

HIGH REFRACTIVE INDEX GLASS PRODUCTION USING LOCAL RAW MATERIALS

**MASTER OF ARTS INDUSTRIAL DESIGN
(GLASS TECHNOLOGY)**

BY

HAUWA ISA (MRS.)

NOVEMBER, 2000.

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Thesis submitted to Department of Industrial
Design Faculty of Environmental Design
Ahmadu Bello University, Zaria.

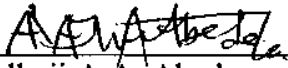
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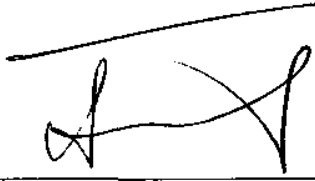
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CERTIFICATION

This thesis entitled "High Refractive Index Glass Production Using Local Raw Materials" by Hauwa Isa (Mrs.) meets the requirements and regulations for the award of the degree of Master of Art Industrial Design (Glass Technology) in the Department of Industrial Design, Ahmadu Bello University, Zaria is approved for its contribution to knowledge and literary presentation.


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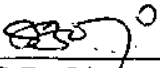
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DECLARATION

I hereby certify that all the contents of this research are the result of my work and no research of this type has been previously submitted for any degree award of Ahmadu Bello University or elsewhere.



Hauwa Isa (Mrs.)

DEDICATION

This thesis is dedicated to my late father Mallam Isa Dauda and my little daughter Asiya who has suffered along with me at infancy during the period of this research.

ACKNOWLEDGEMENT

In the name of Allah the Beneficent the Merciful, All thanks be to Allah who taught man what he knew not and gave him the knowledge of interpretation.

I once again thank God for giving me the health, the courage, the knowledge and the ability to successfully finish this course through His Guidance and Mercy.

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ABSTRACT

Glasses of relatively high refractive index were produced using barite from Azara in Nasarawa State and sand from Kenyi in Kachia Local Government of Kaduna State. Prior to the glass production, preliminary chemical analysis of the barite and sand were carried for moisture content, loss on ignition and elemental composition by the use of Atomic Absorption Spectrophotometer (AAS) and Flame Photometer. The oxide value of each element was calculated and the following percentage compositions were obtained using 1.000g of each sample for the determination. The average of three determinations for each element in both barite samples are shown below:

Sand Sample: Moisture content = 0.02, Loss on ignition = 0.06, Na_2O = 0.121, K_2O = 0.947, SiO_2 = 98.39, CaO = 0.056, Al_2O_3 = 0.180, Fe_2O_3 = 0.029 MgO = 0.008 and R_2O_3 = 0.150. Baryte Sample A: Moisture content = 0.02, loss on ignition = 0.06, Na_2O = 0.025, K_2O = 0.015. **Baryte Sample B:** Moisture content = 0.026, loss on ignition = 0.044, CaO = 0.006, MgO = 0.024, Na_2O = 0.028, K_2O = 0.001, SiO_2 = 18.12, BaO = 65.02, Fe_2O_3 = 0.029, Al_2O_3 = 16.62.

Three batches were formulated considering the oxide composition of the sand and the barite sample A due to its high BaO and low SiO_2 content. B_2O_3 and ZnO were introduced as additional fluxing and fining agents in the case of batch II, and only ZnO in batch III. The batches were test melted at a temperature of $1,175^\circ\text{C}$ in an electric furnace of heating capacity $1,200^\circ\text{C}$.

Batches II and III melted but batch I sintered. Similarly the batches were also test melted by gas firing at 1,350°C. All the batches melted giving a reddish brown paste due to contaminants. The three properties tested were refractive index, density and thermal endurance. Refractive index and density were determined by floatation method. The following results were obtained.

Batch number	Density (d)	Refractive index (n)	Thermal Endurance (F)
I	-	-	-
II	2.75	1.49	99.20
III	2.78	1.54	88.60

Based on the above results, the barite is good enough for optical glass production.

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CHAPTER ONE

1.0 INTRODUCTION

Glass in the general usage of the term is a hard, brittle, non-crystalline substance which may be either transparent or opaque, resulting from fusing silica with alkalies.

According to Frank Giffin (1963) as an engineering material, glass is unique and distinguishable from other materials. Indeed it is one of the most curious and interesting of substances in many ways. Roberts (1978) defined glass as a material formed by cooling from the normal liquid state which has shown no discontinuous change at any temperature but has become more or less rigid through a progressive increase in its viscosity.

The American society for testing material (A.S.T.M; 1963) defined glass as an inorganic product of fusion which has been cooled to a rigid condition without crystallization. Considering the two definitions above, the A.S.T.M. is limited to inorganic constituents and that glass are non-crystalline, amorphous in nature which means that their condition is similar to that of the liquid state.

Roberts (1978) added that, their lack of crystallization during cooling is as a result of their flow properties and thermodynamic behaviour which enables their viscosity to increase rapidly as their temperatures decrease thereby ensuring that their viscosity is already very high at the liquid temperature. At this point there would be insufficient time for the molecules

to arrange themselves for nucleation and crystal growth, hence the resultant liquid will be transparent, strong and brittle.

The transparency of glass may be thought of as a property more usually characterized by a liquid than the solid crystalline state. The X-ray diffraction pattern given by glass is virtually indistinguishable from that given by a liquid. This also provides confirmation of the liquid-like nature of glass. Roberts (1978).

Glass differs from solid crystalline substances by a number of characteristic properties. They are plastic at high temperature while rigid at low temperatures, under normal manufacturing, they do not crystallize. Roberts (1978).

Morrey (1938) further added that glass is isotropic; its properties are the same regardless of the directions in which they are measured. These properties are more characteristics of a liquid structure than of a crystalline structure. Moreover, the structure of glass is permeable to small particles such as sodium ions, so that it behaves as an electrolytic conductor.

1.1 GLASS CONSTITUTION

The various constituents of glass can be classified according to their functions in the glass structure and the properties they introduce into the glass.

Elliot and Lyle (1965) reported that a large variety of glasses with different chemical and physical properties can be made by suitable adjustment of their chemical composition.

The main constituent of practically all commercial glasses is sand which is abundant locally. Analysis carried out on locally available sand proved that it contains silica, sodium, calcium, magnesium and aluminum oxides among other raw materials. Elliot and Lyle (1965).

Silica (SiO_2) is the outstanding glass forming oxide; for it possess in the highest degree and desirable qualities of freedom from devitrification, resistance to attack by water and acids and coefficient of expansion. Elliot and Lyle (1965).

Modifying and intermediate oxides are two other oxides that play a unique role in the glass structure. They are incapable of building up a continuous network but have the effect of weakening the glass network. The alkali metal oxides, such as sodium and potassium oxides and alkaline earth metal oxides such as those of magnesium and calcium are examples of this category of oxides. The introduction of modifying oxides into the glass results in changes of properties which include lowering of melting point and reduction of the viscosity of the glass as well as increase in the thermal expansion coefficient. Elliot and Lyle (1965).

The intermediate oxide particularly the Aluminum oxide also serves to lower the melting point of a glass and to retard devitrification.

1.2 GLASS MAKING RAW MATERIALS

The main raw materials used in the manufacture of various types of glasses are found naturally. Silica being the main glass former exists in great abundance combined with other oxides in nature.

According to Griffin (1963) glass was originally manufacture from silica obtained by grinding flints, but today white sand is mostly used, which is essentially rock that has been disintegrated into fine particles by wind, water and ice-weathering. Griffin (1963).

Elliot (1965) further added that silica sand is combined with one or more basic oxides, which are usually alkali or alkaline earth metal. These serve as fluxing agents to melt the silica at a lower temperature. Soda ash is the main raw material that supplies the alkali in the form of sodium oxide (Na_2O). Other sources include sodium carbonate obtained from salt-cake and sodium nitrate.

Pilkington (1980) relates that the end product of the silica sand and alkali is water glass which is soluble in water. To overcome this, lime is added to stabilize the glass. Limestone and burnt dolomite are important sources of lime while dolomite in most cases introduces the magnesium oxide component.

A variety of minor constituents maybe added to serve as auxiliary raw materials which may include colouring and decolourising materials. Sand most often contains certain amount of Iron (III) oxide which gives the glass a

greenish tinge. This can be masked by adding a decolourising agent such as selenium.

For the production of special glasses there are certain components which need to be added to get the required product. In the case of optical glasses batch to impart the optical property of refractive index are mainly lead oxide or barium oxide. The raw materials that introduces these oxides are litharge and witherite respectively, which are found abundantly in nature.

1.3 GLASS MANUFACTURE

The art of making glass in the same manner as that of pottery has evolved over thousands of years. The exact date and place where glass was first manufactured remain unknown. However, it is evident that the industry has been established by 1500BC. Discoveries made by archaeologists have revealed the existence of simple decorative glass object and vessel being quite common in the Mediterranean civilization of that period. By the 3rd century A.D. most of the important processes of glass manufacture were well established and the techniques for making and shaping articles of glass spread throughout the Roman Empires.

Glass making first started with the hand made glass articles. Production by automation was a subsequent development. It is also believed that the first man-made glass is incidental rather than deliberate.

Glass manufacturing processes involves different steps before getting to the end product. These processes in the past used the crude methods manually before the industrial era but today mechanization has replaced the old methods and at the same time leading to mass production.

The different steps, the raw materials have to undergo include batching and melting, forming, annealing and finishing. These steps have to pass through certain degrees of temperature range depending upon the glass composition and the type of glass to be produced.

1.3.1 BATCHING AND MELTING

The initial step in every glass manufacturing processes is the batch formation. This is the accurate weighing and thorough mixing of the raw material before feeding into the furnace. While most of the materials to be used are usually dry, it is common to use wet sand. For this purpose it is necessary to make regular determination of the moisture content of the raw materials in order to ensure correct weight of dry materials obtained.

In large batch, the main material are weighed and mixed with the minor constituents. Refining agents and colouring agents are weighed separately and mixed.

Melting starts when the mixed glass batch is introduced into the furnace and ends when molten glass free from solid inclusions and gas bubbles and homogeneously mixed before being formed into articles. In the furnace the

mixture of the raw materials has to be in the crucible or pot; but for large-scale production, the melting is done in continuous furnaces or tank furnace. At a temperature range of 600 – 700°C, the reaction between the alkali and the sand takes place resulting to a liquid product. High temperature ensures vigorous reaction within the furnace whereby the alkaline carbonate reacts with the silica resulting in the evolution of carbon (IV) oxide gas. For the complete evolution of these gases refining agent are usually introduced into the glass batch.

It is also essential that the whole operation is correctly timed to prevent devitrification. Above a certain temperature known as devitrification temperature, the glass remains a liquid, but if the temperature is allowed to drop below this level it could crystallize or devitrify.

1.3.2 FORMING

Shaping of the glass depends on the type of glass to be produced. So due to its viscosity changing from a syrupy consistency to a rigid solid as it cools, the fabrication of glass differs from that of other materials in that all the shaping operations must be carried out within a limited time depending upon the size and shape of the article being formed.

In hand production and in the case of complicated shapes, additional “gathers” of glass are often brought from the furnace and fused with the original mass to form a handle or foot. During such operations the glass is

reheated many times to maintain it in a pliant state by inserting the partially formed article into the furnace.

By reason of its unusual physical properties only four main methods of shaping glass have been developed so far. These are blowing, pressing, casting and drawing. All of these with the exception of casting are used in both automatic and small-scale hand production methods. Glass casting has not been efficiently applied to large-scale working.

1.3.3 ANNEALING AND FINISHING

Annealing is the method of controlling the rate at which the glass is cooled to release the internal stress acquired due to temperature gradient within the glass. This annealing is achieved by bringing the glass to a uniform temperature range in the intermittent kilns and often in continuous furnace.

Finishing is the last operation to be carried out on the glass product once it has undergone annealing. The finishing operation includes cleaning, grinding, polishing, cutting and grading. All these may not necessarily be carried out on every glass object.

1.4 TYPES OF GLASSES

Glasses are grouped according to their different compositions, these categories of glasses include silica, soda lime, borosilicate, lead alkali, borate and optical glasses.

i) Silica Glasses

Silica glass which is considerably of technical importance are expensive because of its high softening temperature usually in the range of $1500^{\circ}\text{C} - 1700^{\circ}\text{C}$. It possesses a very low coefficient of expansion, high resistance to thermal shock and when purity is high it possesses high transmission qualities of ultra-violet light.

ii) Soda Lime Glasses

These glasses are the most common commercial glasses suitable for a wide variety of applications due to their physical and chemical properties. The colourless type transmit a very high percentage of visible light and hence are used for windows. They are also used as containers because they are relatively chemically inert and so cannot contaminate the content or affect their taste, that is, they are resistant to chemical attack from aqueous.

The main disadvantages of soda lime glass is their relatively high thermal expansion coefficient compared to silica glass which does not expand very greatly when heated. The addition of soda has a dramatic effect in increasing the expansion rate and in general, the higher the content of soda in a glass, the poorer will be its resistance to sudden changes of temperature.

Chemical durability is greatly improved by the addition of calcium oxide and small amount of alumina and magnesia as intermediate oxides.

iii) Borosilicate Glasses

The third major group is the borosilicate glasses. They are composed mainly of silica and boric oxide with small amount of alkali and aluminum oxide. These groups of glasses are characterized by a relatively low alkali content and consequently good chemical durability and thermal shock resistance.

They are predominantly used in plants in the chemical industry, for laboratory apparatus and as pharmaceutical containers and for various high intensity lighting applications as well as glass fibres for textiles and plastic reinforcement.

iv) Lead Glasses

Lead alkali are another group formed by the use of lead oxide combined with calcium and potassium oxides as replacement of all or part of the sodium oxide content. This category of glasses have refractive indices and a relatively soft surface. As such they can easily be decorated by grinding, cutting and engraving. The effect of the cut crystal is the brilliance of the surface as the light is caught and refracted by the facets. They are some what used extensively in the electrical industry because of their good insulating properties due to the presence of lead oxide and the partial replacement of soda content by potassium oxide. High percentage of lead oxide content in the glass qualifies it to be for radiation shield due to the well-known ability of lead to absorb gamma rays and other forms of radiation, which are harmful.

v) Optical Glasses

These glasses are produced by the addition of a wide range of metal oxide in order to obtain the various refractive properties. They can be designed to meet almost any specified combination.

Glasses with high dispersion relative to refractive index are called flint glasses while those with low dispersion are the crown glasses.

vi) Opal Glasses

The opal glasses are another group of glasses that usually contain finely ground particles of feldspar or cryolite which cause it to appear translucent without becoming transparent by scattering the light which falls on it.

vii) Other Types of Glasses

Other special kinds of glasses include the Aluminosilicate, alkali-barium silicate, phosphate, borate, Glass-ceramic, chaliogenite and photosensitive glasses. These groups of glasses have different ranges of compositions depending on their applications.

1.5 STATEMENT OF THE PROBLEM

It is a known fact that the use of optical glasses in research and medicine and in wider application for aiding sight among majority of Nigerians who would have gone blind without the use of this special material. Any country aiming for meaningful development should in addition to other forms of technology have a knowledge and means of producing optical glasses which is very essential. With this in mind, it is therefore, imperative to undertake a research aimed at possible production of this material locally.

1.6 AIMS AND OBJECTIVES OF THE STUDY

The objectives of this study are:

- i) To locate sources of suitable raw materials for optical glass production in Nigeria.
- ii) To analyze the raw materials in order to determine their chemical compositions.
- iii) To produce different glasses with different batch compositions
To test the glasses produced for the following properties:
 - Refractive Index (n)
 - Density (d)
 - Thermal endurance (F)

1.7 RESEARCH QUESTIONS

Based on the problems and the objectives of this study, the following research questions were drawn.

- i) What are the necessary raw materials used to impart optical activity on a glass?
- ii) How do we get these raw materials, if available, in pure form?
- iii) If the desired are produced, what conditions are necessary to maintain the desired property?
- iv) What equipment or apparatus is necessary to evaluate the properties of the glasses produced and to what extent?

1.8 SCOPE AND DELIMITATION

The basic raw-materials for any kind of glass manufacture is sand which is silica (SiO_2). This is found abundantly in almost all parts of the country, but for the purpose of this study it has been delimited to the sand sourced from Kenyi in Kachia Local Government of Kaduna

State and the Baryte from Azara in Anwe Local Government of Nasarawa State due to the pre-knowledge of the extent and purity of the deposit.

1.9 LIMITATION

Optical activities in glass include refraction, dispersion etc. However this study is limited to the investigation of refractive property and density which are interrelated and also the thermal endurance.

1.9.1 SIGNIFICANCE OF THE STUDY

It is hoped that the research findings will help researchers and glass manufacturers to have an insight into:

- i) The quality of locally available baryte for optical glass production
- ii) The effect of varying the composition of baryte on the properties of the glasses produced vis-à-vis refractive index.
- iii) The possibility of using the local barite for optical glass production hence enabling industries to spring up for that purpose.

1.9.2 DEFINITION OF TERMS

Ash-less paper:	Special filter paper that does not leave any ash behind when it is completely burnt.
Calibration Curve:	A graph of various concentration of solution plotted against absorbance from which concentration of ions in an unknown sample is determined.
Dispersion:	Splitting of white light ray into its various component colours.
Devitrification:	The crystallization of one or more substances present in the molten glass when maintained below its melting temperature.

Fluxing Agent:	A substance which induces rapid chemical reaction and causes the batch to melt easily to form glass.
Fining Agent:	A substance which decomposes giving some gaseous by-products liberating a large number of gas bubbles that rises to the surface helping to stir the batch.
Furnace:	A thermal plant or thermal insulation made of high refractory bricks in which fuels are burnt to attain very high temperature with little loss of heat to the environment.
Flint Glass:	Colourless glass.
Fusion:	State of being melted together.
Kiln:	A furnace made of refractory clay materials for firing glass and ceramic products.
Parts Per Million (ppm):	The amount of solute in milligram (mg) in one million milligram part of the solvent (10^6).
Refractory Crucibles:	Pots made of Refractory materials that are specially made for melting metals and glass.
Refractive Index:	It is the ration of the sine of angle of incidence to the sine of angle of refraction for a ray of light passing from a less dense to a denser medium.
Sintering:	Fusion of the glass batch without complete melting due to low temperature and low fluxing agent.
Stoichiometric equation:	A balanced chemical equation which shows the mole ratio of reacting substances and products.

CHAPTER TWO

2.0 LITERATURE REVIEW

The review of related literature is in accordance with suggestions of Nworgu (1991) and Adetoro (1997) who viewed the synthesis of related literature as an essential ingredient to the development of sound research design. In the scheme of this study, available research materials were reviewed accordingly.

Barite (BaSO_4) – Barium sulphate according to Othmer (1964) is found naturally in the form of witherite. It has various colours but mostly yellow, Isomorphous Orthorhombic crystals in shape associated with galena and of specific gravity 4.3, a Mohr's hardness level of 3.00 – 3.75. The Raw Material Research and Development Council (1989) revealed that extensive deposit of barite occurs in Plateau and Benue states with an estimated reserve of over 500,000 metric tones in Nassarawa State which is yet to be fully exploited. The Ore varies from normal opaque to the rare transparent crystals.

Barium carbonate (BaCO_3) which is manufactured from Barium sulphate (BaSO_4) reacts with silica (SiO_2) to form Barium silicate with the evolution of carbon (iv) oxide (CO_2). In the glass industry large amount of the coarsely ground barite act as a flux to increase fluidity at lower temperatures as well as increasing brilliance by increasing the index of refraction of the glass.

Frank (1963) describes glass as one of man's most "taken – for – granted" materials. In his words it is "A man – made substance which is hardly ever out of arms – reach wherever we maybe in the civilized world". However, the first definite mention of a magnifying lens is in the works of the Arab Optician, Alhazen, who says that an object placed under a segment of a glass sphere appears enlarged. By the time of Isaac Newton (1642 – 1727) the art had advanced so much that the deficiencies of optical instruments, especially telescopes were beginning to be felt acutely, so glasses can be put into various use considering their properties, sizes, thickness and the condition under which a given type is manufactured.

Joseph Fraunhofer (1787 – 1826) made accurate measurements of refractive indices for different colours and found that with flint glass, the results depended on the condition of manufacture.

Abbe and Scott (1870) described optical glasses in terms of their refractive index at the sodium D-line (589 Å) and "V" value known as Abbe number which is a measure of the dispersion or variation of index with wavelength. Furthermore, the refractive index as well as the dispersion of a glass is increased by increase in density. So heavy oxide glasses possess such qualities and are termed "flints" while glasses with low density are the "crowns". The chemical compositions and the size of the molecules due to greater number of outer electrons on the complex structural unit in the glass greatly affect the refractive index. Examples include sodium iodide (NaI) and

potassium iodide (KI) present in the composition greatly increase the refractive index, also the cations have greater effect on refractive index than the anions. (Bacanov, 1965).

Bacanov, (1965) showed that studies carried out on the refractive indices in various glass composition containing sodium, potassium, gold and barium, found that glass containing barium ions have higher refractive index of about 4.67. Othmer (1964) added that glasses with Abbe number 55 or above are defined as crown glasses; and those with Abbe number 50 are the flint glasses. Experiment conducted by Faraday on glasses resulted in the ultimate production of a glass of remarkable purity, consisting of silicate, lead and borate of lead. These materials were perfectly pure and melted in a platinum crucible, powdered spongy platinum being added to assist in the disengagement of any air bubbles, while the vitreous mass stirred with a platinum spatula.

Elliot and Smyth (1965) observed that the homogeneity of the materials in optical glasses have homogenous optical properties throughout the compositions and these can be detected by sensitive and elaborate instruments. To decrease the crystal capacity of the optical glass, Zimina (1965) observed that the composition of the batch has to contain 30 – 33% lead oxide (PbO) and 7 – 19% Barium oxide (BaO). Gastev (1968) continued that addition of 15 – 19% of BaO combined with other oxides lowers the softening point of the glass. Walter (1968) revealed that, the chemical durability or corrosion

resistance of many of such glass make them quite vulnerable because service problems are frequently encountered, this include weathering by atmospheric moisture and leaching during processing especially in polishing or handling.

Budd (1971) stated that the choice of a suitable optical glass composition however, will depend not only on these two important physical properties, refractive index and dispersion but on a number of auxiliary properties such as density and thermal endurance which are important in the final use of the glass. He further stated that glass for optical use falls into two general categories, which comprised of those used for the manufacture of spectacles and photographic lenses and those exemplified by driving mirrors used on automobiles and signal lenses.

Experiment carried out by Vasudaran and Krishnan (1972) on eighteen optical glasses of different compositions in the wavelength range of 3200 – 5700Å to determine their stress optic coefficient were all negative except for a high lead content glass of dispersion 6.7 and refractive index 1.89. The numerical value of the coefficient decreases as one proceeds to the ultraviolet. This behaviour is just the opposite of what is observed in fused silicon (iv) oxide, but by applying Mueller's theory the strain polarizability constant and is dispersion have been evaluated.

Masuda (1973) identified optical glasses which contains 5 – 18% BaO and 20 – 30% PbO to have high refractive index, low optical dispersibility and improved weathering resistance but Nagai (1975) observed that lead oxide

free optical glasses containing 40% BaO had a density of 3.32 g/dm^3 and a refractive index of 1.79. Tacheuchi (1975) in his research further observed that glasses with refractive index 1.68 – 1.85 and Abbe number 29 – 52 contain 5.5 – 60% Barium Oxide (BaO).

According to Vasil'Kova (1978) glasses containing 7 – 38% BaO have increased chemical resistance and refractive index while the dispersion coefficient and crystallinity were decreased but the dispersion near U.V, transmittance increases by 35 – 48% Barium Oxide. Fedrova (1978) observed that glasses containing 0.6 – 7 weight % by weight of BaO in its composition had improved refining and manufacturing properties. The translucency of such glasses also increased due to the presence of BaO.

Watzk (1979) contributed by adding that optical glasses with high chemical resistance is prepared from a composition of 43 – 45% BaO and refining agent of 0 – 1% Arsenic oxide and potassium iodide of 0.03% weight has refractive index of 1.62 and Abbe number 58.7.

Enomoto (1994) discovered that optical glasses comprising 37 – 55% BaO and other alkali metals have excellent chemical resistance but that with low percentage of BaO (0 – 5%) and high percentage of phosphate (40 – 53%) they have low refractive index and high dispersibility as well as devitrification resistance. Those with lead free composition have improved resistance against devitrification and light transmissivity.

It was found that optical containing Barium oxide and other elements or their oxides such as Na_2O , K_2O , ZnO was found to increase the optical properties such as refractive index and dispersion.

Although an optical glasses composition containing alkali metals but high percentage of BaO was found to have a refractive index of 1.54. Regression analysis revealed that optimization in imparting optical properties is also possible.

CHAPTER THREE

3.0 RESEARCH DESIGN, METHODS AND PROCEDURE

Research design as described by Afolabi (1963) is the plan, structure and strategy of investigation conceived so as to obtain answers to research questions and to control variance. In line with this, the following methods were adopted in this research.

- i) Population of the study.
- ii) Data collecting instruments/field work.
- iii) Data treatment and laboratory analysis.
- iv) Batch formulation and test melting.
- v) Property determination of the test melted products.

3.1 POPULATION OF THE STUDY

According to Nworgu (1991) a researcher can collect some information needed in one particular environment. Population of this nature are termed as accessible which in line with the research conducted on both the sand and the Baryte which was obtained from Kenyi and Azara respectively.

3.2 DATA COLLECTING INSTRUMENTS/FIELD WORK

The information and data used in writing this study were collected from various sources. These includes both primary and secondary sources. Pelto (1970) recommended the use of variety of instrument to give greater credibility to research result.

The secondary source of data collection were information obtained from available literature in published studies and texts, unpublished dissertation, these journals, conference and seminar papers. Documents from Raw-material Research Institute, Geological Survey and the Nigerian Mining Corporation were also utilized.

The primary source entails field study approach in order to determine the sources of the raw-material as it is available locally. At the site of the deposit diggers and shovels were used for collecting the samples at the surface and at a depth of about 0.5meter.

3.3 DATA TREATMENT AND LABORATORY ANALYSIS

For the purpose of this study, only one source of sand sample and also that of barite sample were treated and analyzed. The elemental and subsequent oxide composition of the various substances associated with each were determined because this will give a guide towards the batch formulation and also their interference with the optical activity of the glass produced.

3.4 ANALYSIS OF SAND SAMPLE

3.4.1 SAND SAMPLE AND SAMPLING TECHNIQUES

Kenner (1971) described proper sampling as a vital, pre-requisite for the analytical determination of elements.

The sample was collected at various distances apart, across the site of the deposit on the surface and at a depth of 0.5 metre this was done in such a way as to have representative sample from the site. Vogel (1962) explained sampling as the process of extracting from a large, a small portion which serve as good representative of the sample.

3.4.2 SIEVING

The sand sample was crushed sieved with British standard sieve (BSS) 20 mesh (0.5mm) for proper grain size distribution. Pott (1944) stated that proper sieving is necessary because the grain size determines the melting point of the batch. Particle sizes of 0.1 – 0.5mm in diameter makes melting of the batch to occur within a short time.

3.4.3 EXPERIMENTAL PROCEDURE

The sieved sample was dried, weighed on an Ohaus digital balance before being subjected for the chemical analysis to determine the metal oxides present in the samples using the Atomic Absorption Spectrophotometer, flame photometer and by complexometric titration using Ethylene Diammine Tera Acetic Acid (EDTA).

All determination of the moisture content, loss on ignition and oxides content were carried out in triplicate and the calculated average result reported.

3.4.4 DETERMINATION OF MOISTURE CONTENT

The moisture content is taken as loss in mass on heating at 105°C or 110°C to constant weight, it can be defined as the moisture observed or associated with the material and the water held by certain forces not much higher than the forces between the water molecules.

O'Brian (1971) described moisture content as the amount of moisture loosely held by the solid minerals which may be removed by simply heating to a temperature slightly above the boiling temperature of water.

3.4.5 PROCEDURE

1.0000g of the sample was weighed and kept in an oven at a temperature of 110°C for 2 hours. The sample was removed, cooled in a desiccator at room temperature. The process was repeated until constant weight was obtained. The result was calculated as:

$$\text{Percentage Moisture Content} = \frac{(\text{Weight loss at } 110^{\circ}\text{C})}{\text{Sample weight}} \times (100)$$

3.4.6 DETERMINATION OF LOSS ON IGNITION

The loss on ignition as described by Reed, et al (1971) is taken as the constant mass obtained on heating the sample at 1000°C. At this temperature

all organic matter, carbonates and sulphates decompose giving off gaseous by-products.

3.4.7 PROCEDURE

The sample after the moisture content determination was further heated in a platinum at 900°C in a muffle furnace for an hour, similar method was adopted for heating and reweighing as in the moisture content until a constant weight was obtained. The percentage loss on ignition was calculated and shown in table I as:

$$\text{Percentage Loss on ignition} = \frac{(\text{Weight loss at } 900^{\circ}\text{C}) \times (100)}{\text{Sample weight}}$$

3.4.8 DETERMINATION OF SODIUM AND POTASSIUM OXIDES

The sodium and potassium content of sand partly depend on the silicate material and primarily on the degree of weathering of the area where it was sourced. The potassium in sand is in non-exchangeable forms.

Williams (1962) further added that there are three types of compounds of potassium found in the sand, some are immediately available and water soluble while some are only slightly water-soluble.

3.4.9 PROCEDURE

All reagents used in the subsequent chemical analysis are of analytical grade (Analar grade) 0.10g of the sample was placed in a crucible and ignited at 1000°C for 10 minutes to destroy the organic matter. The crucible was

allowed to cool and 5ml perchloric acid added and was then heated on a hot plate to dissolve the sample. The solution was transferred into a 50ml volumetric flask and water added to mark. This served as the stock solution. Hesse (1971) stated that once sodium and potassium are in solution, they could be determined by spectrographic, volumetric, colorimetric and gravimetric methods. However, the flame photometric method has superseded the others for speed and convenience, as such it was the one adopted for this study.

3.5.0 METHOD OF CALIBRATION USING THE FLAME PHOTOMETER

The flame photometer was lit and air turned on by adjustment. Water was sprayed and gas flow adjusted to give well defined blue cone. It was then allowed to warm for 10 minutes before the appropriate filter was inserted into the filter apartment of the instrument.

The galvanometer reading was noted checking the top-scale and zero scale frequently, the part per million (ppm) of the element in the stock solution was obtained from the calibration curves in Fig. 1 for potassium and Fig. 2 for sodium from which the total ppm and subsequent oxide value for each element was determined using the following formula.

$$\text{Total ppm} = \frac{(\text{ppm of element in the sample}) \times (\text{Blank reading}) \times (\text{Volume of solution})}{(\text{photometer reading}) \times (\text{Initial weight of the sample})}$$

$$\text{Total ppm} \frac{(2.5) (18) (50)}{(50) (1) (0.10)} = 450$$

$$\text{Percentage Sodium (Na)} = \frac{\text{Total ppm}}{10^6} \times 100$$

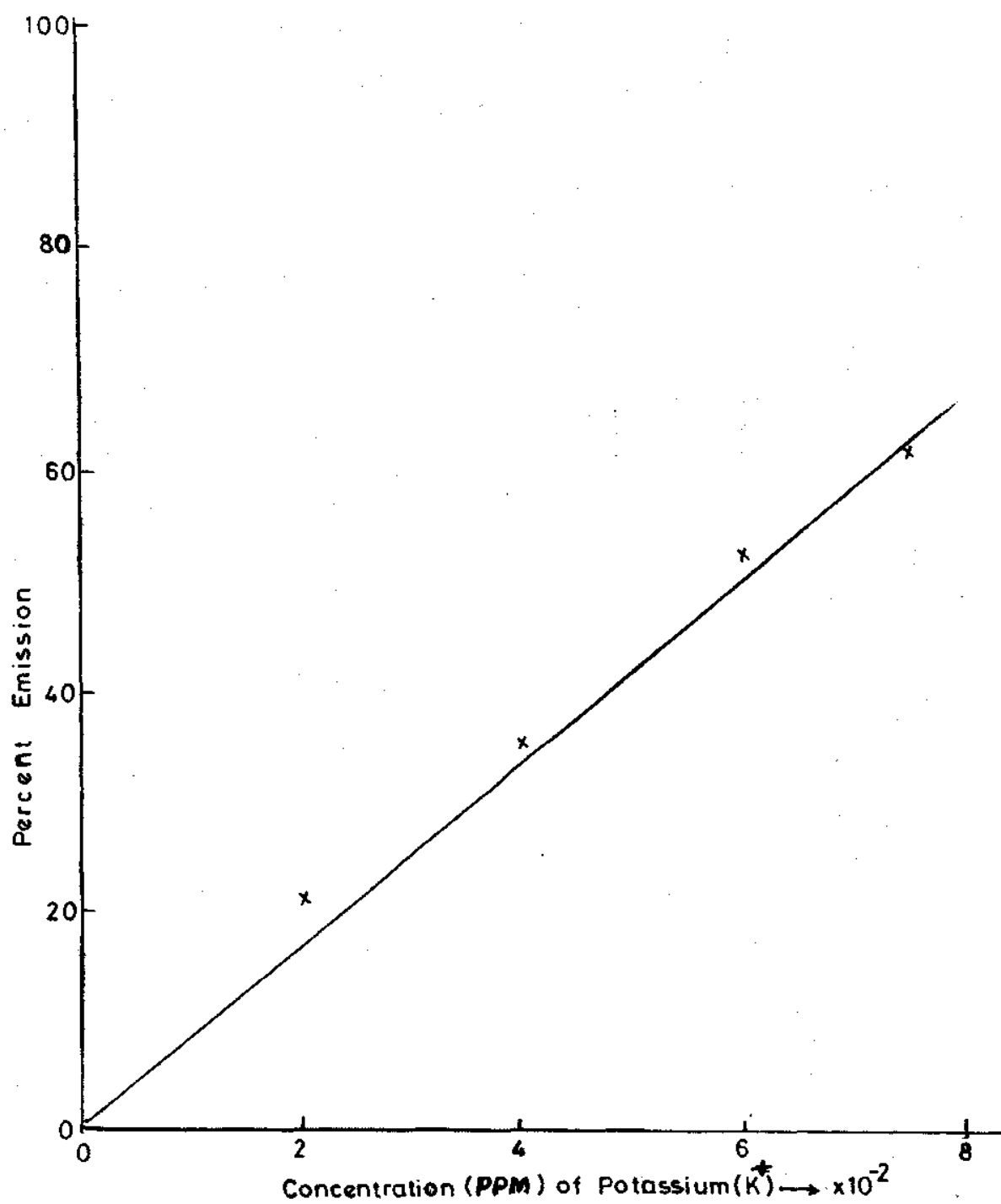


FIG.1:CALIBRATION CURVE FOR THE DETERMINATION OF POTASSIUM

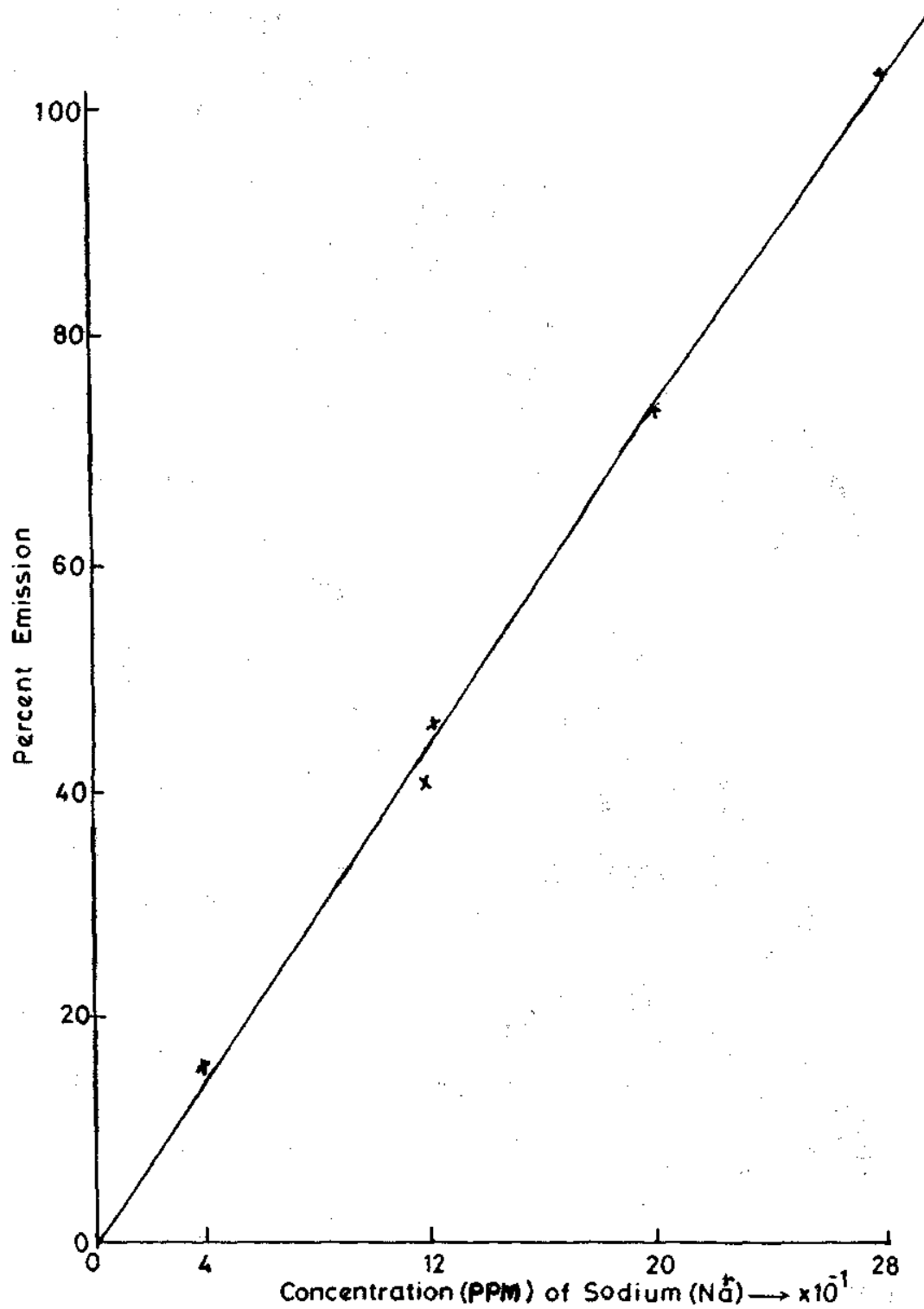


FIG-2: CALIBRATION CURVE FOR THE DETERMINATION OF SODIUM

$$\text{Percentage sodium oxide (Na}_2\text{O)} = \text{percentage} \times \frac{\text{Molar mass of Na}_2\text{O}}{\text{Atomic Mass of Na}}$$

The same formula was adopted for potassium and the values obtained for each code was recorded as shown in Table 1.

3.5.1 DETERMINATION OF CALCIUM AND MAGNESIUM OXIDES

Calcium and magnesium in sand occurs in combined form such as carbonates, phosphates and fluorides (Hesse *et al* 1971). The sample to be analyzed was brought into solution by digestion using perchloric acid as adopted after Allen *et al* (1974).

3.5.2 PROCEDURE

A stock solution was prepared and various concentrations (1 ppm – 8 ppm) were made and the Atomic Absorption Spectrophotometer (AAS) was used to measure the absorbance.

A graph of absorbance versus concentration was plotted to serve as the calibration curve and shown in figures 3 and 4. The elemental concentration and the oxides values were obtained using the formula as shown below.

$$\text{Total ppm} = \frac{\text{ppm of element in the sample} \times \text{Dilution factor} \times \text{Volume of sample in solution}}{(1) (\text{Sample weight in gram})}$$

$$\text{Total ppm of magnesium (Mg)} = \frac{1}{50} \times \frac{10}{1} \times \frac{50}{0.1} \times 0.5 = 0.5$$

$$\text{Percentage Magnesium} = \frac{\text{Total ppm}}{10^6} \times 100$$

$$\text{Percentage Magnesium Oxide} = \text{Percentage Magnesium} \times \frac{\text{Molar Mass of MgO}}{\text{Atomic mass of Magnesium}}$$

$$\text{Total ppm for Calcium} = \frac{0.1 \times 10 \times (50)}{0.1} = 500$$

$$\text{Percentage Calcium} = \frac{\text{Total ppm}}{10^6} \times 100$$

$$\text{Percentage Calcium Oxide} = \text{Percentage Calcium} \times \frac{\text{Molar Mass of Calcium Oxide}}{\text{Atomic Mass of Calcium}}$$

The value of each oxide are recorded in Table 1.

3.5.3 DETERMINATION OF IRON OXIDE (Fe₂O₃)

Iron is found in free or combined state in the form of oxide or in form of organic complexes. The compound of Iron in the sand affect the structures of the materials and also impart colour to the sand. Bennett (1971) explained that total iron in sand can be brought in solution by acid digestion or by fusion with sodium carbonate and Melnick (1963) discussed several methods of determining iron content once brought into solution. For the purpose of this work the Atomic Absorption Spectrophotometric method was used.

3.5.4 PROCEDURE

A mixture of 10ml stock solution with bromine water and 5ml KSCN solution was obtained as the standard solution. It was aspirated and the absorbance noted at 380nm. A graph was plotted for absorbance against concentration in ppm as indicated in Fig. 5 and the value of the ppm for the element was obtained from the graph and calculated as shown below:

$$\text{Total ppm of Iron (Fe}_2\text{O}_3) = \frac{(0.20) \times (50) (1)}{(0.1)} = 100$$

$$\text{Percentage Iron (Fe)} = \frac{\text{Total ppm}}{10^6} \times 100$$

$$\text{Percentage Fe}_2\text{O}_3 = \text{Percentage Fe} \times \frac{\text{Molar Mass of Fe}_2\text{O}_3}{\text{Atomic Mass of Fe.}}$$

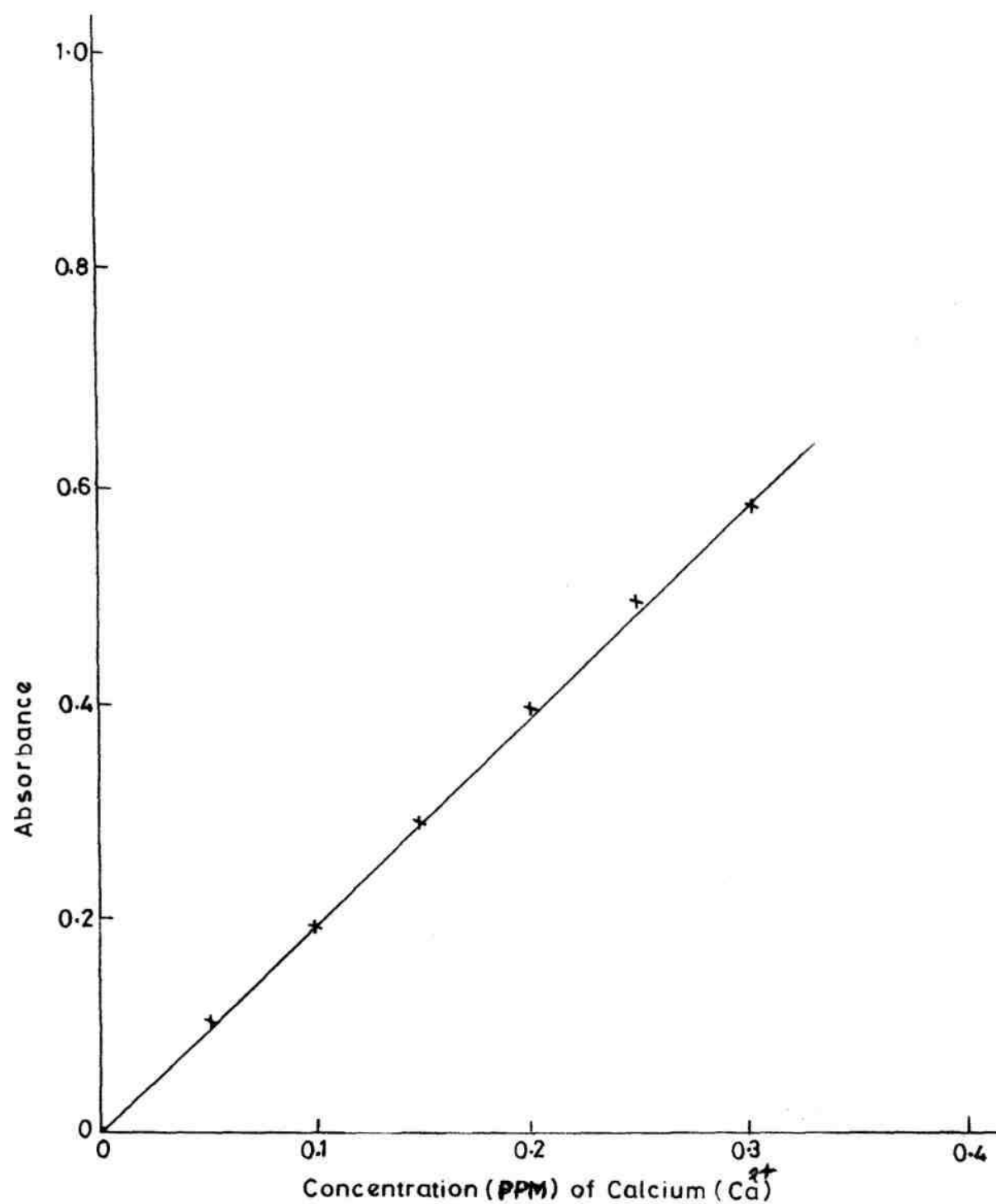


FIG.3: CALIBRATION CURVE FOR THE DETERMINATION OF CALCIUM

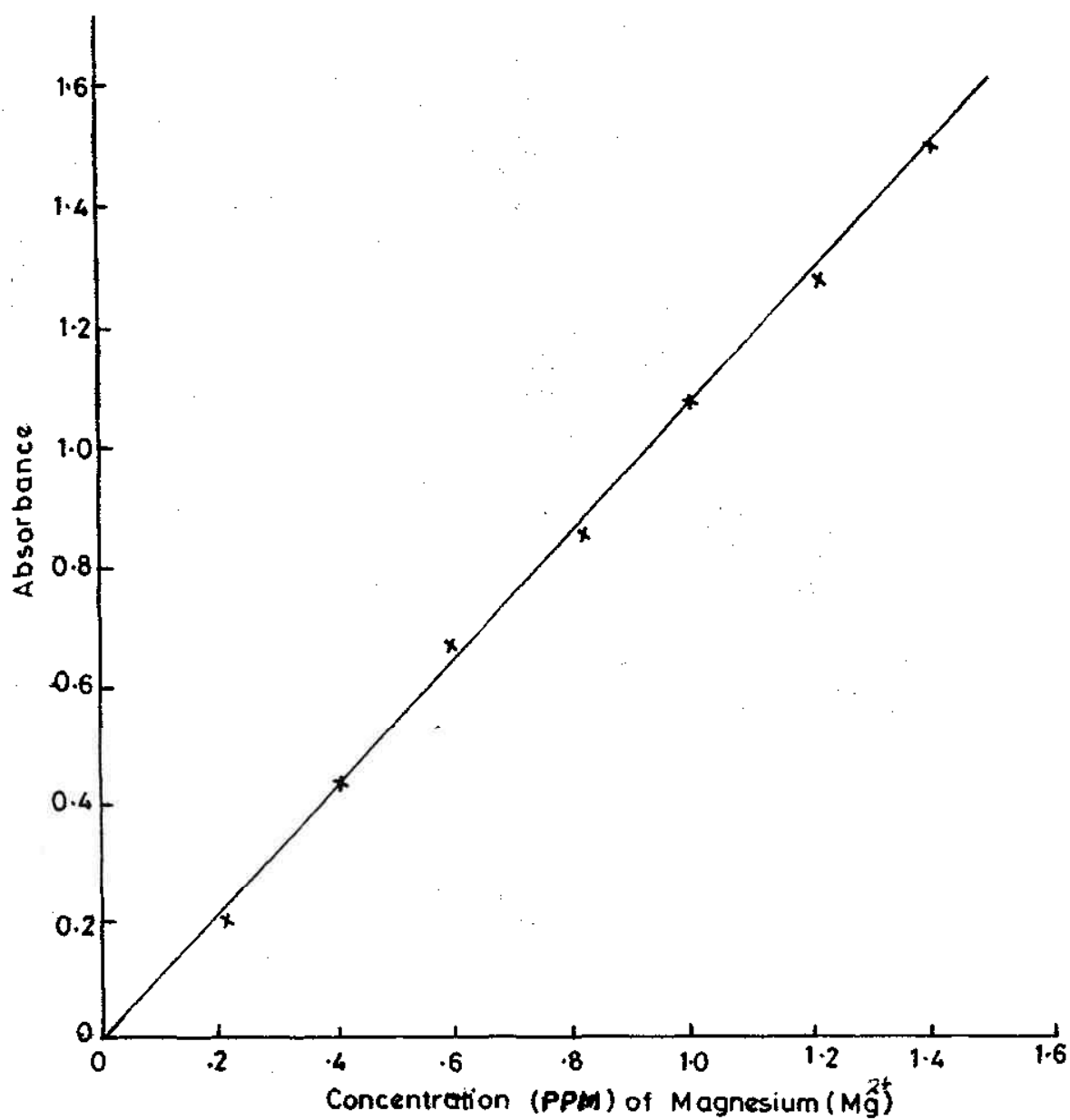


FIG. 4: CALIBRATION CURVE FOR THE DETERMINATION OF MAGNESIUM

3.5.5 DETERMINATION OF ALUMINA (Al₂O₃)

In the soil analysis carried out by E.O. McLean in 1965, it was pointed out that aluminum oxide (Al₂O₃) can be determined to a certain degree of accuracy by many different methods; interference of other ions makes the exact determination relatively difficult. But to minimize these interferences, volumetric method was adopted in this study as follows.

3.5.6 PROCEDURE

A stock solution of 25ml was pipetted into 250ml beaker and to it 4.00g of ammonium chloride (NH₄Cl) was added and a small quantity of ammonia solution (NH₃.H₂O) was added with drops of methyl orange as indicator. The solution was warmed and content was ashed at 800°C for an hour.

Percentage of Al₂O₃ was determined by the difference between the masses of empty crucible used and the crucible plus its content.

$$\text{Percentage Al}_2\text{O}_3 = \frac{(\text{weight of Al}_2\text{O}_3) \times (100)}{(\text{weight of sample})}$$

The result is indicated in Table 1.

3.5.7 DETERMINATION OF R_2O_3

R_2O_3 are the oxides of elements with +3 oxidation state. Fe_2O_3 and Al_2O_3 were already determined, R_2O_3 is obtained as follows:

$$Al_2O_3 = Fe_2O_3 + R_2O_3$$

$$R_2O_3 = Al_2O_3 - Fe_2O_3$$

Based on this, the result was obtained and recorded in Table 1.

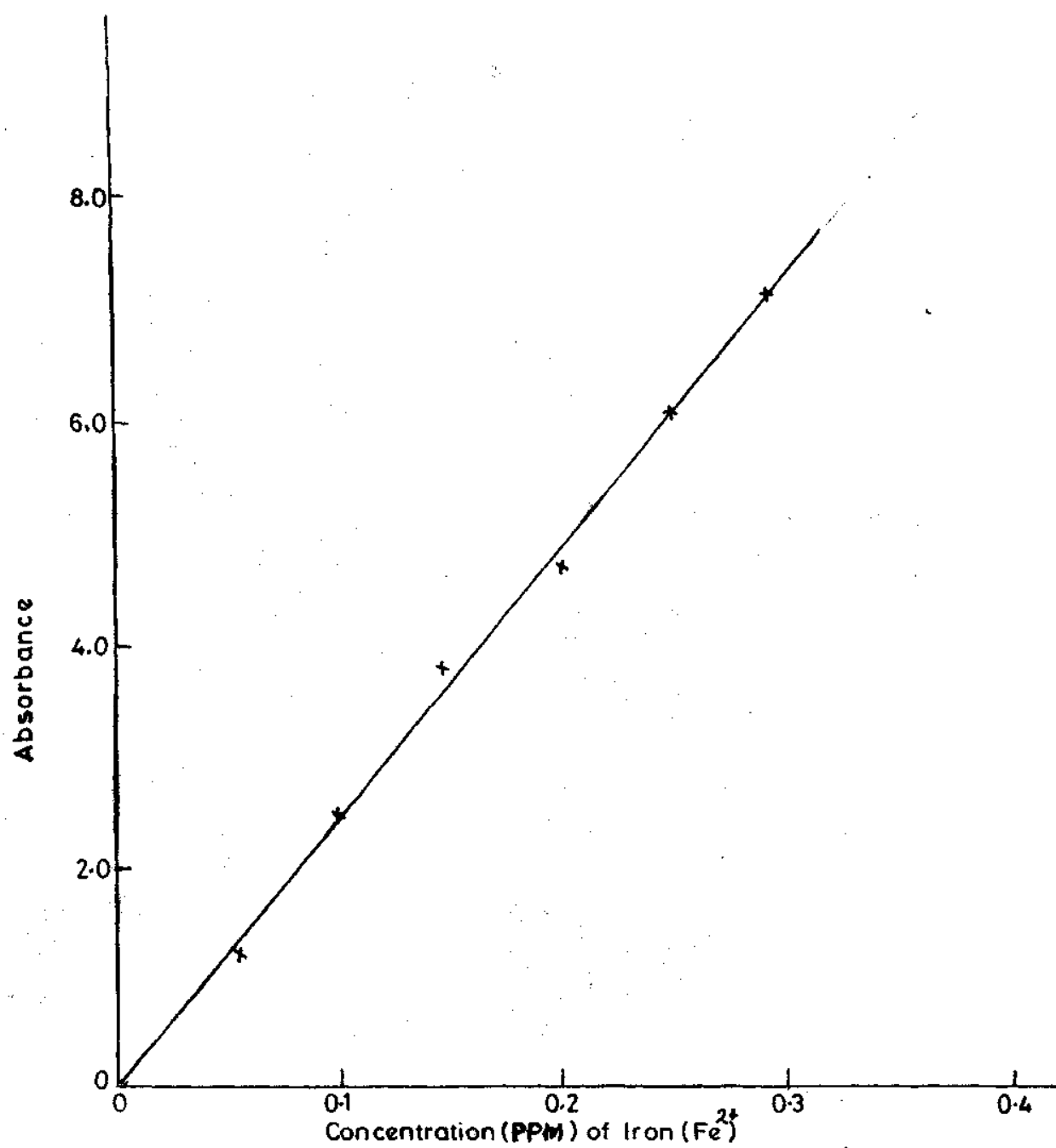


FIG.5: CALIBRATION CURVE FOR THE DETERMINATION OF IRON

3.5.8 DETERMINATION OF SILICA CONTENT (SiO₂)

The greater portion of any sand especially that used in glass production contains SiO₂, any other oxide in association is termed as an impurity. Snell (1973) determined silica content of sand by gravimetric method after fusion of the sand. A different approach which is also effective was applied in this analysis. The difference of the sum total of other oxides, moisture content and loss on ignition from 100%. This gave the actual percentage of the SiO₂ content which is recorded in table 1.

3.6.0 ANALYSIS OF BARYTE SAMPLES

3.6.1 BARYTE SAMPLES AND SAMPLING TECHNIQUES

Based on the report obtained from the Nigerian Mining Corporation (1988) the barite deposit comprises of exposed surface layers and the underneath layer. Each layer varies in composition of some elements ranging from sandstones, calcite, ironstone and galena. The degree of purity varies with depth, because the purest is found underneath, so the samples collected were from both layers.

3.6.2 LABORATORY ANALYSIS

It is mandatory to analyze and ascertain the proportion of the different elements or their oxides and other substances associated with the barite and this could be done after the screening analysis. Pott (1944) reported that

crushing and sieving of sample is the simplest method to be employed to screen solids to different grain sizes. The samples were crushed and sieved with BSS 20 mesh to obtain the required grain sizes for quick melting of the composition.

Table 1: Result of Sand Analysis

Oxides	Average Percentage Composition
Moisture content	0.018
Sodium Oxide (Na_2O)	0.121
Potassium Oxide (K_2O)	0.947
Magnesium Oxide (MgO)	0.008
Calcium Oxide (CaO)	0.056
Aluminum Oxide (Al_2O_3)	0.180
Iron Oxide (Fe_2O_3)	0.029
Silica (SiO_2)	98.39
R_2O_3	0.151
Loss on ignition	0.099

**** Other oxides with the oxidation number + 3.**

3.6.3 EXPERIMENTAL PROCEDURES

The two samples, the lower layer sample A and the upper layer sample B were both analyzed for oxide contents using the method reported by Snell and Etere (1973). For each sample, three separate analyses using the same mass and the average result of each determination was taken and the values recorded in Tables II and III respectively.

All the metal oxides determination of the samples was done using the Atomic Absorption Spectrophotometer and the reagents used are of Analytical grade (Analar).

3.6.4 MOISTURE CONTENT AND LOSS ON IGNITION DETERMINATION

1.0000g of each sample were placed in different crucibles, heated at 110°C for 2 hours cooled in a desicator and weighed. This was repeated until constant weight was obtained, and the value for moisture contents calculated as:

$$\text{Percentage moisture} = \frac{(\text{weight loss at } 110^{\circ}\text{C}) \times (100)}{\text{Sample weight}}$$

The dried samples from the moisture content determination was transferred into a muffle furnace and ignited at 800°C for 2 hours, cooled and

weighed. This was again repeated until constant weight was obtained and the result calculated as:

$$\text{Percentage loss on ignition} = \frac{(\text{weight loss at } 800^{\circ}\text{C}) \times (100)}{\text{Sample weight}}$$

3.6.5 DETERMINATION OF SILICA CONTENT

PROCEDURE

The residues obtained from the loss on ignition were dissolved by adding concentrated H_2SO_4 . It was evaporated to dryness, heated further strongly to expel all SO_3 fumes and further ignited in a muffle furnace at $800 - 900^{\circ}\text{C}$ for 30 minutes. The residues were dissolved in 10ml 48% Hydrofluoric acid. It was evaporated to dryness, allowed to cool and 5ml HF was again added, evaporated to dryness, ignited, cooled and weighed.

The loss in weight was calculated as percentage silica as shown below:

$$\% \text{ Silica} = \frac{(\text{weight loss}) \times (100)}{\text{Sample weight}}$$

Subsequent determination of other elements and their oxides was done by the use of the product of fusion and leaching of the residues obtained from the silica determination.

3.7.0 FUSION AND LEACHING PROCEDURE

About 10.00g of sodium carbonate (Na_2CO_3) were added to the residue from the silica determination. The mixture was thoroughly mixed and fused to about 45% of the size in a crucible, cooled and the fusion cake removed from the crucible with hot water, transferred into a 250ml beaker; water was added to make the volume to 100ml and further digested on a steam bath with occasional stirring.

The supernatant liquid was decanted from the leached residue and filtered, washed with 2% Na_2CO_3 . The filtrate was collected in a beaker labeled A while the residue B the residue was dissolved in a 100ml beaker of 10% dilute hydro chloric acid (HCl) and then digested to near boiling for 30 minutes and then filtered, transferred into another crucible and ignited. The residue then reserved, the filtrate was diluted to 100ml and used for the determination of Fe_2O_3 , Al_2O_3 , MgO , CaO , Na_2O , K_2O and BaO . The effect of other interfering elements like lead and nitrates were removed by perchloric acid during digestion.

3.7.1 DETERMINATION OF ALUMINUM OXIDE (Al_2O_3)

50ml of the aliquot was transferred to a beaker containing the filtrate. 100ml of water was added and heated, 2 drops of methyl orange added as indicator to sodium hydroxide (NaOH). The solution was digested to boiling for 5 minutes, it was filtered and precipitate washed 5 times with 2% NH_4Cl

and then transferred into a crucible, ignited at 900°C for an hour and weighed.

The value calculated as:

$$\% \text{Al}_2\text{O}_3 = \frac{\text{weight of residue} \times 100}{\text{Sample weight}}$$

3.7.2 DETERMINATION OF Fe₂O₃, CaO AND MgO

For the determination of Iron, calcium and magnesium, the use of Atomic Absorption Spectrophotometer was adopted for accuracy. The filtrate from the result of fusion was used as the stock solution which was sprayed into the instrument alternately corresponding with the lamps for the elements. The content in ppm of the elements was obtained from the calibration curve in Figures 3, 4 and 5.

The percentage oxides values are calculated using the formula below:

$$\text{Total ppm} = \frac{(\text{conc. ppm of element}) (\text{Dilution}) (\text{Volume of sample in solution})}{(\text{Sample weight})}$$

$$\text{Total ppm in Calcium} = \frac{(0.2) (50) (1.0)}{(0.1)} = 100$$

$$\text{Percentage Calcium (Ca)} = \frac{\text{Total ppm}}{10^6} \times 100$$

$$\text{Percentage CaO} = \text{Percentage Ca} \times \frac{\text{Molar Mass CaO}}{\text{Atomic Mass of Ca}}$$

$$\text{Total ppm for Magnesium} = \frac{(0.1) (50) (5.0)}{(0.1)}$$

$$\text{Percentage Magnesium (Mg)} = \frac{\text{Total ppm}}{10^6} \times 100$$

Percentage Magnesium oxide

$$(\text{MgO}) = \text{Percentage Magnesium} \times \frac{\text{Molar Mass of MgO}}{\text{Atomic Mass of Mg}}$$

$$\text{Total ppm for Iron} = \frac{(0.1) (50) (2.0)}{0.1} = 100$$

$$\text{Percentage Iron} = \frac{\text{Total ppm}}{10^6} \times 100$$

Percentage Iron (III) oxide

$$\text{Fe}_2\text{O}_3 = \text{Percentage Fe} \times \frac{\text{Molar Mass of Fe}_2\text{O}_3}{\text{Atomic Mass of Fe}}$$

3.7.3 DETERMINATION OF SODIUM, POTASSIUM AND BARIUM

The aliquot obtained from the result of the leaching was used for the determination using the flame photometer.

The ppm of the element was obtained from a curve plotted by emission against concentration as shown in Figures 1 and 6. The total ppm was calculated as shown below:

$$\text{Total ppm} = \frac{(\text{ppm of element}) \times (\text{Dilution}) \times (\text{Volume of sample in solution})}{(\text{Sample weight})}$$

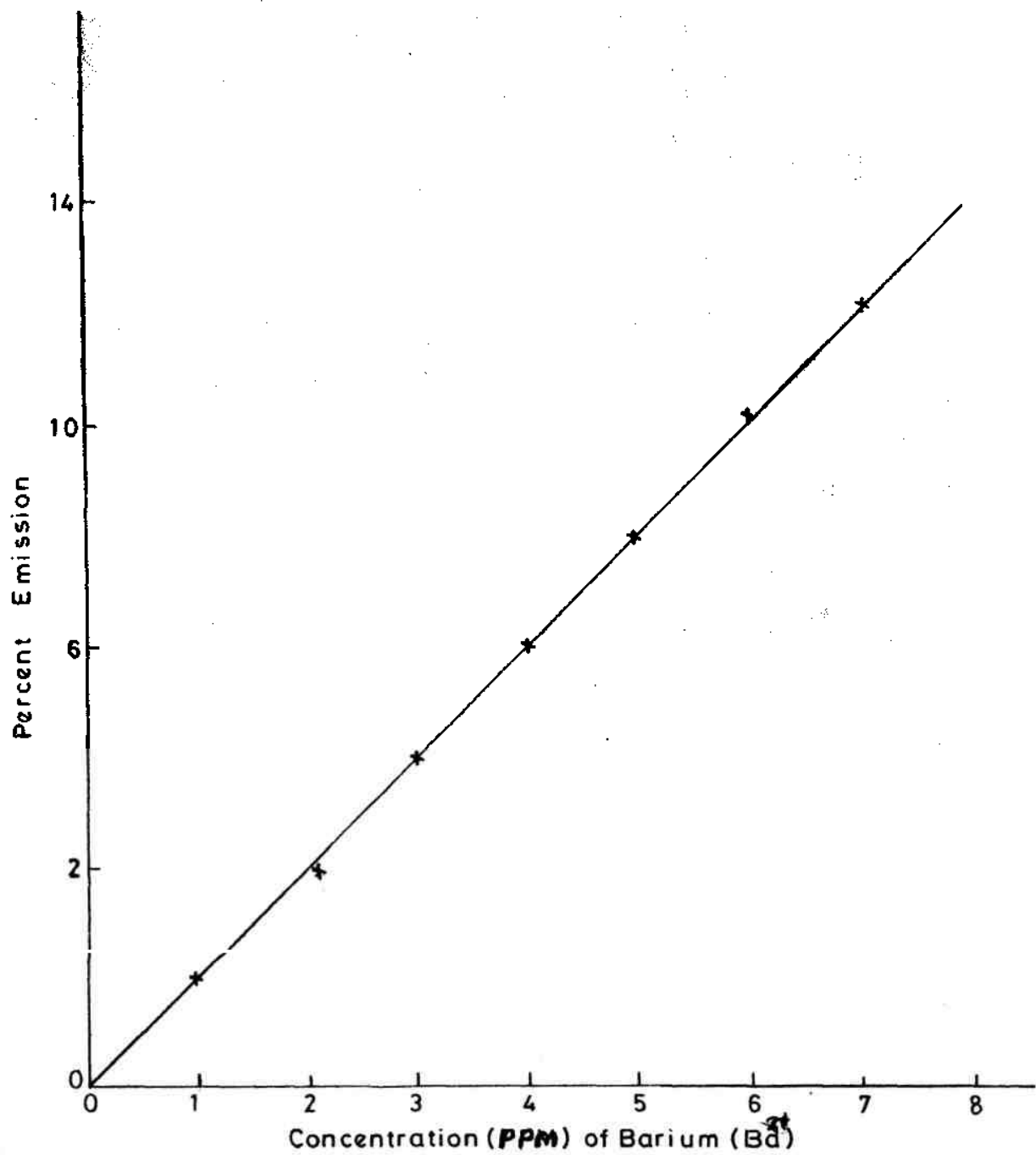


FIG.6; CALIBRATION CURVE FOR THE DETERMINATION OF BARIUM

$$\text{Total ppm for Sodium (Na)} = \frac{(0.1)(50)(2.5)}{(0.1)} = 125$$

$$\text{Percentage Sodium} = \frac{\text{Total ppm}}{10^6} \times 100$$

Percentage Sodium Oxide

$$(\text{Na}_2\text{O}) = \text{Percentage Na} \times \frac{\text{Molar Mass Na}_2\text{O}}{\text{Atomic Mass Na}}$$

$$\text{Total ppm of potassium (K)} = \frac{(0.083)(50)(1.5)}{(0.1)} = 62.25$$

$$\text{Percentage Potassium (K)} = \frac{\text{Total ppm}}{10^6} \times 100$$

Percentage Potassium Oxide

$$\text{K}_2\text{O} = \text{Percentage Potassium} \times \frac{\text{Molar Mass K}_2\text{O}}{\text{Atomic Mass of K}}$$

3.7.4 DETERMINATION OF BARIUM

$$\text{Total ppm} = \frac{(8.052) \times (100) \times (50)}{(1)(5)} = 8052$$

$$\text{Percentage Barium} = \frac{\text{Total ppm}}{10^6} \times 100$$

Percentage Barium Oxide

$$\text{BaO} = \text{Percentage Barium} \times \frac{\text{Molar Mass BaO}}{\text{Atomic Mass Ba}}$$

3.8.0 BATCH FORMULATION AND TEST MELTING

Glass production is only successful when appropriate batch is formulated and this can only be realized by detailed knowledge of the raw material compositions, obtained by analysis. Samuel (1974) reported that when glasses are known by their composition it becomes possible to modify them intelligently and to vary the materials in which the different oxides are introduced while maintaining a predetermined composition in the final product.

Table II: Result of Baryte Sample A

Oxides	Average Percentage Composition
Moisture content	0.020
Barium Oxide (BaO)	89.880
Sodium Oxide (Na ₂ O)	0.025
Potassium Oxide (K ₂ O)	0.015
Magnesium Oxide (MgO)	0.040
Calcium Oxide (CaO)	0.014
Aluminum Oxide (Al ₂ O ₃)	0.620
Iron Iodide (Fe ₂ O ₃)	0.028
Silica (SiO ₂)	9.310
Loss of ignition	0.060

Table III: Result of Baryte Analysis Sample B

Oxides	Average Percentage Composition
Moisture content	0.026
Barium Oxide (BaO)	65.020
Sodium Oxide (Na ₂ O)	0.028
Potassium Oxide (K ₂ O)	0.001
Magnesium Oxide (MgO)	0.024
Calcium Oxide (CaO)	0.006
Aluminum Oxide (Al ₂ O ₃)	16.620
Silica (SiO ₂)	18.120
Iron Oxide (Fe ₂ O ₃)	0.029
Loss on ignition	0.044

Optical glass which is the type that is intended in various optical instrument is also characterized primarily by its homogeneity and must also posses definite optical properties which are secured by its treatment during melting and annealing and a more careful selection and compounding of the batch material than any other variety of glass.

3.8.1 BATCH CALCULATION AND FORMULATION

Three batches were formulated and the different compositions were obtained from the percentage of the oxides in the two raw materials, that is the sand and the baryte. The sum total of individual oxide in each case was taken as the oxide composition in the batch.

i) Batch I

The oxide calculation in this batch was based on 66.27% SiO_2 from 65.00g of the sand and 22.47% BaO obtained from 25.00g of the baryte. The various oxides compositions were computed from the masses of the baryte and the sand. Their values was indicated on Table IV^A. The sum total of the oxides amounts to 85.82%, the composition by mass is as shown in Table IV^B.

ii) Batch II

The calculation was based on 67.90% SiO_2 and 9.88% BaO obtained from 69.00g of sand and 11.00g of barite respectively. The various oxide compositions includes zinc oxide (ZnO) and Borax ($\text{Na}_4\text{B}_2\text{O}_7$) which introduces Boric oxide (B_2O_3) was introduced as fining and fluxing agents respectively. These gave a total of 89.98% and the balance distributed to sodium and potassium based on their ratio in their composition. The appropriate percentage composition of the oxides is shown in Table V^A and the composition by mass shown in Table V^B.

Table IV^A – Percentage Oxide Composition of Batch I

Oxides	Percentage
SiO ₂	66.270
BaO	22.470
Na ₂ O	1.880
K ₂ O	13.010
Al ₂ O ₃	0.330
CaO	0.044

Table IV^B – Composition by Mass of Batch I

Oxides	Average Percentage Composition
Sand	65.00
Baryte	25.00
Sodium Carbonate (Na ₂ CO ₃)	1.05
Potassium Hydrogen Carbonate (KHCO ₃)	26.41

Table V^A – Percentage Oxide Composition of Batch II

Oxides	Percentage
SiO ₂	67.90
BaO	9.88
Na ₂ O	1.52
CaO	0.04
K ₂ O	9.17
Al ₂ O ₃	0.19
ZnO	7.70
B ₂ O ₃	3.50

Table V^B – Composition by Mass of Batch II

Raw material	Masses in gram
Sand	69.00
Baryte	11.00
Sodium Carbonate (Na ₂ CO ₃)	2.850
Potassium Hydrogen Carbonate (KHCO ₃)	11.860
Borax (Na ₂ B ₄ O ₇)	18.210
Zinc Carbonate (KHCO ₃)	5.050

iii) Batch III

The calculation was based on 60.00% SiO₂ and 12.13% BaO obtained from 59.70G of sand and 13.50g barite. The various oxides composition, which includes ZnO, gave a total sum of 80.70% and the remaining balance of

19.30% was also rationed among sodium and potassium. The appropriate percentage composition of the oxides and their composition by mass are shown in tables VI^A and VI^B respectively.

The rationing of the remaining balance in all the three batches is only among potassium and sodium and this is principally due to their important property of increasing fusion of the batch.

Samuel (1974) explained that calcium and aluminum oxides in excess in any batch composition might lead to devitrification, so their proportion in the raw materials is within the range that minimizes the defect.

The compositions by mass of the oxides in the batches were introduced in the form of their salts in grams. Na₂O in form of Na₂CO₃, K₂O in form of KHCO₃, ZnO form ZnCO₃ and B₂O₃ in the form of borax (Na₄B₂O₇). The oxides were obtained based on their decomposition from their Stoichiometric equations.

3.8.2 TEST MELTING

All the three formulated batches were heated in an open refractory crucible in an electric furnace (carbolite) of heating capacity 1,200°C at a temperature of 1,175°C for 24 hours.

Table VI^A – Percentage Oxide Composition of Batch III

Oxides	Percentage
SiO ₂	60.00
BaO	12.13
K ₂ O	17.62
Na ₂ O	2.33
CaO	0.04
Al ₂ O ₃	0.19
ZnO	7.70

Table VI^B – Composition by Mass of Batch III

Raw material	Masses in gram
Sand	59.70
Baryte	13.50
Sodium Carbonate (Na ₂ CO ₃)	3.85
Potassium Hydrogen Carbonate (KHCO ₃)	36.35
Zinc Carbonate (KHCO ₃)	11.86

The composition, after heating, batches II and III melted completely but batch I only sintered. Another set of similar batches were gas-fired in locally constructed kiln at 1,350°C and all melted, but with a lot of impurities, which might have come from the gas or from the kiln.

3.9.0 TESTING OF PROPERTIES

The three major properties associated with an optical glass are dispersion, refractive index and density; the latter two properties are linearly related. But refractive index is the most important property, which qualifies a glass for optical use, so the refractive index and density were measured in addition to the thermal endurance, which was also determined so as to find the effect of heat on the final product due to the nature of our environment or the climatic condition.

The refractive index and density were measured using liquids of relatively high refractive index and density as applied by Debussy (1971). For the purpose of these determination series of liquids like carbon tetrachloride, tetrachlorethane and bromoform were employed. But bromoform was found to be suitable and was used.

3.9.1 DENSITY DETERMINATION

The density was determined by placing a piece of the glass produced in bromoform of 20ml. Glass floats at room temperature and immediately sinks by elevating the temperature by 2 – 3°C. This indicates that the density of the glass is approximately same as that of the bromoform at the elevated temperature. In this way the density of the glass samples were obtained by a method which according to Winkle mann and Schott (1974) is a very accurate

method of density determination. To further prove this assertion, the method of calculating this density was adopted as follows:

$P_1 P_2 \dots P_x$ are the respective percentages of the oxides in the glass.

$d_1 d_2 \dots d_x$ are the corresponding density factors of the oxides, as shown in appendix I.

The density of the glass is given by formula $\frac{100}{D} = \sum \frac{p}{d}$

where D = density of the glass.

3.9.2 REFRACTIVE INDEX DETERMINATION

The refractive indices of the pieces of glasses of batches II and III was each determined by submerging the piece of the glass in bromoform liquid and then heated for 5 minutes and when viewed from the top the glass underneath was blurred at a temperature of 35°C, indicating that the refractive index of the glass approximates that of the liquid as proposed by Debussy (1971). This method was based on the law of refraction as a result of the differences of densities of the two media.

3.9.3 THERMAL ENDURANCE

This property was determined using the formula $F = \sum P_i a_i$ where,

P = Percentage of the oxide in the composition.

a = Thermal endurance factor of the oxides in the glass, as shown in

f = Thermal endurance expressed in percentage.

The values were substituted in the formula and evaluated for the two batches II and III the results recorded in Table VII.

Table VII: Results of Refractive Indices, Densities and Thermal Endurance of Batches I, II and III

Batch Number	Density g/cm ³	Refractive Index	Thermal Endurance
*I	-	-	-
II	2.75	1.49	99.20
III	2.78	1.54	88.60

* The batch sintered, no glass was formed.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

The application of any raw material in any production depends on so many factors. For optical glasses, the purity and nature of the composition is very important, prior to the formation of the glass from the raw materials, chemical analysis, to ascertain the proportion of the oxides was conducted on the two major raw materials, the sand and the baryte used in this study.

4.1 SIEVING

Proper screening analysis is an important factor for homogeneous melting of a glass composition. Pott (1944) explained that particle sizes of 0.5mm in diameter obtained by using the British standard sieve of 20 mesh were found to give a well melted glass. Manring (1964) have earlier stated that grains of this size, when properly mixed permits rapid reaction at initial stage, which is an important stage for proper sintering of the batch.

4.2 MOISTURE CONTENT AND VOLATILE MATTER

The sand and the baryte samples A and B contains 0.018, 0.020 and 0.026 respectively. These values are very low and it is an indication that hygroscopic and deliquescence substances if at all present are in a very low

quantity. The low content is also an advantage on the application of the product under humid atmosphere.

The volatile matters content is also low as revealed by the low value of loss on ignition, this shows that there is low organic materials.

4.3 CHEMICAL ANALYSIS

The result of the analysis of the sand and the two baryte samples are tabulated in Tables I, II and III. The three samples were analyzed for the oxides that are principally needed in the glass batch due to the role they play in the glass production, particularly in optical glass, which is the focus of this study.

Iron III oxide (Fe_2O_3) is known to impart colour, which is quite a nuisance particularly in optical glass production, but its presence in the samples is in low concentration, which will not interfere with the product.

Other oxides such as Magnesium oxide (MgO) and Aluminum oxide (Al_2O_3) according to Samuel (1994) if present in high concentration may affect the homogeneous melting of the glass their presence in a reasonably low concentration is that the above condition is overcome.

Oxides like Calcium oxide (CaO), Potassium oxide (K_2O) and Sodium oxide (Na_2O) are needed in the production to act as fining and fluxing agents. The proportion of these oxides in the raw materials is within permissible range to impart the two desirable properties.

The silica content of the sand as revealed in Table I is pure enough for optical glass production and the proportion of the oxide in the two raw materials will augument. The percentage proportion of the sand in the batch to almost 100%. For the purpose of this study sample A of the baryte was used in conjunction with the sand to formulate batches for the glasses produced. This is mainly due to the high content of Barium oxide (BaO), low Fe_2O_3 and Al_2O_3 in the samples.

4.4 BATCH FORMULATION

The results of chemical analysis provide a guide for appropriate batch composition and formulation. The oxides content of the samples leads to the amount of each individual oxide to be added in the batch.

Samuel (1974) related that to formulate a batch composition for optical glass is a tedious process that involves trial and error to arrive to a composition that melt to produce a glass of required optical properties. The two major optical properties that are required to qualify a glass for optical use are refractive index and dispersion. Density is also a property that has linear relationship with refractive index so its determination can invariably leads to that of refractive index.

After the work of Abbe and Scott (1870) on optical glass production, it was later found that these properties can be imparted to a glass by incorporating heavy metal oxides in the batch formulation. The heavy metals

mainly used for optical glass production are the Lead and Barium, even though Lead has an advantage over barium, but the later also has an advantage over the former because it does not corrode refractories during the melting process at the production line.

Zimina (1965) and Walter (1968) produced optical glasses containing 5 – 50% Barium oxide and the products gave a glass of 1.79, which is high for optical activity.

In this study three batches were formulated containing BaO of 22.47%, 9.88% and 12.13%. The batch constituents include Na₂O, K₂O, Al₂O₃, SiO₂ and CaO. For batch I the proportion of Na₂O is low while B₂O₃ and ZnO were not added because the batch was formed based on the oxides analyzed in the two raw materials only. Na₂O and K₂O play the role of fluxing agents; their proportion was raised compared to the other components in the batch.

In batch II the percentage of BaO was lowered and SiO₂ raised to 67.90%, Na₂O concentration decreases as well as K₂O but ZnO and B₂O₃ were introduced for their role as fining and fluxing agents respectively.

In the case of batch III the percentage compositions of BaO was raised so as to test its effect in increasing refractive index, B₂O₃ was removed from the composition because it enhanced refractive index and so as to ascertain the effect of the BaO alone.

The proportion of Al_2O_3 and CaO in all the three batches were not altered because their proportion in whatever composition are enough for glass production.

4.5 TEST MELTING

The three batches formulated were test melted in an electric furnace of capacity of 1200°C for 24 hours. Batch I sintered, this may arise due to insufficient temperature and more importantly the low percentage of fluxing agents.

The two batches II and III all melted at 1175°C due to the effect of Na_2O , K_2O and B_2O_3 , which act as fluxing agents in the batches.

The result of this test melting is remarkable because it was produced at a relatively low temperature; this is due to the fact that the two batches were well formulated with appropriate compositions. The same set of batches was subjected to gas firing in a locally constructed kiln for 24 hours. The batches melted to a viscous reddish brown paste, this indicates the presence of contaminants either from the gas nozzle or from the furnace roof.

4.6 TESTING OF PROPERTIES

The three main properties tested, refractive indices, densities and thermal endurance of the two melted batches. The refractive index of the two

batches (II and III) is greater than 1.4. Samuel (1974) explained that the minimum value to qualify a glass as an optical glass is 1.4 to 1.7.

Glasses with refractive indices below 1.50 are termed as light crown glasses and those with above 1.50 are said to be barium crowns. So the glasses produced in bath II falls into the former category while batch III falls into the later category. This classification is based on peddle's classification of optical glasses.

The result of density determination for the two glasses formed also falls within the Peddle's classification.

The results for the properties, that is refractive index and density from the batches formulated and the composition of the raw materials showed that an optical glass can be produced from it.

The result of the thermal endurance as indicated in Table XII showed that the two glasses have a very high thermal endurance. The low thermal endurance in batch III compared to batch II is due to the absence of borax (B_2O_3), which was removed so as to establish its role in increasing refractive index, which was found to be insignificant.

Greater thermal endurance is associated with glasses containing low alkali and high ZnO , B_2O_3 , Al_2O_3 and (Samuel 1974).

CONCLUSION

The availability of the two raw materials, their purity especially the low iron content and the high refractive index of the glass produced and baryte concentration in the batch indicated that the raw materials can be used to produce the optical glass locally.

The melting of the batch at a very low temperature showed that the material could be produced at a minimum cost.

RECOMMENDATIONS

Based on the findings and conclusions drawn from the study, the following recommendations are made:

1. More deposits of the raw materials should be sourced so as to undergo large-scale production.
2. Comprehensive investigation should be taken on other properties such as dispersion.
3. There is the need to mould the glass produced into various shapes, polished and determine the focal length for their appropriate use.

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Appendix 1: Oxides in the batches and their respective density factors

Oxides	Density
SiO	2.3
Na ₂ O	2.6
K ₂ O	2.8
CaO	3.3
Al ₂ O ₃	4.1
BaO	7.0
B ₂ O ₃	1.9
ZnO	5.9

Winklemann & Schott

Appendix 2: Thermal Endurance Factors for Oxides in the batches

Oxides	Density
SiO ₂	1.23
CaO	0.48
Al ₂ O ₃	1.00
B ₂ O ₃	0.90
BaO	0.65
ZnO	0.60
Na ₂ O	0.52
K ₂ O	0.05
ZnO	

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Appendix 3:

Table 1 for PPM and percentage emission for Potassium, Sodium

Potassium

PPM $\times 10^{-2}$	2	4	6	8
% emission	20	36	56	64

Sodium

PPM $\times 10^{-1}$	4	12	20	28
% emission	18	38	70	98

PPM and absorbance for calcium, magnesium and iron

Calcium

PPM $\times 10^{-1}$	1	2	3	4
Absorbance	0.2	0.4	0.6	0.8

Magnesium

PPM $\times 10^{-1}$	1	2	3	4
Absorbance	2.5	5.0	6.0	

Iron

PPM $\times 10^{-1}$	2	4	6	8	10	12
Absorbance	0.2	0.4	0.6	0.8	1.0	1.2

PPM and percentage emission for Barium

PPM	2	4	6	8
% emission	2	6	8	64