



Comparative analysis of groundnut oil quality in the north-central zone of Nigeria: Determination and evaluation of heavy metals, fatty acids, phospholipids, and iodine values in groundnut oil

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ABSTRACT

The research presents a comparative analysis of the quality of locally produced groundnut oil (*Arachis hypogaea*) sold in the north-central zone of Nigeria markets (Benue, Nasarawa, Kogi, Kwara, Niger and Plateau States). The aim was to assess and compare the qualities of the oils and to know the safety of human consumption. The groundnut oil produced biodiesel, shampoo lubricants, and soap-making industries. The concentrations of the heavy metals were analyzed with atomic absorption spectrometry (AAS). It showed that the lead, zinc, and copper (Pb, Zn, Cu) were within the FAO/WHO recommended limit, while Cd (0.201-0.331 mg kg⁻¹) was above the limit (0.07 mg kg⁻¹). Also, the gas chromatography (GC-FID) results indicated that twelve fatty acids (linoleic > oleic > palmitic > stearic > lignoceric > arachidic acid > behenic > erucic > arachidonic > margaric > linolenic > palmitoleic) were obtained in the groundnut oils in all markets and fatty acids include caprylic acid, capric acid, lauric acid, and myristic acid were absent in oils. In addition, the magnitude of six phospholipids (phosphatidylcholine > phosphatidylethanolamine > phosphatidylinositol > phosphatidylserine > phosphatidic acid > lysophosphatidylcholine) were also achieved, respectively. The results showed that iodine, peroxide, saponification value and refractive index were below the FAO/WHO recommended level, and the acid value was higher than the normal range.

1. Introduction

Groundnut oil is a tasting oil derived from the groundnut plant (*Arachishypogaea*), a species in the legumes family (Fabaceae). Some common synonyms for groundnut are peanut, earthnut, goober, pinder, and ground pea. It is called “*abum*” by the Tiv people, “*emansak*” by the Ibibios, “*epa*” by the Yorubas, “*Gyada*” by the Hausas and

Asiboko by the Ibos. In 1753, Linnaeus described the domesticated groundnut species as *Arachis* (derived from the Greek “*arachis*,” meaning a weed), *hypogaea* (meaning an underground chamber) or a weed with fruit produced below the soil. Groundnut is eaten fresh or roasted and is used in cooking, confectionery and pressed for edible oil. Palm oil and groundnut oil are both vegetable oils. Vegetable oils are water-insoluble, edible liquids derived from plants, which consist predominantly of long-chain fatty acid esters derived from the

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simple alcohol glycerol. Oil plays a crucial role in our everyday life. There are different types of oils, including edible, non-edible, essential oils [1], etc. Edible oils include palm oil, coconut oil, groundnut oil, etc. Rubber seed oil is an example of non-edible oil. Essential oils include Jasmine oil, sandalwood oils, etc. The quality of groundnut oil could be affected by improper post-harvest handling, processing and storage. Again, there is widespread speculation that groundnut oil is being adulterated for profit maximization. The adulteration ranges from using dyes, water and other illegal food additives, which could affect the quality of these oils regarding nutritional value, wholesomeness, utilization, safety and shelf-life. The percentage of free fatty acid, moisture and dirt content generally determines the quality of this oil. The produce is traditionally bought on a 5% free fatty acid basis with penalties for exceeding this figure [2]. Hence, there is a need to assess the quality of groundnut oils sold in major markets in the north-central zone of Nigeria. Heavy metals have relatively high densities of 4.0g cm^{-3} and above [3]. Heavy metals in trace amounts are of significant benefit to man. Inadequate trace elements in diet may constitute a health problem that may be devastating. In large doses, heavy metals are generally characterized as toxic or poisonous. Since trace elements provide nutritional value, they are sometimes called micronutrients [3]. Groundnut oils are essential daily condiments because of their various uses in our everyday lives. Unfortunately, it has been reported that some brands of groundnut and palm oils are adulterated with diesel automobile hydrocarbon oil, which is miscible with vegetable oils. This impurity is alleged to change the quality of vegetable oils and consequently negatively affect consumers [4]. Vegetable oils and fats contain trace levels of various metals depending on many factors such as species, soil used for cultivation, irrigational water, variety and stage of maturity, pollution, mode of processing, storage, and contaminations. These metals may enter the food material from the soil through mineral uptake by crops, food processing, and environmental

contamination (as in fertilizer application). Metals play essential negative and positive roles in human life [5]. Hence, there is a need to determine the concentration of heavy metals, trace elements and some physicochemical parameters in these groundnut oils in the north-central zone so that consumers will know the qualities of these groundnut oils. Atomic absorption spectroscopy (AAS) is a widely used analytical technique for determining heavy metals concentration in water, fats and oils [6-8]. It is a sensitive and reliable method for measuring trace amounts of heavy metals in water and oil samples. AAS has been used in several studies to assess drinking water quality and food samples from various sources, including oils. Gas chromatography (GC) Flame ionization detector (FID) is a well-established technique which is used to identify and quantify the incorporation of fatty acids into lipid pools. Chromatographic separation of lipids is typically extracted from the sample using the solubility of lipids in solvent mixtures of chloroform and methanol. Sodium chloride is added to facilitate the separation of the mixture into aqueous and organic lipid-containing phases [9]. Complex lipid classes of interest can be separated from the total lipid extract by solid phase extraction (SPE).

The study aimed to assess the quality and Nutritional values of locally produced groundnut oil in the northern central zone of Nigeria (Benue, Nasarawa, Kogi, Kwara, Niger and Plateau states). Therefore, the AAS and GC-FID determined the physicochemical parameters, the concentration of heavy metals, and the concentration of fatty acids and phospholipids in groundnut oil.

2. Material and Methods

2.1. Reagents and Materials

The reagents used for the analysis were all analytical grades purchased from Emole Nigeria (NO: 33 Old Otukpo Road high level, Makurdi, Benue State, Nigeria). Cadmium, lead, zinc, and copper standard solutions (500 mL ; 1000 mg L^{-1}) purchased from Merck, Germany. The reagents such as nitric acid (CAS number : 7697-37-2), sulfuric acid

(CAS number: 7664-93-9), hydrochloric acid (CAS number: 7647-01-0), hydrogen peroxide (CAS number: 7722-84-1), sodium hydroxide (CAS number: 1310-73-2), sodium thiosulphate (CAS number: 7772-98-7), glacial acetic acid (CAS number: 64-19-7), potassium hydroxide (CAS number: 1310-58-3), potassium iodide (CAS number: 7681-11-0), ethanol (CAS number: 64-17-5), tetrachloromethane (CAS number: 56-23-5), chloroform (CAS number: 67-66-3), Wiji's solution (CAS number: 7790-99-0), phloroglucinol (CAS number: 108-73-6), diethyl ether (CAS number: 60-29-7), methanol (CAS number: 67-56-1), boron trifluoride (CAS number: 7637-07-2), n-hexane (CAS number: 110-54-3) were purchased from Merck, Germany. Also, the phenolphthalein indicator (Sigma), starch indicator (Sigma), polyethylene bottles (plastic bottles), weighing balance, beakers, oven, filter paper, deionized water (DW), bottles, bath water and heating were used for analysis groundnut oil.

2.2. Instrumental

The measurements were made from Ahmadu Bello University Zaria Laboratory for the analysis of heavy metal samples using a Phoenix 986 atomic absorption spectrometer (Biotech Engineering Management Co. Ltd, UK) and Shimadzu GC-FID (model GC-2014; Sweden) for the analysis of Fatty acids and phospholipids in the groundnut oils. Cadmium, lead, zinc and copper hollow cathode lamps were operated according to the AAS manufacturer's instructions.

2.2.1. Atomic Absorption Spectrophotometer

A Phoenix 986 model (Biotech Engineering Management Co. Ltd, UK) atomic absorption spectrometer with four hollow cathode lamp positions was employed. The light sources of the

different elements were hollow-cathode lamps from Cathoden, UK. The light beam through Air-Acetylene was controlled by an aperture for measuring absorbance in different slit widths depending on the calculated element. The oxidant rate was 4.5 L min⁻¹ and the fuel rate (C₂H₂) was 1.5 L min⁻¹. The most sensitive Cd, Cu, Pb and Zn absorption lines were used [10]. Standard solutions were inspired into the flames after the burner had been allowed to operate for 5-10 min. This way, thermal equilibrium was attained before any final adjustment to the absorbance mode, measuring time, burner height, gas flows or amplifier gain. In this case, maximum sensitivity will be expected. All absorbance values are the average of ten readings recorded successively from the different absorbance modes. The background absorption is measured and subtracted from the total absorption to determine the actual atomic absorption signal. For this reason, a continuum source of deuterium arc lamp in ultraviolet has been used to measure only the background contribution to the absorption signal, which has essentially zero atomic absorption sensitivity at the regular resolution for atomic absorption instruments. In this case, the background correction is automatically carried out by a background correction system [11]. The limit of detection (LOD) and limit of quantification (LOQ) for heavy metal (Pb, Zn, Cu, Cd) determination was achieved by AAS and is shown in Table 1. The lowest qualitative and quantitative concentrations for the tested linearity range were calculated for each metal according to the guidelines of ICH,2000. LOD and LOQ were calculated using the expression $m \times S/c$, where $m = 3.3$ for the LOD and 10 for the LOQ, S is the standard deviation of the intercept, and c is the slope of the calibration curve tested for linearity.

Table 1. The LOD and LOQ of AAS For heavy metal determination

Parameter	Pb	Zn	Cu	Cd	Average
LOD (mg L ⁻¹)	0.088	0.052	0.077	0.028	0.06125
LOQ (mg L ⁻¹)	0.433	0.208	0.231	0.112	0.2455

2.2.2. Gas chromatography analysis

Shimadzu GC-FID model GC-2014 Sweden was equipped with a flame ionization detector and capillary column (30 m, 0.53 mm) with a stationary phase fused silica. The chromatographic conditions were detector temperature 280°C, injector temperature 250°C, initial column temperature 120°C for 1 min, programmed to increase at a rate of 10°C per minute up to 200°C and then at four °C per minute up to the final temperature of 220°C. Nitrogen and hydrogen for chromatography R, as the carrier and auxiliary gas, respectively, have a 1.3 mL min⁻¹ flow rate. As a determination, one µL of the derived sample was injected, alternatively with a sample volume/internal standard ratio of 80/20. Fatty acids and phospholipids were identified by comparing the standards' retention times and relative retention times with those of the samples. The quantification was by internal standardization using the methyl esters of lauric acid as the internal standard. The value of fatty acids and phospholipids were calculated according to AOCS methodology (mg per 100 g⁻¹) [12].

2.3. General Procedure

First, the *groundnut oil (Arachis hypogaea)* samples were prepared by digestion procedure, and then parameters such as iodine value, the concentration of free fatty acid, Acid value, color, odour, peroxide value, saponification value and refractive index were determined. Also, heavy metals (Cd, Pb Zn and Cu), Fatty acids and phospholipids in groundnut oil were determined.

2.3.1. Digestion of groundnut oil (*Arachis hypogaea*)

First, 2.0 g of each sample was weighed in a beaker. Concentrated nitric and sulphuric acids (5cm³) were added, followed by hydrogen peroxide (2cm³), then heated on a heating mantle until a clear solution was obtained. The content of the beaker was allowed to cool and then filtered. The resulting solutions were made up to 50cm³ using de-ionized water and then transferred into a plastic bottle for metal analysis by the AAS method [13].

2.3.2. Procedure for determination of parameters in groundnut oil

Acid value was determined by the titrimetric method of Kupwade and Desai [14]. 5g of the oil sample was weighed, and 75 mL of hot, neutral alcohol was added with a few drops of phenolphthalein. The mixture was shaken vigorously and titrated with 0.1M NaOH solution with constant shaking until the pink coloration remained permanent. The acid value was calculated using Equation 1 (V= titration endpoint value).

$$\text{Acid value} = (V \times 5.6) / (\text{Weight of sample}) \quad (\text{Eq.1})$$

The iodine value was determined according to the titrimetric method of Pearson [15]. 2.0 g of oil sample was weighed into a dry glass stopper bottle of 250 mL Capacity, and 10 mL of carbon tetrachloride was added to the oil. About 20 mL of Wij's solutions were then added and allowed to stand in the dark for 30 min. 15 mL of (10%) potassium iodide and 100 mL of water were added and then titrated with 0.1M sodium thiosulphate solution using starch as indicator just before the endpoint. A blank was also prepared alongside the oil samples. The iodine value was calculated by Equation 2.

$$\text{Iodine value} = (V_2 - V_1) \times 1.269 / \text{Weight (g)} \quad (\text{Eq.2})$$

Where V₂ = titre value for blank, V₁ = titre value for sample(s)

The peroxide value was evaluated according to AOAC [16]. A 2.0 g oil sample was weighed into a tube, and 1g of powdered potassium iodide with 20 mL of solvent mixture (glacial acetic acid and Chloroform) was added. This was then placed in boiling water for 30s. The content was poured into a flask containing 20 mL of 5% iodide solution. The tube was washed with 25ml of distilled water and titrated with 0.002N sodium thiosulphate solution using

starch as an indicator. A blank was prepared alongside the oil samples. Peroxide was obtained by Equation 3.

$$\text{Peroxide Value} = \frac{2(V_1 - V_2) \text{ mEq/kg}}{\text{Weight of sample (g)}} \quad (\text{Eq.3})$$

Where V_2 = titre value for blank, V_1 = titre value for sample(s)

The Saponification value was determined according to the titrimetric method of Pearson [15].

2.0 g of oil sample was weighed into a conical flask, and 25 mL of alcoholic potassium hydroxide was added. The solution was heated in boiling water for one hour. 1 mL of 1% phenolphthalein was added and titrated with 0.5N HCl. A blank was prepared alongside the oil samples. The formula calculated the value by Equation 4.

$$\text{Saponification Value} = \frac{5.61N(A - B)}{W} \quad (\text{Eq.4})$$

Where N= Concentration of HCl acid used,

A= Volume of H_2SO_4 , for blank (mL),

B= Volume of H_2SO_4 (mL),

56.1= Equivalent weight of potassium hydroxide,

W= weight of oil

The colour of the oil samples was determined by visual comparison, while the odour of the oil samples were determined using a glass stoppered bottle rinsed with 4 M HCl internally and externally and rinsed with distilled water. The bottle was halfway filled with the oil sample and shaken vigorously for about 2 minutes. The stopper was then removed, and the odour was observed by putting nostrils near the mouth of the bottle. The rancidity of the oil samples was determined qualitatively using the Kries Test, as described by Pearson [15]. 5.0 cm³ of the oil samples was placed in a 100 cm³ test tube vigorously mixed with 5cm³ of 0.1% phloroglucinol solution in diethyl ether and 5 cm³ of concentrated HCl for about 20s.

The presence of pink colour indicates incipient rancidity. The refractive index (RI) was determined using a mathematical expression [17] and shown in Equation 5.

$$\text{RI} = 1.45765 + 0.0001164/V \quad (\text{Eq.5})$$

RI: the Refractive Index

V : Iodine Value

2.3.3. Procedure for analysis of fatty acid, phospholipid, and heavy metals

50 mg of the extracted fat content of the sample was saponified (esterified) for five minutes at 95°C with 3.4 mL of 0.5M KOH in dry methanol (CH_3OH). The mixture was neutralized by using 0.7M HCl. 3 mL of the 14% boron trifluoride in methanol was added. The mixture was heated for five minutes at the temperature of 900°C to achieve a complete methylation process. The fatty acid methyl ester was thrice extracted from the mixture with redistilled n-hexane. The content was concentrated to 1.0 mL for Gas Chromatography analysis (GC-FID), and 1µm was injected into the injection pot of GC-FID. The modified method of Liu *et al.* [18] was employed to determine the extracted oil phospholipid content. 0.01g of the extracted fat was added to the test tubes to ensure complete dryness of the oil for phospholipid analysis. The solvent was completely removed by passing the stream of nitrogen gas on the oil. 0.4 mL of chloroform was added to the test tube's content, followed by the addition of 0.10 mL of the chromogenic solution. The range of the tube was heated at the temperature of 100°C in a water bath for about 1min and 20s. The content was allowed to cool to the laboratory temperature, and 5 mL of the hexane was added, and the tube with its content shook gently several times. The solvent and the aqueous layer were allowed to be separated, and the hexane layer was recovered and allowed to be concentrated to 1.0 mL for gas chromatography analysis (GC) using a pulse flame photometric detector (FPD). Also, the heavy metals determined by F-AAS after sample preparation (Acid digestion; microwave) of groundnut oil (Fig.1)

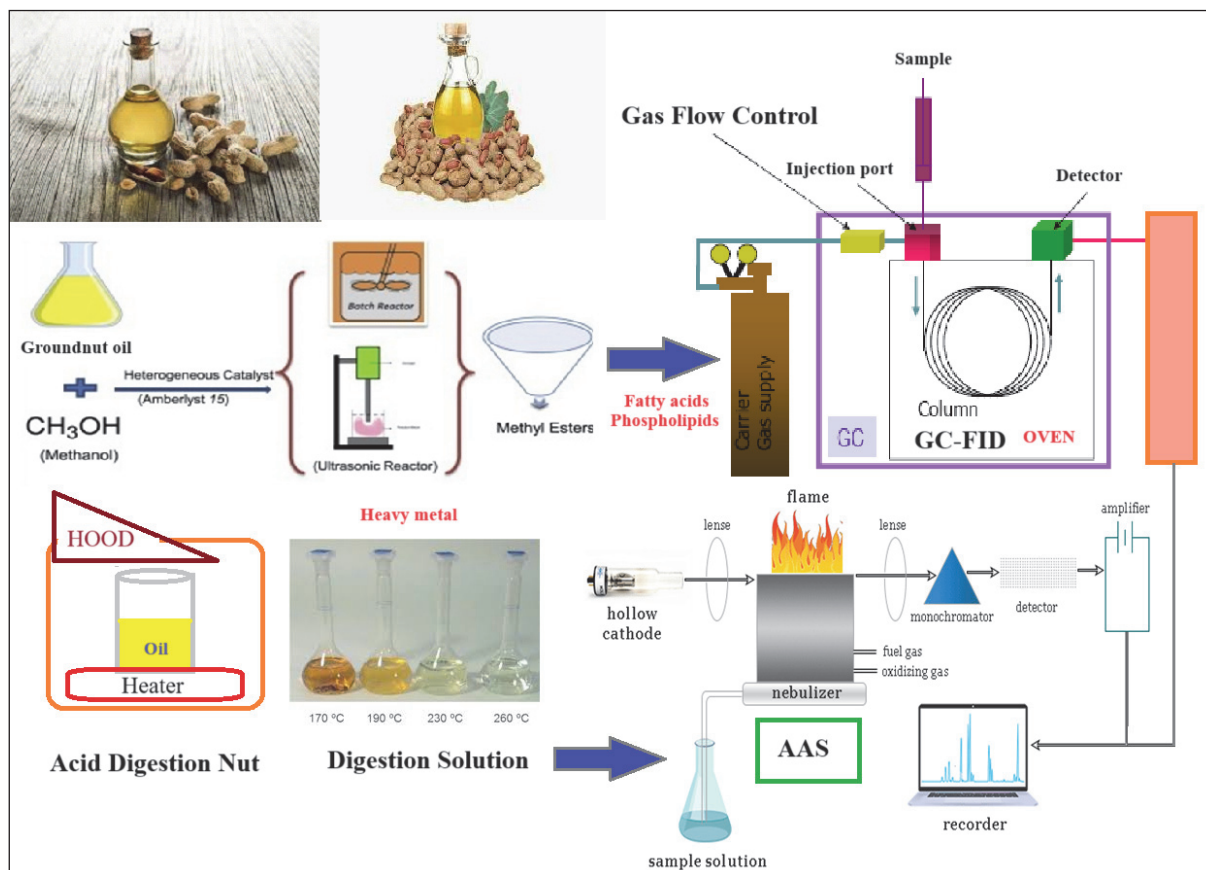


Fig.1. Procedure for sample extraction/separation of fatty acid, phospholipid and heavy metals from groundnut oil before determination by GC-FID and F-AAS

2.4. Scope of the study, collection of oil samples, and study area

The study was restricted to parameters such as iodine value, fatty acid/phospholipid concentration, acid value, colour, odour, peroxide value, saponification value, refractive index, heavy metals, Fatty acid and phospholipid in groundnut oil in North central Nigeria. The concentration of heavy metals (Cd, Pb Zn and Cu), fatty acid and phospholipid in groundnut oil were determined by F-AAS and GC-FID, respectively. The study covered an analysis of groundnut oil in 2022. Groundnut oil was bought from six states in north-central Nigeria markets for two months (September and October 2022). Three groundnut oil samples of 100 cm³ each were collected from three sellers in each market, giving eighteen samples. The collected oil samples were packed in

polyethylene bottles and stored below 20°C until analyses were used. The study was conducted in north-central Nigeria, one of Nigeria's geopolitical zones. It comprises six states, including the federal capital territory, Abuja. The states include Benue, Nasarawa, Plateau, Kogi, Niger and Kwara (Fig. 2).

3. Results and Discussion

The results obtained from the physical and chemical analysis of locally produced groundnut oil (*Arachis hypogaea* oil) sold in six markets in North Central Nigeria are presented in Table 2, 3 and Figure 3. The physical parameters of the ground nut oil are shown in Table 2. Also, the oil's heavy metal contents, the percentage composition of fatty acids, saturated and unsaturated fatty acids, and phospholipids were presented in Tables 4, 5, 6 and 7 and Figures 3, 4, 5 and 6. Oil constitutes a significant composition of

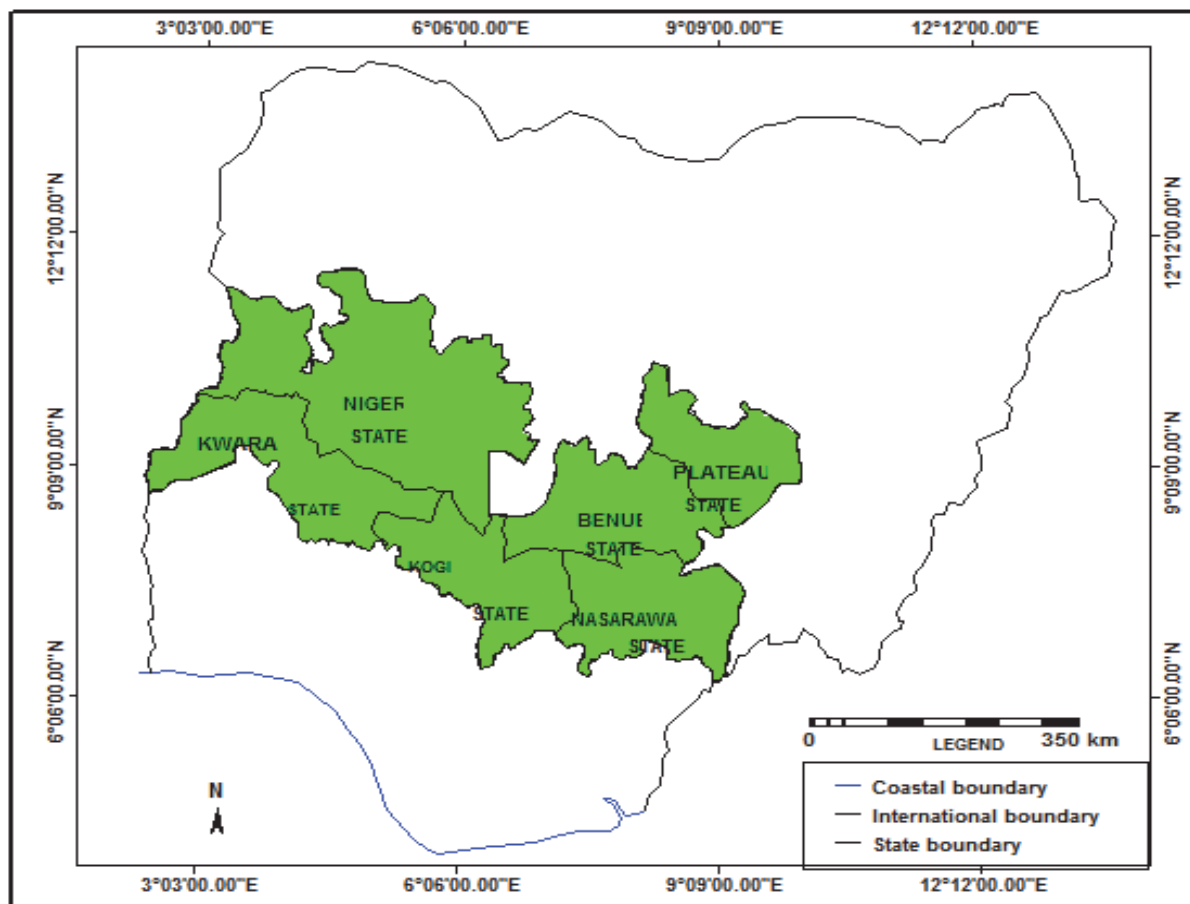


Fig. 2. Map of north central Nigeria showing the sampling states.

our daily diet consumption, and its market growth is now considered for its acceptability and economy, not minding the composition and nature.

3.1. Physical parameters

The sampled groundnut oil in Makurdi, Lafia and

Lokoja was amber-yellow, while Jos, Minna and Ilorin were golden yellow. No abnormal odour of the sampled oil was noticed; hence, it was agreeable or acceptable. The state of all the oil was liquid (Table 2).

Table 2: The physical parameters of the groundnut oil purchased in the North Central Nigeria markets

Market	Colour	Odour	State (25°C)
Makurdi	Amber Yellow	Agreeable	Liquid
Lafia	Amber Yellow	Agreeable	Liquid
Jos	Golden Yellow	Agreeable	Liquid
Minna	Golden Yellow	Agreeable	Liquid
Lokoja	Amber Yellow	Agreeable	Liquid
Ilorin	Golden Yellow	Agreeable	Liquid

3.2. Chemical properties of the oil

The study indicated that oil in the Makurdi market was relatively high in fat content (135%), while the Lokoja market has the lowest value (70%), as shown in Table 3 and Figure 3. The order of fats content was Makurdi<Jos< Ilorin<Minna<Lafia<Lokoja. The iodine value is a measure of the total unsaturation of oils, as well as an indicator of their susceptibility to oxidation. The iodine values of all oil samples from the Northcentral markets were below the WHO specification (86-166 g I₂/100g of oil) range. The higher the iodine number, the more C=C bonds in the fat [19]. This shows that the groundnut oil samples from the Lokoja market contain higher unsaturated fatty acids than any other market sampled. The chemical analysis of iodine value indicated that the Lokoja market has the highest value, followed by the Lafia market. The increasing order was Lokoja >Lafia> Minna >Makurdi> Jos >Ilorin. A high iodine value denotes a high degree of unsaturation caused by the extent of oxidation and degree of heat treatment during oil processing. The peroxide value is the weight of active oxygen contained in one gram of oil or fat [20]. Peroxide value measures peroxides and hydroperoxides formed in the initial phases of lipid oxidation. It, therefore, determines the degree of oil oxidation and indicates the level of deterioration of oils and fats. Freshly refined oil should have no peroxide value. In this study, it was observed that the groundnut oil from all the markets showed peroxide values (Table 3 and Figure 3) lower than the FAO/WHO (14) recommendation range (≤ 10 mili equivalent oxygen per kg), thus indicating less susceptibility to oxidation with Lokoja market having the highest (1.13 meq per kg) and Minna market having the lowest (0.42 meq per kg). According to Hassan [21], a low peroxide value indicates the oil's oxidative stability and a high peroxide value indicates poor oil resistance to peroxidation during storage [22]. Therefore, it is likely that storage for a long time may lead to rancidity of the oil. A rancid taste often becomes noticeable when the peroxidative value exceeds 20 meq per kg [23]. Peroxide value is critical for

examining the quality and stability of fats and oils, stages of oxidation and spoilage extent [24]. Thus, the ground nut oil obtained from these locations will not harm human health due to its nonprone oxidation. The acid value is used to measure the quality of the oil since the acid value indicates the extent of hydrolysis and deterioration. The higher the fatty acid value, the higher the level of free fatty acids, which translates into decreased oil quality. The acid values from Lafia and Minna markets were approximately similar in value. In this study, the acid value in all the markets was higher compared to FAO/WHO [10] specification (≤ 0.6 mg KOH per gram of oil), and it followed Lokoja >Lafia >Minna>Jos> Ilorin >Makurdi order. The high acid values indicate free fatty acids present in the groundnut oil, which may be due to exposure to atmospheric oxygen or due to the method used for the extraction. According to Demian [25], acid values measure the extent to which glyceride in the oil has been decomposed by lipase and other actions such as light and heat. The determination is often used as a general indication of the condition and edibility of oil. According to Badmos *et al.* [26], a low acid value indicates the stability of oils over a long period and protection against rancidity and peroxidation. No rancidity was detected in any of the sampled groundnut oil in north-central Nigeria (Table 3 and Figure 3).

The saponification value measures the fatty acids' average molecular weight (or chain length). It is a measure of oxidation during storage and indicates the oil deterioration. An increase in saponification value in oil increases the volatility of the oils. It enhances the quality of the oil because it shows the presence of lower molecular weight components in 1.0 g of the oil, which will yield more energy on combustion [27]. The saponification values from the Northcentral markets were below the FAO/WHO [10] specification (187-196 mg KOH per gram of oil) range. This property makes it less useful in soap making. The lower saponification value observed in this study suggests that the mean molecular weight of fatty acids is high, as low saponification indicates the presence of long-chain

fatty acids, and higher saponification value indicates lower chain fatty acids since saponification value is inversely proportional to the average molecular or chain length of the fatty acid. The study shows that the Jos market has the highest saponification (142.25 mg KOH per gram) while the Minna

market has the lowest value (37.23 mg KOH per gr). The increasing order of saponification was Minna >Lokoja>Ilorin>Lafia >Makurdi >Jos. All the groundnut oil sampled has the same refractive index (1.46) in North Central Nigeria.

Table 3. Chemical Analysis of the groundnut oil sold in north-central Nigeria

Market	Fat content (%)	Iodine Value (wij's)	Peroxide value (meq kg ⁻¹)	Acid Value (%)	Rancidity	Saponification value(mgKOH g ⁻¹)	Refractive Index
Makurdi	135	1.35	0.70	4.43	Nil	127.02	1.46
Lafia	78	1.73	0.60	2.12	Nil	113.10	1.46
Jos	128	0.67	0.80	2.52	Nil	142.25	1.46
Minna	89	1.67	0.42	2.22	Nil	37.23	1.46
Lokoja	70	2.62	1.13	1.62	Nil	46.44	1.46
Ilorin	97	0.12	0.84	3.01	Nil	52.46	1.46

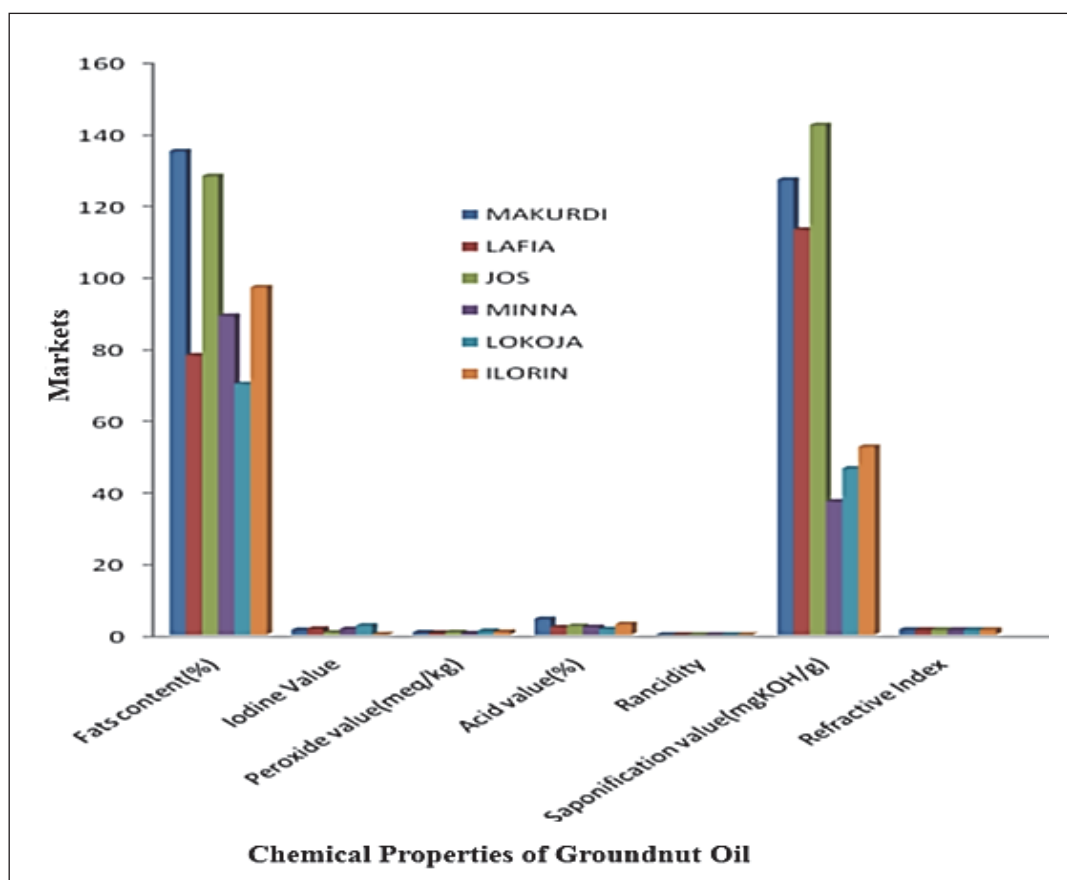


Fig.3. Chemical properties of the groundnut oil sold in north-central Nigeria

3.3. Heavy metals analysis

Lead serves no useful purpose in the human body, but its presence in the body can lead to toxic effects, regardless of the exposure pathway. In this study, the minimum (0.052 mg kg⁻¹) and maximum (0.114 mg kg⁻¹) levels of lead in the groundnut oil recorded were approximately equal to the threshold limit of lead established by WHO [28]. The highest and lowest values were noticed from Lafia and Ilorin markets, respectively. Lead in the oil may result from anthropogenic activities such as using leaded petrol during extraction. The order of lead in the oil was Ilorin>Makurdi>Jos>Lokoja>Minna>Lafia (Table 4 and Figure 4). *Cadmium* mean concentration (Saponification of groundnut oil) in the groundnut oil samples in North central Nigeria was above the recommended limit of daily tolerable intake level of 70 µg for Cd for the average 70kg man and 60 µg of Cd per day for average 60 kg woman [4]. The highest and lowest values were found in Lafia and Jos, respectively (Table 4 and Figure 4). The increased order of cadmium was Jos<Makurdi<Minna<Ilorin<Lokoja< Lafia. The element is toxic even at low levels, resulting in nausea, vomiting, abdominal cramps, headache, diarrhea, and shock. The increase in the mean levels of Cd observed in the groundnut oil was attributed to environmental pollution from emissions from municipal waste incinerates, industrial effluents, and plants'

absorption. *Zinc* content of the samples ranged from 0.119 -0.061 mg kg⁻¹. However, the concentration of zinc in the oil samples from the four markets (Makurdi, Jos, Lokoja and Ilorin) analyzed were within the threshold limit (0.1mg kg⁻¹) specified by WHO [28], while Lafia and Minna market values were above the threshold limit established by the world health organization (WHO). Therefore, groundnut oils from these four markets were within the acceptable nutritional margins regarding zinc (Table 4 and Figure 4). *Copper* is essential for the human body, but high intake can cause adverse health problems like headaches, stomachaches, dizziness, vomiting and diarrhea [29]. In Figure 4, the copper content of samples of groundnut oil from all the markets was below the threshold limit; this may probably be a result of low industrial activity in the area, low contamination of the soil in which the groundnut seed used in the production of the oil were cultivated [30]. The highest and lowest values from the research were 0.110 and 0.011 mg kg⁻¹, respectively. The order was Jos>Makurdi>Minna>Ilorin>Lokoja>Lafia. The maximum level of Cu tolerable for a healthy man and woman is 0.9 mg kg⁻¹ daily. The results obtained were within acceptable limits of Cu specified by the WHO. Also, heavy metal and VOCs can be extracted /separated from different matrix by nanotechnology before determination by F-AAS, ET-AAS and GC-FID [31-37].

Table 4. Mean Concentration of heavy metals (mg kg⁻¹) in groundnut oil Purchased in North Central Nigeria

Market	Pb Mean	Cd Mean	Zn Mean	Cu Mean
Makurdi	0.061	0.202	0.061	0.105
Lafia	0.110	0.333	0.119	0.011
Jos	0.062	0.201	0.063	0.110
Minna	0.113	0.212	0.115	0.103
Lokoja	0.072	0.331	0.071	0.101
Ilorin	0.052	0.322	0.082	0.102
FAO/WHO,1999	0.114	0.07	0.1	0.9

S.D: Standard Deviation

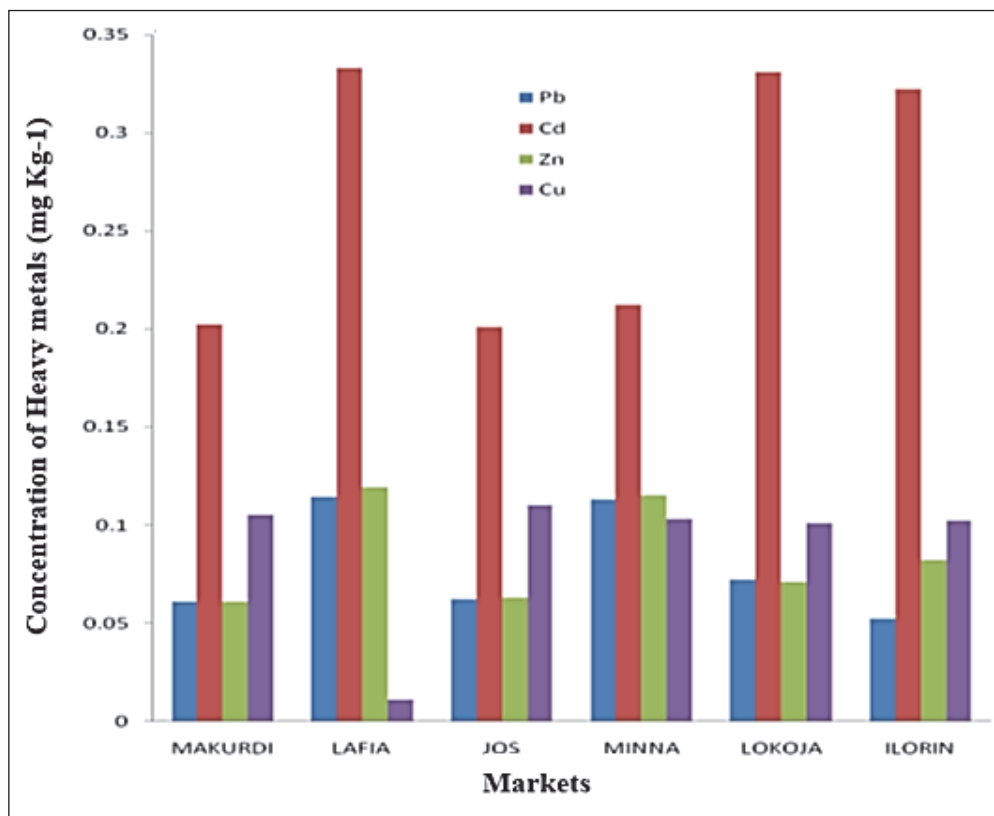


Fig. 4. Concentration of heavy metals (mg kg⁻¹) in groundnut oil

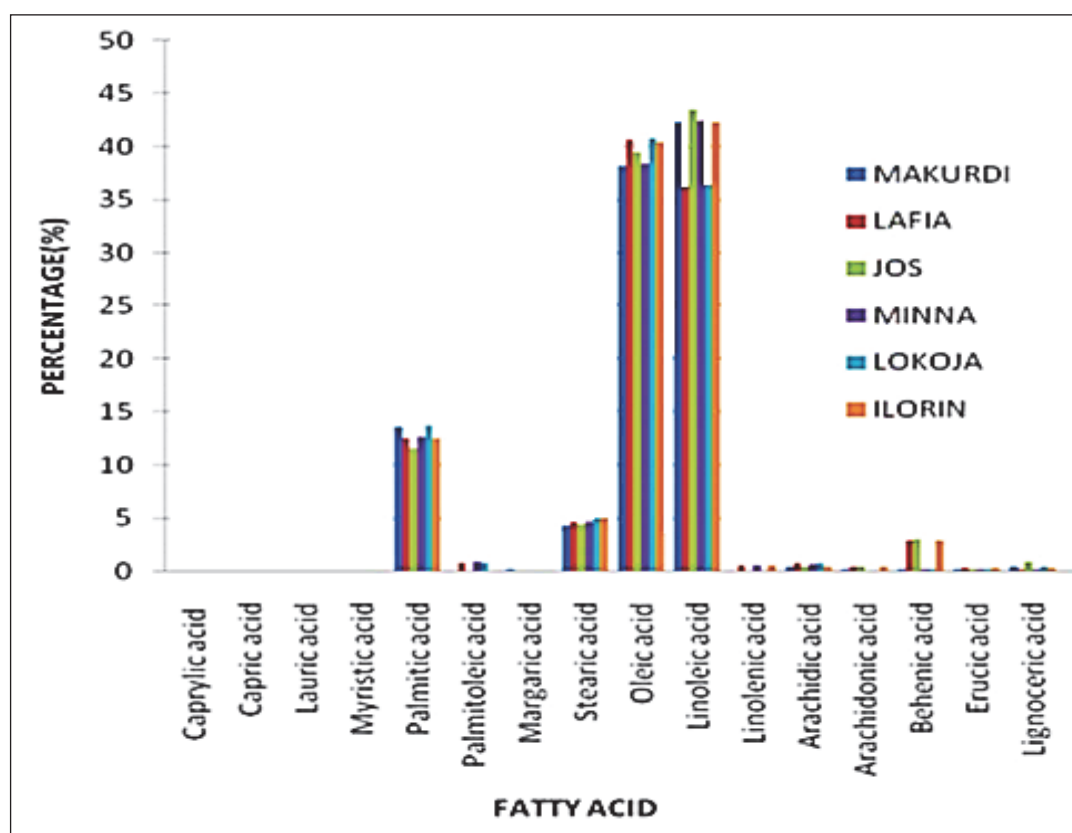
3.4. Analysis of fatty acids composition

Table 5 and Figure 5 show the percentage composition of fatty acids in locally produced groundnut oil in six markets in north-central Nigeria. The results indicated twelve fatty acids in the oils. Comparatively, fatty acid detected in both markets in North central Nigeria includes palmitic acid, palmitoleic acid, margaric acid, stearic acid, oleic acid, linoleic acid, linolenic acid, arachidic acid, arachidonic acid, behenic acid, erucic acid and lignoceric acid. Fatty acids absent in the oils include caprylic, capric, lauric, and myristic acid. The order of fatty acid composition in all the samples in all the markets is linoleic > oleic > palmitic > stearic > lignoceric > arachidic acid > behenic > erucic > arachidonic > margaric > linolenic > palmitoleic acids. Phospholipids results showed six phospholipids: phosphatidylcholine,

phosphatidylethanolamine, phosphatidylinositol, phosphatidylserine, phosphatidic acid and Lysophosphatidylcholine. The order of magnitude was phosphatidylcholine > phosphatidylethanolamine > phosphatidylinositol > phosphatidylserine > phosphatidic acid > Lysophosphatidylcholine [23]. The study establishes that all the fatty acid types present were found in the sampled locally produced groundnut oil in all the markets in north-central Nigeria. This result obtained was like that of Kupwade and Desai [14], except that they detected caprylic acid, capric, lauric, and myristic acids and detected oleic acid to be the most predominant, with a percentage of 58.68%. Linoleic acid, the predominant acid in all the sampled markets, is an omega-six fatty acid and plays a vital role in pro-inflammatory reactions, blood clots, and allergic reactions.

Table 5. Percentage composition of fatty acid in locally produced groundnut oils

Fatty acid	Makurdi Market	Lafia Market	Jos Market	Minna Market	Lokoja Market	Ilorin Market
Caprylic acid (C8:0)	0.00	0.00	0.00	0.00	0.00	0.00
Capric acid (C10:0)	0.00	0.00	0.00	0.00	0.00	0.00
Lauric acid (C12:0)	0.00	0.00	0.00	0.00	0.00	0.00
Myristic acid (C14:0)	0.00	0.00	0.00	0.00	0.00	0.00
Palmitic acid (C16:0)	13.58	12.51	11.59	12.65	13.68	12.55
Palmitoleic acid (C16:1)	0.02	0.70	0.03	0.87	0.71	0.02
Margaric acid (C17:0)	0.08	0.05	0.06	0.09	0.09	0.06
Stearic acid (C18:0)	4.27	4.59	4.37	4.69	5.00	4.91
Oleic acid (C18:2)	38.25	40.75	39.46	38.43	40.87	40.46
Linoleic acid (C18:2)	42.39	36.38	43.49	42.49	36.48	42.29
Linolenic acid (C18:3)	0.06	0.56	0.06	0.57	0.06	0.55
Arachidic acid (C20:0)	0.38	0.71	0.39	0.63	0.78	0.33
Arachidonic acid C20:4)	0.09	0.42	0.42	0.09	0.09	0.42
Behenic acid (C22:0)	0.16	2.89	2.99	0.17	0.16	2.87
Erucic acid (C22:1)	0.12	0.23	0.13	0.24	0.22	0.23
Lignoceric acid (C24:0)	0.39	0.22	0.83	0.22	0.37	0.21

**Fig. 5.** Percentage of saturated and unsaturated fatty acids found in locally produced groundnut oil in north-central Nigeria

The result of the percentage composition of saturated, unsaturated, and monounsaturated fatty acids are presented in Table 6 and Figure 6, which showed that the percentage composition of total unsaturated fatty acid is more than saturated and monounsaturated fatty acid in all the locally produced groundnut oil marketed in North central Nigeria (Makurdi, Lafia, Jos, Lokoja, Minna and Ilorin) with Makurdi (81.85%) and Jos (78.03%) having the highest and lowest values respectively. The highest composition

of TSFA, MUFA and PUFA was found in Lafia (20.97%), Ilorin (41.88%) and Jos (42.80%), while the lowest composition was found in Lokoja (18.85%), Makurdi (38.39%) and Minna (37.22%) respectively. The higher the composition of unsaturated fatty acid, the higher its potential as an industrial feedstock and vice versa. In the polymer industry, unsaturated fatty acids are converted to epoxides poly oils, precursors in making plastics. The order of fatty acids was TUFA>PUFA>MUFA>TSFA.

Table 6. Percentage of saturated, unsaturated, and monounsaturated fatty acids composition

Fatty acid	Makurdi market	Lafia market	Jos market	Minna market	Lokoja market	Ilorin market
TSFA%	18.86	20.97	18.96	20.79	18.85	20.79
TUFA%	81.85	79.03	78.03	81.49	79.21	81.83
MUFA%	38.39	41.68	38.39	41.77	38.48	41.88
PUFA%	42.56	37.35	42.80	37.22	42.11	37.76

* % = Percentage; * TSFA = Total saturated fatty acid

* TUFA = Total unsaturated fatty acid.

* MUFA = Monounsaturated fatty acid.

* PUFA = Polyunsaturated fatty acid.

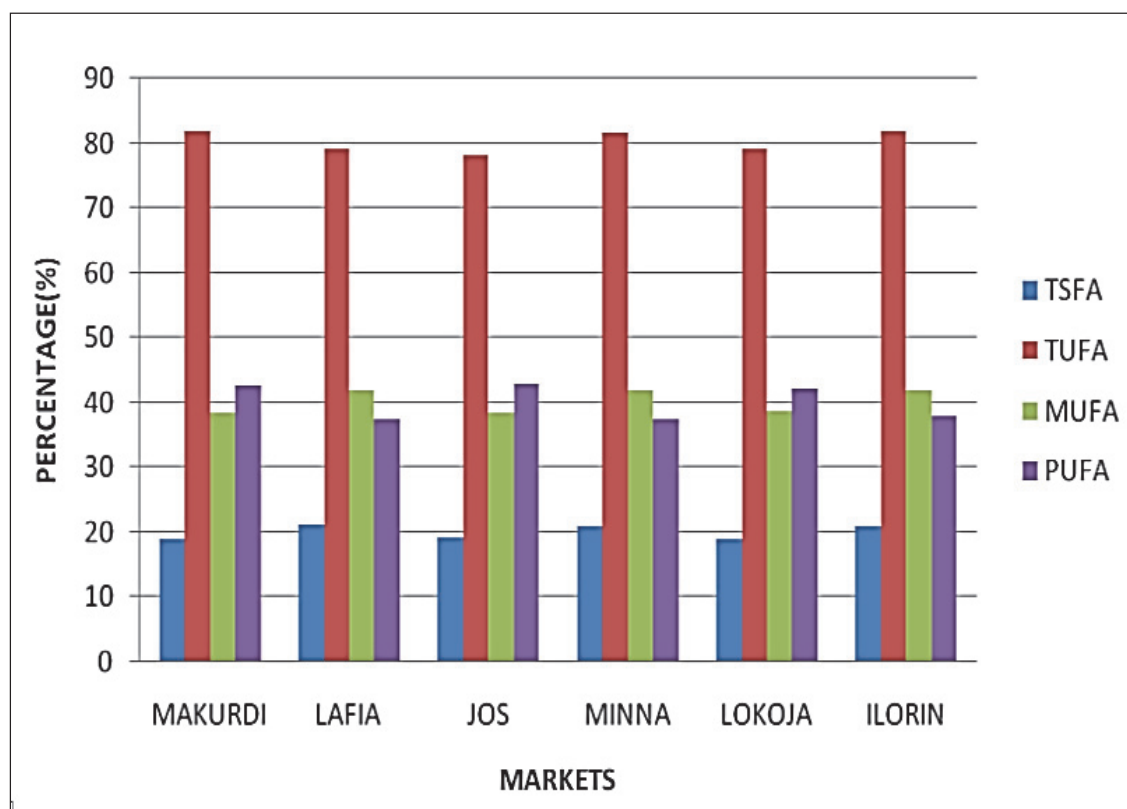


Fig. 6. Percentage of saturated, unsaturated, and monounsaturated fatty acids composition in north-central Nigeria

* TSFA = Total saturated fatty acid * TUFA = Total unsaturated fatty acid;

* MUFA = Monounsaturated fatty acid * PUFA = Polyunsaturated fatty acid;

3.5. Analysis of phospholipids composition

The phospholipids analyzed in locally produced groundnut oil sold in north central Nigeria are presented in Table 7 and Figure 7. Six phospholipids were identified, with phosphatidylcholine having the most significant percentage of phospholipid composition in all the markets and sampled groundnut oil. In contrast, lysophosphatidylcholine had the least in all the markets. The order of magnitude was phosphatidylcholine > phosphatidylethanolamine > phosphatidylinositol > phosphatidylserine > phosphatidic acid > lysophosphatidylcholine.

The highest concentration of phosphatidylcholine was found in Ilorin market (349.22) and the least in Makurdi market (259.86). This research analysis agrees with Adeyeye et al. [38] who reported phosphatidylcholine as the most abundant phospholipid in animals and plants as the main building blocks of membrane bilayers. Phosphatidylcholine, known to reduce body fat and required in the body for cell functioning Williams, Dowhan [39], was detected in large oil concentrations.

Table 7. Percentage composition of phospholipids found in locally produced Groundnut oil in north central Nigeria (mg per 100 gram)

Phospholipid	Makurdi Market	Lafia Market	Jos Market	Minna Market	Lokoja Market	Ilorin Market
Phosphatidylethanolamine	84.87	64.35	85.78	65.53	83.86	63.34
Phosphatidylcholine	259.86	347.04	295.86	346.11	260.84	349.22
Phosphatidylserine	3.39	9.93	3.45	9.68	3.29	9.90
Lysophosphatidylcholine	1.18	2.52	1.19	2.51	1.17	2.50
Phosphatidylinositol	79.53	67.89	78.60	68.98	79.43	69.89
Phosphatidic acid	2.93	10.81	2.99	10.76	2.79	10.18

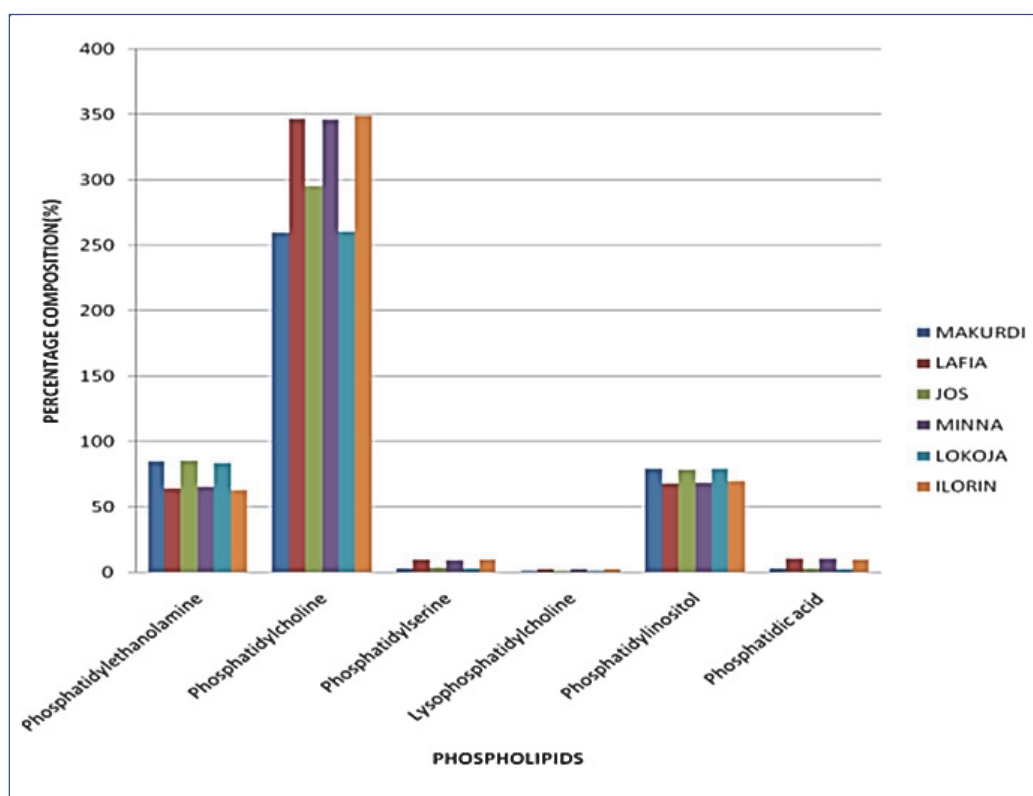


Fig. 7. Percentage composition of phospholipids found in groundnut oil in north-central Nigeria

4. Conclusion

The work compared locally produced groundnut oils produced and sold within and around north-central Nigeria markets. The assessment of the physicochemical parameters of the groundnut oil samples revealed that iodine, saponification, and peroxide values were lower than the threshold limit values (TLVs) except for acids greater than the reference value (FDA/WHO). Heavy metals (Zn, Pb, Cu, and Cd) contents of the groundnut oil from the six markets were detected by F-AAS and GC-FID. The results showed cadmium and zinc appeared to be the predominant metal contaminants and were the only elements that exceeded the recommended safe dietary exposure level. The oils had twelve fatty acids, which include palmitic acid (C16:0), palmitoleic acid (C16:1), margaric acid (C17:0), stearic acid (C18:0), oleic acid (C18:1), linoleic acid (C18:2), linolenic acid (C18:3), arachidic acid (C20:0), arachidonic acid (C20:4), behenic acid (C22:0), erucic acid (C22:1) and lignoceric acid (C24:0). It establishes that capric acid, caprylic acid, lauric acid and myristic acids are absent in the oil while linoleic acid was the highest in composition in all the sampled oil in all the markets in north central Nigeria followed by oleic acid which GC-FID analyzed. The oils show potential for industrial application as biodiesel, lubricants, plastics, and soap due to the presence of unsaturated and some saturated fatty acids. However, the oils will also help make shampoo. The assessment of phospholipid levels of the groundnut oils was also carried out with GC-FID, producing six phospholipids, namely phosphatidylcholine, phosphatidylethanolamine, phosphatidylinositol, phosphatidylserine, phosphatidic acid and Lys phosphatidylcholine. Phosphatidylcholine can help treat liver diseases and serves as a precursor of choline, a compound in the synthesis of acetylcholine, which can improve memory and muscle function.

5. Recommendation

It is recommended that further research into the use of these oils for some industrial processes

be embarked upon, and medical value should be checked. Also, groundnut oil contains high levels of phosphatidylcholine, among other legumes. Hence, it is advised that people should consume locally produced groundnut oil more often than other vegetable oils.

6. Significance of the Study

Groundnut oil is the chief source of edible oil. For the production of soap, margarine, and cosmetics and with the growing awareness in environmental pollution, groundnut oil is to be analyzed to ascertain its pollution level and nutritional value. This study is significant for the following reasons; (i) To provide a physicochemical database for groundnut oil that could be used as a basis for future studies. (ii) To create awareness of its contamination/pollution level.

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