# INVESTIGATION OF THE MAJOR CHARACTERISTICS OF SOME VEGETABLE OILS USED IN NIGERIAN FROM LOCAL AND FOREIGN SOURCES

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# D E C L A R A T I O N

This is to certify that this research project is original, and that it has not been presented in part or full anywhere for the purpose of the award of a degree.

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# D E D I C A T I O N

This project is dedicated to the Memory of my father, late Chief JOSEPH OYADIJI AJALA, the late Esa of Oyan, and to ALMIGHTY GOD, the Giver of knowledge and wisdom who saw me through the period of my tribulations.

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

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## ABSTRACT

Analysis was carried out on seventeen oil samples namely, palm oils from Kano, Samaru, Funtua and Oyan, Sunflower oil made by Boulogue Cedex from France, Corn oil made by Lindenberg from Federal Republic of Germany, Salad oil, cookwell oil, Melon Seed oil (extracted in the laboratory) Groundnut oils from Samaru, Funtua and Kano respectively,

The results show that, Coconut oil and palm kernels oils have the highest saponification values while the refined oils or the seed oils have the lower saponification values. It is evident from the results that all the refined oils, sunflower, salad, melon, cookwell, corn, coconut, and groundnut have high iodine numbers while coconut and palm kernel oils have the least iodine numbers.

It is also evident from the result that acid value and percentage free fatty acid are very low for oils like, sunflower, salad, cotton, melon corn, groundnut and palm oils have high acid and percentage free fatty acids.

Finally, the amount of trace elements found in the oils are lower in the refined oils than the oils which are obtained locally.

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# CHAPTER 1

# INTRODUCTION

# C H A P T E R  1

## I N T R O D U C T I O N

### 1.0 DEFINITION OF OIL

Fats and fatty oils are water insoluble substances of plants and animals origin[1] which consist mainly of glyceryl esters of long-chain fatty acids. As a matter of fact, there is no scientific differentiation between edible oils and fats and the two terms may be used interchangeably.

The common distinction between them is to consider solid product as fats, and liquid ones as oils, this difference is temperature dependent at high temperatures all the edible oils and fats are liquid and at low temperatures they appear to be solid. Even this latter statement is only apparently true, as most natural fats, while appearing solid at ambient temperature are strictly a blend of solid and liquid components[2]. The products which form this subject could equally well be referred to either as fatty oils or simply fats, irrespective of consistency at ambient temperature.

### 1.1 CLASSIFICATION:

The term 'Oil'[2] has been applied in general usage to describe certain physical characteristics of various

substances rather than their chemical nature or composition. This common use has led to confusion over the nature of oils and it is essential from the on set to understand their true classification.

Oil and fats can be divided into groups according to both their origin and their chemical nature.

1.1a FIXED OILS AND FATS:

Animal fats derived from the milk and body tissues of animals including Marine animals.

1.1b VEGETABLE OILS AND FATS:

These are obtained from the fruits and seeds of a wide range of plants. These oils and fats are esters of fatty acids (Specifically glycerides) and are non-volatile.

1.1c MINERAL OILS:

These are distilled from petroleum and shale deposits. This group of materials include paraffine, oil, fuel oil and most lubricating oils.

1.1d VOLATILE OR ESSENTIAL OILS:

Oils of lemmon, oil or cloves, and cinnamon oil. These are obtained mainly from plant sources, although some are derived from animals. These oils are complex mixtures of aldehydes, ketones, hydrocarbons, alcohols, acids and short chain esters. They are used for flavours, perfumery and pharmaceutical purposes.

1.1e CRUDE FATS:

These are completely untreated, as isolated from the oil-bearing tissue. Crude oils are unpalatable and hence inedible in this state.

1,1f NATURAL FATS:

This may have been treated to remove the impurities which make them unpalatable, but otherwise have not been altered.

1.1g MODIFIED FATS:

These are fat or oil which has been changed by chemical treatment or physical separation to produce a fat which is different from the original material.

1.1h SYNTHETIC FATS:

These are fats which have been chemically made from various source materials. Some have been produced by oxidation of hydrocarbons to fatty acids which are then esterified with glycerol. This process was operated on a large scale in Germany (1939;45)[3]; however, not only was it costly, but the fats produced contain unnatural fatty acids which were reported, to give rise to toxic effects.

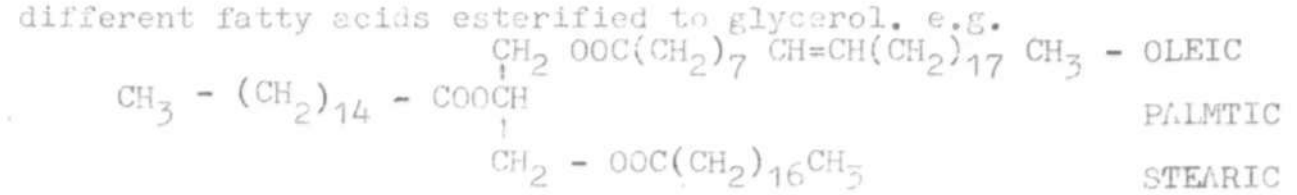
Another process which is partly chemical, partly biological consist of the synthesis of fatty acids from carbohydrates by micro organisms, and the

esterfication of the fatty acids with synthetic glycerol.

1.2 COMPOSITION:

Oils and fats are essentially esters[1] and, in the great majority of commercial oils, the alcohol component is glycerol. The non-ester portion is usually less than 2% of the total oil and may contain sterols, hydrocarbons, aliphatic alcohols, and other organic compounds. A few oils contain one or more long chain alcohols in place of glycerols others contain an ether components as part of the glyceride molecule e.g. certain fish liver oils.

Triglycerides of a single fatty acid do occur in natural oils e.g. glycerol trioleate (triolein), but by far the greater proportion of oils consist of mixed glycerides. Mixed glycerides contain either two or three different fatty acids esterified to glycerol. e.g.




The triglycerides are formed by the reaction of the trihydric alcohol glycerol and fatty acids. The predominant acids in natural fats occur as straight chains containing 12 to 18 carbon atoms. A few shorter chain acids acids present in small proportions are characteristic of milk fats, while longer chains (20 and 22 carbon atoms) are found in

certain types of materials, especially in fish oils. In addition to the chain length of acids another important variable characteristics of the fats, namely the degree of unsaturation. While the number of unsaturated acids which could occur is very large, the number found in natural fats is limited. The common fatty acids are listed below:

Table 1

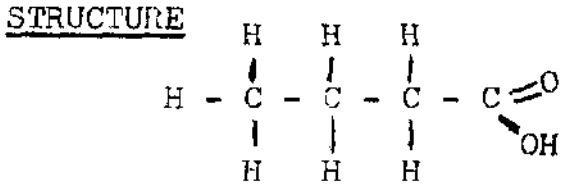
| Common Name | Chain length C-atom | Degree of Unsatura-tion | Abrevated Stctural formula | Melting Point °C |
|---|---|---|---|---|
| Lauric acid | 12 | Saturated | $CH_3(CH_2)_{10}COOH$ | 44.2 |
| Myristic " | 14 | Saturated | $CH_3(CH)_{12}COOH$ | 54.7 |
| Palmitic " | 16 | Saturated | $CH_3(CH_2)_{14}COOH$ | 62.9 |
| Stearic " | 18 | Saturated | $CH_3(CH_2)_{16}COOH$ | 69.9 |
| Palmitoleic acid | 16 | Mono-Un-Saturated | $CH_3(CH_2)_6CH\text{-}CH(CH_2)_7COOH$ | -0.5 |
| Oleic acid | 18 | Mono-Un Saturated | $CH_3(CH_2)_7CH=CH(CH_2)_7COOH$ | 16 |
| Linoleic acid | 18 | Di-Un saturated | $CH_3(CH_2)_4CH=CH(CH_2)_7COOH$ | -5 |

The structure of the fatty acids is relatively simply and follows that of the simplest organic compounds, the normal paraffins. The molecule of a saturated acid consists of a chain of carbon atoms, each with its requisite number

of hydrogen atom attached, except for the terminal carbon which carries a carbonyl organic acid grouping. The following example shows the structure of butyric acid.

$CH_3 - CH_2 - CH_2 - COOH$

STRUCTURE



The Unsaturated acids have a deficiency of hydrogen atoms so that the link between two unsatisfied carbon atoms becomes a double bond. Unsaturated acids have a very low melting point, so that at ambient temperature they are liquid, . whereas the saturated acids are solids with fairly high melting points. The different acids have an influence on the melting point of the corresponding triglycerides, thus a triglyceride with three unsaturated acids will be liquid, and one with three saturated, a hard solid. It follows that when the unsaturated fatty acids are combined with additional hydrogen, as in the process of hydrogenation they are converted to saturated acids of a higher melting point, hence the use of the alternative term 'hardening'[3].

The most abundant fatty acid is Oleic acid $C_{18}$:1 —— cis Oleic. $C_{17}H_{33}COOH$.

STRUCTURE

$$CH_3(CH_2)_7\overset{H}{\underset{|}{C}} = \overset{H}{\underset{|}{C}}(CH_2)_7COOH$$

It is present in all known fats in amounts ranging from less than ten percent in coconut oil up to over eighty percent in some olive oils. Among the saturated fatty acids, Palmitic acids $C_{16}$:O

$$CH_3(CH_2)_{14}COOH$$

is the most common while stearic acid $C_{18}$:O

$$C_{17}H_{35}COOH \longrightarrow CH_3(CH_2)_{16}COOH$$

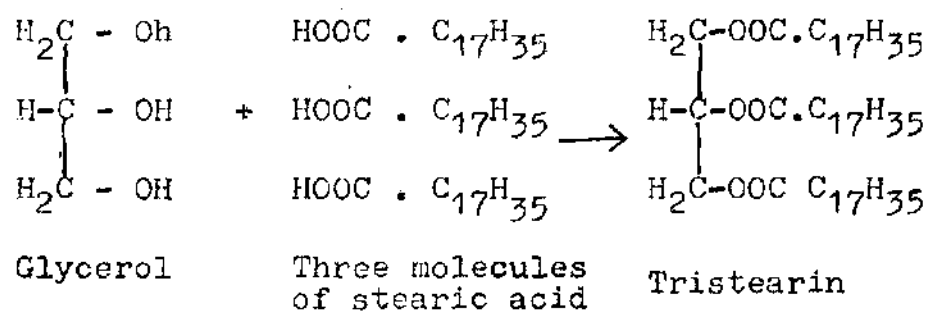
is far less abundant that is generally realized, although it is a major component of many animal fats.

It is the combination of the different acids and glycerol which gives the wide range of triglycerides, and hence the physical characteristics of the various oils which occur in nature are influenced.

As the fatty acid portion of the fat is about ninety-five percent of the total weight of the molecule, the chemical performance is principally dependant on the fatty acids present in the triglycerides.

The structure of triglycerides can be illustrated with the aid of a typical member of the group.

TRISTEARIN



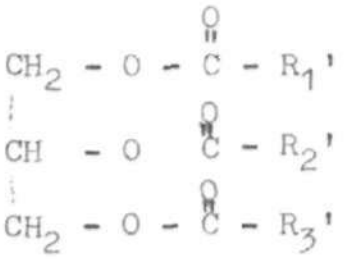

Tristearin is a simply triglycerides with the same fatty acids attached to each carbon of the glycerol chain.

Although fats and oils are predominantly triglycerides, there are minor components present in crude and refined oils. The most important minor constituents are phospholipids, sterols, vitamins, and other impurities of various sorts. Most of the unsaponifiable matters present in oils are made up of these minor constituents[2,3].

## 1.3 GENERAL PROPERTIES

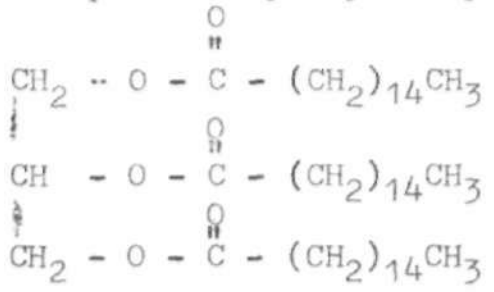
Fats, oils are naturally occurring organic materials called lipids and have general properties of esters of high molecular weight. These in turn are greatly influenced by the fatty acid component[2,3,4].

The general molecular formula is given below where $R_1'$ $R_2'$ $R_3'$ can represent alkyl groups.



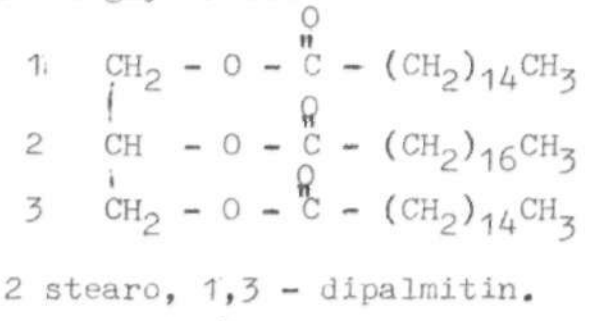
Typical example is Glyceryl tripalmitate palmitin.

(i)



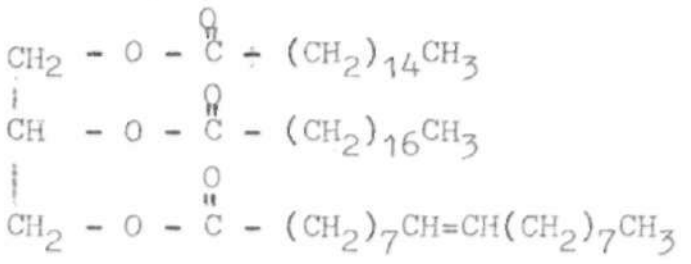
Mixed glycerides

(ii)



2 stearo, 1,3 - dipalmitin.

(iii)



Glyceryl Palmito - Stearo Oleate

The composition of a fat is usually expressed in terms of the acids which may be obtained from it by hydrolysis. Certain fats or oils give mainly one or two acids for example olive oil gives (80% oleic acid, 6% palmtic acid, 4% stearic acid and 7% linoleic acid) Palm oil, (43% palmitic acid, 43% Oleic acid 10% lineoleic acid and 4% stearic acid)[4]. The chemical properties of fats and oils are based on this fatty acid composition.

Fats and oils are essentially neutral, relatively inactive chemically and of very low volatility. They have relatively the same density. They are slightly less dense than water and are almost completely insoluble in it, although small amounts of water will dissolve fats. They will dissolve about 0.1% in water at room temperature and solubility increases with temperature and with the presence of free fatty acids. Both the degree of unsaturation as measured by Iodine value[4], and the average molecular weight as measured by the saponification value affect the density slightly.

Fats when melted are considerably less dense than if present in the solid state.

The specific heat of liquid fats increases slightly with decrease in iodine value and varies almost linearly

with the temperature. The heat of fusion of fats and oils is a function of the compactness of the fat crystals, being higher for fats of high molecular weight than for those of low molecular weight. Heats of fusion of pure trilaurin, trimysistrin, tripalmitin and tristearin are 46.2, 50.3, 53.1 and 54.5g-Cal/g respectively[7].

The vapour pressures of fats and oils are very low. Reported values in mmHg include the following: tristearin 0.001 at 253°C and 0.050 at 313°C, trilaurin 0.001 at 188°C and 0.050 at 244°C [4,7].

Heat of combustion of fats and oils are calculated by Bertram[4]. He found that the heat of combustion of fats and oils is about 9500g - Cal/g in cotton seed oil and lard. It is also found to be as high in other oils.

Fats and oils are relatively poor conductors of heat. The thermal conductivity varies little for different oils and ranges from about 0.00040 cal/(Sec) (1 sq.cm) at 20°C to 0.00039 at 100°C.

Refractive index of fats and oils depends upon its average molecular weight and to a minor degree upon its glyceride structure as well as its degree of unsaturation.

Fats and oils are soluble in most non-aqueous solvents. Their solubility is influenced by the chain length of the component acids and as their degree of unsaturation increased, chain length of the saturated acid decreases solubility, increased unsaturation increases it. Most of the common organic solvents such as acetone diethyl ether chloroform, petroleum spirit, tetra chloromethane will dissolve fats and oils in the liquid state.

Since the alcohol moiety is glycerol in all common oils and fats, the differences in chemical and physical properties of the glycerides are dependent on the nature of the fatty acid moiety. Fatty acids are classified mainly by long chain length and degree of unsaturation. Thus the common acids are short - chain about ($C_4$ - $C_8$), medium ($C_{10}$ - $C_{14}$), and long chain ($C_{16}$ and above). The melting point of acids and their glyceryl esters rises with the chain length. The boiling point of acids also rises but solubility in water and in-organic solvent decreases. Thus the short chain acids have appreciable volatility and solubility in water whereas the long chain acids are, for all practical purposes, non-volatile at ordinary temperature and pressure and are practically insoluble in water.

Fatty acids are classed as saturated (no double bond) Mono-unsaturated (one double bond) and poly unsaturated - (two or more double bonds)[2]. The melting point of the acids and their glycerol esters decreases from saturated to poly unsaturated, solubility increases, but volatility and boiling point change only slightly.

When fat and oil is exposed to the oxygen of the air, it absorb it at a rate dependent on the degree of unsaturation. As oxygen absorption takes place, the rate of oxidation increases, and the fat or oil reaches a state of rancidity. The rate of oxidation is also influenced by temperature and light. As oxidation proceeds, peroxides form and these then break down to form aldehydes, ketones and other shorter chain compounds, which together give the unpleasant smell and taste which we associate with rancid fats.

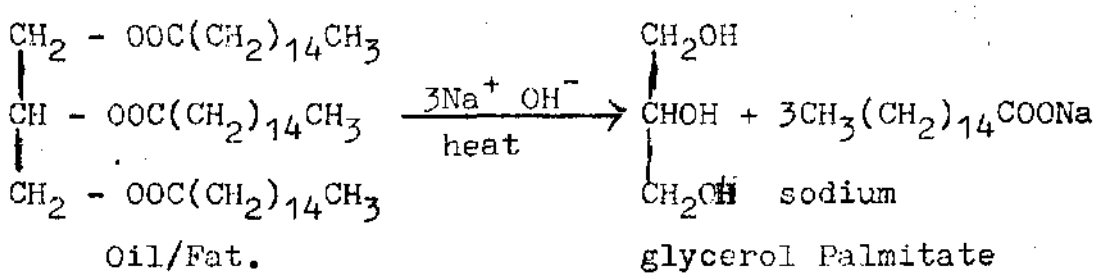
The presence of trace metals in fats and oils increases the rate of oxidation of fats and oils.

Highly unsaturated fats or oils, when heated in air, undergo polymerization[3]. The exact mechanism of this process is not fully understood, but it is sufficient for our purposes to accept that cross-linking takes place between adjacent molecules. The double bonds of the fatty acids are involved in this cross-linking, which is of

great importance to the paint industry. In the edible oil field it can give rise to the deterioration of frying fats owing to polymerisation. Soyabean oil, when used as a frying fat, soon polymerises on the side of the cooking vessel and builds up a yellow 'varnish' of polymerised material. Polymerization is accompanied by a rise in viscosity, a fall in iodine value and deterioration of flavour.

Another property of fats and oils which leads to deterioration is the susceptibility to hydrolysis. Since fats are a combination of glycerol and fatty acids they are chemically classed as esters. Like all esters, the linkage between the alcohol and acid can be broken by hydrolysis, giving the free alcohol and free acid. Since in fats the alcohol is trihydric, each fatty acid can, under suitable condition be separately removed, leaving progressively, diglycerides, monoglycerides and finally glycerol. This type of hydrolysis is mainly due to enzymes called lipases which occur not only in the digestive juices of animals, but are also secreted by bacteria and moulds and are present in many plant tissues.

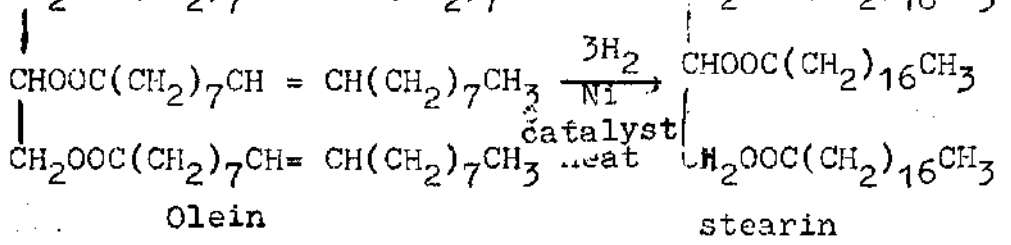
Boiling oils and fats with aqueous alkali hydrolyses it to glycerol and salt of fatty acids. The salt of long chain fatty acids are soaps.




Oil/Fat. glycerol Palmitate

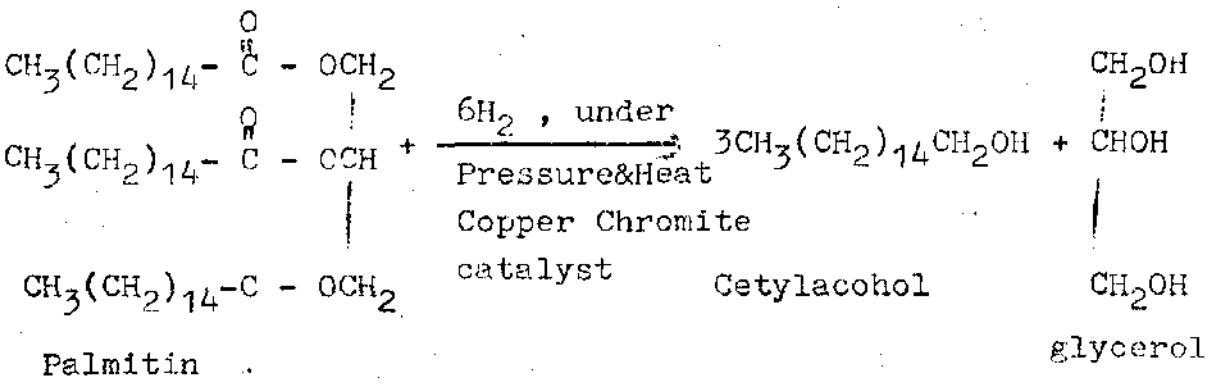
Glycerides that have unsaturated acids can be converted to saturated glyceride by catalytic hydrogenation. This property is used industrially in the process of hydrogenation.

This is illustrated by the conversion of Olein to stearin, wherein hydrogen adds to the carbon - carbon double bonds.




Olein stearin

The ester links in glycerides may be hydrogenolyzed with a saturated glyceride, this leads to long chain saturated alcohols which can be used to manufacture certain synthetic detergents. Two molecules of hydrogen are used per ester linkage in presence of copper chromate as catalyst.




long Chain unsaturated alcohols may be obtained by the analogous hydrogenolysis of unsaturated glycerides, employing a catalyst such as zinc chromite which hydrogenolyses the ester linkage without hydrogenation of the carbon-carbon double bonds.

For example Olein yields oleyl alcohol.

$CH_3(CH_2)_7CH = CH(CH_2)_7CH_2OH$.

## 1.3 VEGETABLE OILS:

Vegetable oils are derived from the seedsof plants which grow in many different parts of the world. Several hundred varieties of plants are known to have oil bearing seeds, but in fact only about a dozen are commercially significant. These are cotton seed, groundnut, sunflower, coconut, Palm oil, Palm kernel, Melon seed is not very common as other oils.

Vegetable plants producing oils may be grouped according to the botanical classification of the plants yielding the oils, but this method of classification may be systematic. Another

method of classification divides them into drying, semi-drying and non-drying oils. This method has its weaknesses and is more suited to classification of industrial use than for edibility.

The alternative method of classification is to group them according to the dominant fatty acids present. On the basis of this last classification, the oils are classified with the dominant fatty acids with which they are associated.

Lauric acid oils:- We have coconut and Palm Kernel.

High saturated acid oils:- These are divided into two

(1) Vegetable butters - Shea nut

(2) Palm Oil - Palm oil.

Oleic/Linoleic Oils:- Groundnut oil, Maize, Cotton seed oil, Sesame, sunflower oil

Linoleic/linolenic acids - Soyabean, linseed

Erucic acid oils - Rape seed, Mustard seed oil.

1.3a LAURIC ACID OILS

There are only three commercially important oils in this group in which Lauric acid content approaches 50% and the unsaturated acid content is low. Coconut oil and Palm kernel oil are the most important.

1.3b COCONUT OIL:

This is obtained from the nut of the coconut palm (Cocos nudifare). The palm is of unknown origin. It is thought to have spread across polynesia from the Indian Ocean. Today, the palm is widely distributed in tropical areas where it grows wild; especially on the tropical coasts and on the islands of the pacific. Malaysia, Indonesis, the philipines, south sea islands and Ceylon are the principal growing areas. In these areas large estates are devoted to the cultivation of the coconut palm. It does equally well inland in well drained, loamy soils of the tropics.

Coconut palms are perennial. Best growth is obtained in areas with rainfall well distributed and amounting to between 50 - 90 inches (130 - 230) annually. It thrives well in a warm sunny climate in which there is little temperature fluctuations, ideal condition being 85°F (29°C). It grows well in deep alluvial soils or sandy loam. The kernel of coconut when dried is known as copra, and from this coconut oil is extracted.

After harvesting, the coconut is split and left to dry. Copra yields about 63% oil. Local inhabitants use this oil for cooking and lighting and for a hair dressing. Industrially, large quantities are required throughout the world in the manufacture of Margarine and cooking oils and fats. Coconut oil is not commonly used in the manufacture of soap and lubricants as other oils. The residue left after extraction of the oil becomes a nutritious food for animals. Another minor source of oil in coconut is the paring, the green skin. The production of paring oil has become quite important in Ceylon[1]. This has not been in practise in Nigeria. A certain amount of fresh kernel is made into desiccated coconut for the confectionery trade.

The oil extracted consists predominantly of saturated fatty acids with Lauric acid accounting for about 55% of the total oil by weight table 11.

It contains only small amounts of unsaturated acids in the form of Oleic and linoleic acids. It is liquid at normal tropical temperature with a low iodine value, high saponification value and the percentage free fatty acid very low.

Table 11

| Fatty Acid composition | | Coconut oil % | Palm Kernel oil % |
|---|---|---|---|
| Caprytic | $C_8$:0 | 6 | 3 |
| Capric | $C_{10}$:0 | 6 | 4 |
| Lauric | $C_{12}$:0 | 44 | 51 |
| Myristic | $C_{14}$:0 | 18 | 17 |
| Palmitic | $C_{16}$:0 | 11 | 8 |
| Stearic | $C_{18}$:0 | 6 | 2 |
| Oleic | $C_{18}$:1 | 7 | 13 |
| Linoleic | $C_{18}$:2 | 2 | 2 |

1.3c PALM KERNEL OIL:

Oil plam (Elacis quineesis) produces a fruit which provides two different oils. The pulp contains palm oil which is highly coloured, is composed mainly of $C_{16}$ and $C_{18}$ fatty acids and behaves like most other vegetable oils apart from its higher melting point.

Within the pulp is a kernel which provides the source material for palm kernel oil.

Records have shown that until recently Nigeria[5] leads the world in production of palm kernels. The rivals are West Malaysia, and Indonesia.

Palm kernels:- World production by Country (10000Mt).

Table III

| HARVEST (a) | 78/79P | 77/78P | 76/77P | 75/76 | 74/75 | 73/74 |
|---|---|---|---|---|---|---|
| Nigeria(b) Oct-Sept | - | 220 | 320 | 320 | 265 | 276 |
| Indonesia (c) " | 110 | 93 | 91 | 83 | 82 | 69 |
| West Malaysia | 405 | 302 | 309 | 244 | 225 | 174 |
| Other Countries | - | 495 | 505 | 448 | 458 | 461 |
| World..... | 1170 | 1110 | 1225 | 1100 | 1030 | 980 |

(a) Bulk of harvesting time, i.e. first of the split years in the case of (1) and second in the case of (2).

(b) Commercial output

(c) Estate production.

The statistics above shows that at the peak years 75/76 abd 76/77, Nigeria produced 320,000 M/T of palm kernels. This level declined sharply to 220,000 M/T Tones in 77/78 whilst production by Malaysia depicts a planned growth from 1973, culminating in a staggering production level of 405,000 M/TONS in 78/79[5].

Although the production figure for Nigeria in 78/79 is not indicated above, there is no doubt that Malaysia retains its world leadership in palm kernel production.

The loss of leadership by Nigeria is caused by the "OIL BOOM".

The kernels are separated from the pulp and fibre and are usually shipped to Europe in this state, very small amount of the kernels is used locally. Palm kernel oil industry is just developing in Nigeria. The kernel are then cracked to release the nut from the shell and the nuts are either solvent extracted or subjected to pressure in order to win the oil from them. The local inhabitants, roast the kernels for a long time to release the oil, then separate the cake from oil and subject the cake to grinding, this is then boiled for a long time to release the remaining oil. The oil is then filtered from the remaining cakes.

This oil, though obtained from the same fruit as palm oil, is a very different product. Its composition and behavic r are very similar to those of coconut oil. Ref. Table II, which for many uses is freely interchangeable with it.

The oil is darker in colour than coconut oil and does not have such a pleasant smell or taste, but after processing it gives an almost white, pleasant flavoured nut oil which can be used in place of coconut oil.

1.3d PALM OIL:

Elacis guineensis[6].

Palm oil a major component of food in Nigeria and other West and Central African Countries, Industrial utilization of Palm oil in Nigeria, primarily for the manufacture of soap and Margarine is estimated at 35,000 tonnes per annum.

In 1960, Nigeria was the largest exporter of palm oil in the world having exported 186,312 tonnes. This figure dropped to 3395 tonnes in 1968, 7643 tonnes in 1970 and nothing was exported in 1979. At the same period, Ivory Coast exported 405 tonnes in 1968, 12,542 tonnes in 1970, and an estimated quantity of 170,000 tonnes in 1979. Similarly, Malaysia made an export of 286 tonnes in 1968. 402 tonnes in 1970 and about 1,830,000 tonnes in 1979. The sharp export drop for Nigeria is due to the "OIL BOOM"[5].

The oil palm is a perenial plant indigenous to tropical West Africa. Oil palm requires hot humid conditions with 1.5 - 1.8 meters annual rainfall. The oil is extracted from the fibrous layer of pulp called the pericarp.

The composition of palm oil is rather unique when compared to that of the other major fats and oils.

Most of the seed oils, such as soyabean, repeseed and sunflower seed oils are composed principally to unsaturated fatty acids. While the palm nut oil, coconut and palm kernel oil, contain predominantly saturated fats. Palm oil, however is composed of approximately 50% saturated fats primarily palmitic acid and 40 per cent unsaturated fats principally linoleic and oleic acids. Thus palm oil will tend to be semi liquid at ambient temperature, separating on standing into a deep red liquid fraction and a yellow solid fraction of about equal volumes.

The distinctive colour of the oil is due to fat soluble carotenoids which is responsible for the high vitamin A content of palm oil.

Composition of palm oil

Table IV

| Fatty acid composition | Percentage |
|---|---|
| Myristic | 1 |
| Palmitic | 48 |
| Stearic | 4 |
| Oleic | 38 |
| Linoleic | 9 |

1.3e COTTON SEED:

The cotton plant is grown primarily to produce cotton fibre. Cotton seed is therefore essentially a by product. Nevertheless it has risen to be the second largest producer of vegetable oil[1,3,6]. Although several other oil seed are more important in world trade. It was not until late in the last century that serious commercial uses were found for cotton seed after the cotton plant itself has been cultivated for several thousand years.

When mature the plant produces round, fluffy white seed vessels known as 'bolls', to which the fibres adhere before the cotton can be used, fibres and seed must be separated in a gin. The seeds are egg-shaped, about 3/8in. long and 3/16in. wide. Some are practically bald, known commercially as black seed, while others have a wolly lint on the cutside.

Cotton is produced in tropical, sub-tropical and cool temperature climates. It can survive with as little rainfuall as 20 inches per annum, there must be a distinct wet and dry season.

The main cotton seed producer in 1966 was the Soviet Union, followed by United State of America, China, Argentina, Brazil, Nigeria, Guatemala, Egypt, Iran, Mexico and Peru. As a result of the amount of cotton produced in Nigeria two cotton seed oil milling are established in Nigeria at Kano and Funtua.

The oil content of cotton seed varies between 15 and 25 per cent. The oil is used in the manufacture of Margarine cooking fats. The cake left when the oil has been expressed is a useful source of Animal foodder, as are the seeds themselves.

Table (V) below shows the fatty acid composition of cotton seed oil.

TABLE V

| Fatty acid Composition | Percentage |
|---|---|
| Myristic | 0.5 - 1.5 |
| Palmitic | 20 - 23 |
| Stearic | 1 - 3 |
| Oleic | 23 - 35 |
| Linoleic | 42 - 54 |

1.3f GROUNDNUT:

Arachis hypogaea[6].

Its natural habitat is sub-tropical part of South America and West Indies. It is now cultivated in most tropical and sub-tropical countries.

There are two types of this low growing annual, one characterized by a spreading or running growth, the other are more bushy type. Both types will grow in tropical and sub-tropical climatic conditions. It takes about four months to reach maturity.

Requirements:- Groundnut cultivation requires 25-50 inches of rainfall, concentrated in the six months of the growing season, temperature requirement is around 80°F (27°C) and growth is favoured by light loamy, sandy soil rich in lime.

The biggest producer of groundnut are India, China, and Nigeria. Both India and China cultivate the groundnut entirely for homeconsumption while Nigeria exports her groundnut. Groundnut have an oil content of forty-five percent[6].

The fatty acid composition is shown below in fig. VI.

Table VI

| Fatty acid Composition | | Percentage |
|---|---|---|
| Palmitic | $C_{16}$ : 0 | 6 - 9 |
| Stearic | $C_{18}$ : 0 | 3 - 6 |
| Oleic | $C_{18}$ : 1 | 53 - 71 |
| Linoleic | $C_{18}$ : 2 | 13 - 27 |
| Arachidic | $C_{2}0$ : 0 | 2 - 4 |

Table VI (CONTD')

| Fatty acid Composition | | Percentage |
|---|---|---|
| Beharic | $C_{22}$ : 0 | 1 - 3 |
| Lignoceric | $C_{24}$ : 0 | 1 - 3 |

1.3g WATER MELON

Citrullus Unlgaris[6].

Water melon is called Egunsi in Yoruba, Ogili in Igbo, and Agusi in Housa.

Melon seed oil is a clear, yellow oil used locally as edible oil with a value equal or higher than groundnut oil. It is widely cultivated in Nigeria, it is a creeping annual which belongs to the gourd (Cucurbitaceae) family.

In Nigeria, the fruit is cultivatedmainly for its seed which form one of the most important sources of protein in the diet. The oil is sometimes extracted and the residue is wrapped and boiled in water giving rise to Igbalo or it may be fried in groundnut oil to Irobo. Melon seeds contain a fair amount of phosporus, Magnesium, potassium and a fair amount of carotene and Vitamin A. In view of its high oil content, it is a high calorific food.

1.3h MAIZE OR CORN:- Zea Mays Iinn

Maize is predominantly the cereal crop of the south, the crop, however, is cultivated to some extent practically throughout the country. It is a sun loving crop, admirably suited to tropical conditions. Maize ranks in importance with wheat, rice and oats in the world production of cereal crop in the United States of America.

In Nigeria Maize offers a fairly cheap source of feeding stuff in the development of livestock production. It also offers a relatively cheap source of food for the rapidly developing piggery industry in Nigeria. The oil content of Nigerian maize is compared to the grains of United States of America, U.S.A. 4.0% Nigeria 4.09%, Nigeria has not grown enough maize as to establish corn oil industry. Maize is richer in oil than any other cereals except oats[3]. Maize oil is a dark golden yellow colour which on standing and cooling, clouds owing to the crystallization of flakes of waxy material derived from the seed coat. The refined oil is a bland yellow product much in demand as a salad oil, for Mayonnaise, and as a cooking oil. It is also used to a limited extent as a raw material for Margarine.

Table VII

| Fatty acid Composition | Percentage |
|---|---|
| Palmitic | 8 - 12 |
| Stearic | 2 - 5 |
| Oleic | 19 - 49 |
| Linoleic | 34 - 62 |
| Linolenic | trace |

1.3i SUNFLOWER SEED OIL: (Helianthus Annus).

It is indigenous to mexico, extensively cultivated in Eastern Europe, Turkey, Argentina and South Africa. It requires a hot summer and fertile soil to produce a food crop

Oil is obtained from the seed either by pressing or by solvent extraction. Refined sunflower seed oil is a pale yellow colour with a pleasant flavour and with a fairly good resistance to oxidation. It is used as salad oil, for frying and as a component for Nargarine.

Table VIII

| Fatty acid composition | Percentage |
|---|---|
| Palmitic | 3 - 6 |
| Stearic | 1 - 3 |
| Oleic | 14 - 43 |
| Linoleic | 44 - 75 |
| Arachidic | 0.5 - 1.0 |

1.3a COOKWELL AND SALAD OILS

Both Cook-well and salad oils are refined oils. They are very pure and highly unsaturated. Salad oil is obtained from purification of oils like maize and sunflower oils. It has a light yellow colour and has a very pleasant flavour.

1.4a OIL MILLING:

The oil in all plants is obtained from the microscopic cells of their seeds. In a single seed there are thousands of cells, the complete seed itself being perhaps no bigger than a small green pea. The methods of removing the oil are in principle very simple. It is either squeezed out of the seeds by sheer physical pressure, much as the juice

is squeezed out of a lemon, or dissolved out by means of a spirit, much as a grease stain can be removed from one's clothes. But these simple principles are not easy to apply, for the walls of the cells which contain the oil are hard to penetrate. It requires the expensive machinery and elaborate processes of an oil mill to achieve this.

In an oil mill the two basic methods of squeezing out the oil or dissolving it with a spirit are after combined. Locally, only physical squeezing is employed, solvent extraction is never practised. The result of sequeezing out the oil and dissolving it is that in the case of groundnut, 46% of the seeds by weight can be extracted as oil, and the remaining 54% contains less than 1% of oil.

1.4b THE OIL MILL:

In Nigeria, oil mills are established where there are large plantations. The commonest oil mills to be found in Nigeria are palm kernel oil mills, groundnut oil mills and cotton seed oil mills, these are situated around the major producing centres in various part of the country. In Britain the mills are constructed near water

because practically all the oil seeds are shipped from abroad.

The general process of oil milling (or extraction) is as follows:-

1.4c CLEANING:

Milling cannot begin until the seeds has been cleaned. As it passes on a conveyor belt from the storage silos to the mill, the seed travels under electromagnet which lift any stray scraps and metal, such, as nuts and bolts from the harvesting machinery or from the ship. Further electro-magnet are situated at various points throughout the plant to remove any remaining Ferrous materials. Then the seed is put through starry sieves which allow the seed itself to pass but stop anything bigger, such as small stones or scraps of straw. The material may then go to a blowing chamber, where a current lifts the seed, while grit being heavier, falls to the bottom of the chamber.

Locally, all the separation is done by hand picking and this waste a lot of time is achieved.

1.4d BREAKING:

The grain is next broken up by rollers. This helps the heat to penetrate during cooking, which takes place at a later stage. Also, the oil flows more readily out of broken cells when they are put under pressure. Seed may be rolled in one of the two ways. Large hard seeds pass through fluted rollers known as cracking rolls. These are heavy steel cylinders whose outer surface is covered with sharp edged grooves running length ways. Two cylinders rotate together, practically touching, one moving slightly faster than the other, and any seed dropped between them is torn to fragments by the edges of the grooves. Palm kernels are one examples of a tough seed which requires this very thorough rolling.

Other seeds go through a series of heavy, plain rollers which break them up by their weight alone. These rollers usually five in number, are mounted one on top of the other on the principle of a clothes wringer. Groundnut seed, which has very little fibre in the walls of its cells, can be broken up by this method.

1.4e COOKING:

To burst the walls of the oil cells the seed is now cooked. It is led through a series of kettles, closed pans piled on top of one another like the tiers of a wedding cake.

Between each kettle, and sometimes round the sides as well, is a steam heated jacket. Metal arms inside the kettles stir the seed as the temperature rises to a maximum of 160 - 230°C (298 - 400 °F) according to the type of seed.

1.4f EXPELLING:

The seed then passes to the expeller where most of the oil is squeezed out. The principle is very similar to that of a kitchen mincer. It has a large, powerful screw which forces the contents of the machine forward through a slotted barrel. The pressure which squeeze the oil out of the seed cells is obtained by three means: The barrel becomes narrower at one point, the central shaft bearing the screw becomes gradually thicker, reducing still further the space into which the moving column of oil seed is squeezed; the "pitch" of the screw (the distance between each turn of the thread) becomes less. Round the barrel are a number of long slots varying in width from 1/20 to 1/100 of an inch. Through these slots the liquid oil can escape, but not the pulped seed.

The mass of squarshed seed is slowly pushed out to the far end of the machine. The oil which has trickled through the slots is pumped through screens and fitters where all traces of vegetables fibre are removed. After

filtering, the oil is automatically weighted and pumped to storage tanks.

The expeller is the basic mechanism of a modern oil mill. There are several kinds. A low pressure expeller with a large capacity will handle three or four tons of seed an hour, expelling about two-thirds of the oil from cooking seed. The oil produced by this method is of very high quality, since oil alone is expelled. To remove the remaining oil, the seed is next put through a solvent extraction process. For solvent extraction the seeds are ground in such a way as to produce flakes rather than very fine particles. The flaked material is then extracted in suitable equipment by means of a low-boiling solvent, usually a petroleum fraction. The crude oil from this process is allowed to settle and is then filtered to remove colloidal matter, free fatty acids and colored impurities. A number of processes are employed for this purpose, including treatment with alkali and adsorbent materials. A further process, known as deodorization may be applied to edible oils. This process consists of treatment with steam at a high temperature and under low pressure to remove volatile materials such a residual solvent certain free acids, and other substances

which would give undesirable tastes or odours. A final treatment of edible oils may consist of hydrogenation and blending of the hydrogenated product with other oils to obtain a product of the desired characteristics.

1.5 ECONOMIC IMPORTANCE OF VEGETABLE OILS & FATS:

The chief importance of vegetable oils is in their food value[1]. Oils and fats are vital ingredients of a balanced diet because they supply bodily warmth and build physical energy, and in recent years vegetable sources have accounted for about three-fifths of the world's consumption, the rest coming from animal fats and marine oils.

These edible oils are consumed in various ways. In their natural liquid state they are used in warmer climates for cooking. In the Western World they are eaten chiefly in spreadable form, and the main demand for them comes from margarine industry. In essence, vegetable oils are very vital in manufacture of margarine. Other food industries which make use of vegetable oils include the manufacture of cooking fats and salad dressings and Ice cream.

In addition to their value as a source of oil, the seeds of several of these plants have high protein content, in particular groundnut, water melon and soyabean. For this reason the residue after the oil has been extracted

in many cases provides animal fodder.

Outside the real of food manufacture, vegetable oils feature in a wide variety of industries ranging from soap manufacture by far the most important to the production of paints, varnishes, lubricants and plastics, protective coatings.

# C H A P T E R 2

## SOURCES OF OILS AND METHODS OF ANALYSIS

# CHAPTER II

## 2.0 SOURCES OF OILS AND METHOD OF ANALYSIS

Oil samples used in this project were collected from different locations. All samples were obtained from local sellers in various markets and imported oils were obtained from supermarkets. Samples analysed in this project included palm oils obtained from Oyan in Oyo State, this is locally produced in that town, palm oil from Samaru, Funtua and Kano.

The sources of palm oil in these three towns mentioned were from Anambra and Imo States. This is because Samaru, Funtua and Kano are non-producers of palm oil due to their geographical locations. Groundnut oil, cotton seed oil were bought from Samaru, Funtua and Kano markets respectively. Palm kernel and coconut oils were obtained from Oyan in Oyo State.

Melon seed was bought from Samaru market, This was roasted for about 2 hours and then grounded. After this, the oil was extracted from the crushed seed using petroleum ether as the solvent by soxhlet method of extraction. Both corn, sunflower, salad were bought at Leventis stores in Zaria. Cookwell oil was bought at Kowa stores Nigeria Limited, Samaru - Zaria.

All oil sampleswere kept in a closely covered container to avoid any contamination before analysis.

## 2.1 ANALYSIS:

Analysis of oils is required for an assessment of their quality[2,3,4], as well as their identification. A number of physical and chemical constants have been established for these purposes. Many of them are empirical, while others are quite specific measurement of the characteristics of the oils.

Each of the ~~constants~~ Parameters that will be discussed are chosen in order to determine the characteristics of the glycerides or fatty acids contained in the oils. The analysis involved oils, which are not soluble in aqueous medium, hence the various determinations were carried out in non-aqueous medium. Solvents used were, Toluene, alcohols (Isopropyl alcohol and ethyl alcohol). Carbon tetra-chloride chloroform and acetic acid. In most of the determinations volumetric method of analysis were used.

Standardization of acids and other reagents and parameters were carried out using volumetric analysis and or spectrophotometric methods.

Unless otherwise stated all reagents used were of Analar grades.

The physical and chemical constants determined are as follows:

2.1a SAPONIFICATION VALUE:

This is a measure of mean weight of the oil, and it denotes the number of miligrammes of potassium hydroxide which is required to saponify 1 gramme of oil, that is to neutralize the free fatty acid and the fatty acids combined as glycerides[3,8].

PRINCIPLE:-

The saponification value was determined by completely saponifying the oil with a known amount of potassium hydroxide, the excess of which was determined by titration[8].

REAGENTS:

Hydrochloric acid: 0.50M aqueous solution accurately standardized. Potassium hydroxide: 0.50M solution in isopropyl alcohol.

Phenolpthalein Indicator:- 1% solution in isopropyl alcohol.

APPARATUS:

250ml conical flasks, condenser and round bottom flasks, burette.

PROCEDURE:

About 2g of oil was weighed, 25ml of 0.5M alcoholic potassium hydroxide was accurately measured to the cold oil and was heated under reflux for one hour. The flask was swirled from time to time. The flask was then allowed to cool a little and the condenser was washed down with a little distilled water. The excess potassium hydroxide was titrated with 0.50M hydrochloric acid, phenolpthalein was used as indicator. Blank determination was carried out under the same conditions with the oil.

CALCULATION:

$$\text{Saponification value} = \frac{56.1M(V_2 - V_1)}{W}$$

where W = weight in grammes of the oil used

$V_1$ = volume (in ml) of hydrochloric acid used in test.

$V_2$ = volume (in ml) of hydrochloric acid used in blank.

NOTE:

Alcoholic potassium hydroxide was prepared by boiling 1 litre of isopropyl alcohol under reflux with 8g. pottassium hydroxide and 5g aluminium grains or (foil) for 1 hour, it was then distilled. 35g of

potassium hydroxide was dissolved in the distilled alcohol. The solution was allowed to stand for some days before use.

2.1b ACID VALUES:

Acid values denote the number of miligrams of potassium hydroxide needed to neutralize the free acids in 1g of oil. It is a measure of the amount of free fatty acid in oil. Some of the deterioration that takes place during storage of either raw material from which the oil is obtained or in the oil itself after isolation, results in hydrolysis of triglycerides to yield free fatty acids[3,8].

PRINCIPLE:-

The oil is dissolved in an appropriate solvent, after which solution was titrated with potassium hydroxide. The amount of potassium hydroxide solution consumed was a measure of the acidity of an oil.

REAGENT:

Solvent:- Equal volumes of toluene and isopropyl alcohol were mixed. It was neutralized with 0.1M potassium hydroxide solution before used. Phenolp. halein was used as indicator.

Potassium hydroxide:- 0.1M KOH prepared by boiling 6.0g of potassium hydroxide in 1 litre of water for 1 hour 2.0g of barium hydroxide was added and boiled for 5 minutes. It was cooled and was allowed to stand for some hours. It was standardized with potassium hydrogen pthalate.

Phenolpthalein Indicator:- 1% solution in alcohol.

APPARATUS:-

250ml conical flasks, burette

PROCEDURE:

5g of the oil was weighed and 30ml of the mixed solvent already neutralized was added. The sample dissolved in the solvent and was titrated against potassium hydroxide solution. The end point was pink.

CALCULATION:

$$\text{Acid value} = \frac{(56.1)\ A\ M}{W}$$

where A = volume of potassium hydroxide solution used in ml.

M = Exact Molarity of the potassium hydroxide solution.

W = Sample weight in g.

2.1c % FREE FATTY ACID:

The free fatty acid was calculated as the percentage by weight of fatty acid of specified molecular weight. Normally, Oleic acid with a molecular weight of 282 was taken or the value obtained is divided by 1.99% for Oleic acid[2].

Procedure:- as for acid values.

2.1d PEROXIDE VALUE:

The peroxide value is expressed in milli-equivalent of peroxide oxygen per kg. oil. The peroxide value is usually used as an indicator of deterioration of oils. As oxidation takes place, the double bounds in the unsaturated fatty acids are attacked. These breakdown to produce secondary oxidation products which indicate a condition known as rancidity.

PRINCIPLE:

The peroxide value is determined by subjecting potassium Iodide at room temperature to the oxidation effect of peroxides. The Iodine thus liberated, was titrated with standardized sodium thiosulphate.

REAGENTS:

2 volumes of glacial acetic acid and 1 volume of chloroform were mixed.

2.1e IODINE VALUE:

The Iodine value of an oil denotes the weight in grammes of halogen, calculated as iodine capable of being absorbed by 100g of sample under specified conditions. It is an approximate measure of the number of Olefinic and acetylenic bonds in the substance. It measures precisely the amount of Unsaturation in the fatty acid radical of the glycerides.

PRINCIPLE:

The Product to be investigated was treated with Iodine monochloride solution. After the addition of the halogen has taken place, the excess of Iodine monochloride was determined by titration with sodium thiosulphate solution.

REAGENTS:

Carbon tetrachloride.

Potassium Iodide: 10% aqueous solution.

Sodium thiosulphate:- 0.1M aqueous solution standardized with potassium dichromate (0.2g of potassium dichromate was weighed dissolved in 50ml of water, 2g of potassium Iodide was added and 5ml concentrated hydrochloric acid was added and standardized with sodium thiosulphate).

Starch Indicator:

Wijs Solution:- This was prepared by dissolving about 9g of iodine trichloride in a mixture of 700ml glacial acetic acid and 300ml carbon tetrachloride.

APPARATUS:

250ml conical flask, burette.

PROCEDURE:-

The amount of sample used depends on the Iodine number of oils as indicated below[2,8].

| Iodine Number | Amount of Substance Used |
|---|---|
| 5 - 20 | 1.0g |
| 20 - 60 | 0.34g |
| 80 - 130 | 0.15 |
| 130 and above | 0.10 |

The amount of oil weighed was put into the conical flask, 10ml of carbon tetrachloride was added to dissolve ~~with~~ oil. 25ml of the Wijs solution was added. The content was mixed thoroughly and it was allowed to stand in the dark for one hour at 27°C.

After standing for 1 hour 15ml of potassium Iodide solution and 100ml of water were added. This was titrated with sodium thiosulphate solution with proper shaking.

starch solution was added when yellow colour appeared sodium thiosulphate was added to the blue colour in the conical flask drop by drop until it disappeared completely.

Blank determination was carried out under the same condition.

CALCULATIONS:

$$\text{Iodine Value} = \frac{12.69\ M(V_2 - V_1)}{W}$$

where $W$ = weight (in g) of sample used

$V_1$ = volume (in ml) of sodium thisulphate used in test

$V_2$ = ~~Molarity~~ Volume of the sodium thiosulphate.

$M$ = Molarity of Sodium thiosulphate

2.1f UNSAPONIFIABLE MATTER:

This is a measurement of the water insoluble components produced after heating the fat with potassium hydroxide. The amount of unsaponifiable matter found in edible oils is usually very small and high values may indicate contamination or adulteration[3].

PRINCIPLE:

The fatty matter was converted into soap by alcoholic potassium hydroxide solution, the solution was diluted with water and the unsaponifiable matter was extracted with diethyl ether.

APPARATUS:

Round bottom flask 250ml fitted with condenser,

Saparating funnels 500ml.

REAGENTS:

Alcoholic potassium hydroxide solution approximately 1M (Reference to note under saponification value for preparation).

Diethyl ether

Potassium hydroxide solution 0.5M Acetone.

PROCEDURE:

2g of oil, was accurately weighed into round bottom flask. 25ml of alcoholic potassium hydroxide solution was added and the mixture was heated under reflux for one and half hours. When saponification was completed the content of the flask was transferred into a separating funnel and the round bottom flask was washed with 50ml distilled water, the washing was added to the separating funnel. The flask was rinsed with 50ml of diethyl ether which was then carefully poured into the separator. The separating funnel was shaken and the mixture was allowed to stand and the two layers separated. 10mls of 1M hydrochloric acid was added because of the emulsion formed.

The aqueous layer was drawn off when the layers had separated. The ether layer was washed two times with 20ml of water and was shaken vigorously. 20ml of 0.5M aqueous potassium hydroxide was added to the ether layer, it was thoroughly shaken. 5mls of 0.1M hydrochloric acid was added because of the emulsion formed. The aqueous layer was discarded and 20ml of distilled water was added shaken and the water layer was discarded. The same process was repeated twice again with 20ml aqueous potassium, hydroxide and 20ml water. The ether layer was washed with 20ml distilled water until the wash water was no longer alkaline to drops of 1% alcoholic phenolpthalein.

The ether solution was transferred to a 250ml conical flask and the ether was evaporated to a small volume. The remaining solvent was transferred to a small conical flask which has been weighed. Few ml of acetone was added when the solvent was almost evaporated. The evaporation was continued until all the solvent was evaporated. The residue was heated to a constant weight at 80$^{o}$C.

CALCULATION:

$$\text{Unsaponifiable Matter} = \frac{\text{Residue} \times 100}{W}$$

where W = weight of oil used.

2.1g HYDROXYL VALUE:-

The hydroxyl value is the number of mg. of potassium hydroxide required to neutralize the amount of acetic acid capable of combining by acetylation with 1g of sample[8,9].

The method of determination of hydroxyl content does not differentiate between OH groups in the fatty acid chains and those present in Mono or diglycerides.

PRINCIPLE:

The hydroxyl groups were acetylated with a known amount of acetic anhydride and 2g of sodium acetate. The excess acetic anhydride was decomposed with water and the acetic acid formed was titrated with ethanolic potassium hydroxide.

REAGENTS:-

Sodium acetate

Acetylating agent - acetic anhydride, potassium hydroxide in alcohol 0.5M.

Phenolpthalein Indicator:- 1% solution in 96% ethanol v/v.

APPARATUS:-

Burette, Conical flasks, round bottom flask, condenser.

PROCEDURE:-

10cc. of oil sample was measured and introduced into a round bottom flask. 10cc. of acetic anhydride was added and accurately weighed 2.0g sodium acetate was added. Condenser was attached in a reflux position; the content was boiled.gently for 1 hour. The flask was allowed to cool for 15 minutes and 50cc. of distilled water was added through the top of the condenser. The flask was heated on a steam bath for 15 minutes with frequent shaking to destroy the excess acetic anhydride. The contents were transferred into a separatory funnel and the flask was rinsed with 10cc. of water two times. These were added to the content in the separatory funnel. This was thoroughly shaken to make sure that the aqueous layer was in contact with the oil layer. After this the aqueous layer was rejected and the oil layer was washed with 50cc of saturated sodium chloride. The washing was done until the washing was neutral to litmus. The oil

was dried with anhydrous sodium sulphate and was filtered.

2g of acetylated oil was weighed and introduced into a round bottom flask. 25ml of 0.5M ethanolic potassium hydroxide solution was introduced to the acetylated oil, and was refluxed for thirty minutes. Two drops of 1% phenolpthalein indicator was added and this was titrated with 0.5M hydrochloric acid. The blank determination was carried out

CALCULATION:-

$$\text{Hydroxyl value} = \frac{56.1(M)(V_2 - V_1)}{W} + \text{Acid Value}$$

where W = weight (mg) of oil

$V_1$ = volume (in ml hydrochloric acid used in test.

$V_2$ = volume (in ml) hydrochloric acid used in blank.

M = Molarity of hydrochloric acid.

2.1h ASH CONTENT:

The ash content is described as the percentage of Inorganic residue remaining after ignition of the oil.

APPARATUS:

Quartz dish.

PROCEDURE:-

10g of oil was weighed into the Quartz dish which had been weighed. The dish was heated carefully to the ignition point. When the burning has finished the dish was heated in the furnace at 700°C. The dish was cooled and weighed again.

CALCULATION:

$$\text{Ash \%} = \frac{100 \times W_2}{W_1}$$

where $W_1$ = weight (in g) of sample

$W_2$ = weight (in g) of ash

2.1i REFRACTIVE INDEX:

Refractive index of an oil is the ratio of the sine of the angle of incidence to the since of the angle of refraction when a ray of light of wavelength 589.3 MN passed from air into the oil[8].

APPARATUS:

Instrument used is Abbe 60 refractometer.

PROCEDURE:-

The space between the prism were filled with oil. Ample time was allowed for the oil and prism to attain steady temperature. After this the prism was closed and properly tightened. The Instrument was adjusted so that the field dividing line was coincidental with the cross wires.

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2.1j SPECIFIC GRAVITY:-

Specific gravity denotes the weight ratio of oil in air of weight of water in air.

APPARATUS:

Glass pycnometer.

PROCEDURE:-

The measurements were carried out at room temperature. The pycnometer was weighted empty and the weight recorded. Then it was filled with air free distilled water, this was weighed again. The water was poured away and the glass was cleaned properly with absolute ethanol. It was then filled with oil and weighed again.

CALCULATION:

$$\text{Specific gravity} = \frac{\text{weight of oil in air}}{\text{weight of water in air}}$$

2.1k TRACE ELEMENTS:

Phosphorus, Iron, Copper, and Magnesium.

Trace elements were obtained in aqueous solution by dry ashing. This was a follow up from the determination of the ash content of the oils. The ash obtained was treated with 5mls of6MHCl to wet it completely and it was carefully heated to dryness at low temperature over hot plate.

15mls of 3M hydrochloric acid was added and it was heated on hot plate until the solution just boiled. The contents were cooled and filtered into 100ml volumetric flask. The dish was washed for at least three times with distilled water. The flask was filled up to the mark.

PHOSPHORUS:

This element was determined using colorimetry method by applying Molybdenum blue method.

PRINCIPLE:-

Orthophosphate and Molybdate ions condense in acidic solution to give Molybdophosphoric acid which upon selective reduction by hydrazine sulphate produces a blue colour, due to Molybdenum blue of uncertain composition.

The intensity of the blue colour is proportional to the amount of phospahte initially incorporated in the heteropoly acid.

REAGENTS:

12.5g of sodium Molybdate was dissolved in 10M - sulphuric acid and was diluted to 500ml with the acid. Hydrazine sulphate solution: 1.5g of hydrozine sulphate dissolved in deionized water and diluted to 1 litre.

PREPARATION OF STANDARD:-

0.4391g of potassium biphosphate was weighed and dissolved in distilled water and made up to 1000ml.

The solution contained 1000ppm. of phosphorus. 10ml of the solution was pipetted into 100ml volumetic flask and was made up to the mark. This was the working standard stock solution. From this, 10ml of it was pipetted into another 100ml flask to obtain 10ppm. From this 0,1, 0.2, 0.3, 0.4 and 0.5mls of the working solution was pipetted into a separate 100ml volumetric flasks respectively. This gave 0.1ppm, 0.2ppm, 0.3ppm, 0.4ppm and 0.5ppm respectively.

10mls of the solutions were pipetted into another of 50mls volumetric flask. 5mls of Molybdate solution was added followed by addition of 2mls of hydrazine sulphate. After the addition, the solution was diluted to the mark. This was warmed in a steam bath until the blue colour developed.

The cuvette of the spectrophotometer was filled with blue solution and the absorbance was measured at a wavelength of 720mm. distilled water was used as blank. These absorbances were used to construct the calibration curve.

The same procedure was repeated for other samples by taking 10mls of the sample solution, and adding 5mls of Molybdate solution and 2ml of hydrazine sulphate solution. This was subsequently warmed to develop the colour. The absorbance was determined at the same wavelength.

APPARATUS:-

Perkin spectrophotometer 1700.

CALCULATION:-

Read the P values (mg/100ml) of the sample from the calibration curve.

Phosphorus content of solution $mg^{P}/100ml$ = a (ppm)

Wt of the sample used = W

Dilution Factor = F

total phosphorus content as % = $\frac{a \times F}{10 \times W}$

Both Iron, Copper and Magnesium were determined by Atomic Absorption spectroscopy.

PREPARATION OF STANDARDS:

2.53g of Magnesium nitrate, 0.981g of copper sulphate and 1.20g of Ferric chloride were weighed respectively and dissolved in distilled water and the solution were made up to 250ml. The solution contained 1000ppm. 10ml from each of copper, Iron and Magnesium stock

solutions respectivcly were pipetted into separate 100ml volumetric flasks and were diluted to the mark with distilled water. These served as the working stock solutions. Final dilutions were made by pipeting out 2,4,6,8, 10mls of the working stock solution respectively into a series of 100ml volumetric flasks. These provided 2ppm, 4ppm, 6ppm, 8ppm, 10ppm.

These solutions were taken to the Atomic Absorption Spectrophotometer for absorbance measurement. The wavelength of the absorption for these elements were Mg ⅄ 285.2 CU ⅄ 324.8 and Fe ⅄ 248.3. The same procedure was repeated for the sample solution

PRINCIPLE:-

Atomic absorption spectrophotometer was used to measure trace amounts of elements present in oil samples by aspirating solution into the atomizer. The solvent was evaporated and the sample compounds were thermally decomposed and converted into the gaseous stage of the atoms. The atoms of the elements became excited and light is emitted.

The neutral atoms absorb light from the hollow cathode tube source that emitted the same characteristic wavelength of the single element to the determined. The selected spectra line were isolated from the emerging beam by a monochromator and its intensity was measured.

# C H A P T E R  III

## DISCUSSION AND RESULTS

## DISCUSSION AND RESULTS

Oils are natural products and are therefore subject to some variations in composition and certain specific constants, so that these constants fail within a range. From time to time when oils are available, their constants could fall outside the normal range. These variations in composition and constants are dependent on a number of factors among which are differences in botanical species, climatic conditions, soil composition rainfall and temperature.

The quality of the oil which in most cases is the more important economically, is determined by the free fatty acid content. The Higher the value of the acid content the lower the quality of the oils. The purpose of quality control is to ensure that oils are produced within a particular specification. The main quality criteria for good oils are low free fatty acid, this could be as low as 0.01%, the peroxide value which is usually used as an indicator for the deterioration of fats and extent of oxidation which should be as low as 2 to 10%[5].

TABLE 1

| N A M E | IODINE NUMBER |
|---|---|
| Coconut oil | 7 - 10 |
| Cotton oil | 99 - 115 |
| Groundnut oil | 84 - 99 |
| Corn oil | 103 - 128 |
| Palm oil | 46 - 60 |
| Palmkernel oil | 14 - 23 |
| Sunflower oil | 122 - 136 |

Other data are determined on the oils in order to assess the quality of the oils.

These include unsaponifiable matter, saponification value, refractive index, specific gravity and the trace elements. All these parameters are used to give an adequate measure of the quality of the oils.

Unsaponifiable matter is a measurement of the water insoluble components produced after heating the oil with potassium hydroxide. The amount of unsaponifiable matter in edible oils is usually small, high figures may indicate contamination or adulteration. It is also used to check the prescence of fuel oil or lubircating

oil in the oils[3]. In most refined oils the content of unsaponifiable matter largely sterols is 0.5 - 1.0%[3,8].

The saponification value is used to characterise and identify oils. It is also used to indicate the mean molecular weight of oils.

The refractive index is a physical attribute of triglycerides, measured by the angle through which a beam of light is bent when passing through a thin film of oils. It is used to characterise oils in checking purity of oil or searching for component of a mixture. It is also used to measure the unsaturation in oils.

The density is widely used for laboratory control of the purity of oil. It is used to check adulteration and contamination. It is usually less than 1.

The maintainance of a correct osmotic equilibrium and fluid pH in the body is essential for the correct transfer of nutrients and metabolites across cell membranes and around the body, and hence essential for life. The most important electrolyte that are present in the body fluids and served to maintain the correct osmotic equilibrium and body building are copper, iron, magnesium, sodium, potassium, chloride, bicarbonate and phosphate ions. In this project only traces of copper, iron, magnesium and phospate ions were determined.

Phosphorus is associated with calcium in bones and teeth and general metabolism. The sources of phosphorus is rather widespread. For the chances of dietary deficiency to be remote both phosphorus and magnesium should be present in sufficient amount in nearly all foods hence they are found in trace amounts in oils.

Iron is necessary for the carrying and exchange of oxygen in the blood of Mammals, and for many systems involving oxidation and reduction in the body. The amount of Iron which is required to supplement vitamins and tolerated by human beings per day is about 12ppm.[11,17].

Copper is an excellent catalyst for oxidation reduction systems in the body. The permissible consumption of copper in the body is very low about 2ppm.

In most cases all these trace elements are present in the vegetable, but greater amount of these elements are removed as a result of subjecting the oils to high temperature and chemical treatment. For example average level of phosporus in crude palm oil of about 15 - 20ppm is significant[15]. Degumming methods certainly reduce the level to less than 4ppm and less than 2ppm at times. Fully refined palm oil have no detectable metallic ions[5].

Table 11 shows a representative analysis of some vegetable oils by L.V. Cocks and Van Rede (1966)[8]. It is a comparison of the various oils.

Each of the constants used in this project in examining each of the oils was chosen to measure the characteristics of the glycerides and fatty acids.

Table 111 shows the results obtained for the determinations carried out in this project.

CHARACTERISTICS OF THE MORE COMMON OILS

TABLE 11

VEGETABLE OILS

| OIL OR FAT | Density at 20°C | Refracture Index | Saponification value | Iodine Value | Unsaponifiable matter % |
|---|---|---|---|---|---|
| Coconut | 0.907 | 1.448 | 263 | 7-10 | 0.5-1.0 |
| Cotton Seed | 0.916 | 1.471 | 198 | 115 | 1.5 |
| Groundnut | 0.913 | 1.468-1.472 | 196 | 99 | 1.0 |
| Corn | 0.917 | 1.472 | 193 | 128 | 2.0 |
| Palm oil | 0.890 | 1.453 | 205 | 46-60 | 1.0 |
| Palm Kernel | 0.905 | 1.451 | 252 | 23 | 1.0 |
| Sunflower | 0.916 | 1.473 | 194 | 136 | 1.5 |

* L.V. Cocks and Van Rede (1966)

TABLE 111 (CONTD.)

| | Peroxide value | Iodine value | %FFA as Olic | % Ash Content | Acid value | %Unsaponifiable Matter |
|---|---|---|---|---|---|---|
| Palm oil (Oyan) | 7.20 | 67.77 | 6.99 | 99.95 | 13.85 | 0.36 |
| Groundnut oil(Samaru) | 4.80 | 91.73 | 0.34 | 99.97 | 0.68 | 0.44 |
| Groundnut oil | 2.40 | 10.83 | 1.05 | 99.96 | 2.10 | 1.48 |
| Cotton seed oil(Samaru) | 4.80 | 101.97 | 0.12 | 99.82 | 0.23 | 0.56 |
| Sunflower oil | 4.80 | 155.35 | 0.08 | 99.96 | 0.18 | 0.68 |
| Corn oil | 4.80 | 155.58 | 0.30 | 99.95 | 0.58 | 1.25 |
| Salad oil | 4.80 | 172.76 | 0.05 | 99.99 | 0.11 | 0.90 |
| Cook well oil | 4.80 | 118.50 | 0.11 | 99.85 | 0.21 | 0.35 |
| Palm Kernel oil | 4.80 | 18.67 | 4.63 | 99.92 | 9.22 | 0.88 |
| Melon seed oil | 4.80 | 132.58 | 1.99 | 99.88 | 3.90 | 1.60 |
| Cotton (Kano) | 4.80 | 120.32 | 0.11 | 99.89 | 0.21 | 0.44 |
| Groundnut oil(Kano) | 4.80 | 114.53 | 0.11 | 99.97 | 0.21 | 0.70 |
| Cotton (Funtua) | 6.00 | 121.35 | 0.32 | 99.95 | 0.64 | 0.48 |
| Groundnut oil(Funtua) | 7.20 | 111.74 | 0.24 | 99.95 | 0.48 | 0.43 |
| Palm oil (Samaru) | 7.20 | 76.27 | 12.64 | 99.96 | 25.06 | 0.45 |
| Palm oil (Funtua) | 6.00 | 53.95 | 31.99 | 99.90 | 63.66 | 0.40 |
| Palm oil (Kano) | 7,20 | 59.12 | 18.66 | 99.93 | 37.03 | 0.45 |

TABLE 111(CONTD.)

| | Phosphorus content % | Iron Content ppm | Magnesium content ppm | Copper content ppm |
|---|---|---|---|---|
| Palm oil (Oyan) | 0.045 | 8.6 | 0.7 | 3.00 |
| Groundnut oil (Samaru) | 0.067 | 2.0 | 0.32 | 1.90 |
| Coconut oil | 0.051 | 2.5 | 1.24 | 3.20 |
| Cotton seed oil (Samaru) | 0.105 | 1.2 | 0.24 | 1.00 |
| Sunflower oil | 0.033 | 0.8 | 0.04 | 1.10 |
| Corn oil | 0.038 | 1.2 | 0.00 | 1.20 |
| Salad oil | 0.033 | 2 | 0.13 | 1.10 |
| Cook well oil | 0.083 | 0.4 | 0.06 | 1.10 |
| Palm kernel oil | 0.065 | 5.8 | 0.26 | 5.50 |
| Melon seed oil | 0.316 | 0.6 | 1.46 | 1.40 |
| Cotton (Kano) | 0.105 | 0.65 | 0.2 | 1.20 |
| Groundnut oil (Kano) | 0.067 | 0.2 | 0.30 | 1.20 |
| Cotton (Funtua) | 0.105 | 0.45 | 0.22 | 1.10 |
| Groundnut oil (Funtua) | 0.067 | 0.4 | 0.32 | 1.80 |
| Palm oil (Samaru) | 0.048 | 6.1 | 0.32 | 3.20 |
| Palm oil (Kano) | 0.052 | 12.6 | 0.14 | 5.20 |

The results obtained are discussed below as folows:-

3.10 SPECIFIC GRAVITY AT $27^{o}C$

TABLE IV

| N A M E | D E N S I T Y |
|---|---|
| Palm Oil (Oyan) | 0.9042 |
| Groundnut oil | 0.9127 |
| Coconut oil | 0.9208 |
| Cotton oil | 0.9161 |
| Sunflower oil | 0.9188 |
| Corn oil | 0.9187 |
| Salad oil | 0.9190 |
| Cook well oil | 0.9094 |
| Palm Kernel oil | 0.9206 |
| Melon seed oil | 0.9158 |
| Cotton oil (Kano) | 0.9138 |
| Groundnut oil (Kano) | 0.9142 |
| Cotton Oil (Funtua) | 0.9176 |
| Groundnut oil (Funtua) | 0.9141 |
| Palm oil (Samaru) | 0.9177 |
| Palm Oil (Funtua) | 0.9010 |
| Palm Oil (Kano) | 0.9291 |

From the above table, the result shows that the density of the oils are almost identical. It shows that the density of all the oils investigated in the project is less than 1. However, there are some in significant differences in their values. Both locally produced oils like palm kernel oil, palm oil have identical density with the more refined oils like sunflower, cookwell oil and others. Since specific

gravity is associated with the purity of the oil it could be concluded that all the vegetable oils used in this work are reasonably pure.

3.11 REFRACTIVE INDEX AT 27°C

TABLE V

| NAME | REFRACTIVE INDEX |
|---|---|
| Coconut oil | 1.451 |
| Groundnut oil(Samaru) | 1.472 |
| Cotton oil(Samaru) | 1.471 |
| Palm oil (Oyan) | 1.465 |
| Palm kernel oil | 1.456 |
| Cookwell oil | 1.463 |
| Salad oil | 1.470 |
| Sunflow oil | 1.470 |
| Corn oil | 1.470 |
| Melon oil | 1.465 |
| Groundnut oil(Kano) | 1.472 |
| Groundnut oil(Funtua) | 1.472 |
| Palm oil (Kano) | 1.465 |
| Palm oil (Funtua) | 1.465 |
| Palm oil (Samaru) | 1.465 |
| Cotton oil (Kano) | 1.471 |
| Cotton oil (Funtua) | 1.471 |

The results show that the refractive index of all the oils investigated in the project are almost identical. The differences in the figures obtained are insignificant. The Figures vary from 1.451 (coconut) to 1.472 (groundnut oil).

Identical values obtained for all the oils also confirms the earlier conclusion reached from specific gravity measurements that all the oils used can be said to be pure.

3.12 PEROXIDE VALUE:

TABLE VI

| NAME | PEROXIDE VALUE |
|---|---|
| Palm oil (Funtua) | 6.00 |
| Ground nut oil (Funtua) | 7.20 |
| Cotton oil (Funtua) | 6.00 |
| Palm oil (Samaru) | 7.20 |
| Groundnut oil (Samaru) | 4.80 |
| Cotton oil (Samaru) | 4.80 |
| Palm oil (Kano) | 7,20 |
| Groundnut oil (Kano) | 4.80 |
| Cotton oil (Kano) | 4.80 |
| Palm oil (Oyan) | 7.20 |
| Coconut oil | 2.40 |
| Sunflower oil | 4.80 |
| Salad oil | 4.80 |
| Palm kernel oil | 4.80 |
| Cookwell oil | 4.80 |
| Corn oil | 4.80 |
| Melon oil | 4.80 |

From the above results, Groundnut (Funtua) 7.20, Palm oil (Samaru 1.20), Palm oil (Kano 7.20) Palm oil (Oyan 7.20) have the highest peroxide values others have 4.80. Only coconut oil has the least peroxide value (2.40) Palm oil (Funtua) and Cotton (Funtua) have (6.00) as their peroxide values.

The results show that oils having high peroxide value of (7.20) can easily oxidised than those with lower values, as a result these oils can go rancid very easily than oils with lower peroxide values.

The results Indicate that all refined oils and some locally produced oil like groundnut Kano (4.80) and others have the same stability towards being oxidized. The oil having the least peroxide value is the one which can be very stable and can not easily go rancid or deteriorate.

All the oils under investigation in this project show a very low peroxide values ranging from 2.00 - 7.20. The could therefore be regarded as very good oils,

3.13 HYDROXYL VALUE

TABLE VII

| NAME | HYDROXYL VALUE |
|---|---|
| Coconut oil | 47.57 |
| Cook well oil | 39.05 |
| Salad oil | 38.22 |
| Sunflower oil | 42.68 |
| Corn oil | 41.25 |
| Cotton oil (Samaru) | 19.91 |
| Groundnut (Samaru) | 17.52 |
| Palm oil (Funtua) | 27.33 |
| Palm oil (Samaru) | 42.73 |
| Groundnut oil (Funtua) | 18.45 |
| Cotton oil (Funtua) | 11.71 |
| Palm oil (Kano) | 51.97 |
| Cotton oil (Kano) | 12.87 |
| Groundnut oil (Kano) | 20.87 |
| Palm oil (Oyan) | 15.30 |
| Melon oil | 68.72 |
| Palm kernel oil | 25.85 |

The above result shows the same pattern with the percentage free alcohol. Melon seed oil has the highest value of hydroxyl value (68.72). This is closely followed by palm oil (Kano) (51.97). Others having very closely related figures are coconut oil 47.57, sunflower oil 42.68, corn oil 41.25, palm oil Samaru 42.73 respectively.

The lowest value is cotton (Funtua) 11.71. This is an indication that not all the alcohols present in the oils are released during the reaction.

3.14 PERCENTAGE FREE ALCOHOL:

TABLE VIII

| NAME | % |
|---|---|
| Coconut oil | 8.09 |
| Cook well oil | 6.60 |
| Salad oil | 6.45 |
| Sunflower oil | 7.23 |
| Corn oil | 6.98 |
| Cotton oil (Samaru) | 3.32 |
| Groundnut oil (Samaru) | 2.91 |
| Palm oil (Samaru) | 7.24 |
| Palm oil (Funtua) | 4.58 |
| Groundnut oil (Funtua) | 3.07 |
| Cotton oil (Funtua) | 2.00 |
| Palm oil (Kano) | 8.87 |
| Cotton oil (Kano) | 2.13 |
| Groundnut oil (Kano) | 3.48 |
| Melon seed oil | 11.88 |
| Palm kernel oil | 4.32 |
| Palm oil (Oyan) | 5.54 |

The table above shows that the percentage free elcohol present in each of the oils varied from one oil to the other.

The result Indicates that melon seed oil extracted in the laboratory has the highest percentage free alcohol (11.88), Coconut (8.09) both sunflower oil and palm oil Samaru have (7.23 and 7.24) respectively. Palm oil Kano (8.87). Three oils have very close percentage free alcohol namely Cook well oil (6.60), Salad oil (6.45) and Corn oil (6.98). The least percentage free alcohol is cotton (Funtua) it has 2.00. The differences in the percentage free alcohols might be due to difference in composition of the triglycerides. It can be concluded that the percentage free alcohols in most of the oils are low.

3.15 SAPONIFICATION VALUE:

TABLE IX

| NAME | SAPONIFICATION VALUE |
|---|---|
| Coconut oil | 276.15 |
| Cotton (Samaru) | 221.39 |
| Groundnut (Samaru) | 226.01 |
| Palm oil (Samaru) | 226.24 |
| Palm oil (Oyan) | 227.56 |
| Palm oil (Funtua) | 265.41 |
| Cotton oil (Funtua | 227.84 |
| Groundnut oil (Funtua) | 230.23 |
| Palm oil (Kano) | 245.42 |
| Cotton oil (Kano) | 226.42 |

SAPONIFICATION VALUE (CONTD.)

TABLE IX (CONTD.)

| NAME | SAPONIFICATION VALUE |
|---|---|
| Groundnut oil (Kano) | 223.04 |
| Palm kernel oil | 286.95 |
| Corn oil | 177.39 |
| Sunflower | 195.99 |
| Melon oil | 181.69 |
| Salad oil | 195.27 |
| Cookwell oil | 195.27 |

The above result show that coconut oil and palm kernel oils have the highest saponification value. The values are (276.15) and (286.95) respectively. Cotton (Samaru), Groundnut Samaru, Palm oil Samaru, Palm oil (Oyan), Cotton oil (Funtua), Groundnut oil Funtua, Cotton oil (Kano) and Groundnut oil (Kano) have almost identical values. The values are (221.39), (226.01), (226.24) (227.56), (227.84), (230.23), (226.24) and (223.04) respectively.

The values for palm oil Funtua (265.41) palm oil (Kano) (245.42) are higher than that of palm oil (Oyan) (227.56) and that of Samaru palm oil (226.24). The differences in values could be attributed to the fact that all these oils

are not produced in the same locality. The mode of preparation could affect the result.

Oils obtained from Funtua (265.41) and Kano (245.42) could be very economical for the manufacture of soap due to their high saponification values. Other oils under investigation have lower saponification values than the one considered above. The values ranges from 177.39 - 195.97 for sunflower, salad, melon sald respectively.

3.16 IODINE VALUES:

TABLE X

| NAME | IODINE VALUES |
|---|---|
| Salad oil | 172.76 |
| Sunflower oil | 155.35 |
| Corn oil | 155.58 |
| Melon oil | 132.58 |
| Coconut oil | 10.83 |
| Palm kernel oil | 18.67 |
| Groundnut oil (Samaru) | 91.73 |
| Cotton oil (Samaru) | 101.97 |
| Palm oil (Samaru) | 76.27 |
| Palm oil (Funtua) | 53.95 |
| Cotton oil (Funtua) | 121.35 |
| Groundnut oil (Funtua) | 111.74 |
| Palm oil (Oyan) | 67.77 |
| Palm oil (Kano) | 59.12 |
| Cotton oil (Kano) | 120.32 |
| Groundnut oil (Kano) | 114.53 |
| Cook well oil | 118.50 |

Iodine number indicates the degree of unsaturation in oils. The above results show the degree of unsaturation in the oils. Investigated in the project.

The result show that salad oil (172.76) has the highest Iodine number. This is closely followed by sunflower oil (155.35) Corn oil (155.58) others in the same category include Cookwell oil (118.00) melon seed oil (132.58) Cotton (Funtua) (121.35) Cotton (Kano) (120.32).

All the palm oils fall into the same category despite the fact that they were obtained from different sources and by implication perhaps different methods of preparation. Their values ranges from (53.95) palm oil (Funtua) to (76.27) palm oil (Samaru) Coconut oil has the lowest value of Iodine number 10.83.

The result indicates that all the oil seeds groundnut, sunflower, etc, have very high degree of unsaturation due to a larger percentage of unsaturated fatty acids present in the oil. Coconut has the least value of unsaturated fatty acid followed closely by palm kernel oil.

3.17 ACID VALUES:

TABLE XI

| NAME | ACID VALUES |
|---|---|
| Palm oil (Oyan) | 13.85 |
| Palm oil (Samaru) | 25.06 |
| Palm oil (Funtua) | 63.65 |
| Palm oil (Kano) | 37.03 |
| Groundnut (Funtua) | 0.48 |
| Groundnut (Kano) | 0.21 |
| Groundnut (Samaru) | 0.68 |
| Cotton (Funtua) | 0.64 |
| Cotton (Kano) | 0.21 |
| Cotton (Samaru) | 0.23 |
| Palm kernel oil | 9.22 |
| Coconut oil | 2.10 |
| Cookwell oil | 0.21 |
| Sunflower oil | 0.18 |
| Salad oil | 0.11 |
| Corn oil | 0.58 |
| Melon oil | 3.90 |

The results above could be classified into two categories. Those refined and those that are not refined.

The results showed that the acid values for palm oils were very high. Palm Oil (Funtua) has the highest acid values (63.66), Palm oil (Kano) (37.03), Palm oil (Samaru (25.06) and Palm oil (Oyan) (13.85). Palm kernel oil which was produced locally also has (9.22) as its acid values. The refined oils have their acid values ranging from (0.11) (Salad oil) to (0.68) Groundnut oil Samaru and others. The wide differences in the acid value of the oils showed varied qualities of the oil, since acid values is one of the determinants of the quality of an oil. Those produced locally did not undergo any chemical treatment or refining. The oil is just extracted from the seed and it is sold whereas the imported oils such as sunflower, cookwell and salad to mention a few of them undergo chemical treatment during refining process. This leads to their reduction in acid values. For example the acid value for Palm oil used as raw materials in level brothers Nigeria Limited is about 5% but when it undergoes refining it is reduced to about 0.05%. These processes leads to wide differences in the acid values obtained.

3.18 PERCENTAGE FREE FATTY ACID AS % OLEIC:

TABLE XII

| | |
|---|---|
| Palm oil (Oyan) | 6.99 |
| Palm oil (Samaru) | 12.64 |
| Palm oil (Funtua) | 31.99 |
| Palm oil (Kano) | 18.66 |
| Groundnut (Funtua) | 0.24 |
| Groundnut (Samaru) | 0.34 |
| Groundnut (Kano) | 0.11 |
| Cotton (Samaru) | 0.12 |
| Cotton (Kano) | 0.11 |
| Cotton (Funtua) | 0.32 |
| Coconut oil | 1.05 |
| Palm kernel oil | 4.63 |
| Cook well oil | 0.11 |
| Sunflower oil | 0.08 |
| Salad oil | 0.05 |
| Corn oil | 0.80 |
| Melon Seed oil | 1.99 |

The results above showed the same trend as for the acid values. The free fatty acid is obtained as percentage Oleic acid and it is obtained by dividing the acid values by a factor of 1.99% Oleic. The lower the percentage free fatty acid in our oil the greater and better the quality of the oil. Most of the values that are very low are those for the Imported oils and unsaturated oils. The highest percentage free fatty acid is palm oil (Funtua) (31.99%). The lowest being that of salad oil (0.05%). This showed that all unsaturated oils have lower acid values and have better quality. Also if palm oil and others having slightly higher values chemically treated their free fatty acid values could have been reduced considerably. However, palm produced locally are very economical for the production of soaps because of their high free fatty acid value. Though this could be suspected to lower the quality compared to the imported oils yet they are comparable in some aspects.

3.19 % UNSAPONIFIABLE MATTER:

TABLE XIII

| NAME | % |
|---|---|
| Groundnut (Funtua) | 0.43 |
| Groundnut (Kano) | 0.70 |
| Groundnut (Samaru) | 0.44 |

TABLE XIII (CONTD.)

| NAME | % |
|---|---|
| Palm oil (Kano) | 0.45 |
| Palm oil (Funtua) | 0.40 |
| Palm oil (Samaru) | 0.45 |
| Cook well oil | 0.35 |
| Corn oil | 1.25 |
| Salad oil | 0.90 |
| Melon oil | 1.60 |
| Palm oil (Oyan) | 0.36 |
| Palm kernel oil | 0.88 |
| Sunflower oil | 0.68 |
| Cotton seed oil (Samaru) | 0.56 |
| Coconut oil | 1.48 |
| Cotton (Funtua) | 0.48 |
| Cotton (Kano) | 0.44 |

From the results above the percentage unsaponifiable matter are not very high as expected from the literature values. Palm oil from Kano, Samaru and Funtua showed almost the same percentage unsaponifiable matter of (0.45%), (0.44%) and (0.40%) respectively. The values for corn. coconut oil and melon oil (1.25 1.48 and 1.60 respectively) appear to be very high compared to the other oils but it falls within the range of the literature value. This show that all the oils used in this project has not been contamination or adulterated.

3.20 ASH CONTENT:

TABLE XIV

| | |
|---|---|
| Coconut oil | 99.96 |
| Cook well oil | 99.85 |
| Groundnut oil (Kano) | 99.97 |
| Cotton (Kano) | 99.89 |
| Palm oil (Kano) | 99.93 |
| Groundnut oil (Funtua) | 99.95 |
| Cotton (Funtua) | 99.95 |
| Palm oil (Funtua) | 99.90 |
| Palm oil (Samaru) | 99.96 |
| Corn oil | 99.95 |
| Groundnut oil (Samaru) | 99.97 |
| Palm kernel oil | 99.92 |
| Palm oil (Oyan) | 99.95 |
| Sunflower oil | 99.96 |
| Salad oil | 99.99 |
| Cotton (Samaru) | 99.82 |
| Melon Seed oil | 99.88 |

The result show that all the oil samples have very similar values for their ash content.

3.21 PERCENTAGE PHOSPHORUS CONTENT:

TABLE XV

| | % PHOSPHORUS |
|---|---|
| Palm oil (Oyan) | 0.045 |
| Cotton (Samaru) | 0.105 |
| Palm kernel oil | 0.065 |
| Sunflower oil | 0.033 |
| Corn | 0.038 |
| Cookwell | 0.083 |
| Salad | 0.033 |
| Melon | 0.316 |
| Groundnut (Samaru) | 0.067 |
| Coconut | 0.051 |
| Groundnut (Funtua) | 0.067 |
| Groundnut (Kano) | 0.067 |
| Palm oil (Samaru) | 0.048 |
| Palm oil (Funtua) | 0.050 |
| Palm oil (Kano) | 0.052 |
| Cotton oil (Funtua) | 0.105 |
| Cotton (Kano) | 0.105 |

The result show that the amount of phosphorus present in each of the oils differ, Melon has the highest percentage of phosphoru 0.316%.

All the imported oils sunflower, Corn and Salad have almost identical percentage of phosporus content (0.033), 0.038 and 0.033 respectively. The lower values of these oils could be attributed to the fact that most of these trace elements are removed during refining processes.

3.22 AMOUNT OF IRON PRESENT IN PPM:

TABLE XVI

| OIL | PPM |
|---|---|
| Salad | 2ppm |
| Melon | 0.6ppm |
| Corn | 1.2ppm |
| Cookwell | 0.4ppm |
| Palm oil (Kano) | 12.60ppm |
| Palm oil (Funtua) | 7.8ppm |
| Cotton (Kano) | 0.65ppm |
| Palm oil (Samaru) | 6.1ppm |
| Groundnut (Kano) | 0.2ppm |
| Palm kernel oil | 5.8ppm |
| Cotton (Funtua) | 0.45ppm |
| Groundnut (Funtua) | 0.40ppm |
| Sunflower | 0.80ppm |
| Cotton (Samaru) | 1.2ppm |
| Palm oil (Oyan) | 8.6ppm |
| Groundnut (Samaru) | 2.0ppm |
| Coconut | 2.5ppm |

The result above show the amount of iron present in the samples under investigation. Sunflower, Groundnut, (Funtua), (Kano), Cookwell, Melon have comparatively low level of Iron. The values ranges from 0.2ppm to 0.8ppm.

Palm oils generally have very high values. The value ranges from 5.8 to 12.00ppm. Others have lower values ranging from 1.20ppm to 2ppm. The differences in values for palm oil could be attributed to the fact that they are produced from different locations whose soil mineral contents and texture are different. The lower values obtained are due to reduction to very small amount during processing stages. All values obtained are within the literature value of human consumption[16].

3.23 AMOUNT OF MAGNESIUM ION $Mg^{2+}$ in PPM:

TABLE XVII

| Oil | PPm |
|---|---|
| Salad | 0.18 |
| Sunflower | 0.04 |
| Palm oil (Kano) | 0.14 |
| Melon | 1.46 |
| Corn | 0.0 |
| Cookwell | 0.06 |
| Palm oil (Funtua) | 1.36 |
| Palm kernel | 0.26 |
| Palm oil (Oyan) | 0.70 |
| Cotton (Samaru) | 0.24 |
| Coconut | 1.24 diluted 10 times |
| Groundnut (Samaru) | 0.32 diluted 10 times |
| Groundnut (Funtua) | 0.32 diluted 10 times |
| Groundnut (Kano) | 0.30 diluted 10 times |
| Palm oil (Samaru) | 0.32 |
| Cotton (Funtua) | 0.22 |
| Cotton (Kano | 0.20 |

The result showed that groundnut oils have very high values of Magnesium, because the result above showed the values when the samples solution was diluted ten times. Coconut oil also have very high values inspite of its dilution ten times.

Corn oil has zero readings for the Magnesium cothers have low values e.g. sunflower oil, Cookwell oil 0.04 to 0.06 respectively.

The result for palm oils are not consistent due to reasons already given for the differences in amount of trace elements present in oils.

3.24 AMOUNT OF COPPER ION ($CU^{2+}$) IN PPm $\lambda$ 324, 8nm

TABLE XVIII

| OIL | PPm |
|---|---|
| Groundnut (Kano) | 1.20 |
| Palm oil (Samaru) | 3.20 |
| Palm kernel oil | 5.50 |
| Palm oil (Kano) | 5.70 |
| Palm oil (Funtua) | 5.60 |
| Coconut | 3.20 |
| Corn | 1.20 |
| Melon | 1.40 |
| Cookwell | 1.10 |
| Groundnut (Samaru) | 1.90 |
| Palm oil (Oyan) | 3.80 |
| Groundnut (Funtua) | 1.80 |

3.24 AMOUNT OF COPPER ION ($CU^{2+}$) IN PPM $\lambda$ 324.nm

TABLE XVIII

| OIL | PPM |
|---|---|
| Cotton (Kano) | 1.20 |
| Cotton (Samaru) | 1.00 |
| Sunflower | 1.10 |
| Salad | 1.10 |
| Cotton (Funtua) | 1.10 |

The result showed that palm oils, palm kernels and coconut have comparatively high values, ranging from 3.20 to 5.70 ppm. The values for others are very low. The reasons for lower values are due to sources of different oils and differences in climatic conditions. Also different methods of refining could be attributed to their lower values.

The trend of high values of trace elements in locally produced oil samples in followed for all the elements considered.

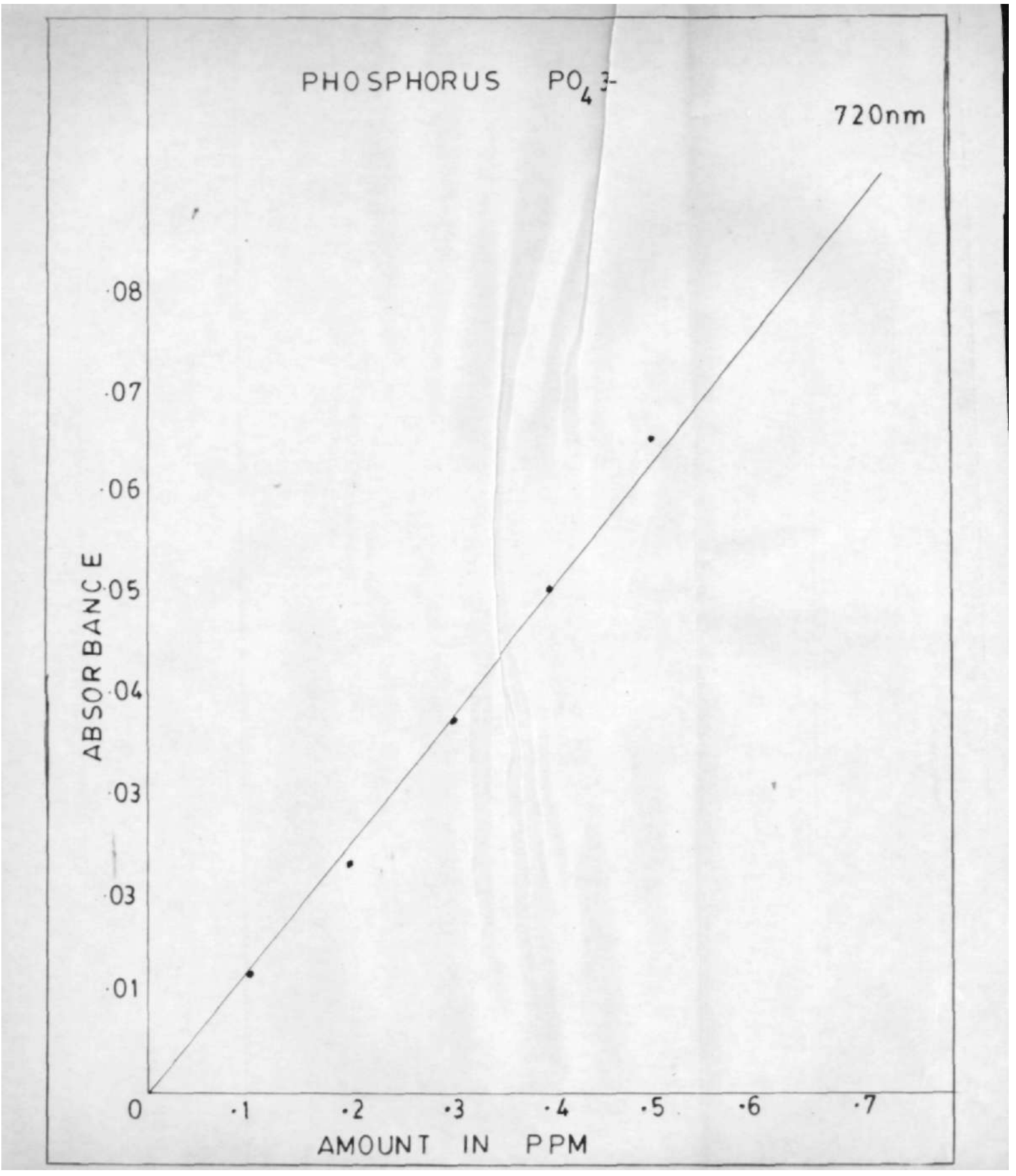
## 3.25 CONCLUSION:

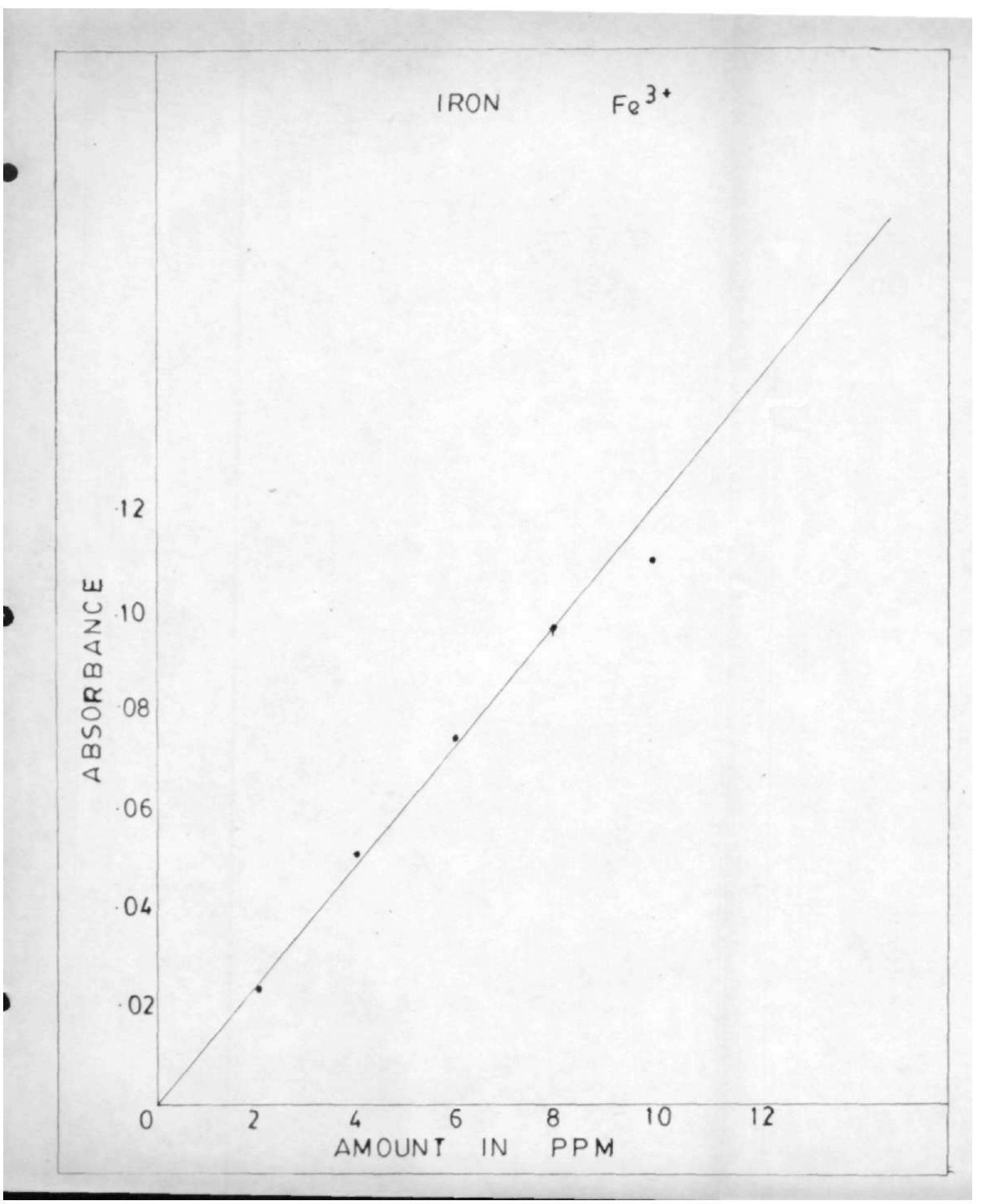
From the analytical results obtained from the work done on these oil samples, it can be concluded that all samples used are good quality oils because most of the characteristics of oils which make oils edible fall within a reasonable range. For example the density of all the oils are less than one as revealed by literature and experimental values the percentage unsaponifiable v values which can indicate adulteration and contamination fall within a good range, this indicates that oil samples used were of good quality. The result also showed that the peroxide values of all the oils are very low indicating that the shelve life, the rate at which the oils go rancid is very low if the oil is properly kept.

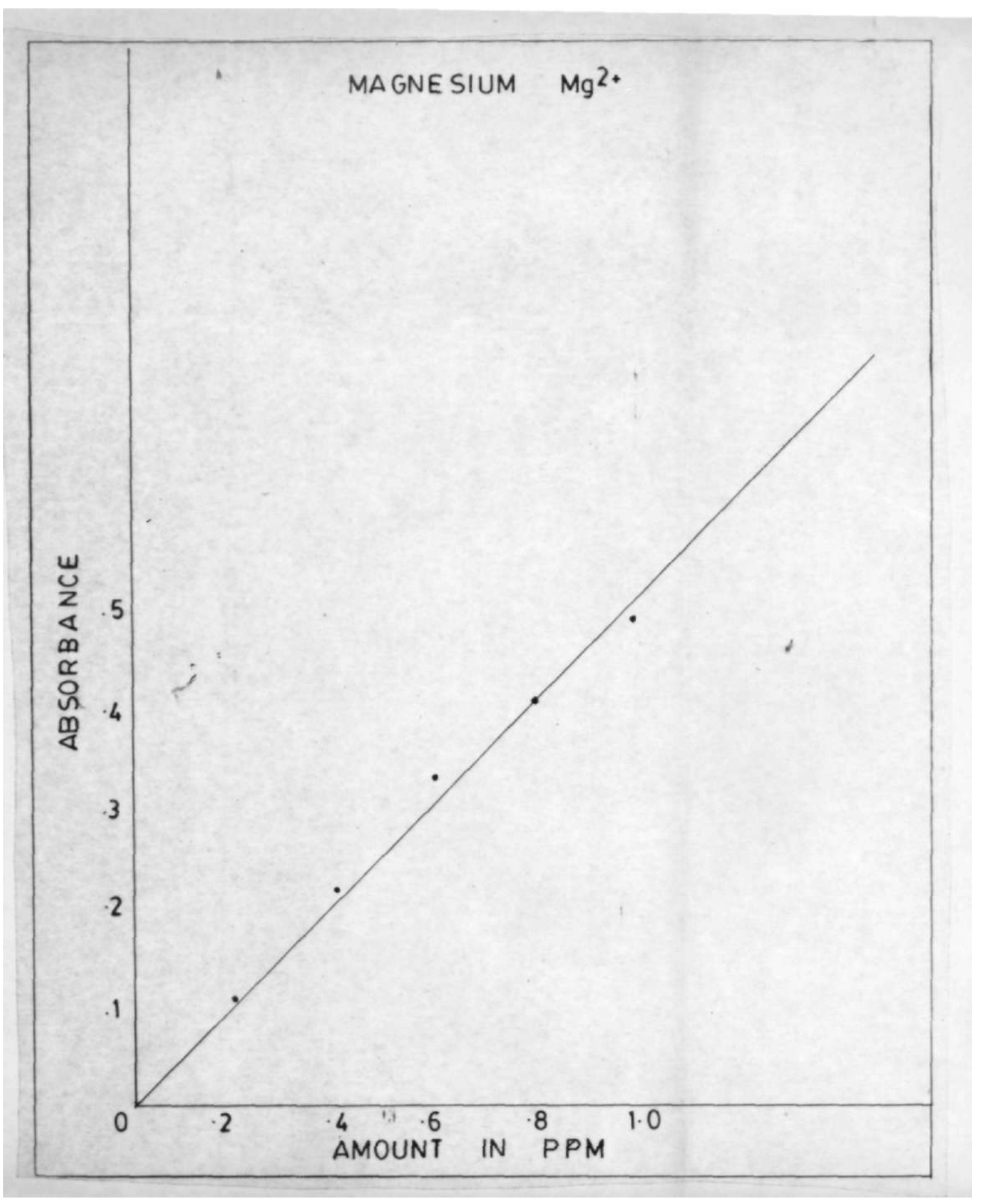
The result also showed that all imported or refined oils have very low acid values hence low free fatty acids as a result of the chemical processes that might have taken place, this in part makes one to conclude that the locally produced oils with their high free fatty acids are lower in quality than the refined oils. With their high values of free fatty acids they are of good quality and are still quite good for consumption, though there is no official standards for the amount of acids to be present in oils.

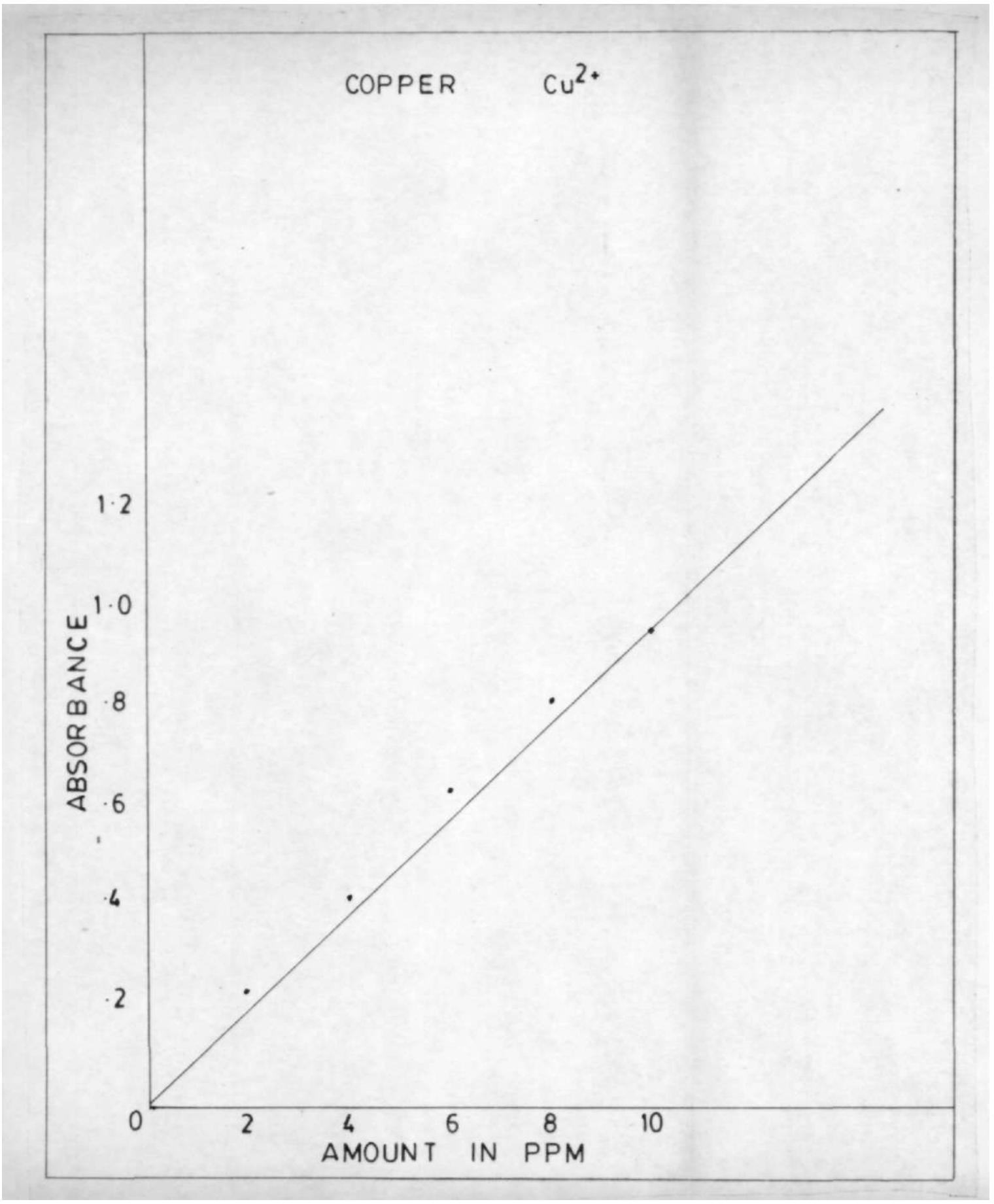
It can also be said that all refined oils and some other oils like groundnut oils, cotton oils have very low amount of trace metals hence are not easily subjected to oxidation or reduction. Palm oils can be said to be easily oxidized due to the presence of relatively high values of copper and Iron even though their presence in the oils investigated can be said to be within tolerable limit (12 ppm).

On the whole, this piece of work seems to be one of the first few attempts to determine the quality of vegetable oils being consumed in Nigeria. The results obtained are likely to be useful to the generality of the people and especially the Nigerian standard organizations who are charged with the formulation of standards for the food and drinks consumed in Nigeria. It would appear that no such standard exist at present for these vegetable oils as confirmed by the Nigerian Institute of food Science and Technology.


PHOSPHORUS PO4 3-
720nm
ABSORBANCE
·08
·07
·06
·05
·04
·03
·03
·01
0
·1
·2
·3
·4
·5
·6
·7
AMOUNT IN PPM


IRON
$Fe^{3+}$
ABSORBANCE
·12
·10
·08
·06
·04
·02
0
2
4
6
8
10
12
AMOUNT IN PPM


MAGNESIUM $Mg^{2+}$
ABSORBANCE
·5
·4
·3
·2
·1
0
·2
·4
·6
·8
1·0
AMOUNT IN PPM


COPPER Cu2+
ABSORBANCE
1·2
1·0
·8
·6
·4
·2
0
2
4
6
8
10
AMOUNT IN PPM

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