

# Introduction

## *1-1 Lubrication and lubricant*

Lubrication involves the addition of some substance to reduce the friction between moving surfaces. This substance is called lubricant. The lubricating oil is basically a mixture of hydrocarbon derived from crude Oil<sup>(1)</sup>. Before the advent of crude oil refining, liquid lubricants were chiefly fatty oils such as olive oil, palm oil and lard oil<sup>(2)</sup>. Such oils had a tendency to oxidize and form sledges and emulsions paraffin. The mineral oils are better in this respect and are much cheaper<sup>(3)</sup>.

The requisites of a good lubricant are body or density, resistance to corrosive acids, fluidity, minimal frictional or tensional resistance, high burning and flash points, and freedom from oxidation or gumming<sup>(4)</sup>. Proper lubrication depends primarily on the chemistry of the lubricants. The ability of the oil to spread over the bearing to resist displacement by heat or pressure, its stability against cracking and oxidation, its viscosity and many other important qualities are determined by its chemical nature. Modern improvements in lubricants have been the result of chemical researches. The chemical as well as the physical properties of the bearing surface are also of major importance<sup>(3)</sup>.

Lubricants enable machine to function continuously by preventing abrasion, or so called seizing of metal parts caused by heat expansion. Some lubricants are also act as coolants and thus prevent material deformities caused by heat. Thin film lubricants are used for heavy loads, where internal frictions in the lubricant and consequent loss of power have to be avoided. Thick film or fluid lubricants are used in machinery in which moving or oscillating conditions are

moderate. Lubricants today are often applied mechanically for better control, usually by valves or rotating rings or chains, immersion devices, splash devices or centralized reservoirs<sup>(5)</sup>.

In an engine, the oil not only serves as a fluid or a boundary lubricant. It also functions as a fluid gasket between the cylinder and the piston rings. It should also act as a cleaning agent and as a scavenger to wash off and transport solid particles produced in combustion or wear<sup>(5)</sup>.

## ***1-2 Classification of lubricants***

Lubricants can be divided into: - solid, semi-solid and liquid:<sup>(6)</sup>

A) Solid lubricants :<sup>(1)</sup> A solid lubricants is a film of solid material interposed between two rubbing surfaces to reduce friction and wear. The films may consist of inorganic material such as graphite, molybdenum sulfide<sup>(7)</sup> and lead monoxide<sup>(6)</sup> or organic compounds such as metallic soaps of aluminum and calcium<sup>(8)</sup> or polymeric films such as polytetrafluoroethylene and polychlorofluoroethylene<sup>(9)</sup>.

B) Semi solid lubricants: Lubricating grease is a semi solid lubricant consisting of a thickening agent <sup>(1)</sup> in a liquid lubricant. Soaps of aluminum, barium, calcium, lithium, sodium, and strontium are the major thickening agents <sup>(8)</sup>. Non soap thickeners consist of such inorganic compounds as modified clays, fine silica solids, usually referred to as fillers added in concentration up to several percent. Fillers are normally inorganic materials such as asbestos, graphite, metal oxide, metal powders, or metal sulfides. Additives are

frequently incorporated to resist oxidation and corrosion and to improve film strength<sup>(6)</sup>.

Lubrication by grease may prove more desirable than lubrication by oil under condition when (I) less frequent lubricant application is necessary (II) grease acts as a seal against loss of lubricant and ingress of contaminants (III) less dripping or splattering of lubricant is called for, or (IV) less sensitivity to inaccuracies in the mating parts is needed<sup>(3)</sup>.

C) Liquid lubricants: liquid lubricant can be classified into two type depending on their origin<sup>(6)</sup>:

1. natural lubricant Products were certainly means first lubricants used as Animal and vegetable lubricants but because they lack chemical inertness and because lubrication requirements have become more demanding they have been largely superseded by petroleum products and by synthetic materials (some organic substances such as lard and sperm oil are still in use as additive because of their special lubricating properties)<sup>(10)</sup>.

2. Petroleum lubricants<sup>(8)</sup>: petroleum products dominate lubricant production with a 98% share of the market for lubricating oils and greases. While lower cost leads to first consideration of these petroleum lubricants, production of various synthetic lubricants covered later has been expanding to take advantage of special properties such as stability at extreme temperatures, chemical

inertness, fire resistance, low toxicity, and environmental compatibility<sup>(6)</sup>.

Petroleum oils generally range from low viscosity with molecular weights as low as 250g/mol to very viscous, to lubricants with molecular weights up to about 1000g/mol. Typical molecular structures of the complex mixtures of hydrocarbon molecules present are shown in figure (1-1). Physical property and performance characteristics depend heavily on the relative distribution of paraffinic, aromatic, and alicyclic (naphthenic) components. Paraffin has a relatively low viscosity and density, and higher freezing temperatures. Aromatics have higher viscosity, which change in rapidly with temperature, higher density, and darker color. Although aromatics have a high degree of oxidation stability, they oxidize to form insoluble black sludge at high temperature. Alicyclic oils are characterized by low pour point and oxidation stability; other properties are intermediate to those of the paraffin and aromatics<sup>(1)</sup>.

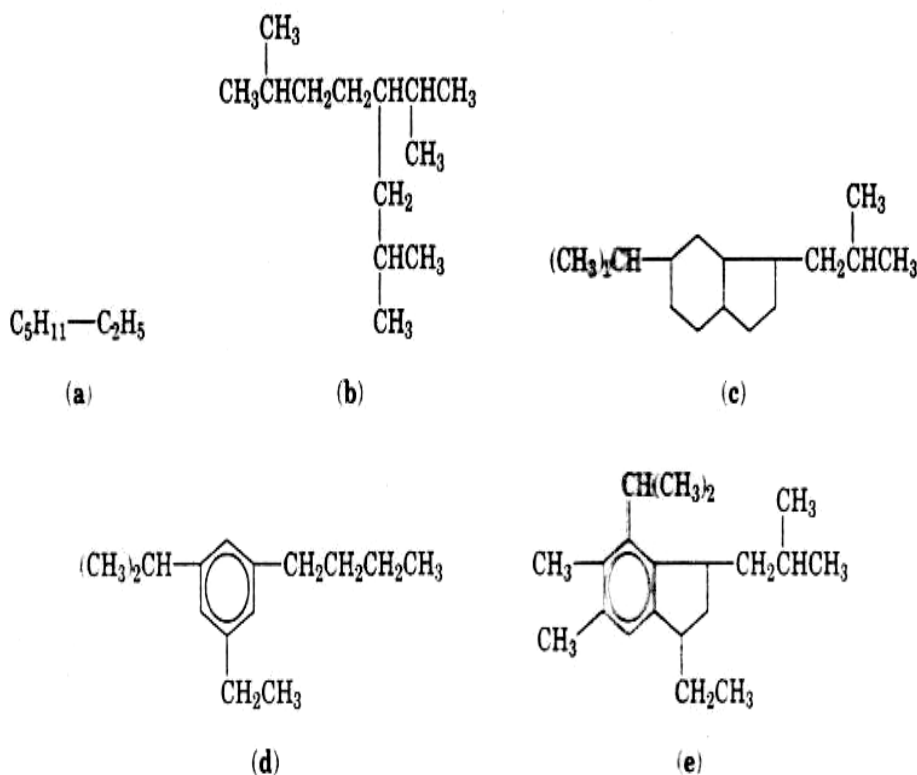


Figure 1-1 typical structures of same compounds present in lube oil: (a) *n*- paraffin, (b) iso paraffin, (c) cycloparaffin, (d) Aromatic hydrocarbon, and (e) mixed aliphatic and aromatic ring<sup>(1)</sup>.

Almost all premium lubricants are so-called paraffinic oils composed primarily of both paraffinic and alicyclic structures, with only a minor portion of aromatics. When stabilized with an oxidation inhibitor and fortified with other appropriate additives, these paraffinic – alicyclic compositions provide non-sludging oils that are satisfactory for almost any type of service<sup>(1)</sup>.

The first step of producing lubricating oil involves distillation of the crude petroleum<sup>(11)</sup>. The lower boiling gasoline, kerosene, and fuel oils are removed first, and the lubricating oil fractions are then divided according to their boiling points into several grades of neutral distillates and a final more viscous residuum. Subsequent refining

steps remove undesirable aromatics and the minor portion of sulfur, nitrogen, and oxygen compounds. Although solvent extraction or sulfuric acid treatment, followed by activated clay to absorb dark-colored and unstable molecules, had been used for this purification step, hydrogen treatment at high pressure and in the presence of a catalyst was introduced in 1955<sup>(12)</sup>. Mild hydrofining involves primarily only the removal of color and some nitrogen, oxygen, and sulfur compounds. More severe hydrofining or hydrocracking at temperatures in the 500-575 °C range further alters the chemical structures to convert aromatics to paraffin and alicyclic in oils of very high viscosity index (VHVI)<sup>(13)</sup>.

Low temperature filtration is a common final refining step to remove paraffin wax in order to lower the pour point of the oil. As an alternative to traditional filtration methyl ethyl ketone solvent, catalytic hydrodewaxing cracks the wax molecules which are then removed as lower boiling products. Finished lubricating oils are then made by blending these refined stocks to the desired viscosity, followed by introducing additives needed to provide the required performance<sup>(14)</sup>.

### ***1-3 Friction***

It is the chief cause of wear in any machine. Friction wastes power almost 20 percent in a modern car. The chief cause of friction is the chemical bonding or Vander Waals attraction, where a few atoms or molecules come into contact. Such contacts may result in dislodgement of particles of colloidal size or larger from one surface by the other. Sometime fusion of a tiny peak or asperity may take

place. The introduction of a lubricant lessens the amount of dislodgement or pick up<sup>(3)</sup>.

The fact of existing free particles in the oil will cause wear in the metallic surface which will generate debris, intensifying in turn the wear process, always in a domino effect until it causes serious damages to the equipment if the cycle is not interrupted. However, this initial wear has been caused by some other factor not duly controlled, such as the lubricant quality or the deterioration of its properties due to excess temperature and the introduction of contaminants such as dust fluid or catalytic metals<sup>(6, 15)</sup>.

The oil degradation is promoted by high temperature. This can be due to an insufficient lubricant level or poor heat transfer because of high environmental temperature or high lubricant viscosity<sup>(16)</sup>.

### ***1-4 Physical and chemical properties of lubricating oil.***

An important information about the lubricant state must be get in order to decide if the oil in good conditions to continue active. An attention to physical and chemical characteristics should be taken. The total acid number (TAN) or total base number (TBN),<sup>(17)</sup> the oxidation, the viscosity, and the viscosity index, the additive content, the nitration, the sulfate formation, the dispersing ability are some common physical and chemical parameters<sup>(4)</sup>.

The analysis labs follow specific predefined routines, according to their experience, with a set of tests, which they consider the most adequate to an established type of equipments. However, it is to the lubrication expert to have sensibility to identify the existence of any important parameter in that equipment in particular, needed to be

evaluated. The following paragraphs discuss list of the physical and chemical oil characteristics<sup>(18)</sup>.

1-**Viscosity:**<sup>(17,19,20)</sup> The viscosity of a liquid is defined as the ratio of the shearing stress to the rate of shear or is the resistance of a liquid to flow. It determines the amount of friction that will be encountered between sliding surfaces and whether a thick film can be built to avoid wear from solid to solid contact. Viscosity customarily is measured by viscometer, which determines the flow rate of the lubricant under standard condition; the higher the flow rate, the lower the Viscosity. Lubricants with low viscosity are generally preferred for bearing subjected to high speed and low pressure. Whereas lubricants with high viscosity are recommended for low speed and high pressure<sup>(3)</sup>.

2. **Viscosity index**<sup>(19,21)</sup>: Since little change of viscosity with fluctuations in temperature is desirable to keep variations in friction at a minimum, fluids frequently are rated in terms of viscosity index. The less the viscosity is changed by temperature higher the viscosity index<sup>(3,6)</sup>.

3. **Oiliness:** The term relates to a lubricant's tendency to wet and adhere to a surface under condition of heavy pressure. A lubricant oil of poor oiliness is subjected to high pressure, it's tendency to be squeezed out of the lubricated machine parts, thereby lubrication action steps. On the other hand, lubricants which have good oiliness stay in between the lubricated surface when they are subjected to high pressure<sup>(7)</sup>.

Oiliness is a very important property of lubricants, particularly for extreme pressure lubrication. Mineral oils have got very poor oiliness. Animal and vegetable oils and fatty acids are considered to be having



high oiliness. In order to improve the oiliness of mineral oils, additives and fatty acids like vegetable oils and fatty acids ( such as oleic and stearic acid ) are added to them<sup>(3,6,8)</sup>.

4. **Acidity**<sup>(22,23)</sup>: The acidic constituents of the oil is referred to as “acid number”. It is defined as the number of milligrams of KOH required to neutralize the free acid in 1 gm of the lubricant. Acidity causes the corrosion of the bearing. It increases if the lubricant suffers oxidizing action during lubricating action. Lubricating oil should possess acid value less than 0.1. Any value greater than 0.1 indicates the oil has been oxidized<sup>(4,6)</sup>.

5. **Emulsification**<sup>(24,25)</sup>: The property of oil to get intimately mixed with water forming a mixture called emulsion. Certain oils form emulsion with water easily. Emulsions have a tendency to pick up dirt, grit, foreign matter etc. thereby causing abrasion and wearing out of the lubricated parts of the machinery. Good lubricating oil should not form any emulsion<sup>(3,6)</sup>.

6. **Flash point**<sup>(26,27)</sup>: It is the lowest temperature at which the oil lubricant gives off enough vapors so as to form an explosive mixture that will flash, if brought into contact with flame. Flash point may in some instances become the major consideration in selecting the proper lubricant:, especially in lubricating machinery handling highly flammable material. A good lubricant flash point should be at least above the temperature at which it is to be use.<sup>(1)</sup>

7. **Fire point**<sup>(26,28)</sup>: It is the lowest temperature at which the vapors of the oil burn continuously for the least five seconds, when a tiny flame is brought near it. In most cases the fire points are 5to40°C higher

then the flash points. The flash and fire point are important when oil is exposed to high temperature service.<sup>(1,3)</sup>

**8. Volatility:** It is the tendency of the lubricant to evaporate. Working with lubricating oils in heavy machinery at high temperature, a portion of oil may vaporize leaving behind a residual oil which have deferent lubricating properties like increased viscosity. A good lubricant should have low volatility<sup>(3,6)</sup>.

**9. Flow point:** It is the temperature at which lubricant ceases to flow. It is of importance in appraising flow properties at low temperature. It can become the determining factor in selecting the one lubricant from among a group with identical properties<sup>(3)</sup>.

**10. Saponification value<sup>(24,25)</sup>:** It is given by the number of milligrams of KOH required to saponify 1 gm of oil. Mineral oils do not safonityat all, but vegetable and animal oils do. This test helps fined weather the oil under reference is animal and vegetable oil or mineral oil or compounded oil containing vegetable and mineral oils<sup>(3)</sup>.

### ***1-5 Analysis of lubricating oil***

The analysis of lubricating oil is comparable to blood analysis. The obtained results allow the expert to take immediate conclusions about the blood quality and, with a more careful evaluation, about the patient's health. The oil analysis allows the expert to immediately recognize the state of the lubricant and, through a more detailed

analysis, to conclude about the machine's condition.<sup>(4)</sup> In both cases the exact identification of the problem and to recommend practical measures in order to solve it.<sup>(29,30)</sup>

In the oil analysis we might say that the wearing and contamination present in the oil reflect the equipment states. Table (1-1) show wear metal reference guide of car engine.<sup>(18)</sup> The quantitative determination of wear metals in used lubricating oil is an important application for engine and turbine. Diagnostic purposes, allowing the identification of wearing compounds before severe failure without dismantling the engine.<sup>(31,32)</sup> Thus preventive maintenance (oil changes, equipment overhauled and replacement of components) can be performed as needed. The wearing of metals causes solid metal debris of different sizes, metal oxides and metal organic species, from mechanical wear, oxidative corrosion and chemical corrosion, respectively<sup>(33)</sup>.

Table (1-1) Wear metal reference guide of car engine<sup>(18)</sup>

Probability of metal existence in engine component									
Engine's component	Iron	Copper	Lead	Aluminum	Silicon	Chromium	Tin	Sodium	Potassium
	Fe	Cu	Pb	Al	Si	Cr	Sn	Na	K
Journal Bearings		X	X	X			X		
Bushings		X	X	X			X		
Cam Shaft	X								
Coolant Additives					X	X		X	X
Crankshaft	X								
Cylinder Walls	X					X			
Exhaust Valve	X					X			
Anti-Friction Bearing	X								
Gasket Materials		X			X				
Gasoline Additive			X					X	
Housing/Castings	X			X	X				
Ingested Dirt					X			X	
Oil Additive		X			X			X	
Oil Cooler		X							
Pistons	X			X			X		
Rings	X					X			
Thrust Washers		X	X	X			X		
Timing Gears	X								
Valve Guides	X	X							
Valve Train	X								
Wrist Pin-Bushings		X	X	X			X		
Wrist Pins	X								

X represents the probability of metal existence in Engine component

Flame atomic absorption spectrophotometry has been used extensively for many years to study the trace wear metals in used engine oil.<sup>(34-37)</sup> There are several techniques for the analysis of metals in petroleum matrices by AAS.<sup>(38)</sup> The simplest is dilution of the oil with an organic solvent such as MIBK, xylene or kerosene and analysis using organo-metallic standard.<sup>(39,40)</sup> Another technique called the dry ashing of the sample, where the organics are burned off to leave an inorganic residue (ash).<sup>(41)</sup> The ash is dissolved in acid and analyzed as aqueous solution. Recently the advent of microwave digestion technology enables the chemist to decompose the oil with acids under pressure. This result in a clear, aqueous solution can analyze using simple water-based standards.<sup>(42)</sup>

Each method of these techniques has advantage and disadvantages and the choice depends on the requirements of the wear metals programs<sup>(43)</sup>.

The dissolution of the oil sample in an organic solvent and comparison with a known set of organo-metallic standards made up in the organic solvent is simplest and fast. However, the method has been shown not to measure the total metal content since not all the particulate metal aspirated is atomized.<sup>(44)</sup> The organic solvent acts as a fuel which can disturb the flame condition.<sup>(38)</sup> Disruption of flame conditions can be reduced by using an adjustable uptake nebulizer and flame microsampling techniques<sup>(45)</sup>.

Sample treatment by ashing is time consuming, however; and total metal content of iron, copper, and chromium are determined accurately. Volatile metals such as lead are lost during the ashing process<sup>(41)</sup>.

Electrothermal atomic absorption spectrometry (ETAAS) was used for analysis of petroleum matrices since it tolerates samples of high organic load and allows good sensitivity to achieve.<sup>(46-49)</sup> In the case of refractory elements, which can be related to the wearing of specific parts of engine and turbines<sup>(50)</sup>, AAS methods are not suitable, since those elements have high boiling points and/or tend to form high melting point carbides and oxides, leading to low sensitivity.<sup>(51,52)</sup> For refractory metals, better limit of detection can be obtained using ICPOES because of the efficient atomization, ionization and excitation achieved by the ICP.<sup>(53,54)</sup>

## ***1-6 Determination of metals***

The common methods that usually used to determined the metal concentrations in various sample are:

1. Atomic spectrometry<sup>(55,56)</sup>
2. Molecular absorption Spectrophotometry<sup>(55,56)</sup>

### ***1-6-1 Atomic spectroscopy***

In analytical chemistry, atomic spectroscopy usually applied to qualitative and quantitative analysis of metals. It takes three forms, atomic emission, atomic absorption and atomic fluorescence.<sup>(57)</sup>

Atomic absorption (AA) spectroscopy involves a measurement of the decrease in intensity of a light beam as it passes through a sample. The sample must be in the form of a vapor that contains dissociated atoms. These criteria are meet by subjecting the sample to the highly energetic condition (approximately 3000°C) of a flame or an electrically heated furnace.<sup>(58)</sup> AA measurements are highly spastic

since electronic transition energies are unique for each element. However, since atomic spectral lines are quite narrow (around 0.005 nm),<sup>(55)</sup> the light sources used in this technique must produce well-defined spectral lines. Typically hollow cathode lamps, in which metal atoms, that where dislodge from the cathode surface and excited, emit radiation as they returned to the ground state. This emitted light is sufficiently narrow to be absorbed by the metal atoms of interest in the sample. Generally, a different unique lamp is needed for the analysis of each metal of interest in the sample. Detection limits are in the parts-per-billion (ppb) or parts-per-million (ppm) range for AA methods.<sup>(56,59)</sup>

In atomic emission (AE) spectroscopy,<sup>(56)</sup> the sample is subjected to even higher temperatures than are used in AA methods (up to 6000°C). This high energy environment converts the aqueous sample into a vapor that contents dissociated atoms. Furthermore, those atoms are then excited state. As excited atoms decay to lower energy state, some of the energy is emitted as light. The intensity of this emitted light is measured at various wavelengths to identify and quantify the metal atoms present in the sample.<sup>(55)</sup> The high temperature source employed in AE act to populate a large number of different energy levels for several different elements simultaneously. Therefore, all of the excited atoms can emit their characteristic radiation at the same time and the detector can measure the emission at several different wavelengths. Detection limits are in the ppm for AE methods.<sup>(58)</sup>

Determination of mercury was achieved by cold vapor atomic absorption. The detection limits of inorganic and organomercury species are in the 0.003- 0.005 ppb range and both types of mercury

can be determined in a 1ml sample in about 3 min and this procedure was used to determine the chemical forms of Hg in water, tuna, hair, and urine samples. <sup>(60)</sup>

Jian-xin determined Cu, Zn, Fe, Ca, Mg, Na, and K in serum by FAAS at 324.8nm, 213.9nm, 248.3nm, 422.7nm, 202.5nm, 330.3nm, and 404.4nm, respectively. The recovery of determined metal was ranged 92-104% with relative standard deviations from 6.2% to 9.7%. <sup>(61)</sup>

A modified silica gel (1-8-HOQ) was prepared and used for the preconcentration of Cd, Pb, Zn, Cu, Fe, Mn, Ni, and Co from seawater prior to their determination by GFAAS. The recovery of trace metal (Cd, Pb, Zn, Cu, Fe, Mn, Ni, and Co) from deionized water was 106±8, 100±8, 98±3, 93±2, 98±3, 101±7, 97±2, and 80±4, while from sea water 94±5, 92±10, 94±12, 96±12, 96±10, 115±5, 96±8, and 74±1 respectively. <sup>(62)</sup>

ICP was used as a selective and sensitive detector for the analysis of  $\beta$ -diketonate complexes of Fe, Cu, Zn, Mn, Al, and Cr of in blood serum, when a solution of the chelating complexes in xylene are directly introduced by pneumatic nebulization. <sup>(63)</sup>

Nakamoto et al <sup>(64)</sup>. vanadium was directly determined in heavy oil samples by AAS using a graphite furnace coated with tungsten and Hitachi vanadium halo cathode lump as a radiation source. The interference of sulfur compound was suppressed by choosing the ashing temperature. When the concentration was diluted to 1.0wt% or less, the interference was suppressed. Their proposed method was made important contributions to the quality control of petroleum refineries.



Sasaki et al <sup>(65)</sup> described a procedure for direct determination of V, Ni and Na in crud oil and petroleum fraction based on GFAAS with suitable dilution by organic solvent.

Matousek et al <sup>(66)</sup> have determinate Ag, Cu and Ni in lubricating oils directly using AAS methods at 338.3 nm, 324.8, and 232 nm for Ag, Cu, and Ni, respectively with relative standard deviation of 4%.

McKenzie et al. <sup>(43)</sup> method of direct aspiration of an oil sample was employed for determination of Al, Fe, Cr, Cu, and Si in a sample of used oil from a bulldozer (SEOCD) by dilution with xylene-MIBK mixture. Organometallic compound containing analyte metals in unused oil sample was obtained as a convenient stock standard made up in oil. The viscosity of the samples and standards on dilution were found to be similar when a 1:4 dilution was used. The concentration of Cu, Fe, Al, Si, and Cr was found to be 1.91, 14.1, 6.9, 5.4 and 1.6 respectively

An analytical method for the particle size independent determination of Al, Cr, Fe, Mg, Mo, Ni, Pb, Si, Sn, Ti, and Zn in lubricating oil and hydraulic fluids by atomic emission spectroscopy and atomic absorption spectrophotometry. Improved analysis of Ag, Cd, and Na. metal powder suspension in hydraulic fluids and lubricating oils were reacted with a small amount of an acid mixture containing hydrofluoric, nitric, and hydrochloric acid and analyzed by a DCP emission spectrometer. The recoveries of Al, Cr, Fe, Mg, Mo, Ni, Pb, Si, Sn, Ti, and Zn ranged from 89% to 102% with relative standard deviations from 2% to 12%. In addition to the metal powder suspension, aircraft, automobile, and diesel truck engine oils and aircraft hydrochloric fluids were analyzed by AES and AAS <sup>(67)</sup>.

A method for analysis of Barium, Calcium, Magnesium, and Zinc in unused lubricating oils by AAS was discussed in ASTM D4628-02<sup>(68)</sup> in that method analysis can be applicable for the determination of mass percent Ba from 0.005 to 1% Ca and Mg from 0.002 to 0.3% and Zn from 0.002 to 0.2%. Another method for Determination of 22 elements in wear metals, additive elements, and contaminants in used lubricating and base oils by ICP-AES was discussed in ASTM D5185-02.<sup>(69)</sup> The detestability for most elements was in the low mg/kg range. The viscosity effects was reduced by using peristaltic pump to deliver solutions to nebulizer or by the use of internal standardization.

### ***1-6-2 Molecular Absorption Spectrophotometry***

Ultraviolet-Visible Molecular Absorption Spectrophotometry has a long and continuing history of use in analytical chemistry. This technique is based on measuring the absorption near-UV or visible radiation by molecules. Radiation in this wavelength region causes electronic transitions at wavelength characteristic of the molecular structure of this molecule.<sup>(56)</sup>

The simultaneous determination of Fe, Co, and Cu was carried out as 1-nitroso-2-naphol complex in presence of aqueous solution of nonionic surfactant of Triton-X100. A partial least- squares multivariate calibration method for the analysis of ternary mixture of Fe, Co, and Cu was developed. The total relative standard error for applying the method on synthetic samples was 2.02%. The proposed method was also successfully applied to the determination of Fe, Co, and Cu in several synthetic alloy solutions<sup>(70)</sup>.

Zenovia and Eleonora<sup>(71)</sup> were determined of Fe<sup>+3</sup> as a Fe<sup>+2</sup> o-phenanthroline complex in natural water by spectrophotometer at 520nm, after preconcentration of the trace amount of Fe<sup>+3</sup> by a strong base anion-exchange resin (Dowex 2x4) that loaded with ferron (7-iodo-8-hydroxyquinoline-5-sulfonic acid at pH=2.2. The sensitivity of the method (after preconcentration) was 0.01µgFe<sup>+3</sup>/ml with recovery of Fe<sup>3</sup> at 7µg/l was 97%.

Quinolinol was immobilized on silica surface for enrichment of trace metal ions like Cu<sup>+2</sup>, Ni<sup>+2</sup>, Co<sup>+2</sup>, Fe<sup>+3</sup>, Cr<sup>+3</sup>, Mn<sup>+2</sup>, Zn<sup>+2</sup>, Cd<sup>+2</sup>, Pb<sup>+2</sup>, and Hg<sup>+2</sup> in the pH range 4–6. Metal uptake capacity was found in the range 0.2–0.7 mmol g<sup>-1</sup> (72).

Goswami et al<sup>(73)</sup>. reported the optimum pH ranges for transition metal separation by 8-hydroxyquinoline on modified silica from aqueous mixture are 4.0–7.0 for Cu<sup>+2</sup> and Cd<sup>+2</sup>, 4.5–7.0 for Pb<sup>+2</sup>, 3.0–6.0 for Fe<sup>+3</sup>, 5.0–8.0 for Zn<sup>+2</sup> and Co<sup>+2</sup> and 6.0–8.0 for Ni<sup>+2</sup>. They found the sorption capacity of the modified silica to be in the range 92–448 µmol g<sup>-1</sup>.

## ***1-7 Aim of the work***

The purpose of this work is mainly concern with qualitative and quantitative determination of wear metals that exist in used lubricating oil after operating for different distances. The quantification of trace elements in used lubricating oil is useful for evaluating the wearing of specific component of engine.

## Results and discussion

### *3-1 Qualitative analyses*

Classical methods of identification<sup>(41, 74,75)</sup> were used for analyzing of the wear metal in lubricating oil samples (AVII and B VII'). The aqueous layer that obtained from digestion of the oil samples was found to have a relatively large quantities of Fe, Cu, Pb and Al.

### *3-2 Quantitative analysis*

Calibration curves for the identified metals ion were constructed by UV-vis spectrophotometer for study of the digestion time of the oil samples and determination of wear metals concentration in each oil sample. The constructed curves by FAAS were employed for determination of wear metals (Fe, Cu and Pb).

#### *3-2-1 Analysis by UV-vis spectrophotometer*

##### *3-2-1-1 Lead*

The absorption measurements of the colored complex that formed by extraction of  $Pb^{+2}$  with dithizone reagent fig 3-1 showed that the maximum absorption occurs at 520nm while the maximum absorption of dithizone solution occur at 620nm<sup>(76)</sup>.

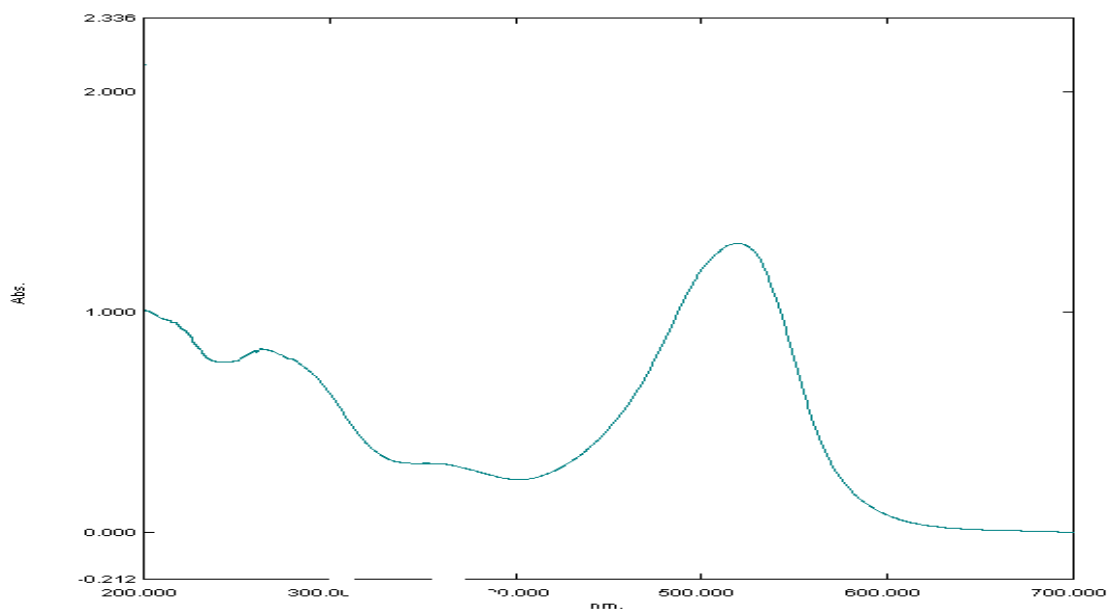


Figure 3-1 Absorption spectrum of lead dithizonate complex

The absorption measurements at 520nm of a mixtures consisted of fixed concentration of dithizone reagent and different concentration of  $Pb^{+2}$  at pH=8.5 were tabulated in table (3-1).

Table 3-1 Absorption measurement for a different mole ratio between  $Pb^{+2}$  and  $H_2Dz$

Mole ratio $Pb^{+2}/H_2Dz$	Absorbance at 520nm
0.1	0.147
0.2	0.3
0.3	0.467
0.4	0.593
0.5	0.756
0.6	0.762
0.7	0.765
0.8	0.763
0.9	0.769
1	0.761

Fig 3-2 shows absorbance at varied mole ratio of the reactants. The two straight line of a different slope were obtained and the intersection occur when the mole ratio was (1/2) that corresponded to the mole ratio between  $Pb^{+2}$  and legand of the complex. This value was agreement with literature(76).

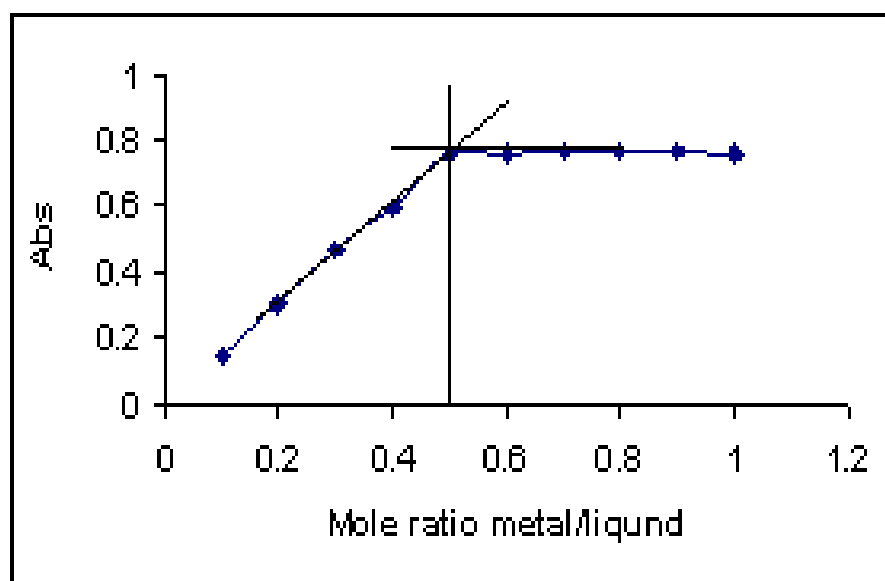


Figure 3-2 Mole ratio plot of  $Pb^{+2}$  with  $H_2Dz$

A lead standard solution was complexed with dithizone reagent in  $CCl_4$  solution. The calibration curve was constructed from (0.061 to 10.0) ppm using 520nm as a measuring wavelength.

A linear calibration curve was obtained as shown in fig 3-3 with a line equation 3-1

$$Y = 0.2576X - 0.0043 \quad \text{----- (3-1)}$$

Where Y represents the absorbance value and X represents the concentration of  $Pb^{+2}$  in ppm.

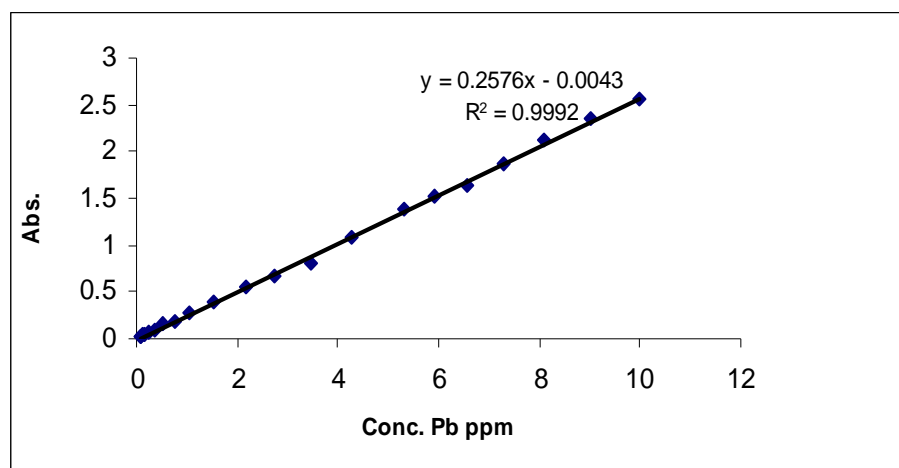


Figure 3-3 Calibration curve of  $\text{Pb}^{+2}$  ppm that measured by UV-visible spectrophotometer

The correlation coefficient for the above line was 0.9992

The recovery of above curve was estimated using freshly prepared standard solution of lead and the results were listed in table 3-2

Table 3-2 Lead recovery study

Concentration of lead in ppm (mg/L)		Recovery %	Relative error %
Prepared	Founded		
5.00	4.999	99.99	0.02
10.00	9.998	99.98	0.02
25.00	24.987	99.95	0.05

The recovery of the lead concentrations was found 99.99 % for the 5.00 ppm and the Relative error % was 0.02% .While the value of the



Relative error % for high concentration (25.00 ppm) was 0.05% and the recovery was 99.95%.

### 3-2-1-2 Copper

The absorption spectrum of copper dithizonate complex showed that the maximum absorption occurs at 550nm as shown in fig 3-4

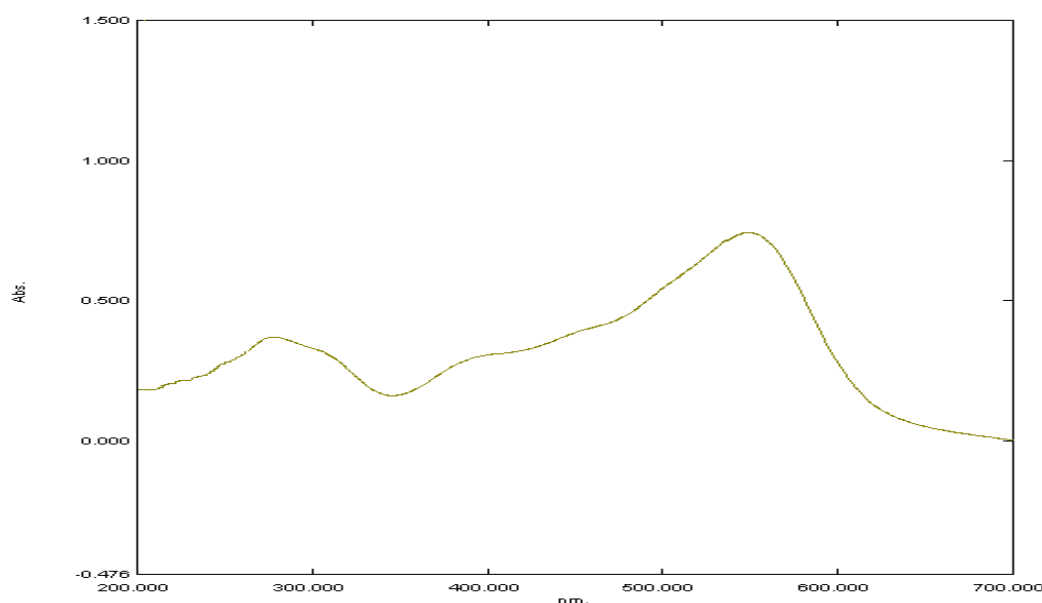


Figure 3-4 Absorption spectrum of copper dithizonate complex

The measurements of absorption at 550nm of a mixtures consisted of fixed concentration of dithizone reagent and different concentration of  $\text{Cu}^{+2}$  at pH=3 were tabulated in table 3-3.

Table 3-3 Absorption measurement of different mole ratio of  $\text{Cu}^{+2}$  with  $\text{H}_2\text{Dz}$

<b>Mole ratio <math>\text{Cu}^{+2}/\text{H}_2\text{Dz}</math></b>	<b>Absorbance at 550nm</b>
<b>0.1</b>	<b>0.23</b>
<b>0.2</b>	<b>0.518</b>
<b>0.3</b>	<b>0.722</b>
<b>0.4</b>	<b>1.009</b>
<b>0.5</b>	<b>1.227</b>
<b>0.6</b>	<b>1.231</b>
<b>0.7</b>	<b>1.239</b>
<b>0.8</b>	<b>1.229</b>
<b>0.9</b>	<b>1.25</b>
<b>1</b>	<b>1.233</b>

The absorption curve as shown in fig 3-5 was obtained when the absorbance plotted against varied mole ratio of the reactants. Two straight lines of a different slope were obtained and the intersection occur when the mole ratio was (1/2) that corresponded to the mole ratio between,  $\text{Cu}^{+2}$  and legand of the complex. The obtained value was in agreement with literature (76).

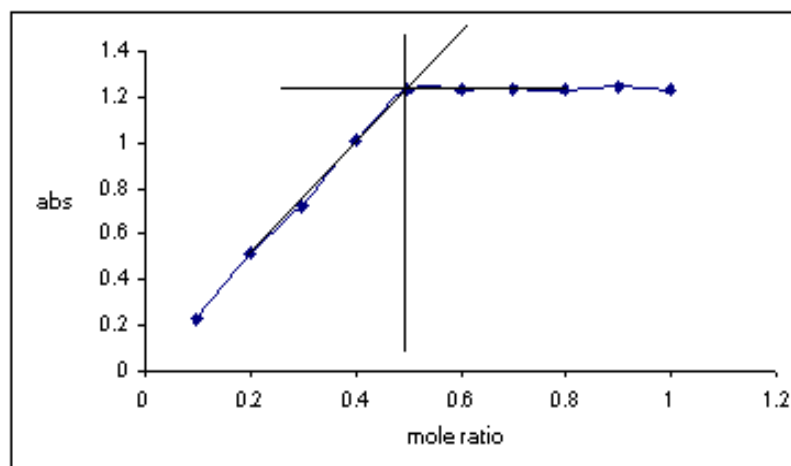


Figure 3-5 Mole ratio plot of  $\text{Cu}^{+2}$  with  $\text{H}_2\text{Dz}$

A copper standard solution was complexed with dithizone reagent in  $\text{CCl}_4$  solution. The calibration curve was constructed from (0.52 to 7) ppm using 550nm as a measuring wavelength.

A linear calibration curve as shown in fig 3-6 was obtained with a line equation 3-2

$$Y = 0.4027X + 0.0252 \quad \text{-----} \quad (3-2)$$

Where Y represents the absorbance value and X represents the concentration of  $\text{Cu}^{+2}$  in ppm.

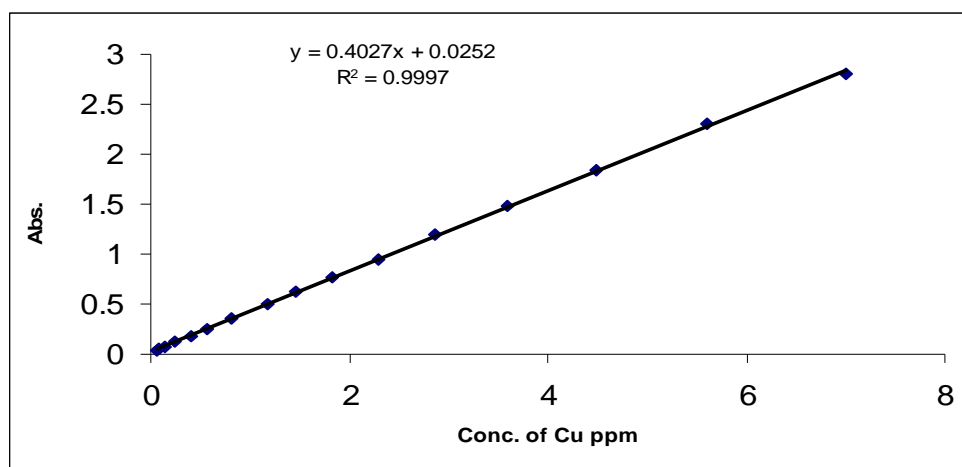


Figure 3-6 Calibration curve for lead that measured by UV-visible spectrophotometer

The correlation coefficient for the above line was 0.9997.

The recovery of above curve was tested using freshly prepared standard solutions of lead and the obtained results was listed in table 3-4

Table 3-4 Copper recovery study

Concentration of copper ppm (mg/L)		Recovery %	Relative error %
Prepared	Founded		
5.00	4.998	99.97	0.03
10.00	10.002	100.02	-0.02
25.00	24.998	99.99	0.01

The recovery of the copper concentrations was found 99.97 % for the 5.00 ppm and the Relative error % was 0.03 .While the value of the Relative error % for high concentration (25.00 ppm) was 0.01% and the recovery was 99.99%.

### 3-2-2-3 Aluminum

The absorption spectrum that shown in fig 3-7 for the colored complex that result from mixing  $Al^{+3}$  with aluminon reagent. The spectrum shows a that maximum absorbances occur at 343 nm and 520nm while for aluminon was 319nm and 524nm .

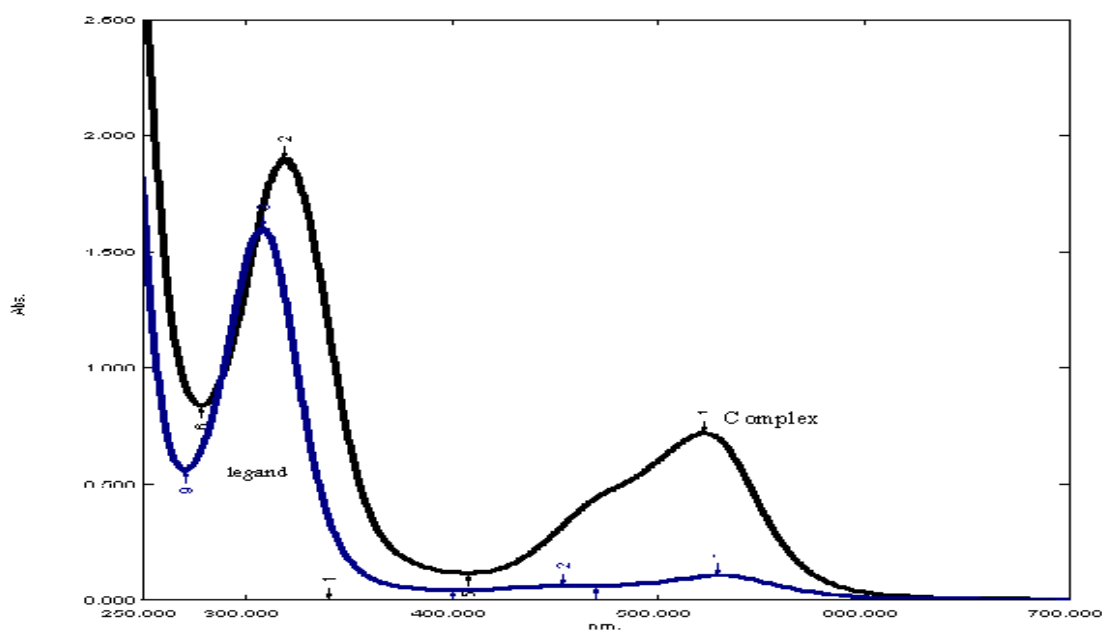


Figure 3-7 Absorption spectrum of aluminum complex

the absorption of aluminum complex was studied at different pH as shown in fig 3-8. The results show that maximum absorption occur at pH=4.25. The obtained value was Closed to the reported value in literature (76)

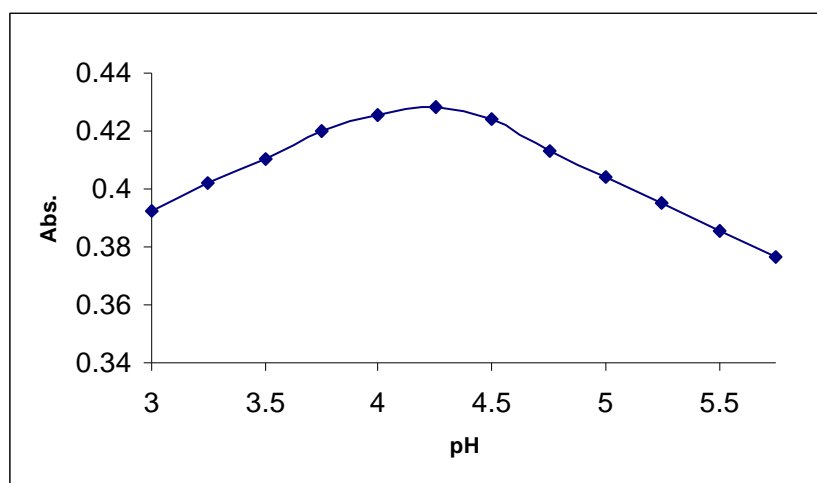


Figure 3-8 Effect of pH on absorption of aluminum complex

The measurements of absorption at 520nm of a mixtures consisted of fixed concentration of aluminon reagent and different concentration of  $Al^{+3}$  at pH=4.25 were tabulated in table (3-8).

Table 3-5 Absorption measurement of different mole ratio of  $Al^{+3}$  with aluminon

<b>Mole ratio <math>Al^{+3}</math>/aluminon</b>	<b>Absorbance at 520nm</b>
<b>0.088</b>	<b>0.131</b>
<b>0.168</b>	<b>0.23</b>
<b>0.25</b>	<b>0.33</b>
<b>0.416</b>	<b>0.416</b>
<b>0.5</b>	<b>0.42</b>
<b>0.583</b>	<b>0.421</b>
<b>0.666</b>	<b>0.42</b>
<b>0.75</b>	<b>0.424</b>

The absorption curve in fig 3-9 was obtained when the absorbance plotted against varied mole ratio of the reactants. Two straight lines of a different slope were obtained and the intersection occurs when the mole ratio was (0.333) that corresponded to the mole ratio of the complex. This value was agreement with literature (76).

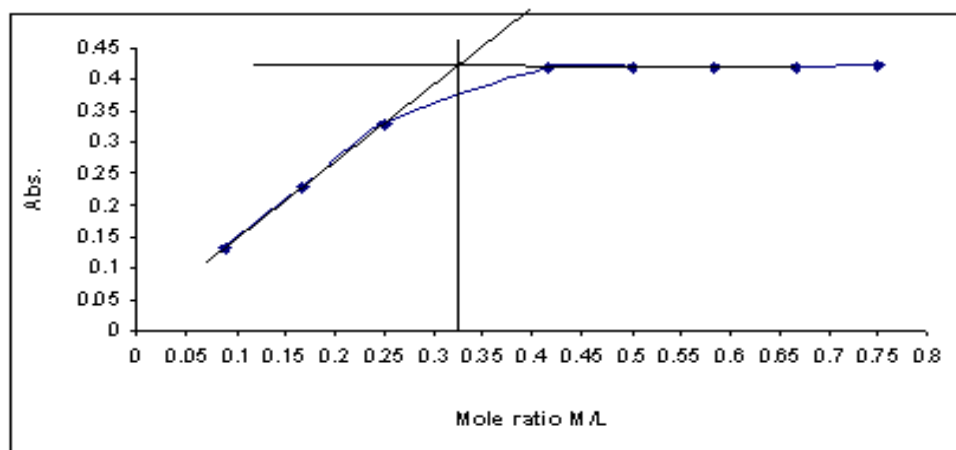


Figure 3-9 Mole ratio plot of  $\text{Al}^{+3}$  with aluminon reagent

A calibration curve was constructed of aluminum standard solution with aluminon reagent. The curve gave a linear range from (0.19-10) ppm. The measurements were carried out at 520 nm as absorption wavelength for the complex as shown in fig 3-10, while the line equation was

$$Y = 0.1893X + 0.0351 \text{ ----- (3-3)}$$

Where Y represents the absorbance value and X represents the concentration of aluminum in ppm.

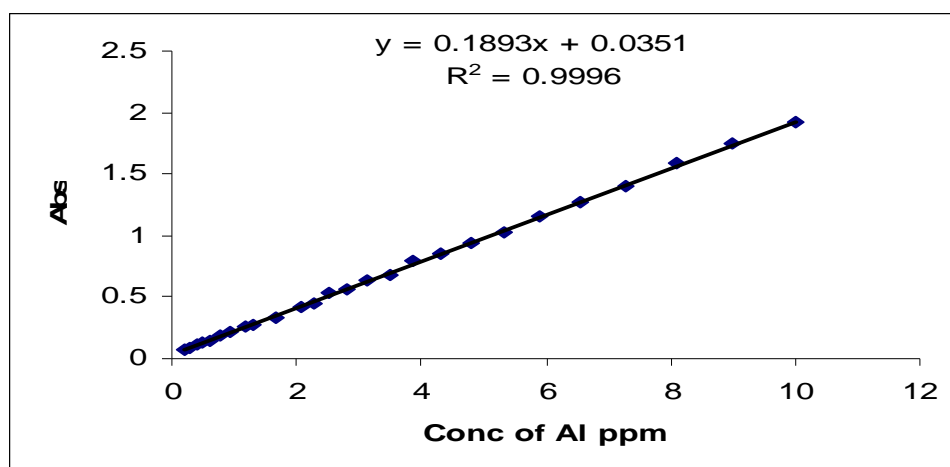


Figure 3-10 Calibration curve of  $\text{Al}^{+3}$  complex that measured by UV-vis spectrophotometer

The correlation coefficient for the above line was 0.9996. The recovery are tested and the results was listed in table 3-6.

Table 3-6 Aluminum recovery study

Concentration of aluminum in ppm (mg/L)		Recovery %	Relative error %
Prepared	Found		
5	5.06	101.2	-1.2
10	10.02	100.2	-0.2
25	25.1	100.4	-0.4

The above table shows that recovery of aluminum standard (5, 10 and 25 ppm) was found to be 101.2%, 100.23% and 100.4% while the Relative error % was -1.2%, -1.9%, and -0.4% respectively.

### 3-2-1-4 Iron

The absorption spectrum shown in Fig 3-11 was obtained for red complex that resulted from mixing  $\text{Fe}^{+3}$  with ammonium thiocyanate reagent in acid media shows maximum absorption occur at 480nm.

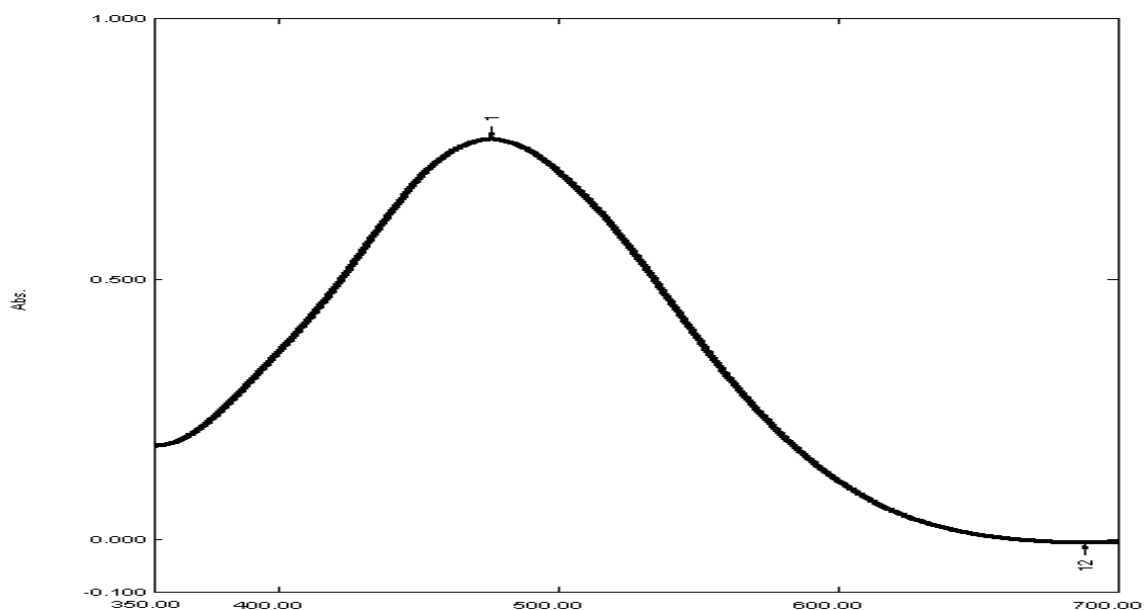


Figure 3-11 Absorption spectrum of iron thiocyanate complex



The absorption of iron thiocyanate complex was studied at different concentration of nitric acid as shown in fig 3-12 the result show that maximum absorption occur when the concentration of  $\text{HNO}_3$  was in the range 0.9-1.5M. The obtained range was in agreement with literature(76).

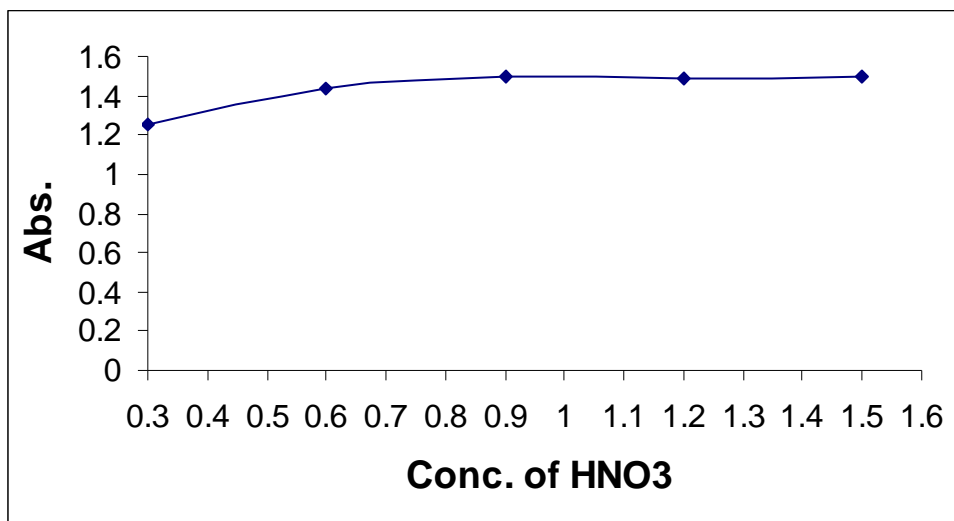


Figure 3-12 Effect of acid concentration on absorption

A calibration curve of iron standard solution was prepared by complexing iron with ammonium thiocyanate reagent. The curve was constructed from (0.016-10) ppm. These measurements were carried at  $\lambda_{\text{max}} = 480\text{nm}$  as the absorption wavelength for the complex.

A linear calibration curve was obtained as shown in fig 3-13 with a line equation

$$Y = 0.1422 X + 0.1034 \text{ ----- (3-4)}$$

Where Y represents the absorbance value and X represents the concentration of iron complex in ppm.

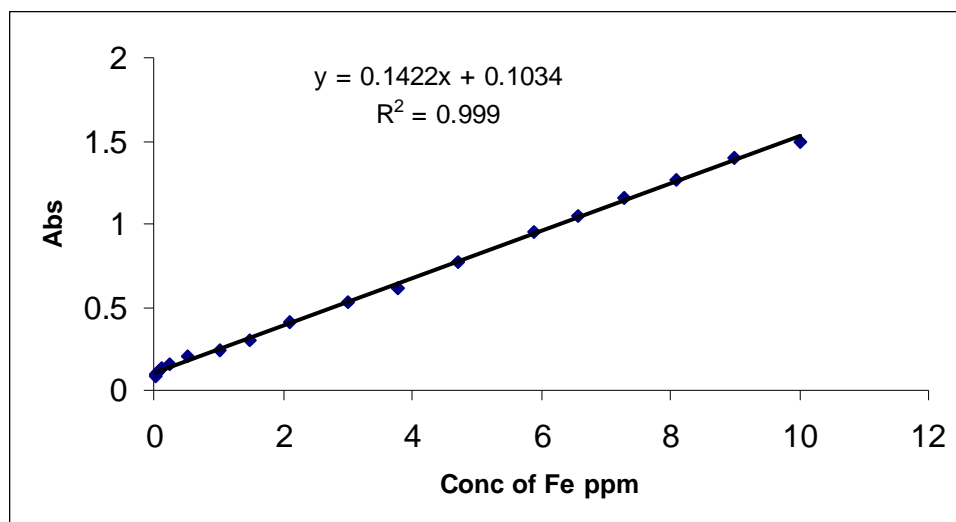


Figure 3-13 Calibration curve for  $\text{Fe}^{+3}$  complex

The correlation coefficient for the above line was 0.9990.

The above calibration curve was tested using freshly prepared standard solutions of iron to measure the recovery; the study results were listed in table 3-7

Table 3-7 Iron recovery study

Concentration of iron in ppm(mg/L)		Recovery %	Relative Error %
Prepared	Found		
5.00	4.99	99.94	0.06
10.00	9.91	99.91	0.90
25.00	24.99	99.98	0.02

The Recovery % of the iron standard solution was found 99.91 % for 10.00 ppm solution, with the relative error of 0.90 %. While the relative error for high concentration 25 ppm was 0.02 %, with recovery% of 99.98%.

### 3-2-1-5 Time effects on samples digestion

The determination of extracted metal ions at a different digestion time showed that 2.5 hours was a suitable time for the digestion of the oil samples as shown in fig 3-14a and 3-14b.

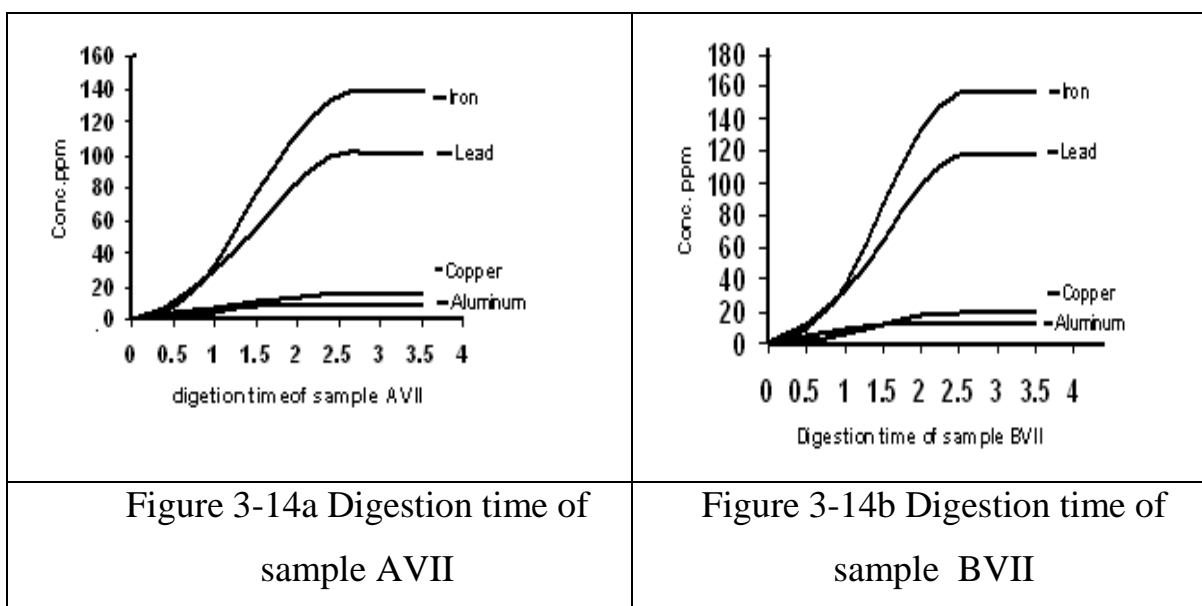


Fig 3-14a and 3-14b showed that the concentration of extracted metals ion from the oil samples increase with an increase of digestion time up to 2.5 hours.

### 3-2-1-5 Isolation of metal ions from the samples and determination by UV-visible spectrophotometer

Iron was quantitatively separated from the sample with diethyl ether in 6M HCl so as to protect the oxidation reduction that occur between dithizone reagent and  $Fe^{+3}$ . The extracted diethyl ether was mixed with deionized water and heated in order to evaporate the organic layer. The remained aqueous layer was treated with equal volume of

0.6M ammonium thiocyanate that prepared in 2M HNO<sub>3</sub>. The absorption was measured at 480nm and the concentration of Fe<sup>+3</sup> was calculating using equation 3-4. The result of measurement was listed in table 3-8a and 3-8b.

Table 3-8a Concentration of Fe<sup>+3</sup> ppm that measured by UV-vis spectrophotometer in sample A.

Sample A	Operating Distance Km	Conc. Ppm	Change of metal conc.
AI	0	1.47	-
AII	500	16.133	14.663
AIII	1000	31.346	15.213
AIV	1500	47.767	16.421
AV	2000	67.872	20.105
AVI	2500	96.351	28.479
AVII	3000	136.470	40.119

Table 3-8b Concentration of Fe<sup>+3</sup> ppm that measured by UV-vis spectrophotometer in sample B.

Sample B	Operating Distance Km	Conc. ppm	Change of metal conc.
BI'	0	1.420	-
BII'	500	17.627	16.207
B III'	1000	34.261	16.634
BIV'	1500	52.426	18.166
BV'	2000	74.792	22.365
BVI'	2500	106.314	31.522
BVII'	3000	155.397	49.083

After separation of iron from the sample, the pH of the remained aqueous layer was adjusted to 3 and shaken with an equal volume of  $3.174 \times 10^{-5}$  M dithizone reagent in order to quantitatively extract of copper ion. The extraction was repeated until no change occurs in the organic layer. The absorption was measured for the extracted organic layer at 550nm. The concentration of Cu was calculated using equation 3-2 and the results are tabulated in table 3-9a and 3-9b.

Table 3-9a Concentration of  $\text{Cu}^{+2}$  ppm that measured by UV-vis spectrophotometer in sample A

<b>Sample A</b>	<b>Operating Distance Km</b>	<b>Conc. ppm</b>	<b>Change of metal conc.</b>
<b>AI</b>	<b>0</b>	<b>0.715</b>	<b>-</b>
<b>AII</b>	<b>500</b>	<b>1.505</b>	<b>0.79</b>
<b>AIII</b>	<b>1000</b>	<b>2.805</b>	<b>1.300</b>
<b>AIV</b>	<b>1500</b>	<b>4.382</b>	<b>1.577</b>
<b>AV</b>	<b>2000</b>	<b>6.625</b>	<b>2.243</b>
<b>AVI</b>	<b>2500</b>	<b>9.958</b>	<b>3.333</b>
<b>AVII</b>	<b>3000</b>	<b>15.164</b>	<b>5.206</b>

Table 3-9b Concentration of  $\text{Cu}^{+2}$  ppm that measured by  
UV-vis spectrophotometer in the sample B

<b>Sample B</b>	<b>Operating Distance Km</b>	<b>Conc. Ppm</b>	<b>Change of metal conc.</b>
<b>BI'</b>	<b>0</b>	<b>0.743</b>	<b>-</b>
<b>BII'</b>	<b>500</b>	<b>1.655</b>	<b>0.912</b>
<b>BIII'</b>	<b>1000</b>	<b>3.074</b>	<b>1.419</b>
<b>BIV'</b>	<b>1500</b>	<b>4.916</b>	<b>1.842</b>
<b>BV'</b>	<b>2000</b>	<b>7.601</b>	<b>2.685</b>
<b>BVI'</b>	<b>2500</b>	<b>11.705</b>	<b>4.104</b>
<b>BVII'</b>	<b>3000</b>	<b>19.469</b>	<b>7.764</b>

The pH of samples was adjusted to be 4.25 in order to measured the concentration of aluminum after treated with aluminon reagent in order to prepare a collared complex. The absorbance was measured at 520nm and the equation 3-3 was employed to calculate the concentration of  $\text{Al}^{+3}$  and the results are tabulated in table 3-10a and 3-10b.

Table 3-10a Concentration of  $\text{Al}^{+3}$  ppm that measured  
by UV-vis spectrophotometer in sample A

<b>Sample number</b>	<b>Operating Distance Km</b>	<b>Conc. ppm</b>	<b>Change of metal conc.</b>
<b>AI</b>	<b>0</b>	<b>nd</b>	<b>-</b>
<b>AII</b>	<b>500</b>	<b>0.979</b>	<b>0.979</b>
<b>AIII</b>	<b>1000</b>	<b>1.854</b>	<b>0.875</b>
<b>AIV</b>	<b>1500</b>	<b>2.802</b>	<b>0.948</b>
<b>AV</b>	<b>2000</b>	<b>3.989</b>	<b>1.187</b>
<b>AVI</b>	<b>2500</b>	<b>5.640</b>	<b>1.651</b>
<b>AVII</b>	<b>3000</b>	<b>8.071</b>	<b>2.431</b>

Table 3-10b Concentration of  $Al^{+3}$  ppm that measured  
by UV-vis spectrophotometer in sample B

Sample B	Operating Distance Km	Conc. ppm	Change of metal conc.
BI'	0	nd	-
BII'	500	1.101	1.101
BIII'	1000	2.273	1.172
BIV'	1500	3.254	0.981
BV'	2000	5.198	1.944
BVI'	2500	8.462	3.264
BVII'	3000	12.299	3.837

Finally lead was quantitatively extracted from the sample with dithizone reagent at pH=8.5. the extraction was stopped as soon as the color was not change. The absorbance was measured for the organic layer at 520nm. The concentration was calculated using equation 3-1 and the results were listed in table 3-11a and 3-11b.

Table 3-11a Concentration of  $Pb^{+2}$  ppm that measured  
by UV-vis spectrophotometer in sample A

Sample A	Operating Distance Km	Conc. ppm	Change of metal conc.
AI	0	0.691	-
AII	500	18.061	17.370
AIII	1000	34.112	16.051
AIV	1500	53.735	19.623
AV	2000	68.952	15.217
AVI	2500	86.450	17.498
AVII	3000	100.88	14.430

Table 3-11b Concentration of  $Pb^{+2}$  ppm that measured by  
UV-vis spectrophotometer in sample B

<b>Sample number</b>	<b>Operating Distance Km</b>	<b>Conc. ppm</b>	<b>Change of metal conc.</b>
<b>BI'</b>	<b>0</b>	<b>0.895</b>	<b>-</b>
<b>BII'</b>	<b>500</b>	<b>17.984</b>	<b>17.089</b>
<b>BIII'</b>	<b>1000</b>	<b>36.623</b>	<b>21.339</b>
<b>BIV'</b>	<b>1500</b>	<b>59.908</b>	<b>23.285</b>
<b>BV'</b>	<b>2000</b>	<b>77.293</b>	<b>17.385</b>
<b>BVI'</b>	<b>2500</b>	<b>95.178</b>	<b>17.885</b>
<b>BVII'</b>	<b>3000</b>	<b>116.581</b>	<b>21.403</b>

Table 3-8a show that the concentration of iron were increased from 1.47 to 136.470 ppm in sample A (first run), while the concentration of iron in sample B (second run) were increased from 1.420 to 155.397 ppm as showed in table 3-8b during operation from 0 to 3000Km.

Table 3-9a show that the concentration of copper were ringed from 0.715 to 15.164 ppm in sample A (first run), while table 3-9b show that concentration of copper in sample B (second run) were ringed from 0.743 to 19.469 ppm during operation from 0 to 3000Km.

Table 3-10a show that the concentration of aluminum were ringed from 0 to 8.071 ppm in sample A (first run), while the concentration of aluminum in sample B (second run) were increased from 0 to 12.229 ppm as showed in table 3-10b during operation from 0 to 3000Km.

Table 3-11a show that the concentration of lead were increased from 0.691 to 100.88 ppm in sample A (first run), while table 3-11b show that concentration of lead in sample B (second run) were increased from 0.895 to 116.581 ppm during operation from 0 to 3000Km.



Figure (3-15a and 3-15b) show that the concentration of wear iron which was found to increase directly with an increasing the operating distance. The increased concentration of iron may be resulted from the friction that occur between engine components, (Cam Shaft, Crankshaft, Cylinder Walls, Exhaust Valve, Anti-Friction Bearing, Housing/Castings, , Pistons, Rings Timing Gears, Valve Guides, Valve Train and Wrist Pins)<sup>(18)</sup>.

The subsequent increases of the change of iron concentration in a sequence operating distance may be result from the change of physical and chemical properties of the employed lubricating oil especially viscosity, oiliness and/or acidity (TAN)<sup>(18)</sup>.

In the other hand the change of iron concentration in sample A was smaller than the change of iron concentration in sample B during operating distance. This fact reflect that friction was increased in the second run (sample B) during the operation of the car engine.

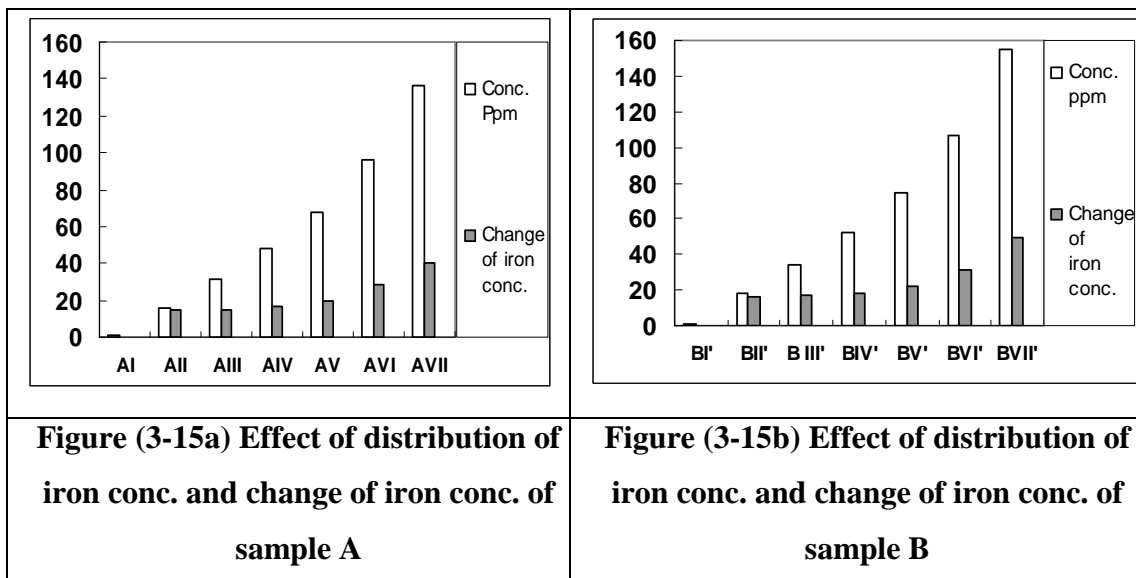


Fig (3-16a and 3-16b) show that the concentration of lead were increase directly with an increase of operating distance. The increase of lead concentration may be result from the friction between engine's

component (Journal Bearings, Bushings, Bushing, Thrust Washers and Wrist Pin-Bushings) or from tetraethyl lead (Gasoline Additive)<sup>(1)</sup>. The random values that resulted from the change in lead concentration could be attributed to the fuel additive.

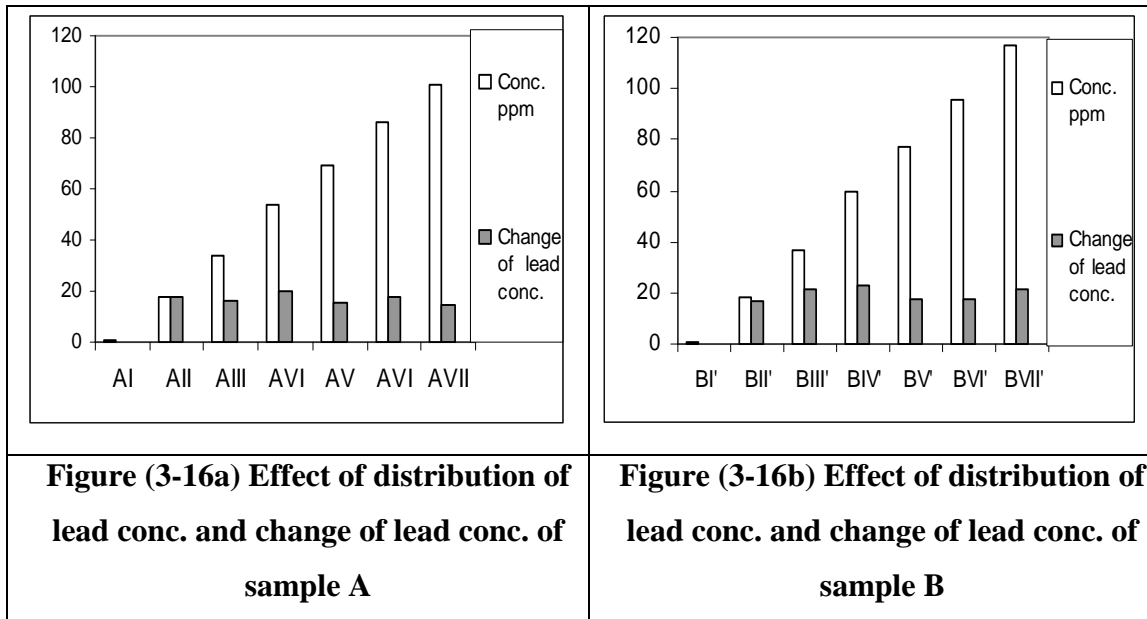


Fig 3-17a and 3-17b show that there were a small increase of aluminum with increased operating distance in the oil samples. The increase of aluminum concentration in each oil samples may be resulted from the friction that occur between engine's component with higher percent of aluminum. Table 1-1 show the engine's component that responsible for wear of aluminum in the used oil samples.

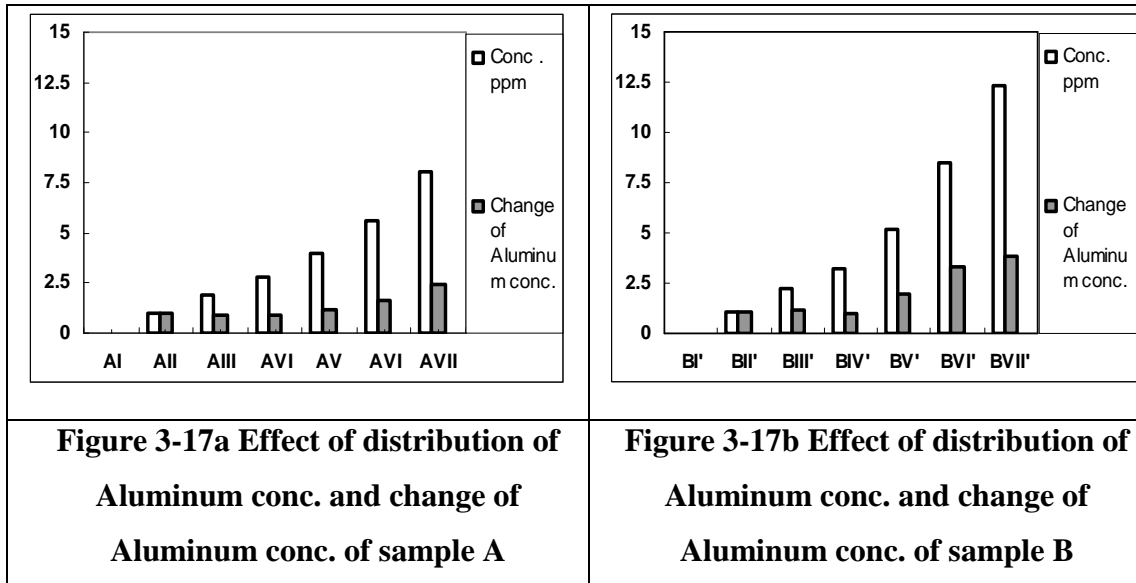
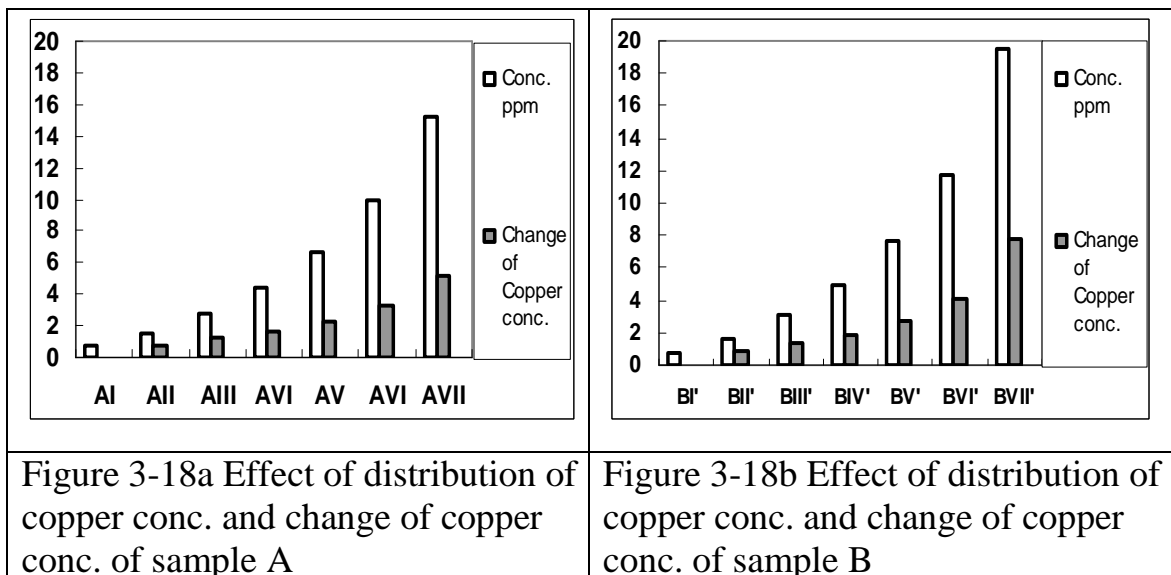


Fig 3-18a and 3-18b show that the existence of copper in the used oil may be resulted from the friction between the component Journal Bearings, Bushings, Gasket Materials, Oil Cooler, Bushing, Thrust Washers, Valve Guides and/or Wrist Pin-Bushings



### 3-2-2 Analysis by flame atomic absorption

#### 3-2-2-1 Iron

A calibration curve was constructed for iron using 0.2-10ppm standard solutions and employing 248.3nm as a measuring wavelength. A linear curve was obtained as shown in fig 3-19 with a line equation of

$$y = 0.0768x + 0.0215 \quad \dots\dots\dots (3-5)$$

Where y represents the absorbance value and x represents the concentration of iron. The correlation coefficient was 0.9997.

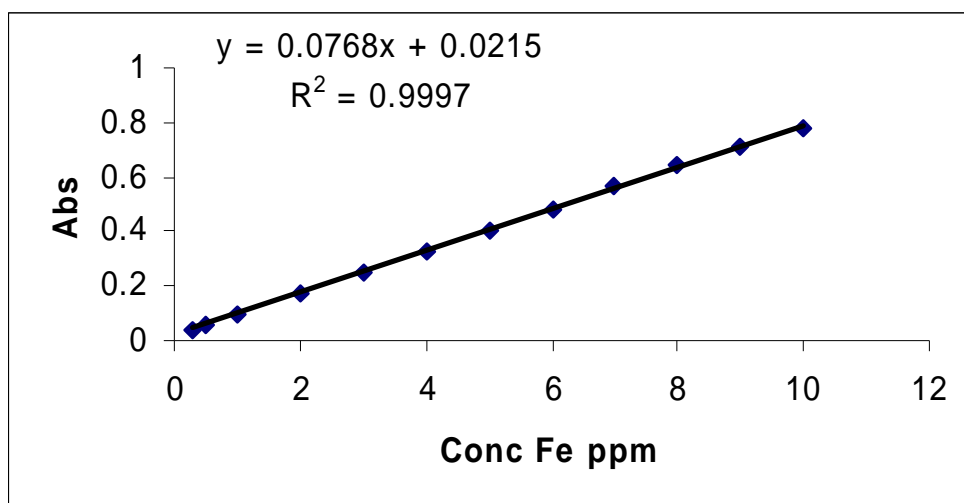


Figure 3-19 Calibration curve of iron measured by AAS

### 3-2-2-2 Lead

Another calibration curve was constructed for lead employing 217.0nm as a measuring wavelength for the metal.

A linear calibration line was obtained extended from 0.2-10ppm, as shown in fig 3-20 with a line equation of

$$y=0.2261x+0.0097 \dots\dots\dots (3-6)$$

Where y represents the absorbance value and x represents the Concentration of lead.

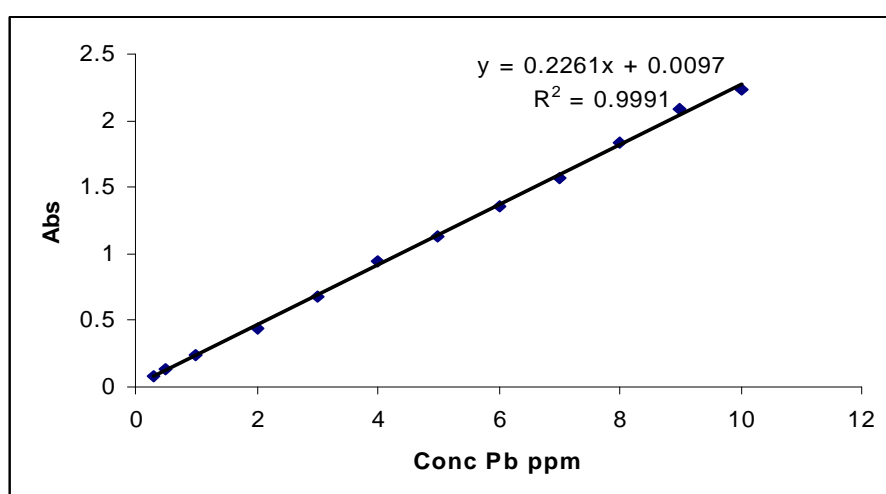


Figure 3-20 Calibration curve of lead measured by AAS

The correlation coefficient for this line was 0.9991.

### 3-2-2-3 copper

A calibration curve was constructed for copper using 0.2-10 ppm standard solutions and employing 324.8nm as a measuring wavelength. A linear curve was obtained as shown in fig 3-21 with a line equation of

$$y=0.0792x+ 0.0646 \dots\dots\dots (3-7)$$

Where y represents the absorbance value and x represents the concentration of copper. The correlation coefficient was 0.9991

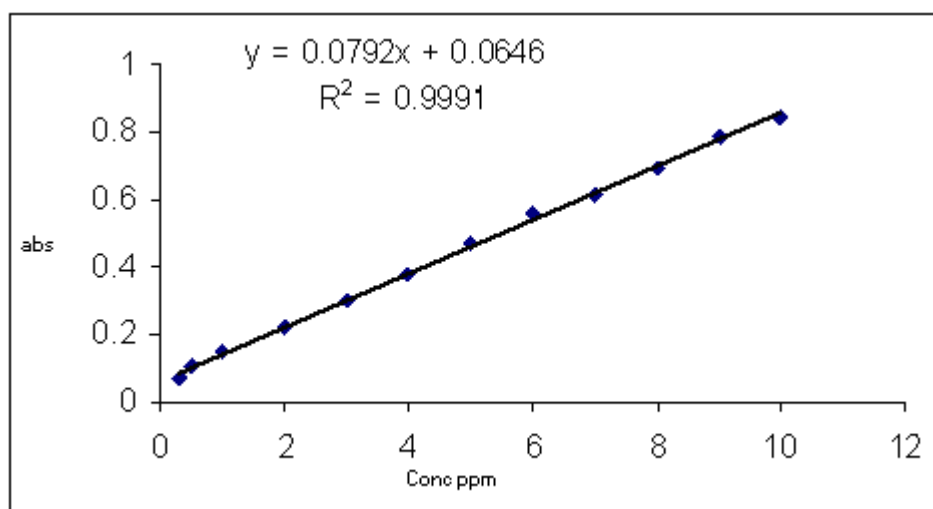


Figure 3-21 Calibration curve of copper measured by AAS

The concentration of iron in different oil sample was measured by FAAS using equation (3-5) and the results are tabulated in table (3-12).

Table 3-12 Concentration of Fe ppm that measured by FAAS of the oil samples (A and B)

Sample Number	Operating Distance Km	Conc. Ppm
<b>AI/BI'</b>	<b>0</b>	<b>1.516/1.461</b>
<b>AII/ BII'</b>	<b>500</b>	<b>16.547/18.210</b>
<b>AIII/ B III'</b>	<b>1000</b>	<b>32.069/34.920</b>
<b>AIV/ BIV'</b>	<b>1500</b>	<b>49.214/53.503</b>
<b>AV/ BV'</b>	<b>2000</b>	<b>69.218/76.145</b>
<b>AVI/ BVI'</b>	<b>2500</b>	<b>98.875/108.626</b>
<b>AVII/ BVII'</b>	<b>3000</b>	<b>139.056/158.568</b>

The concentration of lead in different oil sample was measured by FAAS using equation (3-6) and the results were tabulated in Table (3-13).

Table 3-13 Concentration of Pb ppm that measured by FAAS of the oil samples (A and B)

<b>Sample number</b>	<b>Operating Distance Km</b>	<b>Conc. Ppm</b>
<b>AI/ BI'</b>	<b>0</b>	<b>0.712/0.908</b>
<b>AII/ BII'</b>	<b>500</b>	<b>18.591/18.548</b>
<b>AIII/ BIII'</b>	<b>1000</b>	<b>34.672/37.796</b>
<b>AVI/ BIV'</b>	<b>1500</b>	<b>55.289/61.843</b>
<b>AV/ BV'</b>	<b>2000</b>	<b>70.605/78.782</b>
<b>AVI/ BVI'</b>	<b>2500</b>	<b>88.801/98.606</b>
<b>AVII/ BVII'</b>	<b>3000</b>	<b>104.419/120.045</b>

The concentration of copper in different oil sample was measured by AAS using equation (3-7) and the result were tabulated in table (3-14)

Table 3-14 Concentration of Cu that measured by FAAS of the oil samples (A and B)

<b>Sample number</b>	<b>Operating Distance Km</b>	<b>ppm</b>
<b>AI/ BI'</b>	<b>0</b>	<b>0.722/0.761</b>
<b>AII/ BII'</b>	<b>500</b>	<b>1.529/1.682</b>
<b>AIII/ BIII'</b>	<b>1000</b>	<b>2.846/3.141</b>
<b>AIV/ BIV'</b>	<b>1500</b>	<b>4.440/5.010</b>
<b>AV/ BV'</b>	<b>2000</b>	<b>6.773/7.739</b>
<b>AVI/ BVI'</b>	<b>2500</b>	<b>10.087/11.808</b>
<b>AVII/ BVII'</b>	<b>3000</b>	<b>15.329/19.716</b>

### 3-3 Study of interferences between metal ion

The interference between  $\text{Al}^{+3}$ ,  $\text{Fe}^{+3}$ ,  $\text{Cu}^{+2}$  and  $\text{Pb}^{+2}$  was studied by measuring the concentration of metals ion in three mixture that consisted of (5,10 or 25ppm) of each metal by UV-visible spectrophotometer after separation according to previous methods. Finally the results were listed in table (3-15).

Table 3-15 Interferences between metal ion that measured  
by UV-vis spectrophotometer

Metal	Iron III			Copper II			Aluminum III			Lead III		
	5	10	25	5	10	25	5	10	25	5	10	25
Added ppm	5	10	25	5	10	25	5	10	25	5	10	25
Taken ppm	4.87	9.71	24.34	4.932	9.89	24.83	5.04	10.07	25.06	4.8	9.67	24.37
Recovery %	97.4	97.12	97.35	98.64	98.9	99.32	100.8	100.7	100.24	96.1	96.7	97.5
Relative error	2.6	2.9	2.65	1.36	1.1	0.68	-0.8	-0.7	-0.24	4	3.3	2.52



## Conclusion

UV-vis spectrophotometer was employed for study of the digestion time and determination of some wear metals concentration in the oil samples, while FAAS was employed only for determination of wear metal concentration.

A relatively large quantity of Al, Fe, Cu and Pb were found in used lubricating oil.

The best digestion time of the oil sample was with concentrated HCl found to be 2.5 hour.

The concentration of wear metal were found to increase directly with an increase of operating distance. The friction between engine's component was responsible for the increase of metal concentration especially Fe, Al and Cu. The tetraethyl lead may be responsible for high concentration of lead in the collected used oil samples.

The high concentration of iron may be resulted from the friction between Cam Shaft, Crankshaft, Cylinder Walls, Exhaust Valve, Anti-Friction Bearing, Housing/Castings, Oil Pumps, Pistons, Rings Timing Gears, Turbo-Charger/Super Charger, Valve Guides, Valve Train and/or Wrist Pins<sup>(18)</sup>.

The existence of copper in the used oil may be a result from the friction between the engine components

The existence of aluminum may be resulted from the friction between components that made from aluminum.

## **Future work**

1. Estimation the viscosity and determination of wear metals in lubricating oil at a different operating time of the engine so as to identify the life time of lubricating oil in addition to what is the best lubricating oil viscosity.
2. Use of different kinds of oil brands and study their behavior according to their specifications
3. Use of engines of different ages with same oil and compare their wear effect of oil used.
4. Determination of wear metals by FAAS directly by using organometalic compound as a standard solution and compressed with digestion method. Note that the standard's viscosity must be equal to the sample viscosity.
5. Addition of same materials to waste lubricating oil in order to use it again from engine and study the performance of the treated oil in engine by determination of wear metals in the used treated oil.

---

# **Experimental**

## ***2-1. Instruments and equipment***

1. Flame atomic absorption spectrophotometer, model 5000(USA). Fe, Cu, and Pb hollow cathode lamps were obtained from PERKIN-ELMER instruments.
2. Double-beam UV-VIS spectrophotometer model UV1650 PC (Shimadzu). Equipped with microprocessor, monitor and printer (Canon 800) Japan.
3. pH measurement, Orion Research expandable ion analyzer model (EA 940) with a glass combination electrode

## ***2-2. Chemicals***

All chemical and reagents used in this work were of analytical grade, supplied from Fluka, BDH or Aldrich companies.

## ***2-3. Material and standard solution***

### ***2-3-1. Sampling***

Fuchs lubricating oil was used for 3000Km from Gulf car engine. A 50ml of the oil was collected from the car engine after running for 500Km till 3000Km as shown in table (2-1) this process was repeated twice, A and B.

Table 2-1 Oil samples

Samples	Run distance, Km						
	0	500	1000	1500	2000	2500	3000
A	I	II	III	IV	V	VI	VII
B	I'	II'	III'	IV'	V'	VI'	VII'

### ***2-3-2 Preparation of stock solution***

#### ***2-3-2-1 Iron stock solution***

Iron stock solution (1000ppm) was prepared by dissolving 0.1g Fe metal in 5 ml (5M) HCl and diluted with deionized water to 100ml in a volumetric flask.

#### ***2-3-2-2 Copper stock solution***

Copper stock solution (1000ppm) was prepared by dissolving 0.1g Cu metal in 5 ml (5M) HNO<sub>3</sub> and diluted with deionized water to 100ml in a volumetric flask.

#### ***2-3-2-3 Lead stock solution***

Lead stock solution (1000ppm) was prepared by dissolving 0.1g Pb metal in 5 ml (5M) HNO<sub>3</sub> and diluted with deionized water to 100ml in a volumetric flask.

### ***2-3-2-4 Aluminum stock solution***

Aluminum stock solution (1000ppm) was prepared by dissolving 1.1666g  $\text{Al}_2(\text{SO}_4)\cdot 16\text{H}_2\text{O}$  in 100ml of deionized water in a volumetric flask.

### ***2-3-2-5 Ammonium thiocyanate stock solution***

A 0.6M ammonium thiocyanate solution was prepared by dissolving 4.5672g ammonium thiocyanate in 100 ml of 2M  $\text{HNO}_3$ .

### ***2-3-2-6 Dithizone stock solution***

A  $1.9 \times 10^{-3}$ M Dithizone reagent was prepared by dissolving 0.05g of dithizone reagent in 100ml  $\text{CCl}_4$ . The reagent was kept in a dry cold place.

### ***2-3-2-7 Aluminon stock solution***

A  $5.555 \times 10^{-3}$ M aluminon reagent was prepared by dissolving 0.0525g aluminon reagent in 100ml deionized water.

## ***2-4. Extraction of metal ion from oil sample***

A 20 ml of 17.5% HCl solution was mixed with same volume of oil sample (AVII) in a beaker and digested for 0.5 hour on a magnetic stirrer. The mixture was transferred into a separatory funnel and 30 ml of 95% ethanol were added and shaken for a few minutes then let stand for 5 hours until clear separation of two layers. The aqueous layer was withdrawn and then heated to dryness. The residue was dissolved in 20 ml of deionized water and a few dropper of hydrogen peroxide was added then completed to 50 ml of deionized water. The digestion periods were change from 0.5-3.5 hours at 0.5 intervals. The experiment was repeated with sample (BVII').

## ***2-5. Qualitative analysis.***

Tentative identification of metal ion in a sample was carried out using classical procedure<sup>(41, 73,74)</sup> to a small portion of extracted aqueous layer.

## ***2-6. Quantitative analysis.***

A liquotes of different oil samples were analyzed using flame atomic absorption and UV-VIS spectrometer. The standard solutions of metal ion were used to construct the calibration curve for each ion using the following methods.

### ***2-6-1. Determination of metals ion by UV-vis spectrometer***

#### ***2-6-1-1. Aluminum complex***

The UV-visible spectrum was run from 200-700nm for a mixture of aluminum standard with aluminon reagent<sup>(75)</sup>.

##### ***2-6-1-1-1. Effect of pH on absorption***

A 5 ml of a solution of  $3.7 \times 10^{-4} \text{M}$   $\text{Al}^{+3}$  was mixed with equal volume of  $1.11 \times 10^{-3} \text{M}$  aluminon reagent then 5ml of 0.5M buffer solution at pH=3 was added. The volume was completed to 25 ml with deionized water in a volumetric flask. The maximum absorption was measured at 520 nm. This experiment was repeated at different pH, ranging from 3-6.

### ***2-6-1-1-2 Estimation the composition of the complex***

A different concentration of  $\text{Al}^{+3}$  was mixed with equal volume of fixed concentration of aluminon reagent  $2.222 \times 10^{-4} \text{M}$  as shown in table 2-2.

Table 2-2 Concentration of  $\text{Al}^{+3}$  and the mole ratio of  $\text{Al}^{+3}$  with aluminon reagent

<b>Conc. Of <math>\text{Al}^{+3}</math> M</b>	<b>Mole ratio <math>\text{Al}^{+3}/\text{L}</math></b>
<b><math>1.8518 \times 10^{-5}</math></b>	<b>0.0833</b>
<b><math>3.7037 \times 10^{-5}</math></b>	<b>0.1681</b>
<b><math>5.555 \times 10^{-5}</math></b>	<b>0.250</b>
<b><math>9.2592 \times 10^{-5}</math></b>	<b>0.416</b>
<b><math>1.111 \times 10^{-4}</math></b>	<b>0.500</b>
<b><math>1.296 \times 10^{-4}</math></b>	<b>0.583</b>
<b><math>1.481 \times 10^{-4}</math></b>	<b>0.666</b>
<b><math>1.666 \times 10^{-4}</math></b>	<b>0.750</b>

The maximum absorption was measured at 520nm.

### ***2-6-1-1-3. Calibration curve of aluminum complex***

A 12.5ml of 20ppm  $\text{Al}^{+3}$  solution were mixed with 5ml of  $5.55 \times 10^{-3} \text{M}$  aluminon solution then 5 ml of 0.5M buffer solution at pH=4.25 were added and the volume was completed to 25 ml with deionized water. The subsequent dilution was employed for the construction of calibration curve.

### ***2-6-1-2. Ferric thiocyanate complex***

Absorption spectrum at a range of 200-700 nm was measured for a solution of  $3.58 \times 10^{-3} \text{M}$   $\text{Fe}^{+3}$  with 0.3M ammonium thiocyanate<sup>(75,76)</sup> reagent that prepared in acid media.

#### ***2-6-1-2-1. Effect of acidity on absorption***

A number of mixture was prepared by mixing 1ml of  $1.79 \times 10^{-3} \text{M}$   $\text{Fe}^{+3}$  with 5 ml of 0.6M ammonium thiocyanate that prepared in different concentration of nitric acid then the volume was completed to 10ml with deionized water. The absorption was measured at 480nm.

#### ***2-6-1-2-2. Calibration curve of Ferric thiocyanate complex***

A 12.5 ml of 20 ppm  $\text{Fe}^{+3}$  was mixed with the same volume of 0.6M ammonium thiocyanate that prepared in 2M  $\text{HNO}_3$ . The subsequent dilution was employed for the construction of calibration curve using a solution of 0.3M ammonium thiocyanate in 1M nitric acid.

#### ***2-6-1-3. Lead dithizonate complex***

A 0.5 ml of 0.5M sodium tartarate<sup>(77)</sup> was added to 2.5 ml of 10 ppm  $\text{pb}^{+2}$  then 2 ml of 0.25M buffer at  $\text{pH}=8.5$ <sup>(75,77)</sup> were added. The mixture was shaken for a few minutes in a separatory funnel with 5 ml of  $4.826 \times 10^{-5} \text{M}$  dithizone solution<sup>(78)</sup>. The organic layer was



withdrawn after standing for 5 minutes. The spectrum absorption was measured at a range 200-700nm.

### ***2-6-1-3-1. Estimation the composition of the complex***

A different concentration of  $Pb^{+2}$  was shaken with equal volume of fixed concentration of dithizone reagent ( $2.8957 \times 10^{-5} M$ ) for 5 minutes as shown in table (2-3). The excess dithizone in the organic layer was separated by shaking with equal volume of 0.2M ammonia solution for a few minute, note that the standard solution of  $Pb^{+2}$  was prepared at pH=8.5 in 0.1M sodium tartarate.

Table 2-3 Concentration of  $Pb^{+2}$  and the mole ratio of  $Pb^{+2}$  with dithizone reagent

<b>Conc. Of <math>Pb^{+2}</math></b>	<b>Mole ratio M/L</b>
$2.8957 \times 10^{-5}$	<b>1</b>
$2.6061 \times 10^{-5}$	<b>0.9</b>
$2.3165 \times 10^{-5}$	<b>0.8</b>
$2.0270 \times 10^{-5}$	<b>0.7</b>
$1.7374 \times 10^{-5}$	<b>0.6</b>
$1.4479 \times 10^{-5}$	<b>0.5</b>
$1.1582 \times 10^{-5}$	<b>0.4</b>
$8.6870 \times 10^{-6}$	<b>0.3</b>
$5.7914 \times 10^{-6}$	<b>0.2</b>
$2.8957 \times 10^{-6}$	<b>0.1</b>

The maximum absorption was measured at 520nm.

### ***2-6-1-3-2. Calibration curve of Lead dithizonate complex***

A 2.5 ml of 0.5M sodium tartarate solution was added to 12.5ml of 20 ppm  $Pb^{+2}$  solution then 10 ml of 0.25M buffer at pH=8.5 were added. The mixture was shaken for a few minutes in a separatory funnel with equal volume of  $9.652 \times 10^{-5}$  M dithizone solution then the organic layer was withdrawn after standing for 5 minutes. The absorption was measured at 520nm.

### ***2-6-1-4. Copper dithizonate complex***

A 2.5 ml of 0.2M buffer at pH=3<sup>(75,77)</sup> was added to the same volume of 10ppm  $Cu^{+2}$ . The mixture was shaken for a few minutes in a separatory funnel with 5 ml of ( $1.58 \times 10^{-4}$ ) M dithizone solution<sup>(78)</sup>. After standing for 5 minute the organic layer was withdrawn and the absorption spectrum was measured from 200-700nm.

#### ***2-6-1-4-1. Estimation the composition of complex***

A 2.5 ml of 0.2M buffer at pH=3 was added to the same volume of  $3.17 \times 10^{-5}$  M  $Cu^{+2}$ . The mixture was shaken for a few minutes in a separatory funnel with 5 ml of  $1.58 \times 10^{-4}$  M dithizone reagent. The organic layer was withdrawn and the maximum absorption was measured at 550nm. The experiment was repeated with a different concentration of  $Cu^{+2}$  and fixed concentration of

dithizone reagent as shown in table (2-4). The excess dithizone in the organic layer was separated by shaking with equal volume of 0.2M ammonia solution for a few minutes.

Table 2-4 Concentration of  $\text{Cu}^{+2}$  and the mole ratio between  $\text{Cu}^{+2}$  and dithizone reagent

Conc. Of $\text{Cu}^{+2}$	Mole ratio M/L
$9.5714 \times 10^{-5}$	1
$8.5714 \times 10^{-5}$	0.9
$7.6190 \times 10^{-5}$	0.8
$6.6666 \times 10^{-5}$	0.7
$5.7142 \times 10^{-5}$	0.6
$4.7619 \times 10^{-5}$	0.5
$3.8095 \times 10^{-5}$	0.4
$2.8571 \times 10^{-5}$	0.3
$1.9040 \times 10^{-5}$	0.2
$9.5238 \times 10^{-5}$	0.1

### ***2-6-1-4-2. Calibration curve of Copper dithizonate complex***

A 12.5 ml of 20 ppm  $\text{Cu}^{+2}$  was mixed with 12.5 ml of 0.2M buffer at  $\text{pH}=3^{(76,78)}$ . The mixture was shaken with equal volume of  $3.1746 \times 10^{-4}$  M dithizone reagent for a few minutes in a separatory funnel. The organic layer was separated and subsequent dilution method was employed for construction of calibration curve after dilution with carbon tetrachloride.

## ***2-7 Isolation and determination of metal ions***

### ***2-7-1. Isolation and determination of iron in oil samples***

A 25 ml of the unknown sample was heated to dryness and dissolved in 25 ml of 6M HCl. The mixture was shaken for 5 minutes with 25ml diethyl ether then the aqueous layer was withdrawn. The extraction was repeated again<sup>(79)</sup>. The extracted diethyl ether layer was added to 12.5ml of deionized water and heated to evaporate the organic layer. The resulting solid residue was then dissolved in water completed to 20ml with deionized water and 2 ml of the aqueous layer was treated with equal volume of 0.6M NH<sub>4</sub>SCN that prepared in 2M HNO<sub>3</sub>.

### ***2-7-2 Isolation and determination of copper in oil samples***

The aqueous layer was heated to dryness. The residue was then dissolved in 10ml of deionized water. The solution was neutralized with 0.2M NaOH then mixed with 10 ml of 0.25M buffer solution at pH =3 and the volume was completed to 25 ml of deionized water. The mixture was shaken with equal volume of  $3.174 \times 10^{-5}$ M dithizone reagent. After each extraction, the solution was rinsed with 1 ml CCl<sub>4</sub>. The extraction was stopped as soon as the green color was not change.

The extracted  $\text{CCl}_4$  layers were mixed together and the absorbance was measured at 550 nm.

### ***2-7-3 Isolation and determination of aluminum in oil samples***

The pH of 12.5 ml of the aqueous layer was adjusted with 0.1M NaOH to be 4.25 using pH-meter and the volume was completed with deionized water to 20 ml. The sample was treated with 5 ml of  $8.88 \times 10^{-5}$  M aluminon reagent and the absorbance was measured at 520nm.

### ***2-7-4 Isolation and determination of lead in oil sample***

Another 12.5ml sample was mixed with 5 ml of 0.5M sodium tartarate followed by addition of 2.5 ml of 1M ammonia solution. The pH-meter was employed to adjust pH to be 8.5 with 2M HCl. The solution was filtrated and the precipitated was washed with deionized water Then filtrated was completed to 25 ml with deionized water in a volumetric flask. The mixture was shaken with equal volume of  $4.83 \times 10^{-5}$  M dithizone reagent in a separatory funnel. After each extraction, the solution was rinsed with 1ml  $\text{CCl}_4$ . The extraction was stopped as soon as the color was not change from green to red. The extracted  $\text{CCl}_4$  layers were mixed and the maximum absorbance was measured at 520 nm.

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## **Abbreviation**

<b>VHVI</b>	Very high viscosity index
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<b>MIBK</b>	Methyl isobutyl ketone
<b>AAS</b>	Atomic absorption spectrophotometer
<b>EHAAS</b>	Electrothermal atomic absorption spectrophotometer
<b>ICPOES</b>	Inductive coupled plasma optical emission spectrophotometer
<b>AES</b>	Atomic emission spectrophotometer
<b>GFAAS</b>	Graphite furnace Atomic absorption spectrophotometer
<b>ASTM</b>	American standard testing methods
<b>UV-vis</b>	Ultra violet-visible spectrophotometer

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**DETERMINATION OF TRACE ELEMENT THAT RESULT FROM  
INTERNAL FRICTION OF THE ENGINE IN USED LUBRICATING  
OIL**

**تقدير كمية العناصر الناتجة من الاحتكاك الداخلي للمحرك  
في الزيوت المستخدمة**

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## الخلاصة

يتضمن هذا البحث طرائق طيفية لتقدير العناصر (Fe, Cu, Pb, Al) في زيوت فوكس التجارية والناجمة عن الاحتكاك الداخلي أثناء استخدامها لقطع مسافات مختلفة وبشكل متتالي من خلال محرك سيارة كولف. تم أخذ نماذج للفحص بعد أن استخدم الزيت بواسطة المحرك لقطع المسافات التالية ٠، ٥٠٠، ١٠٠٠، ١٥٠٠، ٢٠٠٠، ٢٥٠٠، ٣٠٠٠ كم وبشكل متتالي.

وقد تضمن الفصل الأول من هذه الرسالة بعض الحقائق والمفاهيم عن زيوت المحركات ومواصفاتها والمواد المضافة لها وخواصها الفيزيائية والكيميائية وتم التطرق إلى بعض البحوث المنجزة بهذا الصدد وبمختلف التقنيات .

الفصل الثاني تضمن وصف للنماذج المأخوذة من زيت المحرك والأجهزة والمواد التي استخدمت في هذه الدراسة وكما تم التطرق إلى الطرق التحليلية التي اتبعت لقياس كمية العناصر التي نتجت عن الاحتكاك الداخلي للمحرك.

أما النتائج فقد تم مناقشتها بالفصل الثالث حيث تم تقدير كمية المعادن (Fe, Cu, Pb, Al) والتي نتجت من الاحتكاك الداخلي للمحرك في الزيت بعد أن استخدم لقطع مسافات مختلفة وبشكل متتالي. تم فصل العناصر أنفة الذكر عن الزيوت من خلال معاملتها مع حامض الهايدروكلوريك. أن تقنية المطيافية الذرية للامتصاص أللهبي ( FAAS ) قد استخدمت لتقدير كل من (Fe, Cu, Pb) بشكل مباشر إما تقنية الامتصاص الطيفي الجزيئي UV-vis spectrophotometer فقد تم بواسطتها تقدير كل من العناصر أسابقه بالإضافة إلى الألمنيوم بطريقة طيفية جزيئية وقد تطلب ذلك فصل العناصر السابقة عن بعضها حيث تم فصل الحديد الثلاثي بواسطة الداى أثيل أثير. النحاس والرصاص تم فصلهما بواسطة محلول الدايتايزون حيث أن النحاس الثنائي يكون معقد بنفسجي اللون الذي ينفصل بشكل تام عن الطبقة المائية عند pH:3 أما الرصاص الثنائي فيكون معقد احمر اللون الذي ينفصل بشكل تام عن الطبقة المائية pH:8.5 . الألمنيوم تم تقديره لونياً مع كاشف الألومينون الذي يكون معقد احمر عند pH4.25 . من خلال تقدير كمية العناصر أنفة الذكر تم تشخيص الأماكن التي يحدث بها الاحتكاك بالاعتماد على دراسة مسبقة (١٨).

لقد وجد أن تركيز الحديد قد ازداد من ١,٤٧ إلى ١٣٦,٤٧٠ ppm في العينة A (التشغيل الأول) بينما تغير تركيزه من ١,٤٢٠ إلى ١٥٥,٣٩٧ ppm في النموذج B خلال التشغيل من (٠- ٣٠٠٠ Km). كما لوحظ أن تركيزا لنحاس قد ازداد من ٠,٧١٥ إلى ١٥,١٦٤ ppm في العينة A (التشغيل الأول) بينما تغير تركيزه من ٠,٧٤٣ إلى ١٩,٤٦٩ ppm في النموذج B خلال

التشغيل من (٣٠٠٠-٠) Km. كما أن التغير بتركيز الألمنيوم كان من ٠ إلى ٨,٠٧١ ppm في العينة A (التشغيل الأول) بينما تغير تركيزه من ٠ إلى ١٢,٢٢٩ ppm في النموذج B خلال التشغيل من (٣٠٠٠-٠) Km. ل وقد وجد أن تركيز الرصاص قد ازداد من ٠,٦٩١ إلى ١٠٠,٨٨٠ ppm في العينة A (التشغيل الأول) بينما تغير تركيزه من ٠,٨٩٥ إلى ١١٦ ز ٥٨١ ppm في النموذج B خلال التشغيل من (٣٠٠٠-٠) Km. أخيراً فقد لوحظ أن الزيادة بتركيز العناصر يتناسب بشكل طردي مع زيادة مسافات التشغيل. كما ان الاحتكاك بين اجزاء المحرك هو المسئول عن الزيادة بتركيز الحديد والنحاس والألمنيوم بينما الزيادة بتركيز الرصاص قد تكون ناتجة عن رابع أثيلات الرصاص (مضافات الوقود).

# *Summery*

Spectrochemical method was employed for determination of wear metals (Fe, Cu, Pb and Al) that result from the internal friction between engine's component after using for a different distances in commercial fuchs lubricating oil. The samples were collected from the engine after running for 0 till 3000Km.

Definitions of lubricating oils, oil additives, their physical and chemical properties of the lubricating oil and oil analyses were illustrated in chapter one in addition to some literature that concerning the determination of metal content in lubricating oil.

The second chapter is concerning with the experimental part which included the kind of oil samples that analyzed in this work. The instruments and material as well as the analytical methods that employed for this task.

Result and discussion are presented in chapter three. The wear metal were determined after digestion of the oil sample with HCl solution. FAAS techniques was employed to determined the extracted metal ions (Fe, Cu and Pb) directly, while UV-vis spectrophotometer was employed for determination of the extracted metal ions after separation of  $Fe^{+3}$  with diethyl ether. The violet complex of  $Cu^{+2}$  with dithizone was separated quantitatively at pH=3, while the red complex of lead with dithizone was separated at pH=8.5. finally  $Al^{+3}$  was treated with aluminon reagent at pH=4.25 and determined at 520nm.



The concentration of iron were increased from 1.47 to 136.470 ppm in sample A (first run), while the concentration of iron in sample B (second run) were increased from 1.420 to 155.397 ppm during operation from 0 to 3000Km.

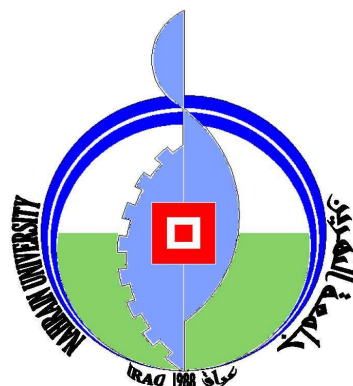
The concentration of copper were ringed from 0.715 to 15.164 ppm in sample A (first run), while copper concentration in sample B (second run) were ringed from 0.743 to 19.469 ppm during operation from 0 to 3000Km.

The concentration of aluminum were ringed from 0 to 8.071 ppm in sample A (first run), while the concentration of aluminum in sample B (second run) were increased from 0 to 12.229 ppm during operation from 0 to 3000Km.

The concentration of lead were increased from 0.691 to 100.88 ppm in sample A (first run), while the concentration of lead in sample B (second run) were increased from 0.895 to 116.581 ppm during operation from 0 to 3000Km.

The concentration of wear metals were found to increase directly with an increase of operating distance. The friction between engine's components was responsible for the increase of metal concentration especially Fe, Al and Cu. The tetraethyl lead may be responsible for high concentration of lead in the collected used oil samples.

Republic of Iraq  
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# **DETERMINATION OF TRACE ELEMENT THAT RESULT FROM INTERNAL FRICTION OF THE ENGINE IN USED LUBRICATING OIL**

**A Thesis**

**Submitted to the College of Science Al-  
Nahrain University in partial fulfillment of  
the requirements for the Degree of Master of  
Science in Chemistry**

**By**

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جمهورية العراق  
وزارة التعليم العالي والبحث العلمي  
جامعة الكوفة  
كلية العلوم  
قسم الكيمياء

## تقدير كمية العناصر الناتجة من الاحتكاك الداخلي للمحرك في الزيوت المستخدمة

رسالة

مقدمة إلى كلية العلوم- جامعة الكوفة  
وهي جزء من متطلبات نيل درجة الماجستير في الكيمياء

من قبل

سلوان بهنام عبو حنا  
بكالوريوس ٢٠٠٠ (جامعة بغداد)

تشرين الأول

رمضان ١٤٢٧

٢٠٠٦

*Supervisor certificate*

I certify that this thesis was prepared under my supervision at the Department of Chemistry, College of Science, Al-Nahrain University as a partial requirements for the Degree of Master of Science in Chemistry.

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**Dr. shahbaz ahmed maki**

In view of the available recommendation, I forward this thesis for debate by the Examining Committee.

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*Examining Committee's Certification*

We, the Examining Committee, certify that we read this thesis and have examined the student **Salwan Bahnam Abo**, in its contents and that, in our opinion; it is adequate as a thesis for the Degree of Master of Science, in Chemistry.

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(Member)

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# الإهداء

إلى كل إنسان أحب الخير لوطني الحبيب وأنار  
دربي وحياتي بالأدب والمعرفة

إلى من رحل بعيدا عني لكنه مازال حاضرا

بالعقل والقلب ..... أخي العزيز بسام

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