate into chloroform.

E X P E R I M E N T A L

Apparatus

Platinum crucible: 25-ml capacity

Hot plate: Gallenkamp, temperature range, 0-250°C

Ion-exchange column

Reagents

All reagents used were of analytical grade unless stated otherwise.

Sodium carbonate (anhydrous)

Sodium peroxide

Concentrated hydrochloric acid (10M)

Amberlite IRA 400 (Cl^- form; exchange capacity-3.9 mmol per gram of dry resin).

Preparation of ion-exchange column

The anion exchange column was prepared as described in chapter two, section 2-5.3 (page 32).

Preparation of the solution for ion-exchange separation

The residue left in the platinum crucible after the volatilisation of silica was carefully fused with a mixture of about 0.5g Na_2CO_3 and 0.1g Na_2O_2. The melt was allowed to cool and then taken up with 15 mls of hot dilute HCl (50% V/V). It was then heated on a hot plate until a clear solution was obtained. The solution was added to the combined filtrates and washings from the separation and determination of silica, and evapourated on a hot plate to about 30 ml. About 30 ml of Conc. HCl

was added and again evapourated to about 10 mls on a hot plate. 20 mls of 10M HCl was added to this and the resulting solution kept for the ion-exchange separation.

Procedure

The solution prepared was passed through the ion-exchange column at a flow rate of 2 ml per minute. The column was washed four times with 50-mls portion of 10M HCl maintaining the same flow rate and the effluent caught in a 400 ml beaker. This fraction was kept for the determination of alumina.

To remove the iron(III) from the column, 150 mls of water was passed through it. The breakthrough for iron was shown by the appearance of a yellow effluent solution through the column. The iron fraction was recieved in a 400 ml beaker and kept for the estimation of iron.

3 - 5.3 Determination of total iron

The separation and determination of iron has been discussed in chapter two, section 2-5.4 (page 35). Suffice it to say here that in the present work, the total iron in the phosphate rock samples was determined colorimetrically by the ortho-phenanthroline method. Ortho-phenantroline is an organic base and reacts rapidly with iron(II) to give an orange red cationic

complex over a wide range of pH, 2 - 9.

In the estimation of total iron by this method, iron(III) has to be reduced to iron(II). Hydroxylamine, ascorbic acid and other reducing agents can be used for this purpose. The main problem encountered in the colorimetric estimation of iron in phosphate rocks have been outlined by Wilson.[16] These arise chiefly due to the formation and precipitation of iron(III) phosphate under the weakly acid conditions often employed. Wilson overcame this problem by employing ascorbic acid as the reducing agent and buffering the solution with chloracetate buffer and substituting 2,2-Bipyridyl in place of hydroxylamine as the colour developing agent. In this way, the precipitation of group-3 phosphates can also be prevented. Fluoride do not interfere in the colorimetric method when the pH of the solution is fess than four.

In the present work, ortho-phenanthroline was employed as the colour developing reagent and acetate was used to buffer the solution to the appropriate pH value. Interferences that can occur due to formation and precipitation of iron(III) phosphate and possibly group-3 phosphates was taken care of by the anion exchange separation carried out in the previous section. Hydroxylamine hydrochloride was used to reduce iron(III) to iron(II).

E X P E R I M E N T A L

Apparatus

pH meter

Spectrometer: Spectronic-20 instrument

Reagents

All reagents used were of analytical grade unless stated otherwise.

Hydroxylamine hydrochloride (10% $^{m}/_{V}$, freshly prepared)

Sulphuric acid (Conc.)

Ferric alum

Sodium acetate (25% $^{m}/_{V}$)

1,10-Phenanthroline (0.25% $^{m}/_{V}$)

Ammonium hydroxide

Standard iron(III) solution (1mg/ml): 8.6350g of ferric alum, $FeNH_4(SO_4)_2 \cdot 12H_2O$, was dissolved in water containing 5 ml conc. H_2SO_4 and made upto the mark in a litre volumetric flask with water.

Preparation of calibration curve

To a series of 50 ml volumetric flasks, aliquots of the standard iron(III) solution were pipetted to give solutions of 0.10, 0.20, 0.30, 0.40, 0.50 and 0.60 mg iron(III) /100 ml. The amount of sodium acetate

required to bring the pH of the solutions to 3.5 was determined in a separate solution using a pH meter. The pH of the standard solutions was then adjusted accordingly. 2 ml of the hydroxylamine hydrochloride solution and 1 ml of the 1,10-Phenanthroline solution was added. After allowing to stand for 1 hour, the solutions were made upto the mark with water and shaken. The absorbance was measured at 512 nm against a reagent blank using Spectronic-20.

A calibration curve was obtained (Fig 3) by plotting absorbance against concentration.

Procedure for the determination of iron

The fraction from the ion-exchange separation was evapourated to about 15 ml on a hot plate. Ammonia solution was added dropwise until the solution was slightly acidic. The solution was transferred to a 100 ml volumetric flask and made upto the mark with water. 5 ml of this solution was pipetted into a 50 ml volumetric flask. The amount of sodium acetate required to bring the pH to 3.5 was determined separately on a separate portion of the sample solution. The pH of the solutions were then adjusted accordingly. The orange red colour was developed as previously described and the absorbance measured at 512 nm against a reagent blank.

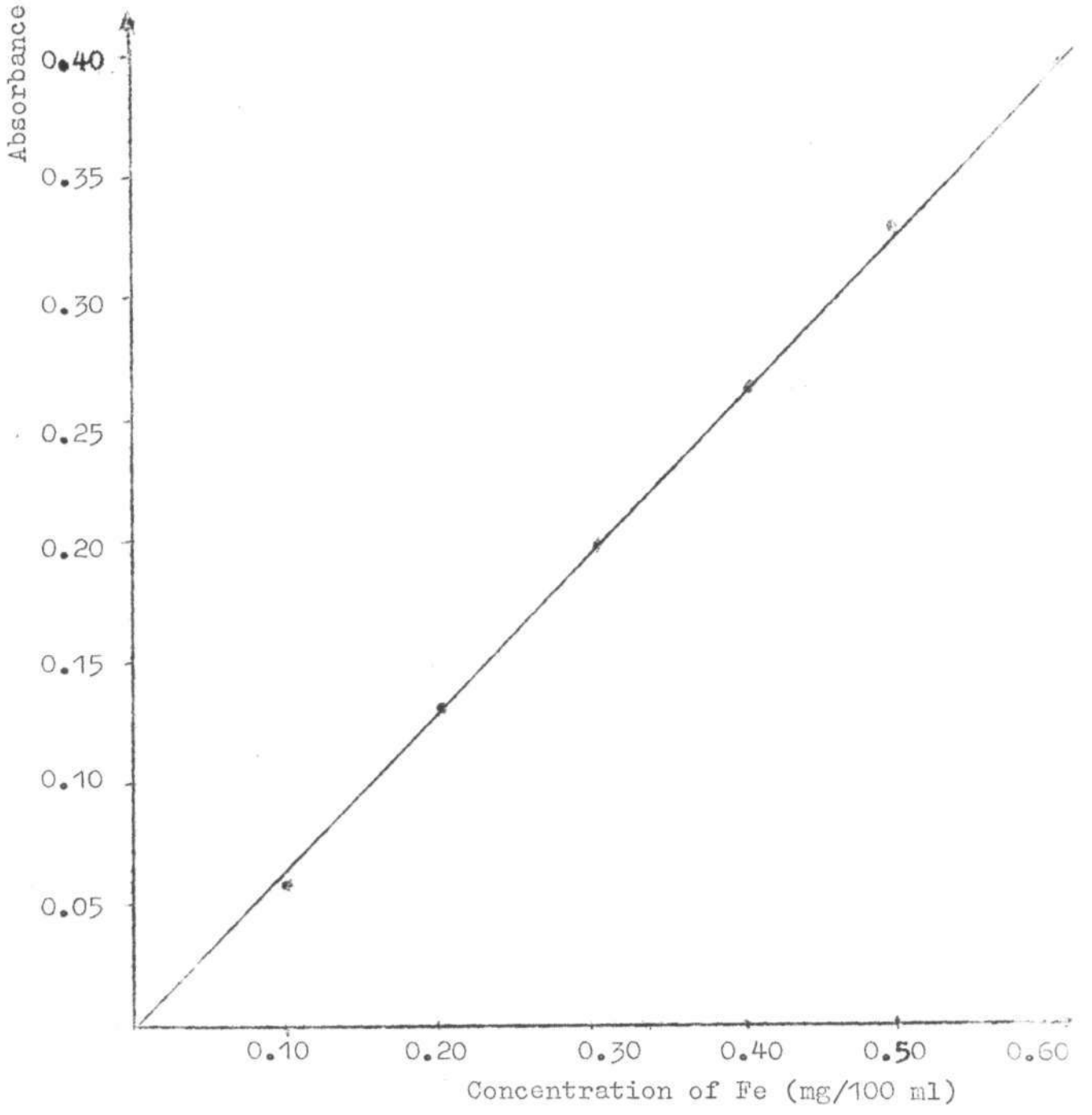


FIG. 3: CALIBRATION CURVE FOR THE DETERMINATION OF Fe_2O_3.

Calculation of percent Fe_2O_3

The concentration of iron in the 5 ml aliquot portion of the sample solutions in mg/100 ml was obtained from the calibration curve (Fig 3). If 'a' is the value obtained, then the percetage of Fe_2O_3 in the samples (with the exception of Niger Rep. sample) is given by the relation:

$$\% Fe_2O_3 = \frac{a \times 1.431 \times 100}{\text{sample weight (mg)}}$$

where, 1.431 is the conversion factor from Fe to Fe_2O_3.
For the Niger Rep. sample the relevant expression is;

$$\% Fe_2O_3 = \frac{2 \times a \times 1.431 \times 100}{\text{sample weight (mg)}}$$

The results obtained are given in table X.

T A B L E X

RESULTS FOR THE COLORIMETRIC DETERMINATION OF IRON AS Fe_2O_3 BY THE 1,10-PHENANTHROLINE METHOD

Sample No.	Sample weight (g)	Absorbance	% Fe_2O_3
FSA 1	0.4416	0.26	1.3
Togo rock	0.5000	0.28	1.2
Senegal (Thiers)	0.6213	0.35	1.2
Niger Republic	0.4122	0.36	3.7

3-5.4 Determination of alumina

Methods for the separation and determination of aluminium have been treated in chapter two, section 2-5.5 (page 40).

The determination of aluminium in phosphate rock by precipitation as the oxinate from ammoniacal solutions have been treated by Wilson.[17]

Evans[18] has described a procedure for the rapid complexometric estimation of aluminium in rocks and minerals that involves no prior separation of interferring elements.

In the present work, aluminium was estimated colorimetrically by measuring the yellow colour of the oxinate in chloroform. The aluminium fraction from the ion-exchange separation was evapourated with perchloric acid to eliminate interference from fluorine, the later being volatilized as hydrofluoric acid. Any fluoride remaining in solution was complexed by the addition of Be(II). Phosphate does not interfere as it is not extracted by oxine. The use of oxine in the colorimetric determination of aluminium has already been discussed (see page 31).

E X P E R I M E N T A L

Apparatus

pH meter

Spectrometer: Spectronic-20 Instrument

Reagents

All reagents used were of analytical grade unless stated otherwise.

8-hydroxyquiniline (Oxine, 2% m/v): 2g of 8-hydroxyquinoline was dissolved in 100 ml of spectroscopic grade chloroform.

Potassium cyanide (13% m/v)

Sodium sulphite (20% m/v)

Tartaric acid (10% m/v)

Perchloric acid (Conc.)

Dilute sulphuric acid (0.01N)

Ammonium nitrate

Hydrogen peroxide (10% v/v)

Beryllium sulphate (4% m/v)

Procedure

The aluminium fraction from the ion-exchange separation (see section 3-5.2) was concentrated to about 15 ml on a hot plate. About 10 ml of perchloric acid was added and the solution evapourated to dryness. Another 10 ml

of perchloric acid was added and the resulting solution again evapourated to dryness. The residue was dissolved in 5 ml perchloric acid and 25 ml water with heating and stirring until a clear solution was obtained. The solution was transferred to a litre volumetric flask and made upto the mark with water.

25 ml of these final solutions (12.5 ml was taken for the Niger and Senegal samples) was pipetted into a 200 ml beaker. 2 ml of tartaric acid, 1 ml of hydrogen peroxide and 2 ml of beryllium sulphate solutions were added. The solution was allowed to stand for 5 minutes and then 5 ml of the sulphite solution was added. After standing for a further 3 minutes, 10 mls of cyanide were added and the solution heated to about 70 - 80°C and then cooled to 25°C. Finally, 2g of ammonium nitrate was added and the pH adjusted to 9 by dropowise addition of ammonia solution using a pH meter.

The extraction of the oxinate and the colorimetric measurement was carried out as previously described (see chapter two, section 2-5.5, page 42).

The concentration of aluminium in mg/100 ml for the aliquots of sample solutions taken was obtained from the calibration curve (Fig. 1, page 44).

Calculation of percent Al_2O_3

The percentage of Al_2O_3 in the phosphate rock samples was calculated from the relations:

a. For FSA 1 and Togo samples;

$$\% Al_2O_3 = \frac{10 \times a \times 1.88 \times 100}{\text{sample weight (mg)}}$$

where,

a = the concentration in mg per 100 ml of the aliquot of sample solution taken,

and 1.88 is the conversion factor from Al to Al_2O_3.

b. For Senegal and Niger Republic samples:

$$\% Al_2O_3 = \frac{20 \times a \times 1.88 \times 100}{\text{sample weight (mg)}}$$

The results obtained are given in table XI.

T A B L E XI

RESULTS FOR THE COLORIMETRIC DETERMINATION OF ALUMINIUM AS Al_2O_3 BY THE 8-HYDROXYQUINOLINE METHOD.

Sample No.	Weight of sample (g)	Absorbance	% Al_2O_3
FSA 1	0.4416	0.68	1.50
Togo rock	0.5000	1.08	2.10
Senegal (Thiors)	0.6213	0.76	2.39
Niger Republic	0.4132	0.62	3.00

3 - 6 Determination of fluoride

The problems encountered in the determination of fluorine in rocks and minerals have been discussed in sections 3-3 and 3-5.1 (pages 68 and 85). These arise chiefly due to the occurance of appreciable amounts of fluorine in the prescence of silica. Virtually all methods for the determination of fluorine are subject to many interferences and as such the separation of the fluorine is the first step in its estimation. This is generally achieved by steam distillation[19,20], pyrolysis or more recently by ion-exchange. Once fluorine is separated, the determination may be done by a variety of titrimetric, colorimetric or gravimetric methods. Horton[21] has given an extensive review of the methods of determination of fluorine.

In the present work, separation was carried out by steam distillation. On heating the sample with one or more acid while steam is being passed through the mixture, fluorine is evolved as a mixture of SiF_4 and HF and is collected in the condensate. Generally, sulphuric and perchloric acids are most frequently used, with the later being the least troublesome. The optimum temperature for the distillation ranges from 125 - 150°C. In general, most of the fluorine is collected in the

first 50 mls or so of the distillate, but the prescence of such elements as aluminium necessitate that a larger volume of the distillate be collected. This is because Al is thought to form a strong complex with fluorine and so retards its recovery. The fluoride in the distillate was then estimated by titration with a standard solution of thorium nitrate using alizarin indicator. The pH of the solution should be kept constant at about 3-3.4. This is achieved by using sodium monochloroacetate buffer. A blank determination is usually necessary or alternatively the sodium nitrate solution can be standardised against known amounts of fluorine.

EXPERIMENTAL

Apparatus

Steam distillation set-up.

Reagents

All reagents used were of analytical grade unless stated otherwise.

Sodium hydroxide solution (1M)

Hydrochloric acid (0.1M)

Ammonium fluoride

Thorium nitrate solution (0.01M)

Perchlori acid (66% $^{v}/_{v}$)

Monochloroacetic acid-sodium hydroxide buffer: 3.9240g of monochloroacetic acid and 0.8g of sodium hydroxide were dissolved in water and made upto the mark in a 100 ml volumetric flask.

Phenolpthalein indicator: Re-crystallized the reagent from ethyl alcohol and dissolved 5g of the purified product in 400 ml ethyl alcohol and diluted to 500 ml with water.

Alizarin indicator (1% $^{m}/_{v}$): dissolved 1g of sodium alizarin sulphonate in 100 ml of water.

Standardisation of thorium nitrate solution

0.1951g of NH_4F (previously dried at 110°C) was accurately weighed and transffered with 15 ml perchloric acid to a steam distillation flask. Distillation was carried out at 125 - 150°C, the temperature being maintained within this range by regulating the supply of steam from the steam generator, and boiling chips were added to the distillation flask to avoid bumping and maintain steady boiling. The distillate was recieved in a 500 ml beaker. Distillation was continued until 150 ml of distillate was obtained.

To the distillate was added a few drops of phenolpthalein indicator and titrated with 1M NaOH solution until just alkaline. The solution was transffered to a 250 ml volumetric flask and made upto the mark with water. A 50 ml aliqout portion was pipetted into a titration flask, 5 drops of alizarin indicator was added and 0.1M HCl was added dropwise until the pink colour of the alizarin indicator was discharged. 2.5 ml of the monochloroacetic acid-sodium hydroxide buffer solution was added and the solution titrated with 0.01M thorium nitrate solution to a faint pink end point.

The average titre reading obtained was 15.20 ml.

Hence,

1 ml 0.01M $Th(NO_3)_4.6H_2O$ = 1.3160mg F^-

Procedure

About 5g of the finely powdered phosphate rock sample (previously dried at 110°C) was accurately weighed and transffered with 15 ml perchloric acid to a steam distillation flask. Distillation was carried out as previously described. About 150 ml of the distillate was collected, and titrated with 1M NaOH solution using phenolpthalein indicator until just alkaline. The solution was transffered to a 250 ml volumetric flask and made upto the mark with water. A 50 ml aliqout portion was taken and titrated

with the standard thorium nitrate solution as previously described.

Calculation of percent F^-

Volume of 0.01M $Th(NO_3)_4.6H_2O$ required for the 50 ml aliquot of sample soluion .. = a ml

$$\therefore \quad \% F^- = \frac{5 \times a \times 1.3160}{\text{sample weight (mg)}} \times 100$$

The results obtained are given in table XII.

T A B L E XII

RESULTS FOR THE TITRIMETRIC DETERMINATION OF FLUORIDE WITH STANDARD THORIUM NITRATE SOLUTION

Sample No.	Sample weight (g)	Titre value (a ml)	% F^-
FSA 1	0.4104	2.40	3.85
Togo rock	0.4000	2.80	4.61
Senegal (Thiers)	0.5000	4.90	6.44
Niger Republic	0.6332	6.00	6.23

3 - 7 Determination of calcium

The analytical chemistry of calcium has been discussed in detail by Turekian et al.[22] In general, calcium is separated as the oxalate ($CaC_2O_4.H_2O$) by neutralizing with aqueous ammonia an acid solution containing the calcium and ammonium oxalate. The calcium can then be determined gravimetrically as the carbonate or oxide or titrimetrically by dissolving the oxalate in dilute H_2SO_4 and titrating with a standard solution of $KMnO_4$.

The determination of cacium by flame emission photometry is rapid but not easy. The chief source of difficulty appears to lie in the anionic supression of the calcium emission line by sulphate, phosphate and aluminate. Stone and Thomas[23] overcame this difficulty by removing R_2O_3 group by a double precipitation with aqueous ammonia prior to the determination. Releasing agents such as lanthanum or strontium can be employed to eliminate the depressive effects of SO_4^{2-}, PO_4^{3-} etc.

In the present work, calcium was estimated on a separate portion of the sample by flame photometry. The depression of the calcium line due to prescence of appreciable amount of phosphate was eliminated by carrying out

ion-exchange separations. Calcium can be separated from PO_4^{3-} by means of a cation exchange resin. Ca^{2+} would be retained by the resin but not the PO_4^{3-}. Weakly basic anionic exchangers can be used for the same purpose, in which case PO_4^{3-} is retained by the resin and the eluate analysed for calcium.

In flame photometry, a solution of the test sample is drawn into the flame region of a flame photometer by aspiration where it is desolvated, evapourated and atomized. The atoms then undergo electronic excitation due to thermal collision with molecules and radicals of the flame gases. During collison, the transfer of thermal energy involves conversion of internal vibrational energy of the flame molecules to electronic energy. The excited atoms then emit radiation equal to the difference in energy from the higher to the lower level, that's when,

$$E = hv$$

The intensity of the emitted radiation is determined by the number of atoms in which identical transitions occur simultaneously, hence it depends upon the concentration of the solution. The emitted radiation is passed through an appropriate filter or monochrometer which selects the desired spectral feature and reject

background radiation and other spectral interferences. Hence, correlation of the emission intensity with concentration of test substance in the solution spray forms the basis of quantitative determination.
In the present work, calcium was separated from phosphate by anion exchange separation and then estimated by flame photometry. The procedure has the disadvantage that excessive dilution of the sample solution has to be done to bring the calcium ion concentration within the optimum concentration range of 1 to 10 ug/ml. Lanthanum was added to ensure complete elimination of depression of the calcium signal. The lower sensitivity of the method is 0.01% and compares favourably with other methods of 0 - 1% range.

E X P E R I M E N T A L

Apparatus

Flame photometer: Corning-Eel; with calcium filter.

Reagents:

All reagents used were of analytical grade unless stated otherwise.

Sodium carbonate (anhydrous)

Sodium peroxide

Lanthanum nitrate (1N)

Amberlite IR_4B (Cl^- form)

Ammonia solution (2N)

Dilute hydrochloric acid (2N)

Standard calcium solution (1mg/ml): 3.6681g of reagent grade calcium chloride dihydrate ($CaCl_2.2H_2O$) was dissolved in de-ionized water, transferred to a litre volumetric flask and made upto the mark with de-ionized water.

Preparation of calibration curve

Aliquots of the standard calcium solution were pipetted into labelled 100 ml volumetric flasks to give solutions of 1.0, 2.0, 3.0, 4.0, 5.0 and 6.0 mg per 100 ml. 2 ml of the lanthanum nitrate solution was pipetted into each flask, and made upto the mark with de-ionized water.

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 calcium filter was fitted. The full scale was set with the 6.0 mg/100 ml calcium top standard and zero with de-ionized 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. 4.

Procedure for the determination of calcium

a. Preparation of ion-exchange column:

Resin: Amberlite IR 4^B (Cl^- form)

Capacity, 75 meq/g.

Column height, 30 cm.

The resin was converted to the Cl^- form by passing 2N HCl through the column and then washed with de-ionized water to nuetrality (bromophenol blue).

b. Preparation of sample solution:

About 3.0g of the phosphate rock powder (previously dried at 110°C) was fused with a mixture of 4g Na_2CO_3 and 1g Na_2O_2. The cake was taken up in de-ionized water to which 10 ml of 2N HCl has been added. The clear solution was transferred to a litre volumetric flask and made upto the mark with de-ionized water.

c. Operating procedure:

25 ml of the sample solution was taken and neutralized with ammonia solution (bromophenol blue). The slightly acidic solution was then passed through the anion-exchange column at the rate of 2 ml per minute. After washing the column, the eluate was concentrated to about 50 ml and

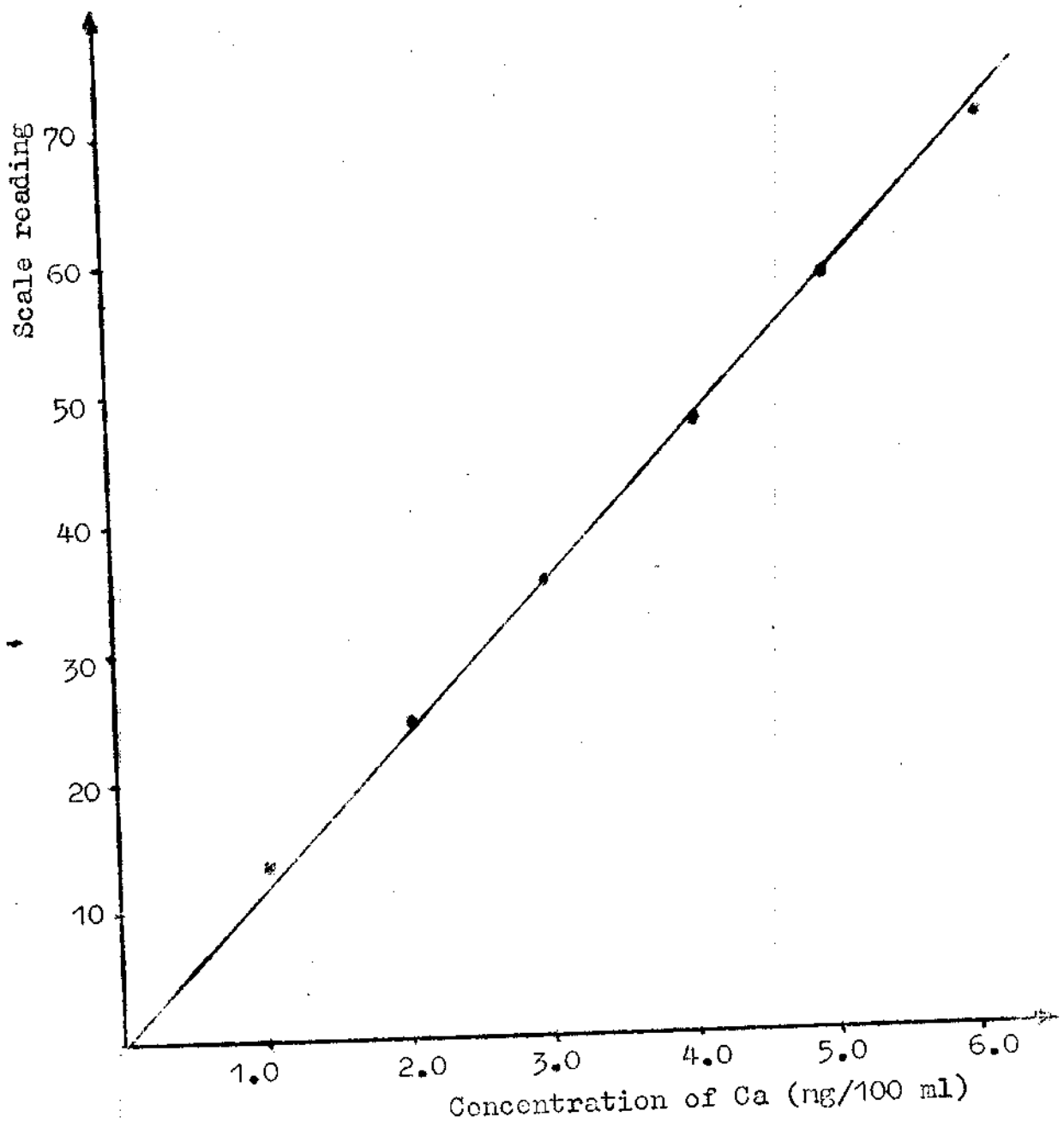


FIG. 4: CALIBRATION CURVE FOR THE DETERMINATION OF CaO.

transferred into a 100 ml volumetric flask. 2 ml of the lanthanum nitrate solution was added and the solution made upto the mark with de-ionized water. Readings were taken on the flame photometer as previously described. The concentration of calcium in the 25 ml aliquot of sample solution was obtained from the calibration curve (Fig. 4).

Calculation of percent CaO

If 'a' is the concentration of calcium in the 25 ml aliquot portion of the sample solution in mg/100 ml, then the number of mg in the 1 litre of sample solution = a x 40.

The percentage of CaO in the sample was then calculated from the relation:

$$\% \text{ CaO} = \frac{a \times 40 \times 1.3992}{\text{sample weight (mg)}} \times 100,$$

where, 1.3992 is the conversion factor from Ca to CaO.

The results obtained are given in table XIII.

T A B L E XIII

RESULTS FOR THE FLAME PHOTOMETRIC DETERMINATION OF CALCIUM AS CaO IN PHOSPHATE ROCK SAMPLES.

Sample No.	Weight of sample (g)	Scale reading	% CaO
FSA I	0.3059	35	52.3
Togo rock	0.3002	33	52.2
Senegal (Thiers)	0.3520	35	46.1
Niger Republic	0.3000	30	47.7

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C H A P T E R IV

RESULTS AND DISCUSSION

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C H A P T E R IV

RESULTS AND DISCUSSION

In this chapter, the results of the analytical studies of iron ore and phosphate rocks are presented. Table XIV (see page 122) summarises the analytical results obtained for the analysis of the iron ore sample from the Agbaja plateau in Kwara State. Table/ XV (see page 130) is a compilation of the results of the phosphate rock samples studied. The iron ore sample and the phosphate rock samples are then graded according to set specifications for the manufacture of steel and phosphatic fertilizers respectively (see Appendices II and IV).
Finally, some conclusions are drawn from the results of the analysis and some suggestions made for futher investigation.

4 - 1 Results for the analysis of iron ore

The results obtained for the analysis of the iron ore sample are given in table XIV. These include the percentage of the following constituents, namely,

SiO_2; Fe_2O_3; Al_2O_3; P_2O_5 and S.

T A B L E XIV

RESULTS FOR THE ANALYSIS OF IRON ORE

Sample No.	% Fe_2O_3	% SiO_2	% Al_2O_3	% P_2O_5	% S
I	72.40	6.20	7.60	2.67	0.13
II	70.50	6.40	7.60	2.84	0.15
III	73.10	6.35	7.60	2.80	0.11
AVARAGE	72.00	6.32	7.60	2.77	0.13

4-1.1 Discussion of results for the analysis of iron ore sample

The results obtained compare well with that obtained by Jones (see Appendix I, page 132).
The characteristic features of commercially preffered iron ores for the manufacture of steel have been discus previously (section 1-1.3, p3-6), and appendix II (page 133) gives the desired specification of a high grade iron ore for the manufacture of steel.
The results of the analytical study of the iron ore sampl reveal that the iron ore of the Agbaja plateau is high in Fe_2O_3 (72%). While a high grade ore is considered to have an Fe_2O_3 content of between 85.8 - 97.2%, any ore containing about 37.2% Fe_2O_3 is considered feasible for the manufacture of steel (see page 4).
The ore has a silica content of 6.32% and compares well with the value specified for a high grade ore(Appendix II)
The ore is high grade with respect to P_2O_5 (2.77%) as the specified value of percent P_2O_5 is $2.3\%_{max}$.
The ore has a low S content (0.13%), a property desirabl in iron ore samples as much sulphur causes objectionable properties in steel.

The alumina content of the ore is high (7.60%), and this is an undesirable property. Alumina, like silica is a slag forming constituent in the blast furnace process and as such a high grade iron ore should contain less than 1% alumina.

In conclusion, it can be said that from the results of the analysis, the iron ore of the Agbaja plateau is a good grade ore. Its one objectionable property is its high alumina content.

4-1.2 Suggestions for further work

Any recommendations with regards to the use of the ore studied for the manufacture of steel would have come a decade too late. The establishment of an iron and steel industry in Nigeria that would make use of the Agbaja iron stones have been the subject of intense negotiations by all the governments of Nigeria since independence. Presently, contracts have been awarded by the Federal Government for the construction of two steel plants in the country that would make use of the iron ore of the Agbaja plateau. So far a sum of five hundred million naira have been commited for the blast furnace plant at Ajaokuta in Kwara state and four hundred and fifty million naira have been commited for the direct reduction plant at Aladja in Warri, Bendel state. It is

expected that more than three billion naira would be spent to get the two steel plants to take off.[1]
As there are other ore deposits in the country, the following suggestions are relevant:

a. The Enugu iron stones (see sec. 1-1.2) should be analysed and characterised.
b. The iron ore deposits to the south of Birnin Kebbi in Sokoto state (see sec. 1-1.2) should be studied and characterized.

4 - 2 Results for the analysis of phosphate rock samples

The analytical study carried out on the phosphate rock samples was aimed at determining the following constituents which have a direct bearing on the manufacture of phosphatic fertilizers, namely;

moisture, total P_2O_5, SiO_2, Fe_2O_3, Al_2O_3, F^- and CaO.

The results obtained are summarized in table XV.

4-2.1 Discussion of results for the analysis of phosphate rock samples

The results obtained for the analysis of the Togo, Senegal (Thiers) and Niger Republic rock samples compare well with that obtained by the Federal Super Phosphate Fertilizer Company (see appendix III)
The characteristic features of a high grade phosphate rock

for the manufacture of phosphatic fertilizers have been outlined in chapter one (sec. 1-2.3, page 8-12) and the desired specification for same given in appendix IV (p 135). The P_2O_5 content of the indigenous FSA 1 rock and that of the Togo and Senegal is characteristic of a high grade ore. That of the Niger Rep. is comparatively low. All the phosphate rock samples studied except that of Niger Rep. have a silica content lower than 5% and hence meet the specification of a high grade rock with respect to SiO_2. The Niger Rep. rock is high in silicious matter (8.19%). The R_2O_3 content of the rocks investigated with the exception of the Niger Rep. rock falls within the range of 2.80 - 3.59% and are therefore of high grade with respect to R_2O_3 for the wet process phosphoric acid manufacture. The Niger Rep. rock is high in R_2O_3 (6.70%).

The F^- content of a high grade ore should not be more than 4%. The analytical results reveal that only the indigenous FSA 1 and Togo rocks meet this specification, the Senegal and Niger Rep. rocks being high in F^-. The moisture content of all the rock samples studied is low. This is desirable as a high moisture content give rise to problems in grinding. From the preceeding discussion, the indigenous FSA 1 rock from Sokoto state and the Togo rock are of high grade and suitable for use in the wet process manufacture of

phosphoric acid. The two rocks are high in P_2O_5, and CaO; low in SiO_2, R_2O_3, F^- and moisture, meeting all the desired specifications of a high grade phosphate rock (see appendix IV). They are of a higher grade than any of the rocks listed in appendix V.

The Senegal (Thiers) rock sample can be classified as high grade with the notable exception of its high SiO_2 and F^- content.

The Niger Rep. rock is a difficult phsphate rock with respect to its high SiO_2, R_2O_3 and F^- content. Coupled with its low P_2O_5 content, the rock is here classified as a low grade rock. It is lower in grade than any of the rocks listed in appendix VI (see p 137).

In Nigeria, there is as yet only one phosphoric acid plant that produces SSP. This is the Federal Super Phosphate Fertilizer Company located in Kaduna, capital of Kaduna State. The plant makes use of imported rock from Togo. The present work classifies the Togo rock as high grade and better in quality than either the Senegal or Niger Rep. rocks. Hence the decision to import the Togo rock in preference to the other two is a laudable one. However, the Togo rock is of the same grade and quality as the indigenous FSA 1 rock and the two rocks are similar in all the aspects investigated in this work. As such, efforts should be geared to the immediate substitution of the

Togo rock with the indigenous FSA 1 rock if found in sufficient quantity to warrant exploitation.
As far as the present work is concerned, the Senegal (Thiers) rock is suitable for use in the wet process phosphoric acid manufacture. The disadvantage in using this rock lies in its high SiO_2 and F^- content.
The Niger Rep. rock is of low grade and its use in the Kaduna plant is not advisable unless it is blended with a high grade rock, in which case the resultant rock-mix would contain the intermediate characteristics within the specified limits (see appendix IV).

4-2.2 Recommendations and suggestions for further work

As a result of the analytical study of the phosphate rock samples, the following recommendations are hereby made:

a. The Federal Government of the Federal Republic of Nigeria or any of its agencies should set about the task of substituting the imported Togo rock with the indigenous FSA 1 rock for use in the Kaduna plant if the latter occurs in sufficient quantity to warrant economic exploitation.

b. The Senegal rock could be used in the Kaduna plant if the indigenous FSA 1 and the imported Togo rocks are not available.

c. The use of the Niger Rep. rock is not recommended. If it has to be used then it should be blended with a high grade rock in a 1;1 mixture.

Some aspects of the analytical studies of the rock samples deserve further investigation, thus:

1. Some constituents of the rocks such as CO_3^{2-}, Cl^- and organic matter have not been determined. As these have some influence in the manufacture of phophatic fertilizers (see sec. 1-2.3), their estimation is worthwhile.
2. The phosphate rock deposits in Oyo State of Nigeria in Kajola and Papa Alanta should be analysed and characterised.
3. There is accumulating evidence that highly ground rock may be as effective as the more expensive soluble phosphate fertilizers in tropical soils. Consequently, the International Fertilizer Development Centre (IFDC) has directed a substential portion of its programme towards the evaluation of various rocks for this purpose in tropical soils [2] The principal advantage of ground rock is its low cost. It would be worthwhile if an investigation could be carried out in this direction, in particular with the indigenous FSA 1 rock.

T A B L E XV

RESULTS FOR THE ANALYSIS OF PHOSPHATE ROCK SAMPLES

Sample	FSA 1	Togo	Senegal (Thiers)	Niger Republic
% moisture	0.76	0.84	0.68	0.75
% P_2O_5 *	36.25	36.60	34.00	27.40
% SiO_2	3.44	3.25	8.19	4.02
% Fe_2O_3	1.30	1.20	1.20	3.70
% Al_2O_3	1.50	2.10	2.39	3.00
% F^-	3.85	4.61	6.44	6.23
% CaO	52.30	52.20	46.10	47.70
% R_2O_3	2.80	3.30	3.59	6.70
CaO/P_2O_5	1.44	1.43	1.35	1.74

*Average of the two determinations.

APPENDIX 1

Composition of the iron ore of the Agbaja Plateau*

Constituent	Percentage
Fe_2O_3	70.63
SiO_2	5.05
Al_2O_3	8.54
P_2O_5	3.01
S	0.08
TiO_2	0.54
MnO	0.05

* Source: Unpublished Reports of the Geological Survey of Nigeria, No. 964, 1952.[3]

APPENDIX 11

Desired specification for a high grade iron ore*

Constituent	Desired limit
Fe_2O_3	85.8 - 97.2%
SiO_2	less than 6%
Al_2O_3	less than 1%
P_2O_5	Not more than 2.3%
S	Very low
TiO_2	Not more than 0.17%

*Source: Geology of Iron Ore Deposits in Canada.[4]

APPENDIX 111

Unpublished results for the analysis of Togo, Senegal (Thiers) and Niger Republic phosphate rock samples*

Particulars	Togo rock	Senegal (Thiers)	Niger Republic
moisture	0.90	0.74	0.90
T P_2O_5	36.29	33.52	31.84
CaO	50.62	45.80	45.36
Fe_2O_3	1.00	1.16	4.04
Al_2O_3	2.28	2.66	5.34
F^-	4.09	6.52	-
CO_2	1.45	1.88	1.28
SiO_2	3.38	8.92	4.27
MgO	0.24	1.31	-
T Cl^-	0.00061	0.04	-
SO_3^{2-}	0.35	0.37	-

*Source: Federal Super Phosphate Fertilizer Company, Kaduna.

APPENDIX 1V

Desired specification for a high grade phosphate rock*

Constituent	Desired limit(%)
P_2O_5	32 - 34
CaO/P_2O_5 by weight	1.5
R_2O_3 max.	3.0
SiO_2	2.5 - 5
F^- max.	4.0
CO_2 max.	3.0
$MgO_{max.}$	0.5
$Organics_{max.}$	1.5
Cl_{ppm}	1.5
SO_3	no limit

*Source:
Fertilizer News, May 1978.[5]

APPENDIX V

Composition of some phosphate rock samples and rock blends*

Rocks & rocks blends	Average composition (dry basis)								
	P_2O_5	CaO	SiO_2	F	Al_2O_3	Fe_2O_3	LOI	CO_2	Cl_{ppm}
Senegal (S)	36.8	51.5	2.9	3.9	1.2	0.67	2.45	1.6	28
Udaipur (U)	36.2	50.2	7.3	3.3	1.3	0.73	1.18	1.0	25
Florida (F)	33.1	48.1	4.9	3.8	1.1	0.70	5.08	2.6	44
Morocco (M)	32.6	50.5	2.3	4.1	0.5	0.15	6.86	4.0	255
Algeria	33.7	54.1	1.4	3.6	0.4	0.32	-	-	-
High grade Jordan	34.3	52.6	1.2	4.0	0.2	0.20	6.39	3.9	177
Low grade Jordan	32.7	51.2	4.4	4.0	0.3	0.30	8.41	6.2	2800
U:F 1:1	34.4	49.4	5.0	3.6	1.2	1.12	2.94	2.0	40
U:S 1:1	35.7	50.9	5.5	3.5	0.6	0.80	2.41	1.6	28
U:M 1:1	34.4	50.2	5.1	3.6	0.8	0.69	3.93	2.9	262
S:F 1:1	34.3	49.0	3.6	3.5	1.2	1.00	-	2.3	50

*Source: Gujarat State Fertilizer Company, Limited, Baroda, India.[6]

APPENDIX V1

Composition of low grade rock phosphates*

Particulars	Jhamar Kotra	Jordan
P_2O_5	30/32	31.57
CaO	47.80	50.51
F^-	2.30	3.21
SiO_2	9.30	4.49
Citrate soluble P_2O_5	5.20	11.40

*Source: Fertilizer News, May 1979.7

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