CHAPTER ONE

1.1 INTRODUCTION AND LITERATURE REVIEW

1.1 INTRODUCTION

Crude oil contains mainly hydrocarbons especially alkanes, naphthenes, and aromatics (Odebunmi and Adeniyi, 2004). It contains also some nitrogen, oxygen and sulphur containing compounds along with trace amounts of elements especially nickel, vanadium, titanium, iron, cadmium etc (Odebunmi andAdeniyi,2004; Olajire and Oderinde,1996). The presence of trace metals and non-metals in the crude oil and petroleum products is destructive, especially in the refining process (Oderinde, 1996).Indigenous petroleum refineries, petroleum depots and filling stations as well as environment in general require enough information on the concentration of trace and heavy metals in Nigerian petroleum products because of its detrimental effects on both equipment and environment.

The trace/heavy metals composition in petroleum products can be used for the identification of environmental fuel pollution. Exhaust from various machine including cars, buses, generators, etc contributed immensely in so many environmental problems due to the concentration of some trace/heavy metals in it. Atomic Absorption Spectrophotometry (AAS) is a well-established extremely valuable technique f or the determination of trace amounts of metals. Since its introduction by Walsh, the method has gone through a number of developmental stages aiming at obtaining an increase in reliability, ease of operation and, above all, improvement in the limit of detection. Atomic absorption spectrometry (AAS) is an analytical method based on the absorption of electromagnetic radiation in the visible and ultraviolet regions of the spectrum by gaseous atoms resulting in changes in electronic structure (Fritz and Schenk, 1987). It is one of the most widely used techniques for the determination of trace and heavy metals in petroleum products. Over sixty elements can be determined in almost any matrix. An example includes petroleum products such as petrol, diesel, kerosene, fuel oil, petrolatum, lubricating oil, etc. So many other samples that can be analyzed using atomic absorption spectroscopy are body fluids, polluted water, foodstuffs, soft drinks, beer, metallurgical and geochemical samples (Fifield and Kealey, 1995).

1.2 Literature Review

Various analytical methods have been reported for the determination of trace metals in petroleum products. Traces of iron, nickel, and vanadium in petroleum and petroleum products were analyzed using spectrophotometry method. The sample was ashed and taking up with the potassium bisulphate. The measurement was b ased on the development of coloured solutions by reagents specific for each element. Henry and George (2016) employed AAS to determined heavy metals in petroleum products. They used two methods which are based on the decomposition and cold water vapor atomic adsorption. Another method involved acid decomposition of the samples in a closed system while the other method used oxy-hydrogen combustion to decompose the sample.

In a work reported by Winston and Harry (2015) used AAS to determine trace quantities of cadmium in petroleum and petroleum products in which the sample was digested with sulphuric acid and then ashed. In another reported work by Oderinde (2009) the vanadium and titanium contents of nine Nigerian crude and petroleum products using a spectrometric method was carried. He reported that in some of the samples the Vanadium and Titanium content were high enough to cause corrosion in turbines and refining processes line in the refinery. Recently, Anthony (2019) reported in his comprehensive analysis of various metallic elements in Nigerian petroleum products using Atomic Absorption Spectroscopy technique, discussed the influence of these trace metals contaminants in the refinery processes.

Farroha *et al.,* (2014) used electrochemical method to determine trace levels of sulphur in petroleum by constant current coulometry. The Tandem mass spectromet er combined with chemical reaction was used to concentrate Sulphur containing poly-nuclear aromatic compound by wood *et al.,* (1994). Oderinde, (2014) thoroughly investigated the types of sulphur compounds present in Ugheli Quality Control Centre (UQCC) of crude oil distillates fractions, and in 2004, Odebunmi and Adeniyi, (2004) analyzed trace metals in petroleum and petroleum products using AAS and they discovered that, the results confirmed that the heavy crude oil contains trace metals higher than the medium and light crudes oil and for the petroleum products shows lubricating oil which has higher viscosity, followed by engine oil and the lubes oil was the least.

1.3 Crude Oil / Composition

Crude Oil is a naturally occurring, toxic, flammable liquid, consisting of a complex mixture of hydrocarbons of various molecular weights, and other organic compounds, that are found in geological formations beneath the Earth's surface (Mendham *et al.,* 2000).

In its strictest sense, petroleum includes only crude oil, but in common usage it includes both crude oil and natural gas. Both crude oil and natural gas are predominantly a mixture of hydrocarbons. Under surface pressure and temperature conditions, the lighter hydrocarbons such as methane, ethane, propane and butane occur as gases, while the heavier ones from pentane and up are in the form of liquids or solids. However, in the underground oil reservoir the proportion which is gas or liquid varies depending on the subsurface conditions and on the phase diagram of the petroleum mixture (Mendham *et al.,* 2000). An oil well produces predominantly crude oil, with some natural gas dissolved in it.

Because the pressure is lower at the surface than underground, some of the gas will come out of solution and be recovered (or burned) as *associated gas* or Solution gas. A gas well produces predominately natural gas. However, because the underground temperature and pressure are higher than at the surface, the gas may contain heavier hydrocarbons such as pentane and hexane in the gaseous state. Under surface conditions these will condense out of the gas and form natural gas condensate, often shortened to condensate (Condensate resembles gasoline in appearance and is similar in composition to some volatile light crude oils). The proportion of light hydrocarbons in the petroleum mixture is highly variable between different oil fields and ranges from as much as 97% by weight in the lighter oils to as little as 50% in the heavier oils and bitumen (Mall,2007). The hydrocarbons in crude oil are mostly alkanes, cycloalkanes and various aromatic hydrocarbons while the other organic compounds contain nitrogen, oxygen and sulphur, and trace amoun ts of metals such as iron, nickel, copper and vanadium. The exact molecular composition varies widely from formation to formation but the proportions of chemical elements vary over fairly narrow limits as shown in Table 1 (Mall, 2007).

Table 1: Composition of Crude Oil.

Element	Percentage range
Carbon	83.00 – 87.00%
Hydrogen	10.0 – 14.00 %
Nitrogen	0.10 – 2.00 %
Oxygen	0.10-1.50 %
Sulphur	0.50 – 6.00 %
Metals	< 0.10 %

Source: Mall, (2007)

I.4. Physical Properties of Petroleum Crude Oil

Petroleum exhibits a wide range of physical properties and several relationships can be made between various physical properties. Whereas properties such as viscosity, density, boiling point, and color of petroleum may vary widely, the ultimate o r elemental analysis varies, as already noted, over a narrow range for a large number of petroleum samples. The carbon content is relatively constant, while the hydrogen and heteroatom contents are responsible for the major differences between petroleum samples. Coupled with the changes brought about to the feedstock constituents by refinery operations, it is not surprising that petroleum characterization is monumental task.

Petroleum refinery processes can be conveniently divided into three different types

1. Separation: division of the feedstock into various streams (or fractions) depending on the nature of the crude material
2. Conversion: that is, the production of saleable materials from the feedstock by skeletal alteration, or even by alteration of the chemical type of the feedstock constituents
3. Finishing: purification of the various product streams by variety of processes that remove impurities from the product. In some case, a fourth category can be added and includes processes such as the reforming (molecular rearrangement) processes. For the purposes of this text, reforming processes are included in the finishing processes because that is precisely what they are: processes designed to fini

sh various refinery streams and render them ready for sale as defined products.

The separation and finishing processes may involve distillation or treatment with a wash solution. The conversion processes are usually regarded as those processes that change the number of carbon atoms per molecule (thermal decomposition), alter the molecular hydrogen–carbon ratio (aromatization, hydrogenation), or even change the molecular structure of the material without affecting the number of carbon atoms per molecule (isomerization).

Evaluation of petroleum for use as a feedstock usually involves an examination of one or more of the physical properties of the material. By this means, a set of basic characteristics can be obtained that can be correlated with utility. To satisfy specific needs with regard to the type of petroleum to be processed, as well as to the nature of the product, various standards organizations, such as the American Society for Testing and Materials in North America and the Institute of Petroleum in Britain, have devoted considerable time and effort to the correlation and standardization of methods for the inspection and evaluation of petroleum and petroleum products. Physical properties of the almost limitless variety of crude oils are generally correlated with aspects of chemical composition.

I.4.1. API gravity

This is the most common measurement performed on petroleum products; density is expressed in terms of API gravity. This measurement determines the weight of a crude oil per unit volume at 60°F, normally measured by the Hydrometer method ASTM D-287.

I.4.2. Aniline point

This point is defined as the lowest temperature at which aniline insoluble in a specified amount of sample. This measure is used to determine the solvency of the hydrocarbons. Typically, paraffinic hydrocarbons have higher aniline points than aromatic hydrocarbons. This method is usually performed under the guidelines of ASTM D-611. Aniline point can be used to determine the quality of ignition in diesel cuts.

I.4.3. Cloud point

This is defined as the temperature at which a haze appears in a sample which is attributed to the formation of wax crystals. Cloud point data is used to determine the tendency of small orifices to plug in cold operating temperatures, normally measured on middle distillate cuts. This property can be measured manually by utilizing ASTM D-2500, since many laboratories utilize similar equipment to perform p our points. With the development of new analytical equipment many laboratories are now utilizing phase technology and are performing ASTM D-5773 which is less labor intensive and more robust.

I.4.4. Freeze point

The temperature at which crystal start to form in hydrocarbon liquids and then disappear when the liquid is heated is the freeze point. Normally performed by ASTM D-2386, this method like cloud point is done by ASTMD-5972 by phase technology.

I.4.5. Metals content

The metals concentration in crude can range from a few to several thousand ppm. Low values of certain elements such as nickel and vanadium can severely affect catalyst activity. In the past metals were determined by Atomic Absorption, but now most metals are determined by Inductively Coupled Plasma Emission Spectroscopy ICPCES. X-ray fluorescence can be a viable technique depending on the concentration.

I.4.6. Mercaptan sulfur

Mercaptan Sulfur species are undesirable in crude oils, and in some cases are toxic. These species are normally attributed to sour crudes. Analysis is normally base d on UOP-163 or ASTM D-3227, a potentiometric titration method. A hydrocarbon sample is added to a solution of isopropyl alcohol containing a small amount of ammonium hydroxide. The solution is then titrated with a solution of silver nitrate.

I.4.7. Micro carbon residue

The carbon residue of a petroleum crude oil is proportional to the asphalt content, normally measured by Conradson Carbon ASTM D-189. In most cases the lower the carbon residue, the higher the value that can be placed on the crude oil.

I.4.8. Nitrogen

Nitrogen species in crude oils can cause catalyst poisoning. ASTM D-3228 or ASTM D-4629 normally determines nitrogen content. Either a syringe inlet or boat inlet analyzes distillate cuts by Oxidative Combustion and Chemiluminescence detection. Whole crude, atmospheric and vacuum residues are analyzed by Kjeldahl methodology, a labour intensive method involving digestion/distillation and finishing up with a titration.

I.4.9. Pour point

The lowest temperature at which a hydrocarbon fraction is observed to pour when cooled under prescribed conditions. The pour point of a sample is determined to b e 3 degrees Celsius above the point at which a sample can be horizontally held and no movement occurs for five seconds. The most frequently utilized method for this test is ASTM D-97, which can be used for all assay fractions/ blends. For whole crudes that have pour points greater than -36°C, a new method has been developed (ASTM D-5853). Also, for fractions that contain wax, a new method utilizing phases technology ASTMD-5949. Normally low pour points are due to low paraffin content and high aromatics.

I.4.10. Refractive index (n)

Refractive index is a ratio technique that takes the velocity of light in air at a specific wavelength and compares that to the velocity in the sample tested. Normally this is performed under the guidelines of ASTM D-1218.

This test method can be performed at various temperatures. The refractive index can be used to estimate the distribution of PNA molecules in oil fractions.

I.4.11. Sulfur content

The sulfur content of crude oils is normally in the range of 0.1-5.0 wt%. Sulfur is n ormally measured by an x-ray technique such as ASTM D-4294 or D-5291. These methods have large dynamic ranges and allow analysis to be completed in about 3-5 min. Samples having sulfur contents greater than 5.0 % are measured by methods such as ASTM D-1552, a combustion technique. For extremely low levels an ultraviolet fluorescence (UV) technique is employed (ASTM D-5453). Again, most of these methods are very robust, but can be influenced by not having a representative sample. Crudes are determined to be sweet or sour based on the amount of dissolved hydrogen sulfide.

I.4.12. Total Acid Number (TAN)

The industry standard for this test is based on ASTM D-664. Normally expressed as Neutralization Number, this test predicts the acidity of an oil/distillate fraction. The sample normally dissolved in Toluene/Isopropyl alcohol / Water is titrated with potassium hydroxide and the results are expressed as mg KOH per gram of sample. Crude Oils having high acid numbers are purchased cautiously due to possible corrosion problems in the refineries. Crudes typically have TAN values form 0.05 -6.0 mg KOH/gm of sample. While whole crudes are outside the scope of this titration method, it is the only recognized method in the industry.

I.4.13. Viscosity

Viscosity is a measurement of a fluid resistance to flow. Most measurements use the force of gravity to produce the flow through a small capillary tube called a viscometer; thus, the measurement is known as kinematic viscosity having a unit of centistoke (cSt). The viscosity of a fluid is always reported with a temperature, since viscosity will vary inversely with temperature. Most viscosity measurements follow the guidelines of ASTM D-445. Normally in an inspection grid the viscosity will be measured at three different temperatures and then plotted on semi-log graph paper. If all measurements are performed properly a straight line will result.

I.4.14. Water & Sediment

Sediment and water values in crude oils are critical parameters as to whether problems will occur in the processing in the refinery. In many cases, desalting equipment may be required in order to handle a given crude slate.

1.5 Types of Hydrocarbon

Generally, there are four different types of hydrocarbon molecules in crude oil. The relative percentage of each varies from oil to oil, depending on the properties of each oil. Table 2 presents the composition of hydrocarbon by weight.

Table 2: Composition by weight of Hydrocarbon

Hydrocarbon	Composition by weight	Average Range
Paraffins	30.00	15.00 – 60.00
Naphthenes	49.00	30.00 – 60.00
Aromatic	15.00	3.00 – 30.00
Asphaltic	6.00	Remainder

Source: Mall, 2007.

1.6 Classification of Petroleum

The oil industry classifies "crude" by the location of its origin (e.g., "West Texas Intermediate, WTI" or "Brent") and often by its relative weight (API gravity) or viscosity ("light", "intermediate" or "heavy"); refiners may also refer to it as "sweet", which means it contains relatively little sulphur, or as "sour", which means it contains substantial amounts of sulphur and requires more refining in order to meet current product specifications (Speight,1999).

a) Paraffin Base: This classification was based on the fact that some petroleum oils separated paraffin wax on cooling leading to the conclusion that, these consisted mainly of paraffins (e.g. methane, ethane, propane, etc. with general formula (C_nH_{2n+2}).

b) Asphaltic Base: These were the petroleum oils which gave no separation of paraffin wax on cooling again leading to the conclusion that these predominantly contained cyclic (or naphthenic) hydrocarbons.

c) Mix Base: These petroleum oils leave a mixture of paraffin wax and asphaltic bitumen when subjected to nondestructive distillation, hence the name.

d) Hybrid Base: These are basically asphaltic oils that contain a small amount of wax.

1.6 Chemistry of Petroleum

Petroleum is a mixture of a very large number of different hydrocarbons; the most commonly found molecules are alkanes (linear or branched), cycloalkanes, aromatic hydrocarbons, or more complicated chemicals like asphaltenes. Each petroleum variety has a unique mix of molecules, which define its physical and chemical properties, like color and viscosity (Speight, 1999).

1.6.1 Paraffin

These consist of straight or branched carbon rings saturated with hydrogen atom s, the simplest of which is methane (CH_4) the main ingredient of natural gas. Others in this group include ethane (C_2H_6), and propane (C_3H_8) (Mall, 2007).

1.6.2 Naphthenes

Naphthenes consist of carbon rings, sometimes with side chains, saturated with hydrogen atoms. Naphthenes are chemically stable; they occur naturally in crude oil and have properties similar to paraffins, examples are 1,3-Dimethyl-cyclopentane and Cyclohexane (Mall, 2007).

1.6.3 Aromatics

Aromatic hydrocarbons are compounds that contain a ring of six carbon atoms with alternating double and single bonds and six attached hydrogen atoms. This type of structure is known as a benzene ring. They occur naturally in crude oil, and can also be created by the refining process. Examples are benzene, toluene and P-xylene (Mall, 2007).

The more carbon atoms a hydrocarbon molecule has, the “heavier” it is (the higher is its molecular weight) and the higher is its boiling point. Small quantities of a crude oil may be composed of compounds containing oxygen, nitrogen, sulphur and metals. Sulphur content ranges from traces to more than 5 percent (Speight, 1999).

1.7 Origin of Petroleum

Most scientists agree that hydrocarbons (oil and natural gas) are of organic origin. A few, however, maintain that some natural gas could have formed deep within the earth, where heat melting the rocks may have generated it inorganically (Gold and Soter, 2009). Nevertheless, the weight of evidence favours an organic origin, most petroleum coming from plants and perhaps also animals, which were buried and fossilized in sedimentary source Rocks (Levorsen, 1997). The petroleum was then chemically altered into crude oil and gas (Tissot and Welte, 1984). The chemistry of oil provides crucial clues as to its origin. Petroleum is a complex mixture of organic compounds. One such chemical in crude oils is called porphyrin. This compound has been identified in a sufficient number of sediments and crude oils to establish a wide distribution of the geochemical fossils, it's also found in and animals (McQueen, 1996).

1.7.1 Biogenic theory

Most geologists view crude oil, like coal and natural gas, as the product of compression and heating of ancient vegetation over geological time scales. According to this theory, it is formed from the decayed remains of prehistoric marine animals and terrestrial plants. (Alboud, 2006).

1.7.2 Abiogenic theory

This theory suggests that large amounts of carbon exist naturally in the planet, some in the form of hydrocarbons. Thermodynamic calculations and experimental studies confirm that n-alkanes (common petroleum components) do not spontaneously evolve from methane at pressures typically found in sedimentary basins, and so the theory of an origin of hydrocarbons suggests deep generation below 200 km (Dean, 1993).

1.7.3 Petroleum movement/migration

Petroleum Migration is a process (or processes) whereby petroleum moves from place of its origin, the source rock to its destruction at the earth's surface. A Length en route, the petroleum's progress may be temporarily arrested and the petroleum may "rest" on its journey within the trap. The process of migration can be divided into three stages;

a) Primary migration is the expulsion of the petroleum products from the source rock

b) Secondary migration is the journey from the source rock to the trap

c) Tertiary migration is the leakage and dissipation of petroleum at the earth's surface.

1.8 History/Exploration of Petroleum in Nigeria

The Nigerian oil and gas industry, taken from when the first known Mineral Survey was carried out (Araromi, present Ondo State) in 1905, is just a 107years today. Real exploration of the hydrocarbon potentials of the country commenced, however, in 1908. The efforts of the Nigerian Bitumen Corporation (NBC), a German concern, in that year were only able to accomplish some 16shallow boreholes, confirming a line of oil seepage in the Eastern Dahomey Basin in Okitipupa, Western Region of Nigeria.

Although the results were not too encouraging and the resultant First World War did stall the efforts, the attempts by NBC nevertheless spurred subsequent efforts by the Shell Overseas Exploration Company and D'Arcy Exploration to open up the country, particularly the subsequently prolific Niger Delta as a world class hydrocarbon prospective region. Although the Royal/Dutch Company initially got the whole of Nigeria as one huge concession, the search was to be narrowed to the Niger Delta where in 1956, after having drilled some 15 dry holes, beginning with the Iho-1 NW in Owerri, the first successful well was spudded at Oloibiri. With that milestone, Nigeria's first shipment of crude oil (5,000 barrels) hit the international market in 1958.By the late sixties and early seventies, Nigeria had attained a production level of over 2 million barrels of crude oil a day. Although production figures dropped in the eighties due to economic slump, 2004 saw a total rejuvenation of oil production to a record level of 2.5 million barrels per day. Current development strategies are aimed at increasing production to 4million barrels per day by the year 2010.

1.9 Petroleum refining process

Refinery processes have developed in response to changing market demands for certain products. The quantities of petrol available from distillation alone were insufficient to satisfy consumers demand, therefore, the main task of refineries became the production of petrol, and as a result the refineries began to look for ways to produce more and better-quality petrol (Speight, 2009). As a result of that, two processes were developed thus, breaking down large, heavy hydrocarbon molecules via catalytic and thermal cracking process and reshaping or rebuilding hydrocarbon molecules via reforming process.

1.9.1 Distillation (Fractionation)

Because crude oil is a mixture of hydrocarbons with different boiling temperatures, it can be separated by distillation into groups of hydrocarbons that boil between two specified boiling points. Two types of distillation are performed: atmospheri c and vacuum distillation (Hobson, 1996).

1.9.2 Atmospheric distillation

Atmospheric distillation takes place in a distilling column at or near atmospheric pressure. The crude oil is heated to 350 – 400oC and the vapour and liquid are piped into the distilling column. The liquid falls to the bottom and the vapour rise, passing through a series of perforated trays (sieve trays). Heavier hydrocarbons condense more quickly and settle on lower trays and lighter hydrocarbons remain as a vapour longer and condense on higher trays. Liquid fractions are drawn from the trays and removed. In this way the light gases, methane, ethane, propane and butane pass out the top of the column, petrol is formed in the top trays, kerosene and gas oils in the middle, and fuel oils at the bottom. Residue drawn of the bottom may be burned as fuel, processed into lubricating oils, waxes and bitumen or used as feedstock for cracking units. To recover additional heavy distillates from this residue, it may be piped to a second distillation column where the process is repeated under vacuum, called vacuum distillation (Hobson, 2006).

1.9.3 Vacuum distillation

This allows heavy hydrocarbons with boiling points of 450^{o}C and higher to be separated without them partly cracking into unwanted products such as coke and ga

s. The heavy distillates recovered by vacuum distillation can be converted into lubricating oils by a variety of processes. The most common of these is called solvent extraction. In one version of this process the heavy distillate is washed with a liquid which does not dissolve in it but which dissolves (and so extracts) the non-lubricating oil components out of it. Another version uses a liquid which does not dissolve in it but which causes the non-lubricating oil components to precipitate (as an extract) from it. Other processes exist which remove impurities by adsorption onto a highly porous solid or which remove any waxes that may be present by causing them to crystallize and precipitate out (Dharia *et al.*, 1992).

1.9.4 Reforming

Reforming is a process which uses heat, pressure and a catalyst (usually containing platinum) to bring about chemical reactions which upgrade naphtha into high octane petrol and petrochemical feedstock. The naphtha is hydrocarbon mixtures containing many paraffins and Naphthenes. In Australia, this naphtha feedstock comes from the crudes oil distillation or catalytic cracking processes, but overseas it also comes from thermal cracking and Hydro cracking processes.

Reforming converts a portion of these compounds to isoparaffins and aromatics, which are used to blend higher octane petroleum product (Dharia *et al.*,1992).

- ✓ paraffins are converted to isoparaffins
- ✓ paraffins are converted to naphthenes
- ✓ naphthenes are converted to aromatics

Equation to illustrate

$C_7H_{16}(l) \rightarrow C_7H_8(l) + 4H_2(g)$ (1)

$C_6H_4(l) \rightarrow C_6H_6(l) + H_2(g)$ (2)

$C_6H_{12}(l) \rightarrow C_6H_6(l) + 3H_2(g)$ (3)

1.9.5 Cracking

Cracking processes break down heavier hydrocarbon molecules (high boiling point oils) into lighter products such as petrol and diesel. These processes include catalytic cracking, thermal cracking and Hydrocracking.

A typical reaction:

$C_{16}H_{34} \rightarrow C_8H_{18} + C_8H_{16}$ (4)

1.9.6 Catalytic cracking

Catalytic cracking is used to convert heavy hydrocarbon fractions obtained by vacuum distillation into a mixture of more useful products such as petrol and light fu el oil. In this process, the feedstock undergoes a chemical breakdown, under controlled heat (450 – $500^{\circ}C$) and pressure, in the presence of a catalyst (a substance which promotes the reaction without itself being chemically changed).Small pellets of silica – alumina or silica – magnesia have proved to be the most effective catalysts. The cracking reaction yields petrol, LPG, unsaturated olefin compounds, cracked gas oils, a liquid residue called cycle oil, light gases and a solid coke residue. Cycle oil is recycled to cause further breakdown and the coke, which forms a layer on the catalyst, is removed by burning. The other products are passed through fractionators to be separated and separately processed (Habsi-Halabi *et al.,* 1997).

A typical reaction:

$$C_{16}H_{34(l)} \rightarrow C_8H_{18(l)} + C_8H_{16(l)} \qquad (5)$$

1.9.7 Fluid catalytic cracking

Fluid catalytic cracking uses a catalyst in the form of a very fine powder which flows like a liquid when agitated by steam, air or vapour. Feedstock entering the process immediately meets a stream of very hot catalyst. The resulting vapours keep the catalyst fluidized as it passes into the reactor, where the cracking takes place and where it is fluidized by the hydrocarbon vapour. The catalyst next passes to a steam stripping section where most of the volatile hydrocarbons are removed. It then passes to a regenerator vessel where it is fluidized by a mixture of air and the products of combustion which are produced as the coke on the catalyst is burnt off. The catalyst then flows back to the reactor. The catalyst thus undergoes a continuous circulation between the reactor, stripper and regenerator sections. The catalyst is usually a mixture of aluminium oxide and silica. Most recently, the introduction of synthetic zeolite catalysts has allowed much shorter reaction times and improved yields and octane numbers of the cracked gasoline (Krishner, 1991).

1.9.8 Thermal cracking

Thermal cracking uses heat to break down the residue from vacuum distillation. The lighter compounds produced from this process can be made into distillate fuels and petrol. Cracked gases are converted to petrol blending components by alkylation or polymerization. Naphtha is upgraded to high quality petrol byre forming. Gas oil can be used as diesel fuel or can be converted to petrol by hydrocracking. The heavy residue is converted into residual oil or coke which issued in the manufacture of electrodes, graphite and carbides (Elliot, 1992).

A typical equation:

$$C_{13}H_{38}(l) \rightarrow C_3H_6(g) + C_{10}H_{22}(l) \qquad (6)$$

1.9.9 Hydrocracking

Hydrocracking can increase the yield of petroleum components, as well as being used to produce light distillates. It produces no residues, only light oils. Hydrocracking is catalytic cracking in the presence of hydrogen. The extra hydrogen saturates, or hydrogenates the chemical bonds of the cracked hydrocarbons and creates isomers with the desired characteristics.

Hydrocracking is also a treating process, because the hydrogen combines with contaminants such as sulphur and nitrogen, allowing them to be removed. Gas oil feed is mixed with hydrogen, heated, and sent to a reactor vessel with a fixed bed catalyst, where cracking and hydrogenation take place. Products are sent to fractionators to be separated. The hydrogen is recycled. Residue from this reaction is mixed again with hydrogen, reheated, and sent to a second reactor for further cracking under higher temperatures and pressures. In addition to cracked naphtha for making petrol, Hydrocracking yields light gases useful for refinery fuel, or alkylation as well as components for high quality fuel oils, lube oils and petrochemical feedstock. Following the cracking processes, it is necessary to build or rearrange some of the lighter hydrocarbon molecules into high quality petrol orient fuel blending components or into petrochemicals. The former can be achieved by several chemica l processes such as alkylation and isomerization.

1.10 Petroleum products

Major products of oil refineries are usually grouped into three categories: light distillates (LPG, gasoline, naphtha), middle distillates (kerosene, diesel), heavy distillates and residuum (fuel oil, lubricating oils, wax, tar).This classification is based on the way crude oil is distilled and separated into fractions (called distillates and residuum). Liquid petroleum gas (LPG), Gasoline (also known as petrol), Naphtha Kerosene and related jet aircraft fuels, Diesel fuel, Fuel oils, Lubricating oils, Paraffin wax, Asphalt and Tar Petroleum coke.

1.10.1 Gasoline

Gasoline or Petrol is a petroleum-derived liquid mixture which is primarily used as a fuel in internal combustion engines. It is also used as a solvent, mainly known for its ability to dilute paints. It consists mostly of aliphatic hydrocarbons obtained by the fractional distillation of petroleum, enhanced with isooctane or the aromatic hydrocarbons e.g. toluene and benzene to increase its octane rating (Fessenden and Fessenden, 1991).

1.10.2 Kerosene

Kerosene is a thin, clear liquid formed from hydrocarbons, with density of 0.78–0.

81 g/cm^3. It is obtained from the fractional distillation of petroleum between150 °C and 275 °C, resulting in a mixture of carbon chains that typically contain between 6 and 16 carbon atoms per molecule. Kerosene is widely used to power jet-engine aircraft (jet fuel) and some rockets, but is also commonly used as a heating fuel and for fire toys (Russell, 2003).

1.10.3 Petroleum Diesel

Petroleum diesel, also called petro-diesel, or fossil diesel is produced from the fractional distillation of crude oil between 200 °C (392 °F) and 350 °C (662 °F) at atmospheric pressure resulting in a mixture of carbon chains that typically contain between 8 and 21 carbon atoms per molecules. Petroleum-derived diesel composed of about 75% saturated hydrocarbons (primarily paraffins including, iso and cyclo paraffins) and 25% aromatic hydro carbon (including naphthalene, alkyl benzene) (Matar, 2002).

1.10.4 Fuel Oil

Fuel oil is a fraction obtained from petroleum distillation, either as a distillate or a residue. Broadly speaking, fuel oil is any liquid petroleum product that is burned in a furnace or boiler for the generation of heat or used in an engine for the generation of power, except oils having a flash point of approximately 40 °C(104 °F) and oils burned in cotton or wool-wick burners (Matar, 2002).

1.10.5 Lubricating Oil

Lubricating oil or engine oil is oil used for lubrication of various internal combustion engines. While the main function is to lubricate moving parts, lubricating oil also cleans, inhibits corrosion, improves sealing, and cools the engine by carrying heat away from moving parts (Chris, 2007).Lubricating oils are derived from petroleum-based and non-petroleum-synthesized chemical compounds .But are today mainly blended by using base oils composed of those organic compound consisting entirely of carbon and hydrogen (Corsico, 2009).

1.10.6 Wax

A wax is a type of hydrocarbon that typically contains long-chain alkanes often containing ester, carboxylic acid, or alcohol groups. The structure and molecular weight of the hydrocarbon chain and the relative concentration of the functional groups determine the hardness of the wax. Waxes are used to make wax paper, impregnating and coating paper and card to waterproof it or make it resistant to staining, or to modify its surface properties. Waxes are also used in shoe polishes, wood polishes, and automotive polishes, as mold release agents in mold making, as a coating for many cheeses, and to waterproof leather and fabric (Corsico, 1999).

1.10.7 Petrolatum

Petroleum jelly, petrolatum or soft paraffin, is a semi-solid mixture of hydrocarbons "with carbon numbers mainly higher than 25" (Schlosberg, 2001), originally promoted as a topical ointment for its healing properties. Its folkloric medicinal value as a "cure-all" has since been limited by better scientific understanding of appropriate and inappropriate uses. However, it is recognized by the U.S. Food and Drug Administration (FDA) as an approved over-the counter (OTC) skin protectant and remains widely used in cosmetic skin care (Muhammad, 1992).

1.10.8 Asphalt

Asphalt is a sticky, black and highly viscous liquid or semi-solid that is present in most crude petroleum and in some natural deposits sometimes termed sphaltum (Abraham, 1938). Asphalt can be separated from the other components in crude oil (such as naphtha, gasoline and diesel) by the process of fractional distillation, usually under vacuum conditions. A better separation can be achieved by further processing of the heavier fractions of the crude oil in a deasphalting unit, which uses either propane or butane in a supercritical phase to dissolve the lighter molecules which are then separated (Abraham, 1998).

1.11 Environmental effects

The presence of oil has significant social and environmental impacts, from accidents and routine activities such as seismic exploration, drilling, and generation of polluting wastes. Oil extraction is costly and sometimes environmentally damaging, although Dr. John Hunt from Woods Hole pointed out in a 1981 paper that over 70% of the reserves in the world are associated with visible macro seepages, and many oil fields are found due to natural leaks.

Offshore exploration and extraction of oil disturbs the surrounding marine environment. Extraction may involve dredging, which stirs up the seabed, killing the sea plants that marine creatures need to survive. Crude oil and refined fuels pills from tanker ship accidents have damaged fragile ecosystems in Alaska, the Galapagos Islands, Spain, and many other places. Burning oil releases carbon dioxide into the atmosphere, which is thought to contribute to global warming.

Petroleum produces less CO_2 than coal, but more than natural gas. However, oil's unique role as a transportation fuel makes reducing its CO_2 emissions a particularly thorny problem; amelioration strategies such as carbon sequestering are generally geared for large power plants, not individual tailpipes (Wilhelm and Hermann, 2005).

1.12 Basic Principle/Components of Atomic Absorption Spectroscopy

Atomic Absorption Spectroscopy is the determination of elemental composition by its electromagnetic or mass spectrum. It can be divided by atomization source or by the type of spectroscopy used. The basic principle is that, light is passed through a collection of atoms. If the wavelength of the light has energy corresponding to the energy difference between two energy levels in the atoms, a portion of the light will be absorbed. The relationship between the concentrations of atoms, the distance the light travels through the collection of atoms, and the portion of the light absorbed is given by the Beer-Lambert law. The main components of an atomic absorption spectrophotometry are radiation source, an atomization cell and a wavelength selector.

1.13 Statements of the Problem

Crude oil and its finished products (Petroleum Products) contains mainly hydrocarbons especially alkanes, naphthenic and aromatics hydrocarbons (Tijjani *et al.*, 2012). It contains also some nitrogen, oxygen and sulphur containing compounds along with trace amounts of elements especially nickel, vanadium, cadmium, iron, zinc and lead etc (Fernandez *et al.*, 2007). The presence of trace metals in the crude oil and petroleum products is destructive, especially in a refining process. This may adversely affect both the processing equipment and storage facilities of the petroleum refinery. The analyses of trace metals in Nigerian petroleum products is very important considering the detrimental effect of these metals in the refining processes and environment in general. And also, the data on the concentration of trace metals in our indigenous petroleum products are lacking, this and other factors necessitates the analyses of trace and heavy metals in this research work by analytical method using atomic absorption spectrophotometry method (AAS).

1.14 Aim and Objectives

This research work was aimed at determining the concentration of trace metals in different Nigerian petroleum products.

The objectives of this research were to:

a) Identify the trace metals in the various petroleum products sample understudy.

b) Compare the different petroleum products samples used in terms of trace metal concentration.

CHAPTER TWO

2.0 MATERIALS AND METHODS

2.1 MATERIALS

All the chemicals and reagents used in this study were of analytical grades, the glass wares used were cleansed, rinsed with distilled water and air dried before used. Some of the reagents and apparatus used are (conc. HCl, HNO_3, pipette, beakers, volumetric flasks, conical flask, beakers, heating mantle and funnels).

The various Nigerian petroleum products used in this research work are kerosene, diesel oil and Petrol; they were collected from Tanke Area, along University of Ilorin, Kwara State, Nigeria. The trace metals analysis was analyzed using Atomic Absorption Spectroscopy (AAS)

2.2 METHODS

There were three sample preparation methods presently being employed prior to determination of metals by atomic absorption technique: —

(a) Solvent dilution.

(b) Total acid digestion of the sample.

(c) Ashing of the sample and dissolution with an appropriate acid.

The Total acid digestion of the sample was employed for the determination of me tals by atomic absorption technique.

2.2.1 Digestion of Petroleum

Acid (Wet) Digestion method was employed; this was carried out using the method reported by Nafiu *et al.*, (2012) with slight modification. After thorough shaking, a mass of 0.5 g of the sample which was weighed in a 250 ml Erlenmeyer and 1ml of concentrated sulphuric acid were carefully added and heated to 170 ± 10 ºC in hot plate for 30 minutes. Then, 1 ml of concentrated nitric acid was added, maintaining the heating for 20 min. Finally, 1 ml of 30% (v/v) hydrogen peroxide was added to complete the digestion.

The digested content, approximately 1.5 ml, was left to cool down to room temperature and quantitatively transferred to volumetric flask and diluted to a final volume of 50 ml with distilled water. The hydrogen peroxide was added to prevent early frothing and deposition of carbon on the wall of the digestion tubes. The digested sample were analyzed using atomic absorption spectrophotometer.

2.2.2 Digestion of Diesel

Acid (Wet) Digestion method was also employed; this was carried out using the method reported by Nafiu *et al.*, (2012) with slight modification. After thorough sha king, a mass of 0.5 g of the sample which was weighed in a 250 ml Erlenmeyer and 1ml of concentrated sulphuric acid were carefully added and heated to 170 ± 10 °C in hot plate for 30 minutes. Then, 1 ml of concentrated nitric acid was added, maintaining the heating for 20 min. Finally, 1 ml of 30% (v/v) hydrogen peroxide was added to complete the digestion.

The digested content, approximately 1.5 ml, was left to cool down to room temperature and quantitatively transferred to volumetric flask and diluted to a final volume of 50 ml with distilled water. The hydrogen peroxide was added to prevent early frothing and deposition of carbon on the wall of the digestion tubes. The digested sample were analyzed using atomic absorption spectrophotometer.

2.2.3 Digestion of Kerosene

Acid (Wet) Digestion method was employed; this was carried out using the method reported by Nafiu *et al.*, (2012) with slight modification. After thorough shaking, a mass of 0.5 g of the sample which was weighed in a 250 ml Erlenmeyer and 1ml of concentrated sulphuric acid were carefully added and heated to 170 ± 10 °C in hot plate for 30 minutes. Then, 1 ml of concentrated nitric acid was added, maintaining the heating for 20 min. Finally, 1 ml of 30% (v/v) hydrogen peroxide was added to complete the digestion.

The digested content, approximately 1.5 ml, was left to cool down to room temperature and quantitatively transferred to volumetric flask and diluted to a final volume of 50 ml with distilled water. The hydrogen peroxide was added to prevent early frothing and deposition of carbon on the wall of the digestion tubes. The digested sample were analyzed using atomic absorption spectrophotometer.

CHAPTER THREE

3.0 RESULTS AND DISCUSSION

The result of concentration of trace metals in petroleum products (kerosene, diesel and petrol) sampled in three different stations are shown in Table 3

Table 3: (STATION 1) Concentration of trace metals in petroleum products (mg/L)

Products	**Mg**	**Ca**	**Cu**	**Fe**	**Pb**	**Zn**
Petrol	0.38	0.82	0.64	3.48	0.5	1.78
Kerosene	0.14	0.48	0.26	1.28	0.16	0.48
Diesel	0.56	0.78	1.05	2.74	0.4	1.38
Control	0.11	0.29	0.09	1.08	0.12	0.29

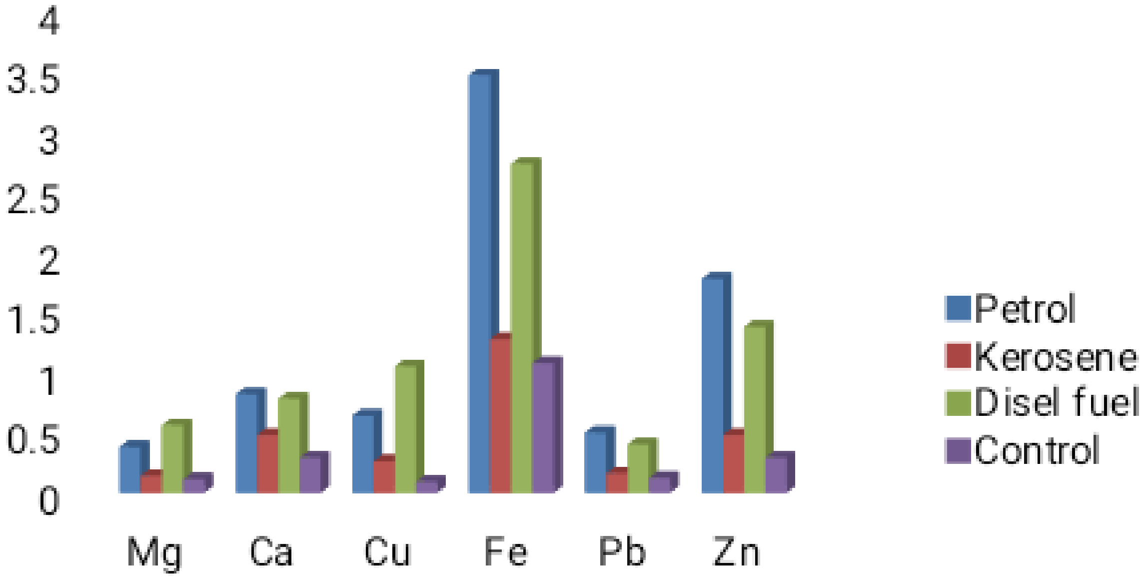

Figure 1: Graph showing comparison between concentration of trace metals in Nigerian Petroleum Products and NNPC products (control)

Table 4: (STATION 2) Concentration of trace metals in petroleum products (mg/L)

Products	**Mg**	**Ca**	**Cu**	**Fe**	**Pb**	**Zn**
Petrol	0.49	0.92	0.69	3.48	0.7	1.83
Kerosene	0.38	0.49	0.33	1.92	0.38	0.65
Diesel	0.27	0.68	0.95	2.63	0.51	1.43

Control	0.11	0.29	0.09	1.08	0.12	0.29

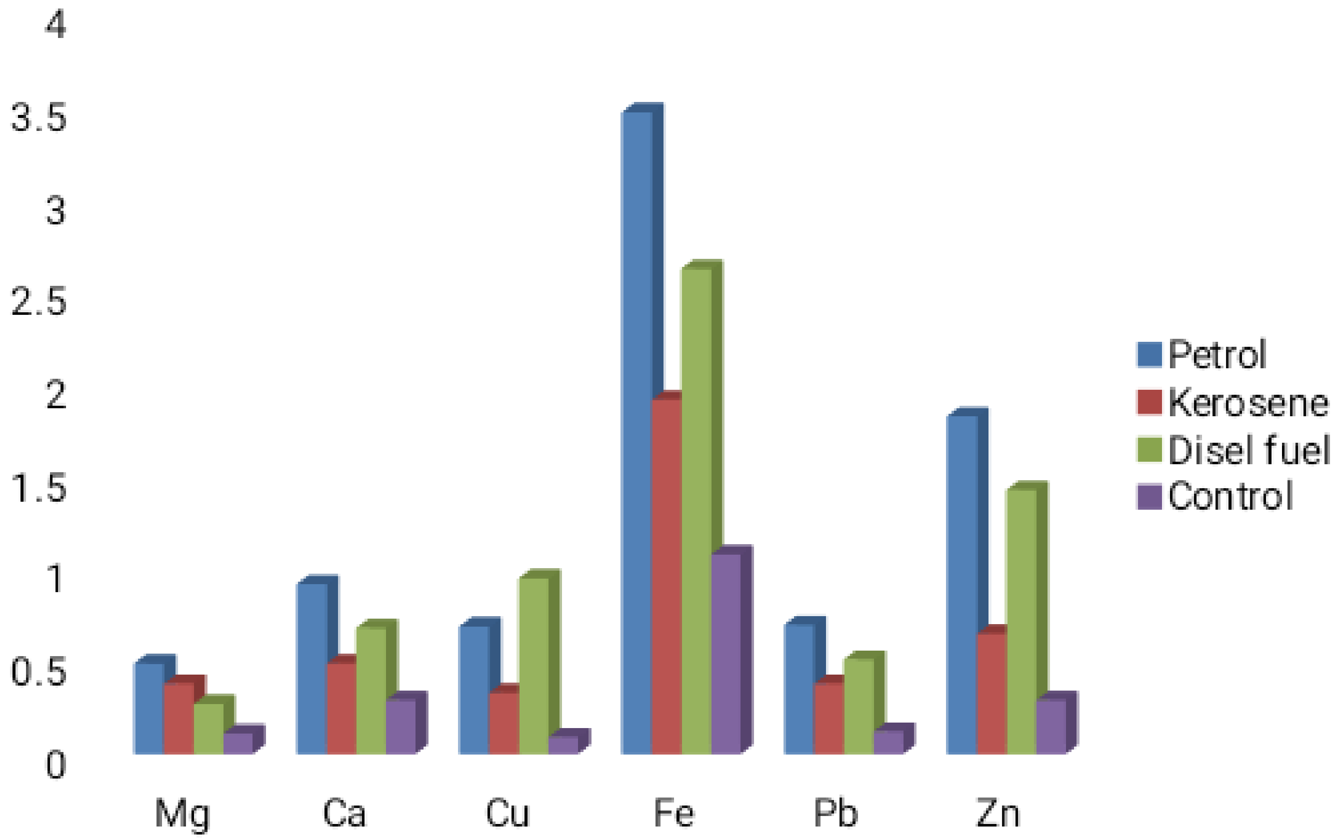

Figure 2: (STATION 2) Graph showing comparison between concentration of trace metals in Nigerian Petroleum Products and NNPC products (control)

Table 5: (STATION 3) Concentration of trace metals in petroleum products (mg/L)

Products	**Mg**	**Ca**	**Cu**	**Fe**	**Pb**	**Zn**
Petrol	0.38	0.87	0.67	2.91	0.74	1.85
Kerosen	0.29	0.51	0.34	1.9	0.35	0.66

e						
Diesel	0.22	0.72	0.97	2.71	0.52	1.51
Control	0.11	0.29	0.09	1.08	0.12	0.29

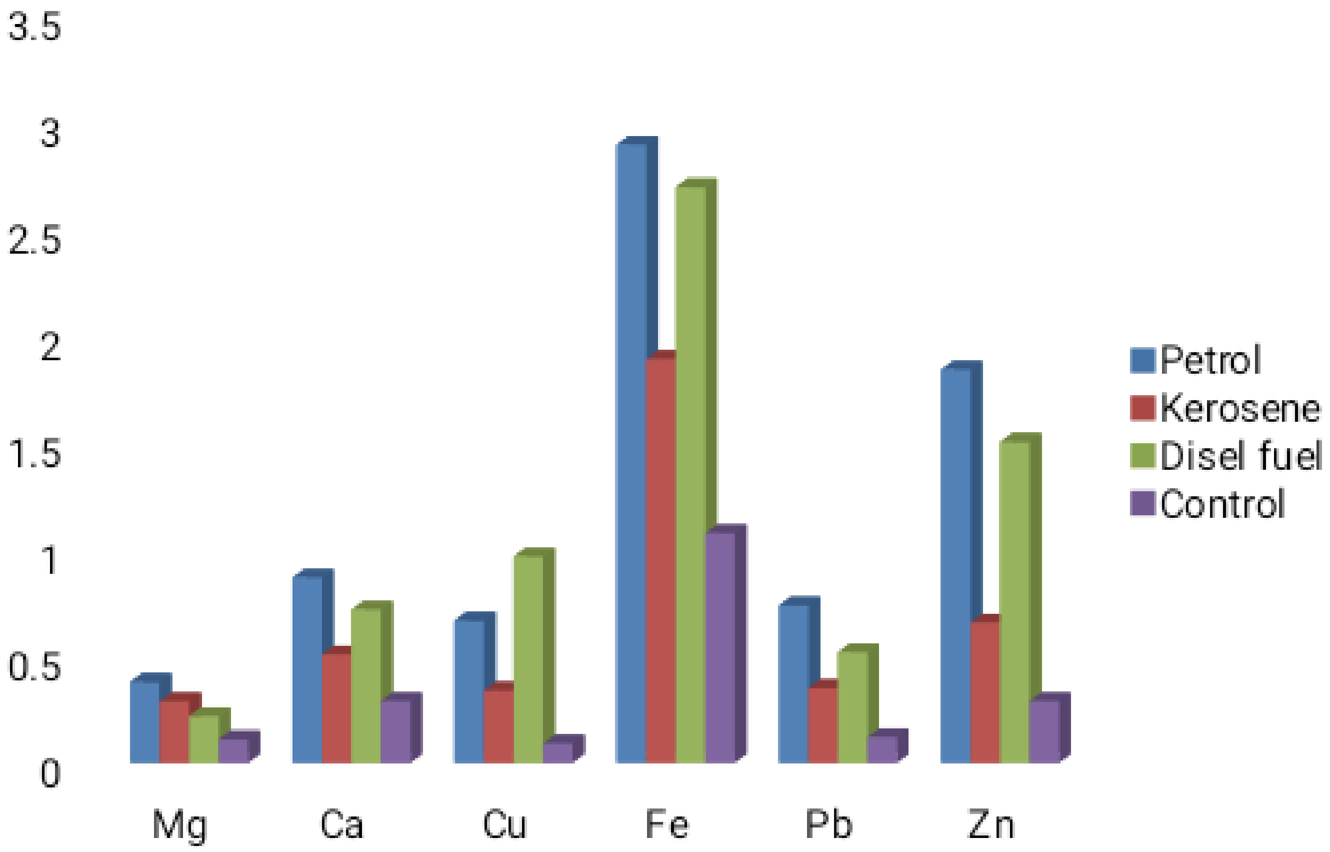

Figure 3: (STATION 3) Graph showing comparison between concentration of trace metals in Nigerian Petroleum Products and NNPC products (control)

The metal content of petroleum products is shown in Tables 3-5 and Figures 1-3 shows an interesting outlay of the concentration of trace metals analyzed in the samples of Nigerian petroleum products. It is observed from the results that the met al contents vary with the viscosity of the petroleum products. The nature of this metals and the abundance in petroleum products may probably provide information on the origin, migration and maturation of raw material of these petroleum products as well as indicating the regional geochemical prospecting base as well as the processing and storage channels in the refinery. As a rule, the metal content increase with viscosity of these petroleum products (i.e. the heavier the petroleum product the higher its metal contents) consequently, the lighter distillates contain less metals. The metal contents of the Nigerian petroleum products in the literature show a wide variation. For example, Odebunmi and Adeniyi, (2004) reported iron content in the range of 10.94-25.00mg/l, while the results obtained in this present work shows range of 1.28-3.48 mg/l compared to the NNPC control which determined to be 1.08 mg/l. The wide variation of the concentrations of iron possibly due to the combination of several factors including the type of petroleum refining equipment (because some of them are made up of different percentage of metallic alloys), sample handling procedures and different analytical techniques adopted. The metal contents of Nigerian petroleum products are in general lower than those of petroleum products from other regions of the world for instant, Adolfo *et al.*, 2007 reported iron contents of 12.39mg/l, 725 mg/land 113.2mg/lin petroleum product s from Central American Region (USA), Mexico and Venezuela respectively.

The concentrations of lead that are present in the samples are within the range of 0.35-0.74 mg/l.

The low amount of lead in the petrol, kerosene and diesel oil might be due to the substitution of methylalkyl lead previously used as additive with ethanol (Stons *et al*,1986; Fessenden and Fessenden, 1991). This is slightly above NNPC control which is 0.12 mg/l.

The concentration of zinc in the petroleum product are in the range for petrol {1.7-1.85 mg/l}, kerosene {0.48-0.66 mg/l} and diesel oil {1.38-1.51 mg/l}. There are all slightly above the NNPC petroleum products used as standard {0.29 mg/l}. The concentration of magnesium, calcium and copper in petroleum products analyzed was found to be in trace amount of concentrations between {0.09-1.05 mg/l}.

However, even as these low levels, the metal contents of Nigerian petroleum products, and especially of iron, lead and zinc high enough to cause corrosion of turbines distillation towers, etc (Oderinde, 2014).

CHAPTER FOUR

4.0 CONCLUSION AND RECOMMENDATIONS

4.1 Conclusion

This work showed that Nigerian petroleum products contains trace amount of iron, zinc, lead, copper, calcium and magnesium. The presence or absence of some elements in Nigerian petroleum products may be associated with the chemical and geological origin of its raw materials and also industrial process and the transportation method adopted. Hence the concentrations of trace and heavy elements in Nigerian petroleum products may reveal information on the environmental friendli ness and quality of petroleum products and probably give an idea of the sources of these trace heavy metals in the petroleum industry. It is obvious from this study, that the Nigerian petroleum products analyzed have low metals contents in petrol, kerosene and diesel oil sample. However, despite the low concentrations, they could still lead to serious health hazard considering their cumulative effects in the environment and high enough to cause corrosion of turbines and distillation towers etc.

4.2 Recommendations

In view of the results obtained from this study, the following recommendations are hereby proffered:

1. Petroleum industries should provide enough fund for the Universities and supply latest analytical machines such as AAS, GC/MS and other very important analytical equipment to Universities/ Research Institutions as part of their public responsibilities.
2. Since most of the sources of these metals are from the alloys used in constructing anti-corrosive pipes, processing equipment and storage materials, there is need for alternative pipes, processing equipment and storage materials constructed from such metallic alloys to be substituted with plastic or fiber material.

3. Government should establish emergency taskforce for the control of industrial and municipal discharge, especially for petroleum and petroleum products discharge.

4. General public should be oriented and alerted on the danger of inhaling the exhaust of different transportation machines and avoid physical contact with these petroleum products.

5. Storage tanks of the filling station must be inspected regularly, and specification of a standard storage tank must be established.

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