SOME PHYSICAL AND CHEMICAL ANALYSIS OF EDIBLE OIL EXTRACTED FROM DIFFERENT VARIETIES OF GROUNDNUTS

BY

ZARMAI SAIDU (B.SC APPLIED CHEMISTRY)
(M.TECH/SSSE/016/96)

A RESEARCH PROJECT REPORT SUBMITTED TO THE DEPARTMENT OF CHEMISTRY, SCHOOL OF SCIENCE AND SCIENCE EDUCATION, FEDERAL UNIVERSITY OF TECHNOLOGY, MINNA

IN PARTIAL FULFILLMENT OF THE REQUIREMENT FOR THE AWARD OF THE MASTER'S DEGREE OF TECHNOLOGY IN ANALYTICAL CHEMISTRY

MARCH, 1998.

CERTIFICATION

This research work has been approved as meeting the requirements of the Department of Chemistry of the Federal University of Technology, Minna for the Award of M.Tech. in Analytical Chemistry.

Dr. M. A. T. Suleiman
(Supervisor)

14th December, 1998
Date

Dr. A. A. Faroq
(Head of Department)

Date

External Examiner

Date

Professor J. M. Baba
(Dean, SSSE)

Date

DEDICATION

This thesis is dedicated to Almighty Allah, the Sustainer, the Nurisher for guiding me always and to my Late Father and Mother for giving me a wonderful life.

ACKNOWLEDGMENT

Thanks and Glory be to the Almighty Allah for whose blessings and mercy were my main inspiration and encouragement that provided the drive to undertake the present study.

My profound gratitude goes to my supervisor Dr. M.A.T Suleiman for his utmost endeavor and admiration despite his engagement in other routine activities of the university. The successful completion of this work within reasonable period is by and large due to his immense sacrifies and dedication. May Almighty Allah bless him in relative abundance. Ameen. I am equally indebted to Dr. A. A. Faroq, the Head of Department of Chemistry for his professional criticisms and advice towards perfecting this work. I am also grateful to the members of academic staff in the department: Mr. P.E.A Ako, Professor M. A. Olatunji, Mr. G. O. Adesina, Dr. E. R. Sadiku, just to mention a few for their eminent contributions.

My special thanks go to the family of Sarkin Ruwa Wana with special recognition to my brothers and sister especially Bazakore, Arewa, Safiya and Lamide for their financial support toward my education. I also acknowledge my uncles particularly Mallam Mohammed Sabo Wana and Late Alhaji Usman Musa Kuta (may his soul rest in perfect peace) for their fatherly advice and

participation in furthering my studies. My thanks also go to my wife, Mallama Hindatu for her understanding, patience and family support without which my work would have been impossible.

My appreciation will not be complete without mentioning the non-teaching staff of the department, friends, colleagues and well wisherswho in one way or the other offered their individual services and encouragement which served as moral booster throughout the period of this project. I wish also to specially recognize Mrs. M. A. Akinbode, Ahmed G. Adamu Kuta, and Mohammed Bawa for their numerous contributions. Finally, I express my sincere gratitude to Mallam Zubayr A. Mohammed (ZAM) for his skill in transforming the manuscripts to a perfect thesis. Thank you and may Allah bless you all.

TABLE OF CONTENTS

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATION

LIST OF TABLES

ABBREVIATIONS/DEFINITIONS

American Oil Chemists Society	AOCS
Ammonia	NH_3
Centimetre Cube	CM^3
Degree Centigrade	C^o
Gram	g
Molar	M
nanometre	nm
Potassium Cyanide	KCN
Potassium hyroxie	KOH
Potassium Iodide	KI
Parts per million	ppm
Volume	V
Weight	W

ABSTRACT

Extraction of oil was carried out on the three varieties i.e Samnut - 10 (RMP-12), Tivi and Kuta Local of groundnuts selected for the purpose of the present study. Oils extracted were refined to obtain purified samples. Some physical and chemical properties analysis of refined samples were carried out. Physical properties values such as relative density (0.91), refractive index (1.466) and boiling point (200°C) and, chemical properties e.g acid value (0.6), iodine value (98), saponification value (188) and peroxide value (0.11mmol kg^{-1}) tend to fall within specified limits, of standard industrial oil i.e Standard Organisation of Nigeria and international Codex standards. Similarly, the low level of impurities (moisture and volatile matter, insoluble impurities, soap content, soluble mineral matter, ash content, unsaponifiable matter, lead) determined for the varieties used indicated high quality materials. For instance, the results for soap content (0.9 X $10^{-7}\%^{m}/_{m}$), insoluble impurities ($0.02\%^{m}/_{m}$), Unsaponifiable matter ($0.06\%^{m}/_{m}$), lead not detected, unsaponifiable matter ($0.7\%^{m}/_{m}$), etc were relatively low. However, comparison of the various results of the varieties used for this study show that variety RMP-12 has more oil content, while variety RMP-12 appeared better than the other two Tivi and Kuta Local variety if the physical and chemical properties determined are conclusive enough. In general all the varieties employed were found to be of satisfactory standard in terms of quality and quantity of oil contents. It is therefore pertinent to state that the materials can be recommended for both industrial and local consumption.

CHAPTER ONE

1.0 INTRODUCTION

1.1 GENERAL SURVEY

Groundnut (Arachis hypogeae) is one of the most valuable legume crops of tropical and sub-tropical countries [1]. It originates from the Latin America. The Portuguese were responsible for its introduction into West Africa from Brazil in 16th Century.

As a source of vegetable oil it is second in importance to Soybeans [9]. It is used as edible oil and important raw materials for industry. This accounts for its considerable increase in the annual acreage plantation and production. For instance 18.9 mt of unshelled nuts was produced in 1980 [2].

Vegetable oils composed of lipids, protein and carbohydrates in ratio normally of 5:2:1 respectively. Fats and oils are the simple lipids which have important physical and chemical properties such as melting point, iodine value etc. It also contains certain impurities such as lead, volatile matters, etc. which may have undesirable effects to consumers if their concentrations and percentages exceed certain limits [3].

The groundnut oil can be extracted, refined and its properties, contaminants investigated and compared with standards values.

THE TERMS VEGETABLE OIL

Vegetable oils are water-insoluble substance of plant origin which consist mainly of long-chain fatty acids esters derived from the single alcohol (glycerol) and are known as triglycerides. Groundnut oil is therefore water insoluble substance from groundnut consisting mainly of long-chain fatty acids esters derived from the glycerol. Oil triglycerides are liquid at room temperature and fats are semi-solids at the same conditions. This difference in their physical state arises from their chemical composition. The oils being composed of low-melting fatty acids that are highly unsaturated, while fats are found from high melting fatty acids that are mostly saturated [4].

1.3 BOTANY OF GROUNDNUT (Arachis hypogeae)

Arachis hypogeae grows to a maximum height of 60cm and is strictly an annual legume. There is a wide variation in the type and strains cultivated in particular localities, but in general the two main types grown commercially are distinct in appearance. One is upright with an erect and vertical branches, the other recumbent with numerous creeping laterals. The first is more commonly grown for mechanized production, the second under peasant farming systems [5]. Erect types often have lower individual nut yields per plant than recumbent types under similar conditions, but because of mechanical cultivation

and harvesting problems with the latter, final in-store yields tends to be lower. However, erect types tend to have slightly higher seed-oil and seed protein content than recumbent varieties, and on a yield per hectare basis there is often little difference [5].

The yellow flowers of the Arachis hypogeae usually appear 4-6 weeks after planting and soon after fertilization, the fertilized ovary generates a pointed stalk-like structure, known as the peg, with the ovary at its top. This peg grows downwards and penetrates the soil to a depth of 2.5-6cm. Fruit enlargement begins at the tip of the peg once it has penetrated below the soil surface. The fruit is a more or less elongated pod and contains 1-6 seeds which are surrounded by thick fibrous shell. The time period from sowing to maturity depends on temperature and variety [2].

1.4 VARIETIES OF Arachis hypogeae

To increase productivity, a number of high yielding varieties of groundnut have been developed. Institute for Agricultural Research (IAR) Samaru, Ahmadu Bello University, Zaria has developed for production six groundnut varieties, namely SAMNUT-10, SAMNUT-11, SAMNUT-14, SAMNUT-16, SAMNUT-17 and SAMNUT-18. The average yield, oil content and period of maturity of these varieties are substantially relatively high. The yield ranged

from 1.6-3.8 tonnes/ha, oil content between 50-60% and maturity period from 95-141 days depending on the variety.

Among the improved varieties which can be profitably established on small to large scale farms as raw materials for the vegetable oil and cake industries, three are early maturing lines, Resistant Red Bulk, (RRB) (SAMNUT-18), 48-115B (SAMNUT-17) and 55-437 (SAMNUT-14). These three have exhibited good agronomic characteristics and high adaptability to drought conditions [1].

1.5 USES OF GROUNDNUT (Arachis hypogeae)

The groundnut is a major cash crop in the West Africa Savanna Region, being an important source of oil; which constitute up to 50% of the kernel. Groundnut oil can be used for a variety of products - margarine, glycerol drugs, salad oil and cooking oil. The crop is also an important component of the local diet and can be eaten raw, roasted or in stews. Groundnut cake, a by-product of oil crushing, and groundnut haulms are useful animal feeds [2].

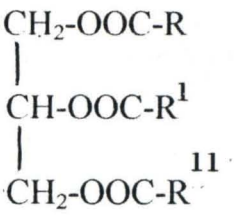
1.6 CHEMICAL CONSTITUENTS OF VEGETABLE OILS

1.6.1 MAJOR CHEMICALS

Fats and oils, also called trigl ycerides, are esters of the trihydric alcohol glycerol and various fatty acids. Most naturally occurring fatty acids are straight chains with a terminal carboxyl group and 4-24 carbon atoms in even numbers.

A few acids have an odd number of carbons and some have a cyclic group or branched chain, but all of these are relatively rare [6].

The generic formula of a triglyceride is shown below:



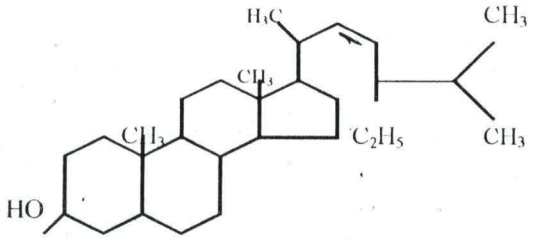
where RCO_2H, R^1CO_2H and $R^{11}CO_2H$ represent molecules of either the same or different fatty acids [7].

The fatty acids may be saturated e.g. palmitic acid, and stearic acids, while others may be unsaturated e.g. oleic and linoleic acids.

In a saturated acid, such as palmitic acid, all bonds between carbon atoms are single bonds, with hydrogen atoms attached to all the carbon atoms, except that of the carboxyl radical. In an unsaturated acid, each of two adjacent carbons lacks one hydrogen, so that the carbon bonds link together to form a double bond. Oleic acid with one double bond is monounsaturated linoleic and linolenic acids are polyunsaturated, having two and three double bonds respectively. Unsaturated acids can be converted to saturated acids by the addition of hydrogen [8]. Fatty acids can be cleaved from a gl ycerides by hydrolysis, or the addition of an OH group to the glycerol back bone and some sort of positive ions to the fatty acid. Alkalis or "bases", are often used to effect this separation [9].

1.6.2.1 STEROLS

These are colourless, odourless and generally inert substances found in oils. They are a group of complex, high melting point crystalline alcohol. One of the sterols found in oil is stigmasterol; having structural formula as shown below:

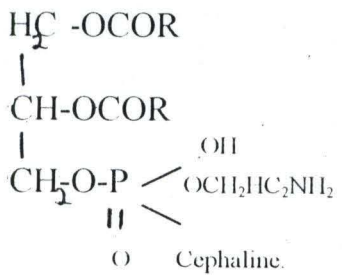


Stigmasterol

Sterols play an important role in biochemical activity being the basic structures from which animals manufacture bile acids and hormones.

1.6.2.2 PHOSPHOLIPIDS OR PHOSPHATEDES

They may be considered as triglycerides in which one of the fatty acid group has been replaced by a phosphoric acid derivatives. Example are cephalin and lecithin.



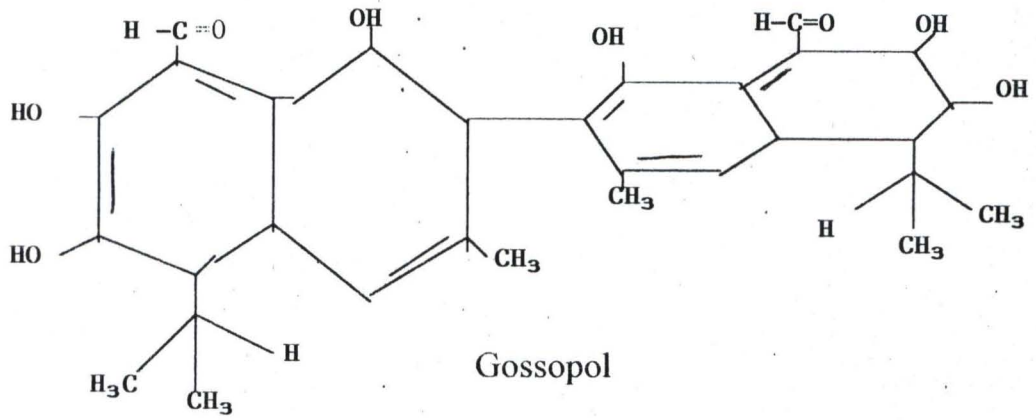
Cephaline.

The phosphlipids are amphipathic and hence surface active like soaps.

1.6.2.3 PIGMENTS

The characteristics yellow-red colour of most vegetable oils is due to the presence of pigments such as gossopol, carotenoids etc.

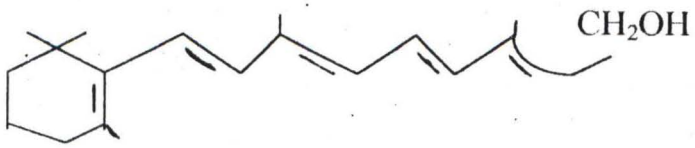
Gossopol is a bitter pigment produced in glands located throughout the cotyledons [9]; which is represented below:



Gossopol

1.6.2.4 VITAMINS

One of the vitamins present in small quantities in vegetable oils is vitamin E which owes its activity to its tocopherol content. Vitamin A is produced by the action of water on the carotene (the precursors of Vitamin A) which occur in unbleached palm oil and in traces in other oils. It is lost in the refined cooking oil due to bleaching [4].



Vitamin A.

1.7 PROCESSING OF VEGETABLE OILS [4]

1.71. STORAGE OF RAW MATERIALS

For certain oil bearing seeds such as soybean, groundnut,melon, corn, etc., it is possible to spread out their processing for oil over the whole year since they can be stored for long periods under cool and dry conditions to prevent germination and possible decay. Some others are not suitable for storage e.g. rubber seed, oil bean seed etc. due to spoilage.

1.7.2 PRETREATMENT OF OIL BEARING SEEDS

Prior to oil extraction, oil bearing seeds are first cleaned to remove dirt consisting mainly of empty and diseased seeds, weeds, sands, small stones, iron particles, etc. The cleaning stages include: sieving to separate the particles according to size and removal of straw, twigs, etc., winnowing to remove chaff, empty grains, etc. in a stream of air, magnetic treatment to remove particles of iron and peeling to remove the husk to minimise losses of oil in the residues during pressing and/or solvent extraction.

The cleansed seeds are then crushed by roller mills to produce thin flakes. The grinding serves to break down the cell walls of the seeds to enable the oil which occurs as small droplets in the cytoplasm to flow out easily during pressing.

1.7.3 OIL EXTRACTION

Two main methods are used: pressing and solvent extraction. The later allows for a much more complete recovery of oil. A combination of pressing and solvent extraction is often practiced in the industry. The seed is first pressed to an oil content of 10-15% and then solvent extracted to leave a residue to less than 1% of oil.

In pressing, pre-heating of the meal is done to bring about the coagulation of the protein matter which is responsible for the extremely fine state of division of the oil within the cells. Heating thus enables the very small oil droplets to coalesce, while the low viscosity facilitates the flow from the materials to the press. A gradual application of pressure on the meal helps to keep the openings and the pores in the press-cake open for the transport of the oil as long as possible and so keep production at a high level. Hydraulic or continuous presses are used.

In solvent extraction, a low boiling petroleum fraction is usually used. The boiling point must not be too low (to minimize solvent loss) or so high that it is not possible to remove the solvent quickly and completely from the oil without employing unduly high temperatures. Extraction can be effected batch wise or continuously.

The oil extract is usually filtered before distilling of the solvent to remove particles which find their way into the solution during the extraction. Distillation is used to recover the oil. The last traces of solvent are removed with the aid of steam.

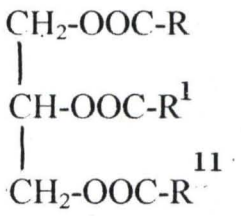
Table 1.2 shows the major vegetable oil industries in the country and the extraction methods employed by each.

1.8 REFINING OF VEGETABLE OIL [4]

Crude fats and oils contain variable amount of non-glycerin impurities. Some, such as sterols, are relatively inert, others like tocopherol are generally desirable; but some, like free fatty acids, phosphatides, mucilaginous materials or foots, and certain pigments, are objectionable, tending to make the fat or oil dark coloured, susceptible to foaming and smoking on heating and liable to precipitation of solid materials when the oil is heated during processing operations.

A few acids have an odd number of carbons and some have a cyclic group or branched chain, but all of these are relatively rare [6].

The generic formula of a triglyceride is shown below:



where RCO_2H, R^1CO_2H and $R^{11}CO_2H$ represent molecules of either the same or different fatty acids [7].

The fatty acids may be saturated e.g. palmitic acid, and stearic acids, while others may be unsaturated e.g. oleic and linoleic acids.

In a saturated acid, such as palmitic acid, all bonds between carbon atoms are single bonds, with hydrogen atoms attached to all the carbon atoms, except that of the carboxyl radical. In an unsaturated acid, each of two adjacent carbons lacks one hydrogen, so that the carbon bonds link together to form a double bond. Oleic acid with one double bond is monounsaturated linoleic and linolenic acids are polyunsaturated, having two and three double bonds respectively. Unsaturated acids can be converted to saturated acids by the addition of hydrogen [8]. Fatty acids can be cleaved from a gl ycerides by hydrolysis, or the addition of an OH group to the glycerol back bone and some sort of positive ions to the fatty acid. Alkalis or "bases", are often used to effect this separation [9].

TABLE 1.2 Major Vegetable Oil Industries in Nigeria [4]

Name of Industry	Location	Processes Undertaken
AVOP	Nachi (Exis)	Refining
Golden Oil	Onitsha	Pressing
Atlantic Farms	Ontisha	Pressing
Tip Top Ind. Ltd.	Lagos	Pressing and Refining
Food Oils Ltd.	Ibadan	Ditto
Gusau Oil Mills	Gusau	Ditto
Life	Nnewi	Ditto
Grand Cereal	Jos	Ditto
AFCOTT	Yola	Ditto
Nigerian Oil Mills	Kano	Ditto
ASAN Oil Ind.	Kano	Ditto
Taraku	Taraku (Benue)	Pressing solvent extraction & refining
New Agro Ind.	Umunza (ANS)	Ditto
General Agro	Port Harcourt	Ditto
Rivoc	Port Harcourt	Ditto
Nalin Ind.	Port Harcourt	Pressing and refining.

Note that the list above shows the major Vegetable Oil Industries in Nigera as at 1992. There may be more of such industries as at now (1998).

The Object of refining is to remove the objectionable impurities with a minimum damage to the neutral oil (glycerides) and tocopherol and minimum loss of oil.

There are various degrees and methods of refining and the one chosen is dictated by the end uses. Solid contaminants of oils are removed simply by filtration or decantation. The main refining operations are degumming, deacidification, decolorisation, deodorisation and acid washing.

1.8.1 DEGUMMING (OR DE-MUNIFICATION)

Some of the vegetable oils contain a quantity of natural gums and phosphatides which are good emulsifying agents and if left in the oil would give rise to substantial losses of oil during alkali refining. Degumming is done by blowing steam into the oil at about 1000°C

1.8.2 DEACIDIFICTION (OR ALKALI-REFINING)

The presence of large amounts of free fatty acids in crude oils is undesirable because of their smell, flavour and corrosive action.

Alkali refining (neutralization) can be carried out with either dilute or concentrated solution. Dilute alkali has advantage of causing very little Saponification of oil. However, there is easy formation of stubborn emulsions which generally limits its use with unde-gummed oils. Concentrated alkali gives rise to a concentrated soap solution (soap stock) which is more easily separated.

from the oil. Concentrated solution of caustic soda has a powerful demunification action and causes greater saponification of the glycerides.

Alkali refining also removes some colouring matter from the oil which makes the alkali-refined oil lighter in colour than the raw oil.

1.8.3 DECOLORISATION (OR BLEACHING)

The process is aimed at removing coloured constituent from the oil.

Decolorisation involves adsorption of the colouring matters on bleaching earth e.g fullers earth and active carbons. Active carbons, for instance absorb colouring matters on its surface thereby rendering oil sample colourless. Some locally available clays have been found effective. Bleaching earth are mostly used, although in many cases the bleaching effect obtained with the carbons is greater; also the latter adsorb various other substances that have objectionable taste or odour [11].

Certain colouring matters such as carotenoids and various quinoid colouring matters can be almost completely removed from the oil by adsorptive bleaching, and a number of oils e.g palm, melon and oil bean are completely decolourised in this way. Some colouring matters resist the treatment and remain coloured after bleaching e.g linseed, soybean and rape oils.

Adsorptive bleaching is carried out by heating and stiring the oil and the bleaching agent under vacuum at a temperature of 70-80°C for sometime (20-45 mins) after which the oil is filtered in presses. Vacuum is employed to prevent oxidation of the soil as much as possible during the treatment [11].

1.8.4 DEODORISATION

Oils and fats contain odiferous substances and substances having peculiar tastes, which must be removed in most cases. These substances may be derived from degradation and oxidation reactions on the fatty acid glycerides and also on certain products occurring in the raw oil (Mucins, Proteins etc.). Deodorisation is effected by means of steam .

Deodorisation is a must for raw materials for edible fat industry; also for technical fats and oils e.g. for soap manufacture.

1.9 PROPERTIES OF VEGETABLE OILS

The properties of oils and fats are needed for an assessment of quality and purity as well as for their identification. A number of physical and chemical properties (constants) are necessary [10, 11, 12].

1.9.1 PHYSICAL PROPERTIES OF VEGETABLE OILS

1.9.1.1 COLOUR

The colour of oils and fats is essential in assessing quality and determining the degree of bleaching. The darker the colour, the poorer the quality. There are methods for determining colour, most of which were developed for a specific product or groups of products.

1.9.1.2 REFRACTIVE INDEX

This is a physical attribute of triglycerides, measured by the angle through a thin film of melting fats. The index of each fat and oil falls within a narrow range and can be used as a characteristics of the fat in checking purity or searching for components of a mixture. It is temperature dependent and is usually measured at $40^{\circ}C$, a temperature coefficient of the refractive index for fatty oils is on the average 0.00036 per $^{\circ}C$.

1.9.1.3 MELTING POINT

This is the temperature at which a solid of a pure substance changes to a liquid. Since oils are mixed triglycerides, they melt over a range of temperature because of the combined effects of the variations in the degree of unsaturation.

In general, triglycerides reflect the melting points of their constituent fatty acids. A low degree of unsaturation, a high molecular mass and the presence of trans rather than Cis isomers of unsaturated acids, all contribute to a relatively high melting point.

1.9.1.4 SPECIFIC GRAVITY

Specific gravity is a ratio of the mass of a given volume of material at $25^{\circ}C$ to that of an equal volume of water at $25^{\circ}C$. For most fats and oils this lies

between 0.90 and 0.94 at 20°C ; in general, it increases with increase in degree of unsaturation and decrease in the mean molecular mass of the fatty acids. It is thus expressed on the following empirical equation:

Specific gravity = 0.8475+0.003 x (sap value) +0.00014 x (I. Value)

where Sap = Saponification and I = iodine.

1.9.1.5 VISCOSITY

This is resistance that fats and oils offers to flow when subjected to a shear stress. The viscosity increases slightly with increase in the average molecular mass and in the degree of unsaturation of the fatty acids; the actual differences however, are very small. Castor oil alone has a viscosity which is much greater than that of the most other fatty oils, hence its use as a lubricant.

1.9.1.6 SOLUBILITY

This is ability of a substance to form a solution with another substance. The solubility of fats and oils plays a part in determining the immiscibility curves of an oil or fat in various solvents. These curves may be used for checking purity. Most fats and oils are miscible with such solvents as petroleum ether, benzene, ether, acetone, etc. The solubility of solid fats and fatty acids is much less, especially that of more saturated products.

1.9.2 CHEMICAL PROPERTIES OF VEGETABLE OILS

1.9.2.1 ACID VALUE (NUMBER)

The acid value is a measure of the amount of free fatty acids present in an oil or fat; it is given by the number of milligrams of caustic potash necessary to neutralise the free fatty acids in one gram of the oil. The acid value is especially important for judging quality of raw oils and for determining the quality of alkali required for alkali refining of an oil at minimal saponification.

1.9.2.2 IODINE VALUE

Iodine value is a measure of the degree of unsaturation of the oil, and is defined as the number of milligrams of iodine absorbed per gram of oil sample. The greater the total unsaturation, the higher, is the iodine value. Iodine value determination is important because depending on its value, oils can be classified into drying, semi-drying and non-dry.

1.9.2.3 SAPONIFICATION VALUE

This is the number of milligrams of potassium hydroxide necessary for saponifying one gram of the oil. Saponification value increases with decrease in the average molecular mass of the oil.

1.9.2.4 HYDROXYL VALUE

This is the milligrams of potassium hydroxide equivalent to the hydroxyl content of one gram of oil sample. The hydroxyl value is a measure of the hydroxyl groups in a given substance. The presence of hydroxyl groups in natural fats is due largely to the presence of substances such as glycerol, mono and diglycerides and sterols.

1.9.2.5 REICHERT, POLENSKE AND KIRSCHNER VALUES

These measure the amount of steam-volatile fatty acids which can be recovered from oils under standard conditions. The acids concerned are Lauric (C_{12}), Capric (C_{10}), Caprylic (C_8), Caproic (C_6), and butyric acid (C_4). The Reichert value measures the water soluble acids, the polenske value measures water insoluble acid and the kirschner value butyric acid by separation from caproic acid precipitating the later as a silver salt.

1.9.2.6 PEROXIDE VALUE (NUMBERS)

This is a measure of millimoles of peroxide or milli equivalents of oxygen taken up by 1000 grams of fats or oil; it is used to measure rancidity.

Table 1.3 Comparison of Some properties of Groundnut oil with Similar nuts [13)

Oil	Refractive Index($40^{\circ}C$)	Iodine Value	Saponification Value
groundnut	1.460 - 1.466	80-106	187-196
Coconut	1.4530^{15} -1.4560	7.5 - 10.5	250-264
Cashewnut (Kernel)	1.4623-1.4633	79-85	187-196

1.10 CONTAMINANTS IN VEGETABLE OILS [14, 15]

Contaminants (impurities), are usually associated with vegetable oils. The concentrations and percentages of the contaminants should be determined in edible oils to ensure that they do not exceed allowable limits. However, if their presence exceed tolerable limits, may have detrimental effects on the consumers.

1.10.1 INSOLUBLE IMPURITIES

Insoluble impurities represent a variety of extraneous matter including nitrogenous material of animal or vegetable origin, earth, carbohydrate material such as vegetable fiber and other substances.

1.10.2 UNSAPONIFIABLE MATTER

The Unsaponifiable content of fats is usually defined as those substances which are soluble in the ordinary fat solvents, but which are not saponified by caustic alkalis. In normal fresh fats and oils these substances consist primarily of higher aliphatic alcohol, sterols, pigments and hydrocarbons.

1.10.3 SOAP CONTENT

Sodium soaps may be present in oil which have been treated with sodium hydroxide or sodium carbonate as in the alkali refining process. Traces of soaps

are difficult to remove in processing and they are not easy to determine analytically.

1.10.4 MOISTURE AND VOLATILE MATTER

Water is only slightly soluble in fats; and is normally present in small quantity. However, when water is present in any quantity above the limit of solubility it is usually found as a separate phase which is settled at the bottom of the container.

Fats contain various substances which are somewhat volatile under the conditions prescribed by some of the methods for determination of moisture. The amount of volatile matter obtained on a given sample is usually determined by the temperature and time of drying. In low grade inedible fats volatile materials may be in greater quantities.

1.10.5 ASH CONTENT

This is incombustible matter remaining after a substance has been incinerated.

1.10.6 SOLUBLE MINERAL MATTER

Soluble mineral matter represents mineral soaps, principally of lime but possibly of iron, lead, copper, arsenic etc.

Table 1.4 Effects and maximum level of contaminants in Vegetable Oils [3]

Contaminants	Effects	Maximum Level
Volatile Matter at 105C°	-	0.2%$^{m}/_{m}$
Insoluble impurities	-	0.05%$^{m}/_{m}$
Soap Content	-	0.005%$^{m}/_{m}$
Iron (Fe)	Colour and taste	1.5Mg/Kg
Load (Pb)	Toxic	0.1Mg/Kg
Copper (Cu)	taste	0.1 Mg/Kg
Arsenic (As)	toxic	0.1 Mg/Kg
Unsaponifiable Matter	-	10 g/kg

1.11 OBJECTIVES OF THE RESEARCH

Vegetable oils have continued to play essential roles in our various communities. They have gained recognition because of their importance as food supplements for both man and animal; and also, as a raw materials for various oil based industrial products.

The sudden rise in private sectors investment in sourcing for local raw materials for the manufacturing industries has brought about establishment of many small and medium scale plants for processing of groundnut. This is to provide the highly demanded cooking oil, animal feed and above all raw materials for oil based industries.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 THE ORIGIN OF GROUNDNUT

Weiss E. A. 1983 established the source of groundnut; Arachis hypogaea L, which is also commonly known as peanut or earthnut. This species is a family member of papilionacea which is the largest and most important of the three division of leguminosae originating from warmer regions [5]. Leppik 1971 gave description of less than a score, but it is probably that there may be nearer 100 varieties in Central South America [16]. Arachis hypogaea is similar to Arachis monticola and can only be identified under cultivation. The Arachis monticola, is regarded as a truly wild conspecific of the cultivated groundnut. In contrast to Arachis monticola, Arachis hypogaea has stronger pods and Carpophores. Smarth et-al 1978 suggested that on a basis of genome donation that Arachis hypogaea originated from a hybrid between Arachis Cardenasi and Arachis batizocoi, both putative parents occurs in reasonable proximity in Bolivia [17].

Weiss E. A. 1983, also reported that, the oldest indications of groundnut cultivation were from the pre-Columbian native societies of Peru,

2000-3000 BC, well to the Northwest, from which it can reasonably have had a much longer history of domestication. It was originally domesticated in the distance past by predecessors of the Arawak-speaking peoples who now live in its homeland. By the time of Columbus, groundnuts were widely distributed in South and Central America and the Caribbean. It was brought to West Africa from Brazil in 16th Century and thence to the African East Coast and so to India [5].

Simpson, B. B. et. al 1986 gave some valuable information on uses of groundnut, methods of its extraction and refining and general processes involved at local and industrial levels.

2.2 USES OF GROUNDNUT OIL

Groundnut on the basis of origin and dispersal is a major world crop. This is evidenced enough from the rise to its modern economic position. Less well known was the beginning of its use as an oil seed crop. Groundnuts were not used for their oil until about 125 years when a French firm began to crush groundnuts imported from Africa in a factory in Marseilles. After this humble beginning, oil extraction spread to other areas of the world. In the United States today, one fourth of the groundnuts goes into oil production and the majority of the groundnut world wide is used for oil [9]. Raw material research and development Council, Nigeria (1993) has reported that groundnut oil can be used

for manufacture of margarine, soaps, glycerol drugs, salad oil and as a cooking oil [1].

2.3 GROUNDNUT OIL EXTRACTION AND REFINING

Man in his usual endeavours had devised various methods of removing oils from groundnuts. Among the earliest methods of extraction was grinding with stones to crush the tissues and release the oil by the Tunisian Workers. Sometimes the seeds were heated to facilitate the flow of the oil from crushed debris. Both a motar and pestle often with a deep, inverted cone and a revolving pestle and a press with a wedge that was manually pounded, have been used for groundnut oil expression since early times. In many undeveloped countries, various types of manual or animal-driven presses are still employed. Almost all the oil extracted by these kinds of methods is consumed locally [9].

The first mechanised oil extraction presses, produced in the seventeenth century, were steam driven and operated on the same principle as the manual press. In 1795, the hydraulic press was developed in England and, in 1900, the first screw presses were used for groundnut oil extraction. Today, this screw pressing mean little because the process of extracting with a screw press generates heat from 65°C to 72°C [9].

Screw press was readily adopted in industrial countries because it made large scale oil production economically feasible. Because screw pressing leaves

a residue that still contains 2 to 4 percent oil, a further refinement using organic solvents usually hexane was developed. Solvent extraction, which leaves a scant 0.5 to 1 percent in the cake, has now been adopted in most large scale operations. The solution containing the oils is separated from the residue and then the solvent itself is driven from the mixture by distillation. Hexane boils off at temperatures between 63 and 65°C leaving the crude oil behind [9].

Oil refining is most often accomplished by mixing the oil with caustic soda (neutralization). In addition to being refined, oil can be degummed (mixing with hot water) and centrifuged. Bleaching can be achieved by adding charcoal or fullers' earth and filtered. Similarly, deodorisation is carried out by heating with steam bath at 140°C [9].

2.4 GENERAL ANALYSIS FOR GROUNDNUT OIL

Numerous methods were used in the past for oil analysis. Many of these numerous methods have been reviewed by Mehlencher (1960) and detailed described by Williams K. A. (1966). This lead to tabulation of the Chemical properties of groundnut and related oils; which are especially useful in data interpretation [18].

Oil routine analysis, determination of the iodine value, Saponification value, and peroxide value of groundnut oil have been reported by Pearson D. 1976 [19].

Whalley, (1955, 1956) outlined micro-analytical procedures for the determination of various chemical and physical constants (Specific gravity, refractive index, oil content and boiling point) and reported by Pearson D. (1976) [19].

Chemical constitution i.e. fatty acids of groundnut oil has been discussed by Hilditch and Williams K. A. (1964) and also reported by Standard Organisation of Nigeria (1992). It was stated that groundnut oil contains about 8.3% Palmitic acid, 3.1% Stearic, 2.4% Arachidic, 56%, Oleic, 26% Linoleic 3.1% Behenic and 1.1% Caprylic acid [3].

Williams K. A. (1964, 1966) and Blachly F. F et al (1973) highlighted the impurities of groundnut oil such as soap content, moisture and volatile matter, insoluble impurities, lead etc. [20]. The maximum tolerable limit of impurities of groundnut oil have been identified and reported by Standard Organisation of Nigeria (1992). For instance, the maximum level of lead and soap content are given as 0.1Mg/Kg (ppm) and 0.005%$^{m}/_{m}$ respectively above these values it may be harmful to consumers [3].

From the foregoing, it is pertinent to state that physical and chemical characteristics of groundnut oils reported by various authors has lead to more understanding of their production, processes, uses and application and above all their economical values.

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 CROP MATERIALS

The seeds (Kernels) of three varieties of Arachis hypogeae were bought in Central Market, Minna. These seeds were individually identified at the school of Agriculture, Federal University of Technology, Minna [21].

Each variety was treated in the same way by first sorting out the impurities and bad species, then washed with water and dried in the oven at 100°C to a constant weight. The kernels were allowed to cool and the chaffs removed to obtain pure kernel, which were later crushed or grounded.

3.2 OIL EXTRACTION

Crushed seeds (40g) was introduced into the thimble of a soxhlet extractor and extraction carried out using hexane as solvent at 50°C for 4 hours. The procedure was repeated several times in order to obtain reasonable quantity of the extracts required for analysis [9].

Each extract was distilled to remove the hexane and the oil obtained were labelled as follows:

Samnut-10 (RMP-12) as EMX20

TIVI Variety as EMX 21

Kuta Local Variety as EMX 22

3.3 OIL REFINING

The extracted oil obtained from each variety of groundnut was refined using degumming, neutralisation and bleaching procedures as stated individually by Ozemoyah P. O. [22] and Ogwala P. [23].

3.3.1 DEGUMMING

A mixture of oil extract and boiled water was properly stirred and allowed to stand in a separatory funnel until the oil and water layers were distinctly formed with gums clearly precipitated out in the aqueous layer. This procedure was repeated many folds until no further precipitate was obtained.

3.3.2 NEUTRALIZATION (ALKALINE REFINING)

Neutralization was effected by adding NaOH (0.5M, $2cm^3$) to the oil (87.32g) and stirring the mixture before carrying out thermal bleaching of the product.

3.3.3 BLEACHING

Two stages process of bleaching was used, that is thermal bleaching and adsorptive bleaching respectively.

3.3.3.1 THERMAL BLEACHING (DEODORISATION)

The degummed - neutralised oil (87.32g) was bleached by heating in an oil bath at 140°C for 10 minutes. The product obtained was used for adsorptive bleaching.

3.3.3.2 ADSORPTIVE BLEACHING (DECOLORISATION)

To each of the thermal bleached oil (87.32g) activated charcoal (1.5g) was added and the content heated in an oil bath to 120°C with constant stirring for 30 minutes. The resultant product was then centrifuged for 1 hour and the purified-decolorised oil decanted.

3.4 DETERMINATIONS

The oil obtained from the above experiments were used to determine the physical, chemical properties and impurities as outlined below:

3.4.1 PHYSICAL PROPERTIES

Physical properties such as refractive index, boiling point, specific gravity, and oil content are special characteristics of a particular oil depending on its variety and source. The various methods used for respective features are discussed below as given by Durst H. D. et. al [24].

3.4.1.1 OIL CONTENT

Oils from crushed samples were extracted according to the method highlighted in section 3.2

The oil content was calculated from the weights of the sample, and that of the actual oil extract and expressed in percentage as:

$$\text{Oil content} = \frac{Wo \times 100}{Ws} = x\%$$

where Wo = Weight of oil

Ws = Weight of sample

X = % extract.

3.4.1.2 SPECIFIC GRAVITY

A clean, dry volumetric flask ($10cm^3$) was accurately weighed (W). The flask was filled to the mark with oil sample and reweighed (Ws). Similarly, the clean, dry flask was filled to the mark with distilled water and weighed again (Ww). Using the weights obtained, the specific gravity of each oil sample was calculated according to the equation:

$$\text{Specific gravity} = \frac{Ws-W}{Ww-W}$$

3.4.1.3 BOILING POINT (MICRO REFLUX METHOD)

Sample of oil ($1Cm^3$) was introduced into a test tube (13 x 100mm size) and a thermometer whose bulb was suspended about 2cm above the top of the oil level was assembled. The bottom of the test tube was then heated with a free

flame until the vapours bathe the bulb of the thermometer. The temperature was noted and this observation was made for each oil specimen prepared.

3.4.1.4 REFRACTIVE INDEX

The prism surface of Abbess refractometer was checked for residue from previous determination and surface cleaned with ethanol (95%). The surface was left to dry by complete evaporation of ethanol. A dropper was used to place the oil sample on a lower prism ensuring that the entire width of the prism plate was covered. The upper prism was brought into contact with the lower prism so that an unbroken layer of oil was formed between the two. The Refractometer Controls were adjusted to bring the light and dark fields into focus with the cross hairs. The reading on the scale was made directly and this was repeated for each of the oil samples.

3.4.1.5 REFINING YIELD

Oils from extracted samples were refined based on the method given in section 3.3. The oil yield was calculated from the weights of crude sample and that of actual refined oil and expressed in percentage;

$$\text{i.e.} \quad \text{refining yield} = \frac{Wr}{Wc} \times 100 = y\%$$

Where Wc = Weight of crude oil

Wr = Weight of refined oil

y% = % refining yield.

3.4.2 CHEMICAL PROPERTIES

Chemical Properties such as acid value, saponification value, iodine value, and peroxide value are special properties of oil. The numerous methods used for these characteristics are described below as given by Pearson D. [25] and William H. [26] respectively.

3.4.2.1 ACID VALUE

NaOH (0.1M) used for determination of acid value was prepared by dissolving NaOH Pallets (1.0g) in a volumetric flask (250cm^3) containing distilled water (20cm^3) and the mixture shaken until the whole NaOH was dissolved. The solution was then made to the mark with distilled water.

The resultant NaOH was used to neutrilise the mixture of diethyl ether (25cm^3), ethanol (25cm^3) and phenolphthalein solution (1cm^3, 1%). Oil sample (1.0g) was then dissolved in the neutral solution and titrated with NaOH (0.1M) by shaking constantly until a pink colour which persisted for about 15 seconds was obtained. This procedure was carried out for each oil sample. The acid value was then calculated according to the equation stated below:

$$\text{Acid Value} = \frac{Vt \times 5.61}{Ws}$$

where Vt = Volume of titrant used and

Ws = Weight of Sample.

3.4.2.2 SAPONIFICATION VALUE

The saponification value was determined using alcoholic solution of KOH and standard solution of HCl prepared in the laboratory as stated below:

(I) Alcoholic solution of KOH was prepared by dissolving KOH pellets (8.75g) in volumetric flask ($250cm^3$) containing distilled water ($5cm^3$) and diluted to the mark with ethanol (95%). The mixture was allowed to stand over night and clear liquid decanted off.

(ii) Standard solution of HCl (0.5m) was also prepared by introducing HCl ($11cm^3$) into volumetric flask ($250cm^3$) containing distilled water ($20cm^3$). The mixture was diluted to the mark with distilled water.

(iii) **DETERMINATION PROCESS**

The oil (1.0g) was added to the alcoholic KOH solution ($12.5cm^3$) and refluxed, with shaking frequently for 30 minutes. Phenolphthalein indicator solution (2 to 3 drops, 1%) was added

and the hot solution titrated with HCl (0.5 M) until it changes from pink to colourless. Similarly, the blank KOH solution (without oil) determination was carried out. The values obtained in both standard and test samples were used to calculate the amount of saponifiable materials as expressed in the equation given below:

$$\text{Saponification Value} = \frac{(b-s) \times 28.05}{Ws}$$

Shere S = Volume of titrant used for the sample

b = Volume of titrant used for blank

Ws = Weight of sample.

3.4.2.3 IODINE VALUE (WIJS' METHOD)

The iodine value was determined using Wijs' solution and standard solution of sodium thiosulphate ($Na_2 S_2 O_3 . 5 H_2O$) prepared as described below:

(I) **Wij's Solution**: The solution was prepared by dissolving iodine (13.0g) in a volumetric flask (100 0 cm^3) containing glacial acetic acid (50cm^3) and made to the mark with the acid. The solution (25cm^3) was removed and dry chlorine gas (prepared from $KMnO_4$, HCl, H_2O and H_2SO_4 [27] was passed into the remaining solution until the deep real colour changed

to orange. Original solution ($25cm^3$) was then added to remove excess chlorine [28].

(ii) **Sodiumthiosulphate Standard Solution (0.1 M):**

The solution was prepared by dissolving $Na_2 S_2O_3, 5H_2O$ (6.2g) in a volumetric flask (250 cm^3) containing distilled water $30cm^3$) and the mixture made up to the mark with distilled water.

(iii) **Determination Process**

The oil (0.2g) was introduced into a dry glass stoppered bottle ($250cm^3$). Carbontetra chloride ($10cm^3$) was added to the oil to dissolve it. Wijs' solution ($200cm^3$) was added to the resultant product and KI solution moistened stopped inserted. The product was then allowed to stand in a dark for 30 minutes. KI solution ($15cm^3$, 10%) and distilled water (100 cm^3) were mixed with the product and solution then titrated with $Na_2 S_2 O_3 5H_2O$ (O.1M) using starch indicator (1 to 2 drops, 1%) just before the end point (yellow to colourless) (S).

Similarly, the blank Wijs' solution (without oil) determination was carried out (b). The values obtained in both standard and test samples were used to calculate the amount of iodine as stated by the equation below:

$$\text{Iodine Value} = \frac{b\text{-}S \times 1.269]}{Ws}$$

Where Ws = Weight of Sample

The procedure was repeated for each oil sample.

3.4.2.4 PEROXIDE VALUE (AOCS METHOD)

The oil (1.0g) was introduced into a conical flask and acetic acid-chloroform solution ($6cm^3$, 3:2 $^{V}/_{V}$) was added. The flask was then swirled until the oil dissolved and saturated KI (1 to 2 drop) was added. The solution was allowed to stand with occasional shaking for 1 minute after which distilled water ($6cm^3$) was added. The mixture was titrated with $Na_2 S_2 O_3, 5H_2O$ (0.1M), adding it gradually with constant and vigorous shaking until the yellow colour almost disappeared. Then starch solution (1 to 2 drops, 1%) was added and titration continued with vigorously shaking near the end point to ensure that the iodine was completely liberated from the chloroform layer. $Na_2 S_2 O_3, 5H_2O$ solution was then added dropwise until the blue colour disappeared. The process was repeated for all the test samples. The equation given below was used to obtain the amount of peroxide present in each specimen.

$$\text{Peroxide Value} = \frac{V_t \times 100}{Ws(Mg)}$$

Where Vt = Volume of titrant used

Ws = Weight of sample

3.4.3 IMPURITIES

Impurities such as moisture and volatile matter, insoluble 'impurities, soap content, soluble matter, ash content and unsaponifiable matter are usually found in the oil in trace amount. The various methods used for each of the listed substance are discussed below as separately outlined by Williams K. A [18] and Standard Organisation of Nigeria [3].

3.4.3.1 MOISTURE AND VOLATILE MATTER (HOT PLATE METHOD)

The hot plate method is most common in routine analysis and was used because it is most convenient.

The well-mixed sample (1.0261 g) was introduced into a weighed beaker ($15cm^3$). The beaker was placed on a hot plate (125 to 130 ^0C) and rotated gently to avoid spattering. The approach of end point was judged by the cessation of rising bubbles of steam as well as the absence of foam. Where as the exact end point was judged at the point of incipient smoking of the oil. The beaker was allowed to cool and weighed again. The percentage moisture and volatile matter was then calculated applying the equation below:

$$\% \text{ Moisture and Volatile Matter} = \frac{W1 \times 100}{Ws}$$

Where W1 = Weight lost in milligram (mg)

Ws = Weight of sample in milligram (mg).

3.4.3.2 INSOLUBLE IMPURITIES

The oil sample (1.0200g) was introduced into a conical flask ($100cm^3$). Petroleum ether ($10cm^3$) was added, the flask was then corked, shaken vigorously and allowed to stand for 30 minutes at room temperature. The mixture was filtered with weighed whatman filter paper (W_1). The filter paper containing the insoluble components was carefully washed with small amount of solvent until the filtrate was free from oil. The filter paper was then dried in the oven (100^oC) to constant weight (W_2). This procedure was repeated for each sample. The percentage insoluble impurities was calculated using equation below:

$$\% \text{ insoluble impurities} = \frac{Wi\ (mg) \times 100}{Ws\ (mg)}$$

Where Wi = Weight increase of filter paper.

Ws = Weight of sample.

3.4.3.3 SOAP CONTENT (TITRIMETRIC METHOD)

This method was used because it is simpler than ashing method.

Soap content was determined by using neutralised acetone solution prepared by introducing distilled water ($2cm^3$) into beaker (100 cm^3) and acetone (98 cm^3) was added. The resultant mixture mixed with bromophenol blue indicator soultion (0.5 cm^3, 0.1%) in ethanol (95%). HCl (0.01 M) was then added to the first appearance of a permanent yellow colour.

The oil (2.0g) was introduced into a beaker ($100cm^3$) and distilled water (1 drop)was added. The mixture was warmed and then shaken vigorously. Neutralised acetone (2.5 cm^3) was added to the soap solution (mixture). The resultant solution was again warmed and shaken, and the solution allowed to stand until it separated into two layers. The presence of soap was indicated by a green-blue colour in the upper layer. The entire solution was titrated with HCl (0.01M) to the appearance of the yellow colour. Warming, shaking and titration continued until the yellow colour of the upper layer remained permanent. The procedure was repeated for each sample. Percentage soap contents was then calculated according to the equation given below:

$$\% \quad \text{Soap content} = \frac{\text{Vt} \times 0.01\text{M acid} \times 0.608}{\text{Ws}}$$

Where 0.01 M = Molarity of HCl.

Vt = Volume of titrant

Ws = Weight of sample in milligram.

3.4.3.4 SOLUBLE MATTER

The oil (2.0200g) was introduced into a conical flask (100 cm^3). Petroleum ether (20Cm^3) was added, the flask corked and shaken vigorously and then allowed to stand for 30 minutes at room temperature. The mixture was filtered using Whatman filter paper. The filter paper containing the insoluble components was carefully washed with small amount of solvent until the filtrate was free from oil. The filtrate and washings was placed in a evaporating dish. A cone of a folded filter paper was placed in a dish containing the filtrate with the apex up and was lighted from the apex where upon the filtrate (petroleum ether) ignited and burnt quietly. The residue was ash to constant weight in a muffle furnace (600 ^0C). The residue was then cooled to room temperature and weighed. The procedure was repeated for each sample, and percentage soluble matter obtained according to the equation below:

$$\% \text{ Soluble Matter} = \frac{Wr \times 100}{Ws}$$

Where Wr = Weight of residue in milligram

Ws = Weight of sample in milligram

3.4.3.5 ASH CONTENT

Oil sample (2.0372g) was introduced into porcelain crucible (15 cm^3). Free flame was applied to heat gently until the oil was ignited by application of

a small flame to the surface. The heating continued just enough to keep the sample burning. When sufficient oil was consumed to allow the addition of more, the heat source was removed and oil allowed to cool until burning ceased. Another portion of the oil (1.0314g) was added and heating continued as before. The heating continued in the same manner until the residue became a black charred mass and then heated in a muffle furnace (600°C) to constant weight. This procedure was carried out for each sample. The percentage ash content was calculated as stated by equation below:

$$\% \text{ ash content} = \frac{Wr \times 100}{Ws}$$

Where Wr = Weight of residue in milligram

Ws = Weight of sample in milligram.

3.4.3.6 UNSAPPONIFIABLE MATTER (PETROLEUM ETHER EXTRACTION METHOD)

This method was chosen because it is easier than ethylether method. The oil (2.5g) and ethanol (15 cm^3, 95%) were added to aqueous potassium hydroxide (2.5 cm^3, 50% $^{W}/_{W}$) and refluxed for 30 minutes or until the oil was completely saponified. The soap solution was transferred into separatory funnel and the total volume of reflux washed with ethanol (20 cm^3, 95%). The transfer was completed with warm and cold distilled water (20cm^3, 20cm^3).

The flask of reflux was rinsed with a little petroleum ether and added to the separatory funnel. The separatory funnel was allowed to cool to room temperature and petroleum ether ($25cm^3$) added.

The mixture in the separatory funnel was shaken for at least 1 minute and allowed to be separated and clarified. Care was taken to separate the upper layer from the lower layer without inclusion. The petroleum ether layer was collected in another separatory funnel ($250cm^3$). The extraction was repeated six more times with portions of petroleum ether ($25cm^3$), shaking vigorously with each extraction. The combined extracts washed in a separatory funnel three times with portions of ethanol ($12.5cm^3$, 10%), shaking vigorously and drawing off the ethanol layer after each wash.

Petroleum ether extract was then transferred into a beaker and evaporated to dryness on a water bath. The residue dried in an oven (80°C) to a constant weight. Finally the residue was then cooled in a desiccator and weighed. The warm ethanol ($25cm^3$, 50^0C, 95%) containing phenolphthalein indicator ($0.5\ cm^3$) previous neutralised to a faint pink colour with NaOH (0.02 M) was added to the residue in a beaker. The mixture was then titrated with NaOH (0.02M) to the same colour. The process outlined was repeated for each sample. the percentage unsaponifiable matter was calculated based on the two equations given below:

Weight of fatty acids in the extract in gram =

V_t x 0.02M NaOH x 0.0056

$$\% \text{ Unsaponifiable Matter} = \frac{(Wr - Wf) \times 100}{Ws}$$

Where Wf = Weight of fatty acids

Wr = Weight of residue

Ws = Weight of sample

3.4.3.7 LEAD

Oil sample (5 g) was ashed. The ash was dissolved in hydrochloric acid ($5cm^3$) and the solution neutralised with ammonia. Citric acid (2g) was then added to the solution and allowed to dissolve. Ammonia solution ($15cm^3$), and KCN (0.1g) were added respectively to the resultant solution. The solution was finally made up to $100cm^3$.

Aliquot ($10cm^3$) was introduced into separatory funnel ($250cm^3$). Solution (10 cm^3) of dithizone - chloroform (5g, 100 cm^3) was then added, closed and shaken for 30 seconds. The lower layer was drawn into a second separatory funnel, containing KCN -NH_3 solution ($25cm^3$) [18].

The funnel was shaken violently and the content allowed to separate. The lower layer was drawn off to a third separatory funnel containing the same

CHAPTER FOUR

4.0 RESULT AND DISCUSSION

4.1 SUMMARY OF RESULTS

Some physical properties, chemical properties and impurities (Contaminants) determination of each oil samples EMX20, 21 and 22 carried out and results obtained are provided in table 4.1, 4.2 and 4.3 respectively.

4.1.1 PHYSICAL PROPERTIES

The following physical properties were determined, namely: percentage oil content, specific gravity, boiling point, refractive index and percentage refining yield by using standard methods and expressions outlined in section 3.4.1.

The results obtained are given in table 4.1 below:

Table 4.1: Results of Some Physical Properties Determination

	SAMPLES		
Properties	Emx20	Emx21	Emx22
Percentage oil content	34	30	25
Specific gravity	0.90	0.91	0.90
Boiling point °C	195	230	200
Refractive index 40°	1.466	1.466	1.465
Percentage Refining yield	87	87	87

4.1.1.1 DISCUSSION OF PHYSICAL PROPERTIES RESULTS

The extraction of oil carried out for the three varieties of groundnut indicated that Sammnut-10 (RMP-12), Emx20 contain more oil (34%), followed by Tivi variety, Emx21 (30%) and then Kuta local variety, Emx22 having about 25% of oil. Various species of groundnuts contains different amount of oil. However, the quantity extracted depend on the solvent and method used.

The efficiency of refining was tested visually and showed transparent, clear, colourless appearance, indicating that refining produced high quality oil, which tend to agrees with most literature (the darker the colour, the poorer the quality) [4].

The specific gravity for Emx 21 agrees with the range given by Standard Organisation of Nigeria (SON), but variety Emx 20 and Emx 22 seems to be slightly different. Though the differences were not so significant they could have arose from the source and method of cultivation in which these varieties experienced and hence the various percentage composition of fatty acids and degree of unsaturation. It was observed that the results obtained lie within the range of most literature of fats and oils (0.90-0.92). [3].

The three oils gave the range of boiling points with the variety Emx 21 having the highest boiling point of 230°C followed by Emx 22 and Emx 20

having 200°C and 195°C respectively. The high boiling point exhibited by Emx 21 may be attributed to its constituents fatty acids of high molecular mass and hence the presence of transisomers of unsaturated acids. Refractive index of the oils tend to lie within the range of Codex Standard (1.460-1.466) [25]. The values obtained (1.466, 1.465) indicated the high purity of the oils. On the other hand, the percentage refining yield (87%) for the three varieties of oils in question show that the refining method employed is viable and economically reliable.

4.1.2 CHEMICAL PROPERTIES

Table 4.2 shows the list of chemical constants of each oil samples determined, namely: acid value, saponification value, iodine value and peroxide value respectively, by using expressions in section 3.4.2.

Table 4.2: Results of Chemical Constants of Oil

	SAMPLES		
Properties	Emx20	Emx21	Emx22
Acid Value	0.6	0.6	0.6
Saponification Value	188	188	188
Iodine Value (WIJS)	99	98	98
Peroxide Value ($M\eta_0 kg^{-1}$)	0.11	0.12	0.11

4.1.2.1 DISCUSSION OF CHEMICAL PROPERTIES RESULTS

The acid, and saponification values for all the oil samples determined tend to agree and fall within the limits specified by previous workers [3,19]. It can be seen from the table that the iodine values for the three varieties conform with the theoretical values of 80-106.

The Emx 21 and Emx 22 varieties have less iodine value while that of Emx 20 is higher. This implies that Emx 21 and Emx 22 varieties are less unsaturated than Emx 20.

It is also evidence enough from the table that the peroxide values for the three oils is about 0.12 $M_{eq}Kg^{-1}$ maximum compared with literature value of 10 $M_{eq}Kg^{-1}$ Maximum. These values are considered relatively low with the Emx 21 variety being higher in comparison to Emx 20 and Emx 21 species which apparently have identical lower values. It is pertinent from the values obtained to state that all the oils samples used were not liable to rancidity and thus considered safe.

4.1.3 IMPURITIES

Various forms of impurities, namely: moisture and volatile matter, insoluble impurities, soap contents, soluble mineral matter, ash content, unsaponifiable matter were determined by using equations in section 3.4.3 and results got are presented in table 4.3 below:

Table 4.3 Results of Impurities in Oil

	SAMPLES		
Impurities % $^{M}/_{M}$	Emx20	Emx21	Emx22
Moisture and Volatile Matters	0.2	0.3	0.2
Insoluble impurities	0.02	0.04	0.07
Soap Content	$0.6x10^{-6}$	$0.9x10^{-7}$	$0.9x10^{-7}$
Soluble mineral matter	0.08	-	-
Ash Content	0.04	-	-
Unsaponifiable matter	0.6	0.9	0.7
Lead (ppm)	-	-	-

KEY

- **Not detected.**

4.1.3.1 DISCUSSION OF IMPURITIES RESULTS

The moisture and volatile matter content determined in each of the oil sample showed that both Emx 20 and Emx 22 have values very close to the

literature value of 0.2% maximum. However for Emx 21 variety, the value gotten is above the range of 0.1%. It can be deduced from the data recorded that the insoluble impurities of the Emx 20 and Emx 21 varieties are below maximum limits of 0.05% while the Emx 22 gave a value slightly higher than the maximum level. The slightly higher level of impurities exhibited by Emx 22 can be attributed to its historical experiences such as the geographical location in which it was grown and amount of fiber and nitrogenous substances it contains.

The amount of soap contained in the groundnut species analysed is lower than the upper limit level of 0.005% in each case. The values represented in table 4.3 show that Emx 20 has the least amount in comparison to Emx 21 and Emx 22 samples.

On the other hand, soluble mineral matter and ash content of Emx 20 are relatively low or infinitesimally small suggesting therefore that sample of groundnut species under investigation can be considered safe enough within limits of experimental errors for local consumption and industrial application.

Also shown in table 4.3 is the unsaponifiable matter, which values obtain lie below the maximum level of 10% $^{M}/_{M}$ which implies that the three oil contained very little percentage of unsaponifiable matter. The Emx 21 has

smallest amount of unsaponifiable matter, followed by Emx 22 and Emx 20 respectively.

Lead content determination method used gave no reading indicating the absence of lead in all samples in comparison with literature value of 0.1ppm maximum. Even though the sensitivity of the method employed may be low, it is evidence enough that the amount of lead content in all the varieties under study is relatively low. Then it can be stated that adverse effect of lead when consumed is within the acceptable limit.

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

Groundnut oil is one of the most important industrial raw materials, that is, in the manufacture of margarine and is highly demanded for human consumption. It is therefore necessary to have good understanding of processes and analysis involved in order to obtain quantitative and qualitative products.

Physical appearances of the three crude oil extracts used appeared to be quite different indicating their types and level of impurities they contained. Though the presence of impurities is inevitable in any given oil, values obtained in our study predict some reasonable quality of the oils in question.

However, after the distillation process, the three refined oil appeared clear and similar. It is evident from the results obtained (table 4.1) to suggest that the amount of oil contained by a particular species of groundnut is a factor of its sources and variety. In the present study variety Emx 20 seems to have higher amount of oil followed by Emx 21 and the least of all is variety Emx 22.

It is also pertinent to note that there is a lot of similarities in chemical behaviour of groundnut oil and cashew-nut oil. These similarities are widely demonstrated by the saponification and iodine values shown in table (4.2). If the

iodine values for the varieties used are meaningful and anything to rely on, it can be stated that the magnitude of the values obtained, suggest that there are more unsaturated fatty acids than saturated ones present in the 3 varieties. This is confirmed by the fact that the extracted oils behaved mostly like liquid at room temperature. The data of physical and chemical analysis of samples used tend to agree with theoretical values. The slight differences observed in some cases can be attributed to differences in the species background and to some extent human and experimental factors.

In the course of the present study, there were limitations such as lack of adequate or essential chemicals, and equipment for instance, determination of palmitic acid, oleic acid, fatty acids composition using gas liquid chromatography could not be carried out. Similarly, Iron, Copper and Arsenic determination were not done because of lack of chemicals e.g. thioglycollic acid, sodium diethyl dithiocarbamate, hydrazine sulphate or silver diethyl dithiocarbamate.

5.2 RECOMMENDATIONS

Sequel to the physical and chemical data revealed by the present study, it is appropriate to recommend variety Emx 20 as the best for both industrial and

local application/uses. The growth of this variety can be encouraged by motivating and educating the peasant farmers who are the main producers.

In view of the fact that some analysis were not carried out due to limitations earlier highlighted, it will be advisable for further work to be done on the varieties used. In this way more information for relative comparison can be obtained and reasonable conclusions drawn. To achieve this, it is recommended that adequate chemicals and equipment be provided or provision be made for inter-organisational collaboration where such items may be available.

Finally, and in conclusion, all the three varieties of groundnuts oil used can be certified in terms of quality and quantity to be of economical valuable.

REFERENCES

1. Raw Material Research & Development Council, Technical Information on Crop Production in Nigeria, (August, 1994), 30-34.

2. Gibbon D. and Pain A., Crop of the Drier Regions of Tropics, Low priced Ed. ELBS (1985), 121.

3. Standards Organisation of Nigeria, Nigerian Industrial Standards for Edible Vegetable Oil, UDC: 664.34 NIS: 289 (1992), 4-12

4. Ibemesi A., Vegetable Oils and Industrial raw Material, Nigerian Perspective, University of Nigeria, Nsukka (1992), 8-19.

5. Weiss E. A., Oil Seed Crops, Longman London and New York (1983), 100-102

6. Weiss J. A., In Mcgraw-Hill Encyclopedia of Science and Technology, 5th Ed., Vol. 5, Mcgraw-Hall (New York, 1982), 319.

7. Gigg O. R. et. al, In Mcgrew-Hill Encyclopedia of Science and Technology. 5th Ed., Vol. 14, Mcgraw-Hill (New York, 1982), 99.

8. Tedder M. J. et. al, Basic Organic Chemistry, Industrial Products, Part 5, John Wiley and sons. London (New York 1975), 535-540.

9. Simpson B. B. and Orgorzaly, C. M. Economic Botany, Plants in our World, Mcgraw-Hill international Ed., Biological Science Series (New York, 1986), 292-316.

10. Parker P. S. In Mcgraw Hill Dictionary of Physics, Mcgraw Hill Book Company (New York, 1985), 624.

11. Ibemesi A., Vegetable Oils as Industrial Raw Material, Nigerian Perspective, University of Nsukka (1992), 20-24.

12. Parker P. S., In Mcgraw-Hill Dictionary of Chemical terms, Mcgraw-Hill Book Company, New York(1985), 321.

13. Goff J. H. and Blachly, F. E., J. Ann. Oil Chemists Society (1973), 320-411.

14. Standard Organisation of Nigeria, Nigerian Industrial Standards for Edible Vegetable Oil NIS: 289/1992, 1.

15. Shappiro H. et. al, In Mcgraw-Hill Encyclopedia of Chemistry, Mcgraw-Hill Book Company, New York, St. Loiusanfrancisco (1983), 558-559.

16. Leppik E. E., Assumed Gene Centres of Groundnut and Soybeans, Economic Botany, Longman (1971), 188-194.

17. Smartt J. J. et. al, The genones of Arachis hypogaea, Euphytica, Longman (1978), 665-675.

18. Williams K. A., Oils, Fats and Fatty foods, their practical examination, 4th Ed; J & A Churchill Ltd. (1966), 30-105.

19. Pearson D., The Chemical analysis of foods, 7th Ed, Churchill Livingstone, Edinburgh London & New York (1976), 448.

20. Blachly F. F. et. al, J.A.M. oil Chemists Society (1948), 234-320.

21. Mohammed J. M., Crop Production Department, Federal University of Technology, Minna, Nigeria.

22. Ozemoyah P. O., Refining of Palm Oil Using Locally developed materials. A paper presented at 15th Annual Conference of Nigerian Society of Agricultural Engineers at Maiduguri (September, 1991).

23. Ogwala P., Refining of Palm Oil Bleaching Capacity of Various Nigerian Clay Deposits, Int. J. of foods Science & technology (1989), 647-651.

24. Durst D. H. and Gokel W. G., Experimental organic Chemistry, 2nd Ed., Mcgraw-Hill Book Company (1980), 31-53 & 560-568.

25. Pearson D., The Chemical Analysis of Foods, 7th Ed., Churchill Livingstone (1976), 488-509.

26. William H., Official Methods of Analysis of he Association of Official Analytical Chemists, 13th Ed., AOAC Washingtone (1980), 437-465.

27. Holderness A. and Lambert J., A Ne Certificate Chemistry, 6th Ed., Heinemann Educational BookNig) ltd. (1984), 402-403.

28. Gabb, H. M. and Latchem, E. W., andbook of Laboratory Solutions, Andre Deutsch Ltondon (1967), 53.