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Maigari IA
Usmanu Danfodiyo University,
Sokoto, Sokoto State, Nigeria

Dabai MU
Usmanu Danfodiyo University,
Sokoto, Sokoto State, Nigeria

Muhammad C
Usmanu Danfodiyo University,
Sokoto, Sokoto State, Nigeria

Eze VC
Usmanu Danfodiyo University,
Sokoto, Sokoto State, Nigeria

Alhassan M
Usmanu Danfodiyo University,
Sokoto, Sokoto State, Nigeria

Assessment of heavy metals and characterization of fresh and used engine oils in different automobile

Maigari IA, Dabai MU, Muhammad C, Eze VC and Alhassan M

Abstract
One samples each of fresh engine oil is categorized as E0 while there used oil counterpart were label as E1, E2, E3, for used engine oil. A dry ash method was adopted for digestion of the sample. The digested samples were separately subjected to Atomic Absorption Spectrometric analysis. The research conducted a comparison of heavy metals (Pb, Fe, Cu, Cr, Ni and additive metals Ca, Mg and Mn) concentration in fresh oil and continuous increase during the usage in 3 different auto-mobile (Toyota bus, Nissan Bus and Sharon). The study divulges the relationship of metals with oil brand and different automobile engine as well as progressive increase in the concentration of metals over distance covered. Physiochemical properties considered include Kinematic Viscosity at 40ºC and 100ºC, Viscosity index, pour point, Flash point, Carbon residue, and Ash contents. Characterization of the samples was also conducted to determine chemical and structural composition using Gas chromatography-mass spectroscopy (GC/MS) and Fourier transformation infrared (FTIR) spectroscopy. A comparison of the obtain results showed connection between chemical properties of fresh oil and the collected used oil. The FTIR spectra showed the bands that are related to the presences of Aromatic Alkanes and carbonyl compound. The analysis of variance showed that there is significant different between the mean concentrations of all the elements studied.

Keywords: Gas chromatography-mass spectroscopy, automobile, elements studied, characterization

1. Introduction
In the present day, the word pollution has become intimate to the world. All human activities in one way or the other generate pollutants or contaminate from either domestic or industrial activities Nwite and Alu, (2015) [24]. However, these pollutants make the environment unhealthy and ultimately uncomfortable as water and land used by inhabitants are most affected Udonne *et al.*, (2016) [36]. The contaminants produced causes significant environmental problems to human health, leading to cancers and other viral diseases Sadeek.*et al.* (2014) [31].

Large amount of engine oil is used and replaced on daily basis. Different method is used to dispose of used oil like; many people use it as a dust cure to prevent dust. Incineration is another method of used oil disposal. But this is not proper way of oil disposal because it pollutes the environment as incineration produce carcinogenic compounds. Many countries are sensitive to this regard. Now recycling is gaining more attention for better use of used engine oil. It is also helpful to conserve crude oil reservoirs due to increasing demand of engine oil as well as help to reduce the environmental pollution Udonne (2011) [36].

2. Materials and Methods
2.1 Materials
The materials and reagents that will be used in carrying out this research are as follows: used and fresh lubricating and gear box oils ((Ammasco Vita Oil 5000SM). was collected from Toyota Hiace bus (2009 Model), Nissan bus (2009 Model) and Sharon Volks Wagen (2009 Model), Hydrogen Chloride (37.0%), Nitric Acid (69.5%). The instruments and equipment that will be used also in carrying out this research work are water bath, Analytical balance capable of determining weights to four decimal places, Conical flasks, Graduated cylinders, Beaker (difference sizes), Thermometer capable of measuring both negative and positive temperatures, Atomic Absorption Spectrophotometer, Furnace, Viscometer, Magnetic Stirrer and whattman filter paper.

Corresponding Author:
Maigari IA
Usmanu Danfodiyo University,
Sokoto, Sokoto State, Nigeria

2.2. Methods
2.2.1. Sample Collection
Sample of used and fresh lubricating oils (Ammasco Vita Oil 5000SM) was collected from Toyota Hiace bus (2009 Model), Nissan bus (2009 Model) and Sharon Volks Wagen (2009 Model), at Sokoto State transport authority maintainers workshop (Tashan Alu) and Sokoto Centre garage within Sokoto, after covering a distance of 3000 km each.

2.3 Physiochemical Analyses of Engine and Gear Oil
A. Determination of Specific Gravity
Specific gravity was determined according to ASTM (D1298) method. A dry empty 50 cm^3 density bottle was weighed and the mass was recorded as W_0, it was then fill with water and weighed again, the mass was recorded as W_1. The bottle was filled with the sample and it was being weighed again, the mass will be recorded as W_2. The specific gravity of the entire sample was calculated using the equation 1. (Al-Harbawy and Al-Mallah, 2014) [2].

$$Specific\ Gravity = \frac{w2 - w0}{w1 - w0} \qquad 1$$

B. Determination of carbon residue and ash content
The known quantity of the sample was weighed and put into a crucible and subjected to heat (T°?) and ignited by flame until leaving a carbonaceous material only. The carbon residue was calculated (ASTM D 482 2003). The residue undergoes cracking and coking reactions during heating at 775°c for about 30 minutes. The crucible containing the carbonaceous residue content was allowed to cooled and weighed. (Hameed *et al.*, 2017) [14].

C. Determination of flash point
The sample was heated in a test cup at 10°C per minute with constant stirring. A small test flame was directed into the cup with simultaneous interruption. The flash point was taken as the temperature when the test flame causes the vapour above the sample to cause a distinct flash in the interior of the test cup.

D. Determination of and pour points
The oil sample was measured in (5 cm^3) test tube and placed in a freezer. The sample was taken out of the freezer every 1 min to check any visible changes and the temperature was measured.

E. Determination of kinematic viscosity
The oil was poured into a viscometer and mounted upright in the viscometric bath maintain at 40 °C and 100 °C, the sample in the tube was allowed to stabilize for 15 minutes when the equilibrium temperature was attained. The sample level was adjusted using a suction pump to 7mm above the upper mark of the viscometer tube, the time taken for the oil move from the upper to lower mark of the viscometer was recorded. The kinematic viscosity was calculated using the equation 3.

$$KV = C(cSts) \times t(s) \qquad 3$$

Where, KV is the kinematic viscosity, C is the calibration constant of the viscometer and t is the time taken for the oil to move from upper timing to the lower timing mark of the viscometer tube.

F. Determination of Viscosity Index
The viscosity of the oil was obtained using the values of kinematic viscosity obtained at 40 and 100 °C with standard measurement

G. Determination of polarity and carbon chain using GC-MS
The chemical composition of the bio lubricant was determined using a combination of gas chromatography and mass spectrometry analytical techniques. The analysis was carried out using gas chromatography-mass spectrometry with helium gas as the mobile phase. Exactly 2 cm^3 of the lubricant sample was injected into sample vial which was fitted into the sample rag manually and then subsequent operations were electronically controlled. A rising vial was used to clean and rinse the injection needle as a precaution against sample contamination. The gas chromatograph was treated with the sample first and then conveyed it to the mass spectrometer for identification and compare with standard values (Nadkami, & Kishore. 2007) [25].

2.4 Metal Analyses
2.4.1 Preparation of Sample
Ashing was carried out to burn off carbonaceous materials in the fresh and used oils. A mixture of 10.0 g of used lubricating oil and 1.0 g sulphuric acid in a 250 cm^3 Pyrex beaker was heated in a heating mantle in the fume cupboard for 45 min. the carbonaceous materials was burnt off and the metals form sulfate with the sulfuric acid which are non-volatile. The charred sulfated part was transferred into silica crucible that was kept in the muffle furnace at 550 °C-25 °C till the sample was reduce to ash in 4-5 hrs. (Xiao, *et al.,* 2011) [41].

3.6 Principle of gas chromatography-mass spectroscopy
GC-MS is a separation technique that is applied to the light ends of a lubricant to separate portions of base stocks, as well as many of the smaller additives. When linked to the mass spectrometer detector, the GC-MS also identify the components being separated and can increase the detectability of the compound separated Maten (2008) [23]. GC-MS measure the concentrations of the additives, such as antioxidants, as low as 10ppm and enables the analyst to identify both the types of molecular species present and their concentrations and accurately determine the concentrations of certain contaminants, especially fuel and glycol-in used oil sample (Livingstone *et al.* 2009) [20].

3.7 Data Analysis and Presentation
The data obtained during this research work was presented in form of mean ± SEM and one-way analysis of variance (ANOVA) at confidence level 95% was performed using statistical software MINITAB 17 to determine the statistical significance and variance.

3. Results and Discussions
3.1. Fourier transform-infrared spectroscopy (FT-IR) characterization
The FT-IR analysis of the characterized both fresh and used engine oil are presented in Table 1-6.

Table 1: Show FT-IR analysis of the characterized both fresh and used engine oil

Compounds of fresh oil (peaks /wavelengths) (E0)	Compounds of used oil by Toyota (peaks /wavelengths) (E1)	Compounds of used oil by Nissan (peaks /wavelengths) (E2)	Compounds of used oil by Sharon (peaks/wavelengths) (E3)
Chloro compound C-Cl stretch /721.2	Chloro compound C-Cl stretch /721.2	Chloro compound C-Cl stretch/725.0	Chloro compound C-Cl stretch/725.0
Methyl C-H asymmetrical/ symmetrical bend/ 1373.5	Methyl C-H asymmetrical/symmetrical bend/1373.5	Methyl C-H asymmetrical/ symmetrical bend/1377.3	Methyl C-H asymmetrical/ symmetrical bend/1377.3
Alkanes/1459.3	Alkanes/1455.5	Alkanes/1459.3	Alkanes/1459.3
1^0Methyne CH stretch/2851.4	1^0Methyne CH stretch /2851.4	1^0Methyne CH stretch /2851.4	1^0Methyne CH stretch /2855.1
2^0Methyne CH Stretch /2922.2	2^0Methyne CH Stretch /2914.8	2^0Methyne CH Stretch /2922.2	2^0Methyne CH Stretch /2922.2
	CH_3 asymmetric stretching in acid /2951.4	Alkane/2953.9	Alkane/2961.4

The gas chromatography-mass spectroscopy result of the fresh engine oil (E0) shows that organosilicon base compound was the predominant which are pentasiloxane, dodecametyl cyclohexasiloxane, dodecamethyl pentasiloxane and some hydrocarbon base compounds which include ethyl hexanol, and heptalene. The result does not show any oxygenated compounds that may results to acids compounds which in a short time usage leads to corrosion and contamination of the engine. The FTIR spectrum for the fresh oils E0 shows peaks at 721 for E0 which shows the presence of halo-compounds in the fresh oils. The bands at 1374 for both oils indicates the presence of ester in the oils. The bands of 1459, 2851, 2922 for E0 shows the presence of saturated alkanes in the oils. This gives the oils it flows characteristics Ugwele et al. (2020) [39]. The peaks obtain are within the range of the peaks result gotten by Dabai and Bello (2019) [6] at 723, 1375, 1461, 2851 and 2922 And also, with peaks of Ugwele et at (2020)

[39]. additional peaks at 2954, 2961, and 2958, respectively, which indicates the presence of carbonyl containing degradation products in the used oils from esters, aldehydes or acids reported by Ugwele et al. (2020) [39]; Dabai and Bello 2019 [6]; Kadam and Zingde (1985) [18]. Although peaks which are detected by Ugwele et al. (2020) [39] at 699 cm^{-1}, 855 cm^{-1} and 1059 cm^{-1} Dabai and Bello (2019) [6] at 1088 cm^{-1}, 2363 cm^{-1}, 1707 cm^{-1}, 1803 cm^{-1} were not detected in all of the used oils (E1, E2, and E3). The peaks obtain in the research is in line with the peaks obtain by Ugwere et al. (2020) at 771 cm^{-1}, 856 cm^{-1}, and 1398 cm^{-1} peaks obtain by Dabai and Bello (2019) [6] at 2851 cm^{-1}, 2922 cm^{-1}.

3.2 Gas Chromatography-Mass Spectrometry (GC-MS) Analysis
The GC-MS analysis of both fresh and used engine oil are presented in Table 2-4.

Table 2: GC-MS Analysis Result for E0 (Fresh Engine Oil)

Group	% Area Peak	Compounds
Benzene	5.54	1-methylethyl Benzene
	4.39	1,3 dimethyl Benzene
	4.81	1-ethyl-2,4 dimethyl Benzene
	5.51	1,2,4,5 tetra methyl Benzene
	1.72	1-methyl-2-(2-propenyl Benzene
Naphthalene	7.96	1-ethyl-3-metyl Benzene
	8.90	Naphthalene
	6.64	2-methyl Naphthalene
	6.64	1 methyl Naphthalene
Carbonyl	o.13	3,5 dimethyl benzaldehyde
Alkene	11.89	Mesitylene
Alkyne	6.26	2,4 Nonadiyne
Acid	0.34	Tricosanoic acid
	0.18	Benzoic acid
	0.12	2-butanoic acid
	0.12	4-aminosalicylic acid

Table 3: GC-MS Analysis Result for E1

Group	% Area Peak	Compounds
Benzene	10.61	1,2,3 tri methyl Benzene
	0.66	Cyclopropyl Benzene
	3.06	1,2,3,4,5 tetra methyl Benzene
	10.61	1-ethyl 3-methyl Benzene
	8.10	3a,4,5,6,7,7a Hexahydro-4, 7 methano Indene
Alkene	0.27	Heptalene
	1.08	Azulene
Naphthalene	4.38	Naphthalene
	18.19	1-methyl Naphthalene
	0.23	2,7-dimethyl Naphthalene
	0.53	2-butyl-Naphthalene
Carbonyl	1.38	Ethanone
	0.27	Pregna-5, 16-dien-20-one
Acid	0.26	2-Butenedioic acid
	0.35	4-Aminosalicylic acid
	0.61	Carbamic acid
	0.25	Tricosanoic acid
	0.30	Acetic acid
	3.04	Glutaric acid

Table 4: GC-MS Analysis Result for E3

Group	% Area Peak	Compounds
Organosilicon	0.29	Tri methyl phosphate silanol
Carbonyl	14.25	Benzaldehyde
Alcohol	0.06	Hexadecanol
Acid	0.15	Benzoic acid
	0.07	o-Toluic acid
	0.24	Docecanoic acid
	0.10	Tetradecanoic acid
	0.05	Azelaic acid
	3.20	Myristic acid
	0.19	Pentadecanoic acid
	0.64	N-Hexadecanoic acid
	0.51	Heptadecanoic acid
	0.32	Oleic acid
	0.18	Glycocylic acid
	0.83	Undecanoic acid
	14.25	Octadecanoic acid
	2.11	Carbamic acid
Alkane	14.25	Octane

The GC/MS spectra of Table E1 and E2 does not reveal any carboxylic acids. Moreover, there was dominance of benzene and naphthalene base compounds which include 1-methyl benzene, 1,3 dimethyl benzene, 1-ethyl-2,4-dimethyl benzene, 1,2,4,5-tetra methyl benzene,1-methyl naphthalene, 2-methyl naphthalene and naphthalene for E1 and 1-methylethyl

benzene, 1-ethyl-3-methyl benzene, Cyclopropyl benzene, 1,2,4,5-tetra methyl benzene and 1-methyl naphthalene for E2. This result is in agreement with the work of Dabai and Bello (2019) [6]; Dabai (2012) [7] who identify 1,2,3-tri methyl benzene, 1-ethyl-2-methyl benzene and propenyl benzene in used oil and slightly with work of Cotton et al. (1997) [5] who detected the presence of naphthalene, di naphthalene anthracenes and ace naphthalene's in used oil samples and also work of Elena-Rosado and John (2003) [9] in which they detected benzene base compounds like 1,2-dimethyl benzene, 1,2,3-tri methyl benzene, 1-ethyl-2-methyl benzene, 1-ethyl-3-methyl benzene, 1,2,3,5-tetra methyl benzene, and also naphthalene base compounds which include 2-methyl naphthalene, naphthalene and 1-methyl naphthalene in used motor oil sample. However, indene was detected in E2.

The GC/MC spectrum for Table E3 reveal acids as the dominant compound found which include benzoic acid, o-toulic acid, Docecanoic acid, Azelaic acid, pentadecanoic acid, heptadecanoic acid and oleic acid. Which is partly in agreement with the work of Elena-Rosado and John (2003) [9] who reported the availability of methyl ester undecanoic acid, 5-methyl undacane, tricosane and 2-methyl tridecane. Furthermore, another hydrocarbon compound such as trimethyl phosphate silanol was detected in the used oil (E3).

Finally, the GC/MC analysis presented the hydrocarbon profile of Ammasco engine oil gives information on what might have occurred during usage used oil.

3.3 Physicochemical properties of fresh and used engine oil

Table 5: Show might have occurred during usage used oil E0-E3

Parameters	E0	E1	E2	E3
FP (ºC)	202.07	106.50	151.87	129.10
PP (ºC)	-20.13	-15.47	-15.90	-15.50
CP (ºC)	-15.20	-14.53	-14.57	-15.63
SG	0.88	0.89	0.94	0.905
CR (w/w%)	0.85	1.51	1.67	0.94
AC (w/w%)	0.99	6.11	2.96	2.59
KV@40	112.8	61.11	50.30	53.80
KV@100	11.36	10.00	9.00	12.00
VI	80.00	151.00	163.00	228.00

Key: PP=Physiochemical Parameters FP=Flash Point, PP=Pour Point, CR=Carbon Residue, SG=Specific Gravity, CP=Cloud Point, AC =Ash Content, KV=Kinematic Viscosity and VI=viscosity Index

I. Flash Point
Flash point is the lowest or minimum temperature at which vaporized lubricating oil can be ignited by external light source. Lowering the value of flash point of used engine and gear oil is due to the presence of light fuels Rincon (2005) [30]. A considerable reduction in flash point of engine and gear oil is an indicator that the oil has being contaminated with volatile products such as gasoline Lenoir (1975) [21]. During determination of the flash point characteristics the result is presented in Table 5 above. The flash point for the fresh engine oil (202.07 ºC) is lower compared to standard which is higher than that obtain by Dabai and Bello (2018) (190ºC). In the case of the used oils, ranging from 106 ºC to 151ºC for engine oil, the decrease in the used oils is due to presence of light fuels. The values obtain are higher than that reported by Dabai and Bello (2018) and within the range reported by Udonne, (2010) [38] and Hamawand et al. (2013) [13] 120ºC and 158 ºC for used oil and flash point below 60ºC may considered to be flammable, the one obtained in this work is within the ASTM specification.

II. Pour Point
Pour point is the lowest temperature at which the oil flow or pour Gobinda et al. (2017) [12]. The decrease in pour point of used lubricating oil is due to degradation of additives, which were present as pour point depressants Rahid et al. (2013) [27]. The pour point of both fresh and used engine oils was found to-20.133 ºC and-15.5 ºC which indicates that both fresh and used oils does not lose its flow characteristics. The fresh engine oil tent to have lower pour point than the used oil. The value obtained for the used oils tend to minimally higher than compared to the fresh ranging from (-15.9 to-15.4 to) for the used engine oil.

III. Cloud Point
The cloud point is the temperature at which wax crystals begin to appear in a liquid. The cloud point is slightly higher than the pour point. When dealing with lubricating oils. The cloud point is a temperature reading at which components that tend to solidify start separating from the oil and begin crystallizing. The cloud point basically determines whether or not the oil will possibly jam filters or small opening

Ratchadaporn *et al.* (2015) [28]. The result recorded from this shows the value of cloud point for fresh and used engine oil to be-15.20ºC which indicates that the used oils contain a little amount of wax thickens which may sludge and vanishes to engine. While for all the used oil to be in the range of (-14.400 to-14.633). The changes between the used oils in minimal.

VI. Specific Gravity
Specific gravity is the ratio of the density of an oil to the density of water or reference substance, this is directly proportional to the amount of solid present in the used engine and gear oil Isah, *et al.* (2013) [17]. The result of the specific gravity for the fresh engine 0.879 and for the used engine oil are 0.891, 0.935 and 0.905 for E1, E2 and E3 respectively, Therefore, its shows that there is an increase in the number of aromatic compounds in the oils which lead to an increase in the density of used oils. These values obtained in this research for fresh oil is higher than that reported by Dabai and Bello (2018) (0,825). While the values for used engine oils are higher than that reported by Dabai and Bello (2019) [6] and lower reported by Hamawand *et al.,* (2013) [13] (0.9261).

V. Carbon Residue
The amount of carbonaceous residue remaining after thermal decomposition of engine and gear oil in a limited amount of air is called carbon forming tendency. The test for carbon residue can be used to evacuate the carbonaceous depositing characteristics of engine oil used in internal combustion Hamawand *et al.* (2013). The increase in carbon residue is due to internal pollutants resulting from the damage of additives, including external pollutants from dust and engine friction product Hameed *et al.* (2017) [14]. The carbon residue of the fresh engine oil is 0.87 wt% which is higher than that reported by Hamawand *et al.* (2013) [13] (0.55 wt%). However, the value for E0 (0.87) is higher compared to that reported by Elaf *et al., (*2019) [8] (0.825). Results obtained from Used oils were 1.53 wt%, and 1.67 wt%, for E1, and E2, respectively, which are lower than (1.82 wt%) reported by Hamawand *et al.,* (2013) [13] with the exception E3 (1.94 wt%) for used oil. Although E3 (1.94 wt%) has the highest carbon residue within the used engine oil. The values obtained explain that the used engine oil contain a lot of carbon deposits, dirt, varnishes, soot, and other solid contaminants that accumulated in oil and it also show the presence of soluble impurities such as heavy metals and other harmful substances.

VI. Ash Content
Increase in ash in used oil is as a result of incidental solids such as dirt and rust (Hussein *et al.* 2014) in addition to oil organic mineral influencers. From experimental result as shown in Table 5 it was found that the percentage of ash in fresh oil is 1.0 wt% for engine (E0) in which (0.1 wt%) as reported by Rashid *et al.* (2013) for fresh oil which is lower than the fresh engine oil (E0) (1.0 wt%). The experimental value for the used oils is 6.0 wt%, 3.0 wt%, and 2.5 wt%, for E1, E2, and E3 respectively, which are above the value reported by Rashid *et al.* (2013). Over roll E1 (6.0 wt%) has the highest ash content among the used engine oil which signifies incombustible component remaining after the oil is completely burned which results in valve and seat wear; this also ultimately reduce the life expectancy of the machine.

VII. Kinematic Viscosity
Kinematic viscosity is an index for analyzing the internal

resistance in motion of lubricating oils. As the temperature increases it also increases Ratchadaporn *et al.* (2015) [28]. Kinematic viscosity can increase in used lubricating oil due to oxidation or contamination, while it may also decrease due to dilution with light fuels Scapin (2007) [33]. Result of kinematic viscosity of fresh and used engine oil was reported in Table 5 above. Kinematic viscosity at 40 ºC and 100 ºC of fresh engine oil is 112.8 cSt/11.36 cSt with the engine oil having slightly higher viscosity than the standard used oils for E1, E2 and E3 are 91.3 cSt/6 cSt, 50.3 cSt/4.9 cSt, 53.8 cSt/5.2 cSt respectively. The result shows low values of viscosity fresh engine oil compared to the used engine oil. This may be due to the being used for a longer period of time compared to the fresh engine oil as a result of that contamination or oxidation may formed. The values obtain are lower than that obtain by Dabai and Bello (2019) (271.13 cSt/20.9 cSt) for fresh oil and (160.94 cSt/13.58 cSt) for used oil.

VIII. Viscosity Index
Viscosity index is the viscosity of a substance in respect to temperature and it's a subjective number indicating the degree of change with temperature Singh and Gulati (1987) [34]. The result presented above indicated the viscosity index for the fresh oils to be 80 for engine oil. However, for the used engine oils are 151, 163 and 228 for E1, E2 and E3 respectively. The result obtained is higher than the fresh engine oil due to particle contamination and slightly lower compared to that reported by Dabai and Bello (2018) [6] (91) and lower than that reported by Syarifah *et al.* (2013) [35] (145) for fresh engine oil.

3.4 Atomic Absorption Spectroscopy (AAS) of the fresh, used engine oil

Table 6: Result for metal content analysis (mg/kg)

Element	E0	E1	E2	E3
Manganese (Mn)	9.5	2.50	18.92	1.0
Chromium (Cr)	0.25	0.25	4.83	0.25
Lead (Pb)	1.08	11.67	58.92	8.67
Copper (Cu)	0.75	1.25	2.25	3.25
Nickel (Ni)	0.75	9.5	11.75	2.50
Magnesium (Mg	4.75	68.25	26.75	50.58
Iron (Fe)	9.5	31.83	59.89	19.50
Calcium (Ca)	16.5	260.5	72.49	235.92

I. Test for Calcium (Ca)
Calcium is present in lubricating oil as an additive. It is intended to detect impurities and keep them in suspension, Calcium is often found in conjunction with magnesium and forms the detergent and corrosion inhibitor part of the additive package. Only when the calcium level deviates more than 25% from the new oil value should be concern to be raised but the likeliest causes are by mixing or topping off with a different product Hopp and Erdoel (1974) [16]. Table 6 show high concentration in almost all of the used engine oil with E1 ($260.5_{kg/kg}$) having the highest concentration among the bunch of used engine oil and E2 ($72.42_{kg/kg}$) with the least of concentration.

II. Test for Nickel (Ni)
Nickel is most commonly seen as an alloy of anti-friction bearings and sometimes along with iron. This is introduced into used oil due to wearing of shafts and sometimes valves and valve guides. The Table 6 shows that the concentration of nickel in E2 ($11.75_{mg/kg}$) is slightly higher than E3 ($2.5_{mg/kg}$),

and E1 (0.00$_{mg/kg}$) does not show any trace of nickel. All are within the range reported by Adebiyi *et al.* (2011) [1] (10.49-27.25mg/kg).

III. Test for Magnesium (Mg)
Magnesium like calcium is an anti-corrosion additive. It neutralizes acids, it also provides some anti-wear properties. Magnesium is mainly introduced into engine oil as an additive. It is regarded as the most common wear metals in used engine oil because it is used in coatings, housing and casings and some engine blocks may contain magnesium making it a wearing element. And is present in fresh oil in the form of magnesium phenates and magnesium salicylates that behave as an antioxidant at high temperatures (Hopp and Erdoel 1974) [16]. Table 6 shows E1 (58.25$_{mg/kg}$) has high concentration of Mg compared to E3 (50.583$_{mg/kg}$) E2 (26.75$_{mg/kg}$) respectively. All are within the range reported by Adebiyi *et al.* (2011) [1] (54.39-123.97mg/kg). And all are below the range reported by Elaf *et al.* (2019) [8] (227.862-888.187ppm).

IV. Test for Lead (Pd)
The existence of lead in used oil is mainly due to wearing of bearing but the contamination source may come from fuel where Pb is used as anti-knock agents. Therefore, in fresh oil it used as an extreme pressure additive mostly in gears than engine oil. It can also be seen as combustion by-product Rauckyte *et al.* (2006) [29]. The result obtained in Table 6 indicates high concentration of lead in E2 (58.917$_{mg/kg}$), compared to other used oil in E1 (11.667$_{mg/kg}$), E3 (8.667$_{mg/kg}$). The result obtained in this research show that E1, E3, are within the range reported by Saif *et al.* (2018) [32] (8.58-12.67ppm). However, E2 prove to be more contaminated with lead with in the Table due to high concentration of lead in them.

V. Test for Iron (Fe)
The Most common wear metal in automobiles engine that is introduced into the engine oil after a period of use is iron. The iron comes from variety of places in the engines such as liners, camshafts, crank shaft, pistons, valves, rust, anti-friction bearings and, rings, oil pump and gears (iron is the major component of the gears, shafts and anti-friction bearings). Iron concentration in engine oil depends on the bearing conditions inside the engine Hamawand *et al.* (2013) [13]. Table 6 shows the level of iron in E2 (59.89 $_{mg/kg}$) to be extremely high compared to E1 (31.833 $_{mg/kg}$), E3 (19.5 $_{mg/kg}$), E2 (59.89 $_{mg/kg}$) suggest there is excessive wear of engine component in Nissan automobile (E2). E1 (31.833 $_{mg/kg}$), E3 (19.5 $_{mg/kg}$), are above the result reported by Dabai and Bello (2019) [6] (1.765ppm), for used oil. Meanwhile the result of E2 is lower than that reported by Hamawand *et al.* (2013) [13] (72ppm) and within the range reported by Adebiyi *et al.* (2011) [1] (41.11-1678.51mg/kg).

VI. Test for Manganese (Mn)
Manganese (Mn) is introduced from wear of cylinder liners, Valves, shafts, anti-friction bearing and gears. Some fuels contain manganese as an anti-knock additive so it can show up as a combustion by-product in oils of petrol engines using these types of fuel. In very rare cases manganese exists as an additive. Lukasiewicz *et al.* (1977) [22]. As shown in Table 6 E2 (18.92 $_{mg/kg}$) in used engine oil, and have higher concentration of Mn than all other used engine oil in the Table. The result is within the range reported by Adebiyi *et al.* (2011) [1] (13.28-92.51mg/kg).

vii. Test for Cupper (Cu)
Copper is almost always found in the form of an alloy brass (copper and zinc) and Bronze (Copper and tin). Copper has many wear metal sources although it too can be contaminated and occasionally an additive. Copper comes from plain bearing, bushes, thrust washes and gears. Bronze gears are frequently used as worm gears in gearboxes. Mostly gear lubricants, contain copper as an anti-wear additive. Some anti-wear and extreme pressure additives can leach and/or corrode copper from these metasl.it is also used in cooler exchangers and can leach into the lubricant. The concentration of Cupper in Table 6 for the used engine oil is minimal compared to Fe, Pb, Ni, Mn, Mg and Ca which suggest that it may have come from decomposition of additives introduced in small quantities or from wearing of piton and valve guides Dabai and Bello (2019) [6]. All the values obtained are lower than the result reported by Saif *et al.* (2018) [32] (4.33-143.33ppm), Adebiyi *et al.* (2011) [1] (68.33-202.48mg/kg) and some are higher of Dabai and Bello (2019) [6] (0.99ppm) and that of Friday *et al.* 2008 [10] (2.4ppm). Overall E3 (3.25 $_{mg/kg}$) have higher concentration of cupper than the rest.

VIII. Test for Chromium (Cr)
Chromium present in engine oil is normally related with piston ring wear. High level can be caused by dirt coming through the air intake or broken rings Chromium can also be used as a surface hardening coating on gears. Can be a contaminant too. It can show up in the oil as an indication of dirt entry. It can also be seen as an indication of an internal coolant leak. Certain type of coolant conditioners contains sodium chromate and once again if water from the cooling system leaks into the oil, then this can evaporate off leaving behind chromium and sodium in the oil (Hamawand *et al.* 2013) [13]. Chromium may indicate excessive wear of chromed parts such as rings and liners (Kahn *et al.* 1970) [19]. Table 6 shows that the concentration of Cr is low in E1 (0.25 $_{mg/kg}$), E3 (0.25 $_{mg/kg}$), compared to E2 (4.833 $_{mg/kg}$). All of which are below the result reported by (Hamawand *et al.* 2013) [13] (1.5ppm) for used oil. While E2 is within the range reported by Adebiyi *et al.* (2011) [1] (4.48-14.69mg/kg).

4. Conclusion
From this research it was concluded that during usage, engine and gear oil gets polluted due to combustion of products and impurities present in the engine and gearbox. Only minute snippet of the used oil is being recycled and the remaining is being dumped into sewage and on land which pollutes our environment and causes serious threat to the environment.
Comparison of the concentration of the selected heavy metals in fresh oil with the used oils shows an increase in metal concentrations. The result reveal that all the used oils were contaminated with heavy metals. They are usually discarded into environment without the necessary precaution to prevent environmental pollution. This is usually the case in many urban cities in Nigeria.

5. References
1. Adebiyi FM, Oluuemi EA, Peter SV. The study of the environmental implications of used lubricating oils by a combination of spectrometric analytical techniques. Energy Sources. 2011;1556-7036(print)/1556-7230. DOI: 10.1080/15567036.2010.515131.
2. Al-Harbawy AW, Al-Mallah MK. Production and

characterization of biodiesel from seed oil of castor (*Ricinus Communis* L.) Plant. International Journal of Science and Technology. 2014;3(9):508-513.

3. Barnes M. Gas Chromatography: The modern analytical tool, oil analysis, machenery lubrication, Noria Corporation; c2003. Online Available from: http://www.practicingoilanalysis.com/article_detail.asp

4. Boyde S. Green Lubricants. Environmental Benefits and impacts of lubrication, Uniqema Lubricants. Green Chemistry. 2002;4:293-307.

5. Cotton FO, Whisman ML, Gowtzinger SW, Reynolds JW. Analysis of 30 used motor oils. Hydrocarbon Processing; c1977, 131-140.

6. Dabai MU, Bello N. Comparative study of regeneration of used lubricating oil using sulphuric and oxalic acid/clay treatment process. International journal of Innovative Science, Engineering & Technology; c2019, 6.

7. Dabai MU. Analysis of Used engine oil as a diagnostic tool for detecting faulty engine parts; c2012, 162-164.

8. Elaf AW, Karim HH, Ahmed NA. Determination of carbon residue, ash content and concentration of heavy metals in virgin and spent Iraqi lubricating oils. J Biochem Tech. 2019;4:65-68. ISSN: 0974-2328.

9. Elena DR, John P. Chemical Characterization of fresh, used and weathered motor oil via GC/MS, NMR and FTIR Techniques. Indiana Academy of Science. 2003;112(2):109-116.

10. Friday ON, Bamidele IO, Kayode OA, Luter L. Comparative investigation of wear metals in virgin and used lubricant oil. Journal of Terrestrial and Aquatic Environmental Toxicology. 2010;4:112-123.

11. Gary DC. Atomic Absorption spectroscopy for determination of elements in medical biological samples. In Organic and Analytical Chemistry. 1972;26:77-112.

12. Gobinda K, Pranab G, Bragendra KS. Chemical Modified Vegetable oils to prepare Green Lubricants. Lubricants. 2017;44:1-17.

13. Hamawand I, Yusaf T, Rafat S. Recycling of waste engine oils using a new washing agent. Energies. 2013;6(2):1023-1049. DOI:10.3390/en6021023

14. Hameed TM, Khudhair MM, Jafar AT, Asaad A, Nifal W, Huseen J. Study using different adsorbents materials in purification of waste lubricating oil. Journal of Engineering and Technology. 2017;35(1):183-190.

15. Houssein AK, Mahmoud ME, Nimir OE. A property-integration approach to solvent screening and conceptual design of solvent-extraction systems for recycling used lubricating oils Techn Eviron Policy. 2013;15:35-44.

16. Hopp HU, Erdoel KE. Atomic absorption spectrophotometric determination of zinc, calcium, barium and magnesium in mineral oil products. Petroleum. Brennst-Chem. 1974;27:435-442.

17. Isah AG, Abdulkadir M, Onifade KR, Musa U, Garba AA, Sani Y. Regeneration of used engine oil. In Proceedings of the World Congress on Engineering. 2013;1:54-.

18. Kadam AN, Zindge. Infrared spectroscopy analysis of used crankcase oil. Scientific Industrial Research. 1985;2:14-18.

19. Kahn HL, Peterson GE, Manning DC. Determination of Iron and Chromium in Used Lubricating oils. At. Absorpt. Newsl. 1970;9:79-80.

20. Livingstone G, Wooton D, Thomson B. Finding the Root Causes of Oil Degradation Analyst Inc. 2009. Available from: http://www.mechinerylubrication.com/Read/989/fluiddeg redation-causes

21. Lenoir JM. Hydrocarbon Processing. 1975;54:95.

22. Lukasiewicz RJ, Buell BE. Direct determination of manganese in gasoline by atomic absorption spectrometry in the nitrous oxide-hydrogen flame. Appl. Spectrose. 1977;31:541-547.

23. Maten TV. X-ray Fluorescence Analysis of additives and wear metals in used lubricating oils analytical instrumentation; c2008, 70-71.

24. Nwite JN, Alu MO. Effect of different levels of spent engine oil on soil properties grain, yield of maize and it's heavy metals up-take in Abakaliki, Southeastern Nigeria. Acadamic Journals. 2015;5(4):44-51.

25. Nadkarni, Kishore RA. Guide to ASTM test methods for the analysis of petroleum products and lubricants. 2nd Edition, ASTM International, West Conshohocken. 2007:1-76.

26. Onwuka MI, Chude VO, Ogwuegbu GC. Remediation of spent engine oil polluted soil using two types of organic manure and their effects on maize growth. Nigeria Journal, Soil Science. 2012;22(2):245.

27. Rahid A, Xiaochun C, Khanji H, Zulifqar AD, Muhammad A. A comparative study of recycling of used engine oil using extraction by composite solvent, single solvent and acid treatment methods. ID: 952589. Doi.org/10.1155/2013/952589.

28. Ratchadaporn I, Nattawud D, Churat T, Jutaporn C, Rameshprabu R. An experimental investigation of palm oil as an environment friendly bio lubricant. International Joint Seminar and Symposium Jiangva University, China; c2015.

29. Raukyte T, Hargreaves DJ, Pawlak Z. Determination of heavy metals and volatile aromatic compounds in used engine oils and sludges. Fuel. 2006;85:481-485.

30. Rincon J. Regeneration of used lubricating oil by polar solvent extraction. Industrial and Engineering Chemistry Research. 2005;44:4373-4379.

31. Sadeek AS, Hoda SA, Ebaa EA, Hussien AE, Asma AA. Hydrotreating of waste lube oil by rejuvenated spent hydrotreating catalyst. Egypt Journal of Petroleum. 2014;23:53-60.

32. Saif-ur RK, Aneesa Z, Farida A, Zubair F. Comparison of heavy metals in fresh and used engine oil. Petroleum Science and Technology. 2018;36(18):1478-1481.

33. Scapin M. Recycling of Used Lubricating Oils by Ionizing. Linking Hub Internet. Klservier.com/retrieval/30969806X0700182X. 2007.

34. Singh Y, Sharma M, Singh N, Singla A, Rastgi PM. Prospects of inedible plant oil driven bio-lubricants for tribological characteristics. A Review. International journal of Ambient Energy. 2018;1-56.

35. Syarifah Y, Amirul A, Syazuan A, Nik RA, Mohamad AA, Abdulhakim A. Comparative study of used and unused engine oil (Perodua Genuine and Castol Magnatee Oil) based on property analysis basis. The Malaysian International Tribology Conference. 2013;68:326-330.

36. Udonne AL, Ayodeji A, Damilola EB. Recycling used lubricating oil using untreated, activated and calcined clay methods. Journal of Engineering and Applied Sciences. 2016;11(6):1396-1401.

37. Udonne JD, Onwuma HO. A study of the effects of waste lubricating oil on the physical and chemical Properties of

soil and possible remedies. Journal of Petroleum and Gas Engineering. 2014;5(1):9-14.

38. Udonne JD. A Comparative study of used lubrication oils using distillation, acid and activated charcoal with clay methods. Journal of Petroleum and Gas Engineering. 2010;28(2):38-43.

39. Ugwele FO, Aninwede CS, Chime TO, Asadu OC, Ike SI. Application of response surface methodology in optimizing the process conditions for the regeneration of used Mobil oil using different kinds of acids. Science Direct. 2020;6(10).

40. Uzairu A, Okunola OJ, Wakawa RJ, Adewusi SG. Bioavailability studies of metals in surface water of River Challawa, Nigeria. Journal of Applied Chemistry; c2014.

41. Xiao R, Chen X, Wang F, Yu G. The Physicochemical properties of different biomass ashes at different ashing temperature. Journal of Renewable Energy Elsevier. 2011;36:244-249.