Experimental part

2.1 Instruments and equipment:

The equipments and material used in this work were:

1. Flame atomic absorption spectrophotometer model AA-670/G U-7/ SHIMADZU, Japan.
2. Double- beam UV –Vis spectrophotometer model (UV-1650 PC) / SHIMADZU, Japan; interfaced with computer via ashimadzu UV- Probe data system program.
3. pH measurement, Orion Research expandable ion analyzer model (EA 940) with a glass combination electrode

2.2Chemicals:

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

2.3Sampling:

Two types of crude oil were obtained from different Iraqi refineries. The first was from Beji refinery which used Kirkuk crude oil (northern); the second was from Al-dowra refinery which was Basra crude oil (southern).The oil samples were delivered to the analysis in clean polyethylene bottles.

The bottles were cleaned with concentrated HNO_3 and washed with deionized water thoroughly and dried before being filled with crude oil.

2.4 Procedure:

2.4.1Sample preparation method:

Two methods were used in the preparation of crude oil samples before analysis:

2.4.1.I Dry ashing:

A volume of 60 ml of each type of crude oil samples was added to 3.0g of sluphur then ignited in platinum dish using burner. After the fire extinguished the platinum dish was placed in furnace and heating continued for 12 hour at 760 °C to ensure complete combustion of all organic matrix. The residue (ash) was then digested with 9 mL of concentrated HCl overnight to dissolve all inorganic materials. The solution was diluted to 500 mL with deionized water in a volumetric flask. The above procedure was repeated using concentrated HNO_3 instead of HCl solution.

2.4.1.II .Wet digestion:

A volume of 10 ml concentrated HCl solution was added to 20ml of crude oil sample, 5ml of xylene and 20ml of deionized water. Xylene was used to decrease the high viscosity of oil then digested for 12 hour. The mixture was transferred to a separating funnel with addition of 3mL of deionized water; the aqueous layer was then collected. The solution was diluted to 500ml with deionized water. The same procedure was repeated using concentrated HNO_3 instead of concentrated HCl.

2.5 Qualitative analysis

Twenty milliliters solution that was previously prepared by dry ashing method was concentrated to 5 mL by evaporation.

Tentative identification of metals was then carried out using classical qualitative methods of analysis (82, 83).This procedure were applied to all samples.

2.6 Quantitative analysis

The quantitative determination of metals was carried out using two techniques molecular absorption spectrophotomety and atomic absorption spectrophotomety.

2.6.1. I Standard solutions of metal for complexes

Nickel:

A 0.1 g of Ni metal was dissolved in 10 mL of concentrated nitric acid and diluted with deonized water to 250mL in a volumetric flask. A 1 mg of DMG was dissolved in 250 mL of concentrated ammonia solution. A volume of 15mL nickel solution was treated with 10ml of 0.1M ammonium citrate solution, 5 mL of 0.1 M potassium iodide solution and 20 ml of DMG solution then diluted to 250 mL in a volumetric flask. The mixture was left for 20 minutes then the absorbance was measured at 440nm as the maximum absorption wavelength of nickel –DMG (84).

Spectrophometric calibration curve was constructed for standard nickel-DMG solution form 0.2 - 5ppm. The extracted oil samples were treated to similarly and the absorbance was measured at 440nm.

Vanadium:

A 0.5740 g ammonium metavanadate was dissolved in 16.2 mL concentrated nitric acid and diluted with deionized water to 250 mL in a volumetric flask. Stock solution of sodium tungstate was prepared by dissolving 0.2 g of sodium tungstate dihydrate (Na_2WO_4. $2H_2O$) in hot water, filters and diluted to 100 mL in a volumetric flask. A 10 ml of vanadium solution was treated by adding 8ml of 0.5M sulphuric acid, 5ml of 0.1M nitric acid, and 8ml of 0.1M phosphoric acid. The mixture was boiled for few minutes to expel the oxides of nitrogen. The mixture was cooled slightly and then 3 ml sodium tungstate solution was added with boiling. The solution was cooled to room temperature and transferred to 50 ml in a volumetric flask.

Spectrophotometric calibration curve was constructed for the absorbance of vanadium tungstate solution from 1 - 15 ppm at λ=400 nm as the maximum absorption wave length (84). The extracted oil samples were treated similarly and the absorbance was measured at λ=400 nm.

Iron:

A 0.123 mg of pure iron powder was dissolved in 10 ml of 0.4 M sulphuric acid and mixed with 3ml of concentrated nitric acid. The solution was transferred to 500ml volumetric flask. A 25ml of iron solution was treated with 3ml buffer solution at pH= 4.00(85) using 0.2 M acetate buffer, 1 ml of 0.5 M 1,10Phenanthroline hydrochloride solution and diluted to 100 ml in a volumetric flask. Then 1.0 ml of 0.1 M hydroxylamine hydrochloride was added to reduce Fe (III). After standing for 1 hour, the solution was measured at λ=512 nm for iron-1,10Phenanthroline solution.

Spectrophotometric calibration curve was constructed for standard iron solution from 1 to 10 ppm. The oil samples from dry ashing and wet digestion were treated using the above procedure and measured the absorbance of the solution at λ=512 nm.

Lead:

A 1.952 x 10^{-5} M Pb^{+2} solution was prepared in a weakly alkaline at pH=7.5(86) from 0.1 M ammonium chloride.

A 4.8309 x 10^{-5} M dithizone was prepared in carbontetrachloride with stirring for 5 minutes. A 2.5mL of Pb^{+2} solution was mixed with 5mL dithizone, 2.5 ml buffer solution and 3 mL of 0.1M sodium tartarte in separating funnel left to 5 minutes. Then measured the absorbance spectrum for the organic layer from 200-700 nm wavelength to ensure the formation of lead dithizonate complex.

The extraction was repeated with different concentration of Pb^{+2} solution from 1 to 5 ppm solution, by measuring the absorbance at λ=520 nm as the maximum absorbance of lead dithizonate.

Spectrophometric calibration curve was constructed for standard lead dithizonate by mixing of 2.5 ml of 15 ppm Pb^{+2} solution and 2ml of buffer solution at pH=7.5(86)shaken with 5ml of dithizone reagent. The organic layer solution was separated and subsequent dilution from 1-10 ppm solution with carbontetrachloride. The absorbance was Measured at λ=520 nm.

A 20 ml of aqueous layer crude oil samples from each of dry ashing and wet digestion samples were treated with 25ml concentrated HCl and placed in separatory funnel after stirring for 2 hours. The aqueous layer was neutralized with 0.1 M sodium hydroxide heated and mixing with 10 ml dithizone reagent, 8ml of deionized water and 2ml buffer solution at pH=7.5(86).

The mixture was shaken in separatory funnel after adding 2ml carbontetrachloride and extraction continues as the complex was formed when the solution color was converted from green to red ,then the absorbance spectrum measured at λ=520 nm.

Zinc:

A 1.12 x 10^{-5} M Zn^{+2}solution was prepared in an acid solution. A 2.409 x 10^{-5} M dithizone was prepared in carbontetrachloride with stirring for few minutes. 2.5mL of Zn^{+2} solutions was transferred in to small separatory funnel containing 5mL dithizone, 1.0mL of 0.02 M sodium thiosulfate solution and 2.5ml buffer. The solution was shaken vigorously for few minutes .Then measured the absorbance spectrum for the organic layer from 200-800 nm wavelengths for zinc dithizonate complex.

The extraction was repeated in different concentration of Zn^{+2} solution from 1 to 10 ppm solution, with measured the absorbance spectrum at λ=530 nm as the maximum absorbance of zinc dithizonate.

Spectrophometric calibration curve was constructed for standard zinc dithizonate with mixing of 2.5 ml of 14 ppm Zn^{+2} solution and 2ml of buffer solution at pH=3.2(85) shaken with 5ml of dithizone reagent. The organic layer solution was separated and subsequent dilution from 1 to 10 ppm solution with carbontetrachloride. Measured the absorbance spectrum at λ=530 nm as the maximum absorbance of zinc dithizonate.

A 20 ml of aqueous layer crude oil samples for dry ashing and wet digestion was neutralized with 0.1 M sodium hydroxide heated; then diluted to 50ml in a volumetric flask. The solution was mixed with 10 ml dithizone reagent, 8ml of deionized water, 1.5ml of 0.02M sodium thiosulfate and 2ml buffer solution shaken in separatory funnel; after each extracted was adding 2ml carbontetrachloride; The extraction was ended as soon as the color of solution changed from green to bright red solution. Measured the absorbance spectrum at λ=530 nm.

Copper:

A 1.102 x 10^{-4} M Cu^{+2} solution was prepared in an acid medium solution at pH=2.5(86). A 2.3309 x 10^{-4} M dithizone was prepared by dissolving 0.0149 mg in carbontetrachloride with stirring for 5 minutes.

A 2.5mL of Cu^{+2} solutions was mixed with 5mL dithizone and 2.5 ml buffer solution in separatory funnel for few minutes .Then measured the absorption spectrum for the organic layer from 200-800 nm wavelengths for copper dithizonate complex.

The extraction was repeated with different concentration of Cu^{+2} solution from 1 to 10 ppm solution, with measured the absorbance spectrum at λ=550 nm as the maximum absorbance of copper Dithizonate.

Spectrophometric calibration curve was constructed for standard copper dithizonate by mixing of 2.5 ml of 14 ppm Cu^{+2} solution and 2ml of buffer solution at pH=2.5(86) .The mixture was shaken with 5ml of dithizone reagent. The organic layer was separated and subsequent dilution with carbontetrachloride from 1-10 ppm solution. Measured the absorbance spectrum at λ=550 nm as the maximum absorbance of copper dithizonate.

A 20 ml of aqueous layer crude oil samples for dry ashing and wet digestion was neutralized with 0.1 M sodium hydroxide ; then diluted to 50ml in a volumetric flask. The solution was mixing with 10 ml dithizone reagent, 8ml of deionized water and 2ml buffer solution(86)shaken in separatory funnel; after each extracted was adding 2ml carbontetrachloride; The extraction was ended the color of the solution changed from green to violet red solution. Measured the absorbance spectrum at λ=550 nm.

2.6.1. II Standard solutions for metals using AAS:

Iron Stock solution (1000ppm) was prepared by dissolving 0.100 g of Fe metal in 3 mL of concentrated HCl and 1 mL of concentrated HNO_3 and diluted to 100 mL with deionized water in a volumetric flask.

Stock solution (1000ppm) of zinc and vanadium were prepared by dissolving 0.1000g of each metal in 25 mL of concentrated HNO_3 and diluted to 100 mL in a volumetric flask with deionized water.

Copper stock solution (1000ppm) was prepared by dissolving 0.3798 g of copper nitrate ($Cu(NO_3)_2.3H_2O$) in 20 mL of deionized water acidified with 5mL concentrated HNO_3 and diluted to 100 mL in a volumetric flask.

Lead standard solution was prepared by dissolving 0.1598 g of lead nitrate ($Pb(NO_3)_2$) in 20 mL of deionized water acidified with 5 mL of concentrated HNO_3 and diluted to 100 mL in a volumetric flask. Nickel standard solution was prepared by dissolving 0.4953 g of nickel nitrate ($Ni(NO_3)_2.6H_2O$) in 20 mL of deionized water acidified with 5 mL of concentrated HNO_3 and diluted to 100 mL in a volumetric flask.

Spectrophometric calibration curve was constructed for each standard metal from different concentrations. A 20 ml of aqueous layer crude oil samples for dry ashing and wet digestion was measured the absorption line for each metal; which employed (324.8, 248.3, 217, 232, 318.5, 213.9) nm respectively for Cu, Fe, Ni, Pb,V, Zn.

1.1Crude Oil

Petroleum is basically a mixture of naturally occurring organic compounds within the earth, usually it is black, green, red or brown oils are not uncommon. Petroleum comes straight out of the ground as a dark and viscous liquid it is called crude oil .There is also natural gas, which can be associated with oil or found alone (1).

1.2 The Origin of crude oil

Crude oil is a liquid mixture of hydrocarbons of varying molecular weights and structures comprise of different chemical and physical characteristics depending on the nature of the crude's and the various refining processes (2). Crude contains between 90% and 95% hydrocarbon by weight, the remainder comprises inorganic material such as vanadium oxide, iron, nickel, calcium, potassium and sodium salts (3).

Oil has no equivalent to the relatively straightforward "swamp model" of coal formation. Indeed, scientists are still debating whether oil has a biological or a non-biological origin. Most petroleum geologists believed that oil is derived ultimately from living organisms, but, the destructive effects of heat and chemical reactions deep in the earth made it difficult to confirm this theory. Distinguished astrophysicist Gold (4) is one who thought that oil has a non-biological origin. He suggested that oil and gas formed from methane in the early part of earth's history.

Oil has been found in many different geological situations, and its chemistry varies from place to place. Yet there is one common factor: oil is always found in or near sedimentary rocks of marine origin. For this reason, it is believed that oil comes from the remains of countless dead plants and animals which collected on an ancient seafloor. This organic matter was then buried under thousands of feet of sediment, and converted by heat and chemical reactions into various kinds of hydrocarbon compounds which known as crude oil (5) .An idea about the origin of oil follows two different lines of thinking: inorganic and organic theories (3).

1.2.1. ***Inorganic theory:***

Early theories postulated an inorganic origin of oil .It became apparent that metallic carbides deep within earth reacted with water at high temperatures to form acetylene (C_2H_2), which subsequently condensed to form heavier hydrocarbons. This reaction is readily reproduced in the laboratory (6). Other hypotheses were a modification of the acetylene theory (7). It has been theorized that the mantle (6,7) contained iron carbide which would react with percolating water to form methane:

$$FeC_2 + 2H_2O \rightarrow CH_4 + FeO_2 \text{ ----------------- } (1.1)$$

The problem was and still lack of evidence for the existence of iron carbide in the mantle. These theories are referred to as the deep-seated terrestrial hypothesis (7).

Another inorganic hypothesis suggested was a cosmic origin (8). This theory was based on that hydrocarbons were precipitated as rain from original nebular matter from which the solar system was formed and then ejected from earth's interior surface rocks. This theory and other are referred to as the extraterrestrial hypothesis.

Two discoveries in 20th Century renewed the interest in the inorganic mode of origin (7). The existence of carbonaceous chondrites (meteorites) and the discovery that atmosphere containing methane exists for some celestial bodies such as Saturn. The only known source for methane is through inorganic reactions. It has been postulated that the original atmosphere of earth contained methane, ammonia, hydrogen, water vapor; add to this photochemical reactions (due to UV radiation) and the result is the creation of an oily, waxy surface layer (9).

The discovery of meteorite led to a renewed interest in an inorganic mechanism for creating organic compounds. Chondritic meteorites contain more than 6% organic matter (not graphite) and traces of various hydrocarbons including amino acids. Liquid hydrocarbons of 90% methane and traces of ethane, propane, isobutene and benzene have been also repeatedly made from inorganic sources (6).

1.2.2 ***Organic theory***

The specialists in geology and geochemistry believed an organic origin of petroleum (7). Most geologists today believed that oil was formed millions years ago from a combination of hydrocarbons synthesized by living organisms and hydrocarbons formed by thermal alteration of organic matter in sedimentary rocks (10). The organic theory became the accepted theory as the oil and gas industry began to fully develop and geologists were exploring for new deposits. The organic theory holds that the carbon and hydrogen necessary for the formation of oil and gas were derived from early marine life forms living on the earth during the geologic primarily marine plankton. The sun provides energy for all living things including plankton and other forms of marine life. As these early life forms died, their remains were captured by the processes of erosion and sedimentation. Successive layers of organic-rich mud and silt covered preceding layers of organic rich sediments and over time created layers on the sea floor rich in the fossil remains of previous life. Thermal maturation processes (decay, heat, and pressure) slowly converted the organic matter into oil and gas (11). The organic rich sediments were converted into layers of rocks. The layers were deformed, broken, and uplifted with time; the liquid petroleum flowed upward through porous rock until it became trapped and could flow no further forming the oil and gas that explored for at present. The chemistry of the hydrocarbons found in the end product (oil and gas) differs somewhat from those found in living things.

Changes, and transformation, took place between the deposition of the organic remains and the creation of the end product.

Plankton is the primary source of all hydrocarbons and the oil by synthesizing fatty acids. Fatty acids are essential constituents of animal fats and plant oils. The general formulas for these acids are $C_nH_{2n}+_2COOH$ or $C_nH_{2n}O_2$ and they form the largest known source of long-chain molecules. This is important because the molecular structure of fatty acids is similar to the molecular structure of hydrocarbons in crude oil. Paraffin or methane series are straight-chain hydrocarbons having general formula C_nH_{2n+2} while the naphthene series has carbon ring compounds having the general formula C_nH_{2n}(11).

1.3. Composition and types of crude oil

Crude oils vary in color, odor, and in the properties from which they consist. They found in two main composition of crude oil; hydrocarbons and non hydrocarbons, the difference is in properties, especially the variations in molecular structure (12). Figure (1.1) shows the average composition of the two main groups in crude oil (13). .

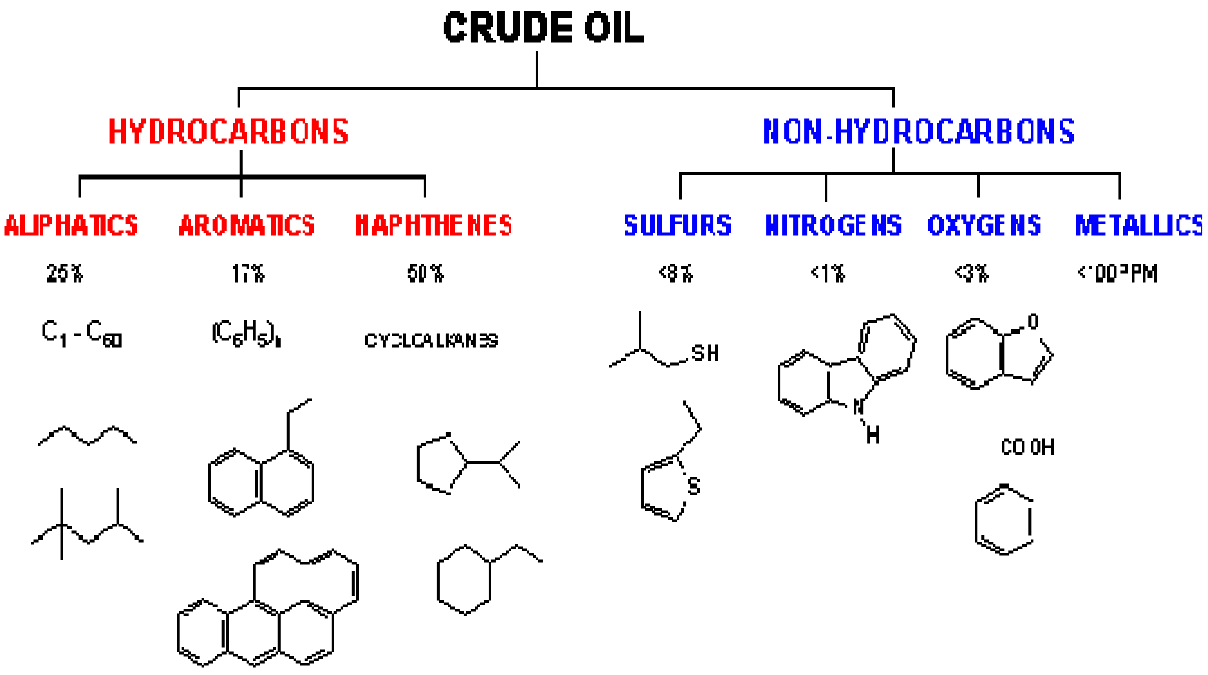


Figure (1.1) Chemical Classification of crude oil

1.3.1. Hydrocarbons: Crude oil is a mixture of hydrocarbon molecules that may include from one to 60 carbon atoms. The properties of hydrocarbons depend on the number and arrangement of the carbon and hydrogen atoms in the molecules (14,15). The simplest hydrocarbon molecule is methane. All other variations of petroleum hydrocarbons evolved from this molecule. Hydrocarbons containing up to four carbon atoms are gases, those with 5 to 19 carbon atoms are liquids, and those with 20 or more are usually solids. The refining process uses chemicals, catalysts, heat, and pressure to separate and combine the basic types of hydrocarbon molecules naturally found in crude oil into groups of similar properties. The refining process also rearranges their structures and bonding patterns into different hydrocarbon molecules and compounds.

Therefore, it is the type of hydrocarbon (paraffinic, naphthenic, or aromatic) rather than its specific chemical compounds that is significant in the refining process (16).

Naturally occurring hydrocarbon in Crude Oil:

I- ***Paraffins**:* The paraffinic series found in crude oil as straight (normal) or branch (isomers) chains of carbon atoms. The lighter, straight-chain paraffin molecules are found in gases and paraffin waxes. The branched-chain paraffin's are usually found in heavier fractions of crude oil and have higher octane numbers than normal paraffin (17).

II - ***Aromatics***: These unsaturated ring-type compounds react readily because of the present of carbon atoms that are deficient in hydrogen. All aromatics have at least one benzene ring as part of their molecular structure. The most complex aromatics, polynuclears are found in heavier fractions of crude oil.

III ***-Naphthenes***: are saturated hydrocarbon with the general formula C_nH_{2n}, arranged in the form of closed rings and found in all fractions of crude oil except the lightest. Single-ring naphthenes with five and six carbon atoms predominate, with two-ring naphthenes found in the heavier ends of naphtha (18).

1.3.2. Basics of non- Hydrocarbons:

Crude oil which also includes the smallest non-hydrocarbon compounds containing sulphur, nitrogen, and oxygen atoms. There may also be small amounts of vanadium, nickel, sodium, iron and potassium compounds (17, 19).

I .Sulfur Compounds

Sulfur may be present in crude oil as hydrogen sulfide (H_2S), or in compounds such as mercaptans, sulfides, disulfides, thiophenes, or as elemental sulfur. Each crude oil has different amounts and types of sulfur compounds, but as a rule the proportion, stability, and complexity of the compounds are greater in heavier crude-oil fractions. Hydrogen sulfide is a primary contributor to corrosion in refinery processing units. Other corrosive substances are elemental sulfur and mercaptans. Prophetic iron sulfide resulted from the corrosive action of sulfur compounds on the iron and steel used in refinery processing equipments, piping, and tanks. The combustion of petroleum products containing sulfur compounds produces undesirable compounds such as sulfuric acid and sulfur dioxide. Catalytic hydrotreating processes such as hydrodesulphurization remove sulfur compounds from refinery product streams(17).

II - ***Nitrogen Compounds***: Nitrogen is found in lighter fractions of crude oil as basic compounds, and more often in heavier fractions of crude oil as nonbiased compounds that may also include nitrogen oxides which formed in process furnaces. The decomposition of nitrogen (20) compounds in catalytic cracking and hydrocracking processes forms ammonia and cyanides that can cause corrosion (17).

III - ***Oxygen Compounds***: Oxygen compounds (21) such as phenols, ketones, and carboxylic acids occurred in crude oils in varying amounts.

IV - ***Metals***.

Metals, including nickel, iron, and vanadium is often found in crude oils in small quantities and is removed during the refining process. Burning heavy fuel oils in refinery furnaces and boilers can leave deposits of vanadium oxide and nickel oxide in furnace boxes and tubes. It is also desirable to remove trace amounts of arsenic, vanadium, and nickel prior to processing as they can poison certain catalysts (22).

V- ***Salts***:

Crude oils often contain inorganic salts such as sodium, magnesium, and calcium chloride in suspension or dissolved in entrained water. These salts must be removed or neutralized before processing to prevent catalyst poisoning, equipment corrosion, and fouling. Salt corrosion is caused by the hydrolysis of some metal chlorides to hydrogen chloride (HCl) and the subsequent formation of hydrochloric acid when crude oil is heated. Hydrogen chloride may also combine with ammonia to form ammonium chloride (NH_4Cl), which causes fouling and corrosion.

VI. ***Carbon Dioxide***:Carbon dioxide may result from the decomposition of bicarbonates present in crude, or from steam used in distillation process.

VII. ***Naphthenic Acids***: Some crude oils contain naphthenic acids, which may become corrosive at temperatures above 450° C when the acid value 20 ppm of the crude is above a certain level (17).

1.4. ***Refining of petroleum***

Refining crude oil involves two kinds of processes to produce the essential products to modern society. There are physical processes which simply refine the crude oil (without altering its molecular structure) into useful products such as lubricating oil or fuel oil. There are also chemical or other processes which alter the molecular structure and produce a wide range of products (12).

Refining by Distillation

The chemical components of petroleum are separated by fractional distillation, which is a separation based on relative boiling points (23). It can be separated by distillation into groups of hydrocarbons that boil between two specified boiling points. Two types of distillation are performed; atmospheric and vacuum.

Atmospheric distillation takes place in a distilling column at or near atmospheric pressure. The crude oil is heated to 350 - 400 ^{o} C and the vapor and liquid are piped into the distilling column (24). The second distillation column where the process is repeated under vacuum, called vacuum distillation. This allows heavy hydrocarbons with boiling point of 450 ^{o} C and higher to be separated without cracking into unwanted products such as coke and gas (19).Refineries produced petrochemicals which can be used by other aspects of the chemical industry. Crude oil produced from refining distillation with six major important fractions is listed in Table (1.2) (25).

Table (1.1) Fraction of crude oil product

Fraction	No. of carbon atoms per molecules	Boiling range degree C°	Uses	Processing
Gases	C1-C4	Below 90°	Calor gas	Gas processing
Straight run gasoline	C5-C10	90°-220°	Cars fuel	Motor gasoline blending
Naphtha	C10-C19	220°-315°	Stoves, airplanes	Cat reforming
kerosine	C15-C25	315°-450°	Trains, lorries	Hydrotreating
Lubricating oil	C20-C70	450°-650°	Machinery	Distillate fuel blending
Bitumen	AboveC70	Solid residue	Roads pavement	Heating

1.5Metals in crud oil

The crude oil consists, as stated before, of carbon with hydrogen and varying amount of sulphur, nitrogen, oxygen and some other elements. The principal elements are found in various combinations quantities (26).

Al-shahristani et al(27). reported a total of 29 elements found in different Iraqi crude oil.

Ag and Pb have been also determined in different Iraqi crude oil samples (27, 28).

These elements were found in two distinct forms:-

I- Metallo-organic complexes of V, Ni and Fe, almost as metallo-porphyrins complexes and other high molecular weight complexes (29, 30).

The porphyrin nucleus is a ring structure consisting of four planners of conjugated pyrrole groups linked by methyne bridges (31). In living organism porphyrin structures commonly chelate iron or magnesium ions in the center of the molecule (32). These metallo- porphyrins complexes are of great physiological significance (33).Corwin (34) studied petroporphyrins and suggested that it may be derived from chlorophyll, hemoglobin or hemin enzymes, which supported the organic theory of the origin of crude oil.

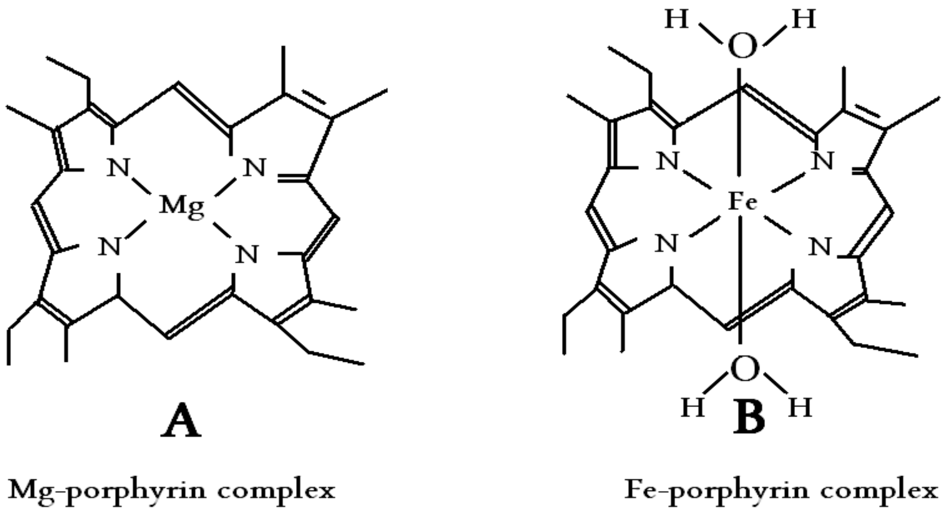
II - Salts, ($CaCl_2$, and NaCl) as solid or liquid suspensions which supported the inorganic theory of the origin of crude oil.

The importance of metallo-porphyrins and other metals:

Erdman (35) and Blumer and Snyder (36) studied the association of porphyrins with other compounds in petroleum and estimated the molecular weights of heavy porphyrin-containing complex molecules.

Hodgson et al. (37) presented preliminary data in the possible origin of petroleum porphyrins and reported an apparent bonding of petroleum porphyrins to amino acids. Such bonds were confirmed between meso-porphyrin and phenylalanine.

The metal ion incorporated in the center of the porphyrin ring may also coordinate with other oxygen- or nitrogen- containing groups such as hydroxyl, water, or ammonia above or below the plane of the ring as shown in figure (1.2):



Mg-porphyrin complex

Fe-porphyrin complex

Figure 1.2 Some metal porphyrin complexes in crude oil

The possible association of high molecular weight compounds greatly aided in understanding the history of migration of oil.

It is generally understood that movement of fluids through porous rock as the case of oil migration (38) is accompanied by tendency for the higher molecular weight and polar constituents to be removed; while the lighter, non-polar constituents are passed essentially unhindered. Causing the reduction in concentration of the larger molecules along the course of migration (29).

The concentration gradients of the elements complexes can therefore be used in the study of the history of formation, migration, and accumulation of oils. The elements that are present, as solid and liquid suspensions are most likely introduced in to oil during migration and/or from reservoir rocks.

The study of their concentrations may throw light on the geochemical nature of the reservoir and/ or path of migration (39).

1.6. Effect of metals present in crude oil

All crude oils naturally contain small quantities of metals (40). In fact highest levels of these metals found in industrial use and during the refining process. Petroleum-refining processes that utilize metal catalysts may leave amount of toxic metals (41, 42); Table (1.2) summarizes the effects and the main problems caused by some metals in crud oil:

Table (1.2) effect of some metals in crude oil and its fraction

metals	Main effect(s)
Pb	Air polluting, high temperature corrosion, Catalytic poison.
Fe	Catalytic poison, fuel system fouling.
V	Catalytic poison, high temperature corrosion.
Ni	Catalytic poison.
Mg	Deposits forming.
Ca	High temperature corrosion, fouling deposits.

Crude oil and refined petroleum products made up an integral mixture of compounds of hydrocarbons and refined petroleum, the actual effective pollutant of oil pollution results from normal tanker operations, offshore oil productions, oil waste in sewage systems and spills (43).

Water environmental concerns about heavy crude oils are of two types:

- Chemical wastes and by- products of heavy crude oil production, upgrading, and refining may cause serious ecological if released to the environment.
- Spills of heavy crude oils are difficult to clean up and may cause long-term to the affected environment (44, 45).Oil spills affect living organisms that use of water surface causes inhibitition to enzyme function in their bodies (46, 47).

The heavy metals are contaminants more than others because of their great effects on living organisms. They are transmitted through direct use of mining and burning of fossil fuels. These elements end up in water systems (48, 49). Some amounts of metals such as vanadium, lead, copper; zinc are left in our environment by human activities (50, 51).

One key factor of metal pollution is that it cannot biologically or chemically breakdown in nature. This stability also can be carried long distances through air and water (52).

Vanadium:

Vanadium is found naturally in crude oils as nitrogen complexes (porphyrins) and has been studied along with nickel, more thoroughly than any other metallic elements found in petroleum (53).

Control of the vanadium content is performed because of the corrosion problems in the combustion chamber that derived from the formation of sodium vandates (54), which have low melting points. The molten vanadates react with the metal surface of the super heaters and form the metal oxide (55).

The major species of vanadium are distributed in the fraction of kerosene, light oil, and heavy oil by the operation of industrial distillation.

These vanadium species behave as a catalyst poison during the catalytic cracking process of a petroleum refinery (56, 57).

1.7The determination of metal

Various method were used for the determination of metals, each method has its special conditions, sensitivity, detection limits and finally application (58, 59). These methods are:

I- Molecular absorption spectrophotometry:

One of the most common methods for the analyzing metal is spectrophotometric methods. Spectrophotometric techniques utilize the property of selective absorption of radiant energy by chemical substances. Photometric methods whether ultraviolet, visible or infrared are characterized by its sensitivity and selectivity (60).

Asia(61) was determined the petroleum samples industry were collected and characterized analysis by UV –Vis spectroscopy was revealed that the amounts of iron, lead, zinc, and copper total contents were 10.3, 0.92, 1.42, 0.52 ppm respectively.

Elchuk et al (62) .used UV/Vis detection for the separation of Ni (II), Zn (II), and Pb (II) by reversed phase ion interaction chromatography which offers high selectivity for determination of variant transition metal than conventional ion exchange methods.

The determination of nickel was carried using this technique after complexing of Ni with dimethylglyoxime (DMG) at wavelength (440) nm after its aqueous extraction from petroleum ashes (63, 64).using the same technique, copper was determined after its complexation with various reagents neocuprione (65) cuprizon (66) and diehyldithiocarbamate (67) at (450, 660, 440) nm, respectively, after its extraction directly from crude oil samples the relative standard deviation was 4.8%.

Kisr (68). was analyzing petroleum oils and products. Analytical activities cover the characterization of crude oils by GC, GC/MS, UV/Vis spectrophotomety, HPLC/UV and GC/FTIR; which determination of the composition of petroleum products; and individual separation and determination of iso-paraffin, naphthene and aromatic hydrocarbons. Also covered are determination of sulphur compounds, and determination of trace metals like V, Ni, Fe, Zn and metal additives in petroleum products. The composition and structural analysis of refining catalysts was made by X-Ray Fluorescence (XRF) and X-Ray Diffraction (XRD). Liquid petroleum gas is analyzed for hydrocarbons and natural gases. Polymers are characterized by GC/MS, and IR fingerprinting. The amounts of trace metals V, Ni, Fe and Zn were found in high concentration of 38.76ppm and17.56 ppm for V, Ni respectively more than Fe and Zn concentrations

II- Atomic spectrophotometry:

Flame atomic absorption is a very common technique for detecting metals and metalloids in environmental samples. It is very reliable and simple to use (69).

Thomas (70, 71, 72), has determined the metals concentration by ion exchange process followed by atomic emission spectrophotometry. Antimony, arsenic, selenium, and tellurium are analyzed after sample treatment by inductively coupled plasma (ICP) which is a powerful analytical, instrumental method for these elements.

The determination of (Ni, Mo, Cr, V, and Ti) was carried out by Martins (73) for determined lubricating oil samples directly using inductively coupled plasma optical emission at detection of limit in 0.3-0.5 ppm.

Yoshikazu (74) has determinate vanadium in light oil and heavy oil, using the tungsten coated graphite-furnace AAS, which gave 39.6 ppm for heavy oils and 22.7 ppm for light oils.

Renae (75) has determined Cadmium (Cd), cobalt (Co), and chromium (Cr); copper (Cu), molybdenum (Mo), nickel (Ni) and vanadium (V) concentrations in digested crude oil by graphite furnace atomic absorption spectrometry (GFAAS), with detection of limit in 0.7 ppm.

Sasaki et al (76).have described a procedure of direct determination of V, Ni and Na in crud oil and petroleum fraction based on graphite furnace atomic absorption spectrometry GFAAS with suitable dilution by organic solvent. The direct determination method of vanadium in the heavy oil was without any preliminary treatment.

Bardes et al. (77) have described a method for determination of Ni in heavy crude oils using carbon rod atomizer in AAS technique at 232.0 nm with detection limit of 0.1 ppm and relative standard deviation of 1.0% after its dilution to 100 times.

Michael et al. (78).have described Fe(III), Mn(II), Cu(II), Zn (II), Co(II), Ni(II), Hg(II), Pb(II), and Ag(I) were sequestered on aploy (acrylamidoxime) resin from laboratory prepared solution.

Recovery of the sequestered metals was achieved by equilibration of the resin matrix with 1:1 HNO_3 / water mixture, or a 1 M thiosulfate solution. Sequestered metals were at least 90% recovered with a standard deviation of $\leq$ 5%. Regeneration of resin with 3 M of NH_3 solution after the acid equilibration. The resin was applied for the separation and simultaneous concentration of Fe (II), Cu (II), Zn (II), and Pb (II) from seawater and pond water. Metals concentrations removed from resin were detected by atomic absorption spectroscopy.

A comparison between non flame-AAS and neutron activation analysis NAA technique in the determination of Fe and Ni in crude oil residue asphalt without pretreatment was carried out by Presley et al (79).

Musa et al (80). have determined the concentration of 25 trace elements in crude petroleum from oil fields by instrumental neutron activation analysis. Crude oil samples were irradiated with a thermal neutron dose rate of 10^{12} and 10^{13} $n \cdot cm^{-2} \cdot s^{-1}$. The concentration of U, Br, Mg, Cu, Na, V, Cl, Al, Mn and Ca was in a range of 0.015 to 84 ppm and that of sulphur of 0.12 to 1.8 ppm. The elements Sc, Cr, Ni, Fe, Co, Zn, Ag, Se, Sb, Ba, Cs, Yb, Hf and Hg have a concentration range of 0.009 to 8747 ppb. The elements V and Ni occur as both porphyrin and non-porphyrin and the ratio of these two forms varies over a wide range. The V/Ni ratios are located between 0.17 and 6.67, in Libyan crude oils which are comparable to the reported values for the crude oils from other countries.

Matousek et al (81) have determinated Ag, Cu, and Ni in lubricating oils directly using AAS methods at 338.3 nm, 327.4 nm and 232.0 nm for Ag, Cu, and Ni, respectively with relative standard deviation of 4%.

1.8. Aim of this work

The purpose of this work is:

- To draw attention to the amount of elements that present in the Iraqi crude oil blends and the comparing the results obtained by the following extraction method, which are dry ashing with HNO_3, dry ashing with HCl, wet digestion with HCl and wet digestion with concentrated HNO_3.
- Focusing on the determined differences between the average concentrations of vanadium, nickel, copper, zinc, lead and iron.

Results and discussion

3.1Qualitative analysis:

The metal qualitative analysis was carried out for both types of crude oils; Aliquot of 25 ml aqueous from dry ashing method, and the same volume was taken from the extract of wet digestion method. Each aliquot volume was evaporated to about 10 ml in order to concentrate metals solution.

The metal ions Fe^{+2}, Ni^{+2} were first identified according to classical methods of analysis.

The aqueous layer from extraction of crude oil samples with sulfuric acid gave negative test for metals; however, the aqueous layer from extract of crude oil samples with nitric acid contained relatively large quantity in metal ions compared with the aqueous layer from extract of crude oil with hydrochloric acid solution.

3.2Quantitative analysis:

Calibration curves were constructed for determination of metals concentration in each sample.

All calibration curves for these metals were constructed by plotting the absorbance of each complex at its maximum absorption wavelength. The metals found in crude oil were:

3.2.1. Copper

A copper standard solution was complxed with dithizone reagent in CCl_4 solution. The complexation of copper in this method was high selective method because it may detect smaller quantities.

The copper range was from 1.0 to 10.0 ppm. The resulting violet complex; showed the absorption wave length at λ max = 550 nm.

A linear calibration curve was obtained as shown in figure (3.1). The line has the equation:

$$\mathbf{Y = 0.0294X - 0.0064} \quad \text{-----------------------} \quad \mathbf{(3.1)}$$

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

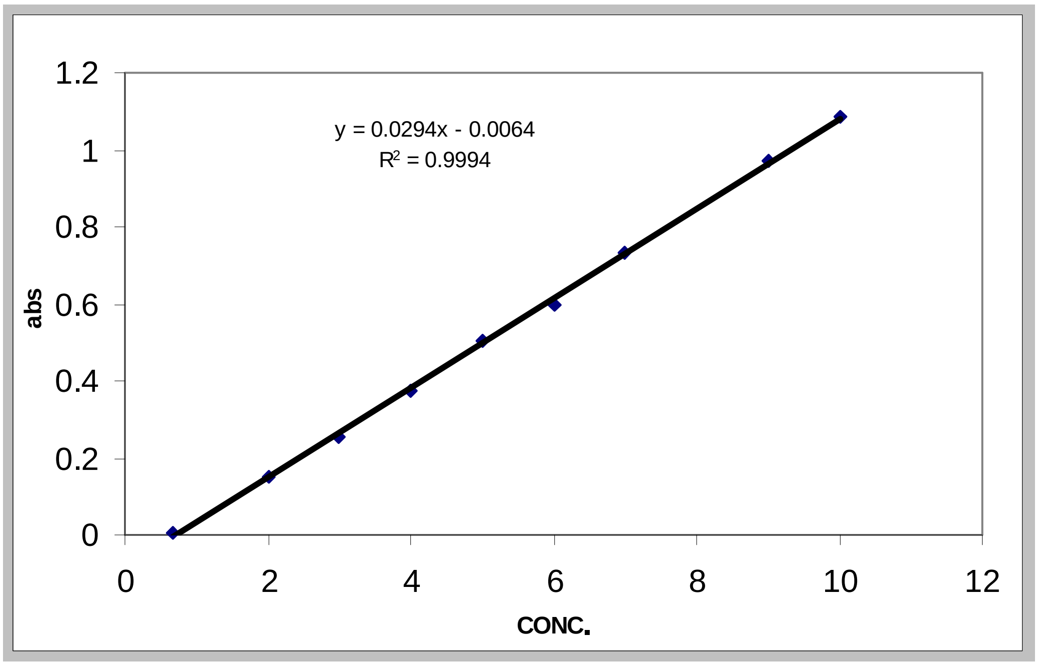


Figure (3.1) The calibration curve for copper using UV-Vis

The correlation coefficient for the above line was 0.9994 with a relative standard deviation of 0.0061%.

The above calibration was tested using prepared standard solution of copper to measure the recovery; the result obtained was listed in table (3.1)

Table 3.1 Copper recovery study

Concentration of copper in ppm(mg/L)		Recovery %	Relative error %
Prepared	Founded		
20.00	**19.41**	**97.04**	**2.96**
40.00	**38.78**	**96.95**	**3.06**
60.00	**58.19**	**96.98**	**3.02**

The accuracy of the copper concentrations was found 97.04 % for 20.00 ppm, with relative error was 2.96% .While the value of relative error for high concentration 60.00 ppm was 3.02 % and the accuracy was 96.98 %.

Table 3.2 shows copper concentrations found in two crude oil samples:

Table 3.2 Cu concentration in Basra and Kirkuk crude oils

Copper concentration* in ppm (mg/L). ±SD				
Crude oil type	Dry ashing with HNO_3	Dry ashing with HCl	Wet digestion with HNO_3	Wet digestion with HCl
Basra crude oil	**0.621 ± 0.002**	**0.761 ± 0.001**	**0.624 ± 0.002**	**0.608 ± 0.007**
Kirkuk crude oil	**0.740 ± 0.001**	**0.776 ± 0.004**	**0.639 ± 0.001**	**0.711 ± 0.001**

*** Each concentration represents an average of at least three measurements**

The concentration ranges of copper in Kirkuk were found higher than in Basra crude oil. The increment percentage was 17.99% for Kirkuk crude digestion with HNO_3 than in Basra crude oil digestion with HNO_3. Also the highest concentration was obtained from the ashing with concentrated HCl solution were (0.761, 0.776)ppm and (0.608, 0.711)ppm with 1.93% and 13.36% increment percentage, respectively found in Kirkuk and Basra crude oil. While the standard deviation of 0.007 wet digestion with HCl method which higher than ashing method with HCl was 0.001%.

3.2.2. Lead

A calibration curve of lead complxing with dithizone reagent in CCl_4 solution was constructed from 1 to 10 ppm .

These measurements were carried at λ max = 520 nm as the maximum absorption for lead dithizonate.

A linear calibration curve was obtained as shown in figure (3.2). The line has the equation:

$$\mathbf{Y = 0.1769X - 0.0659} \qquad \text{--------------------- } \mathbf{(3.2)}$$

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

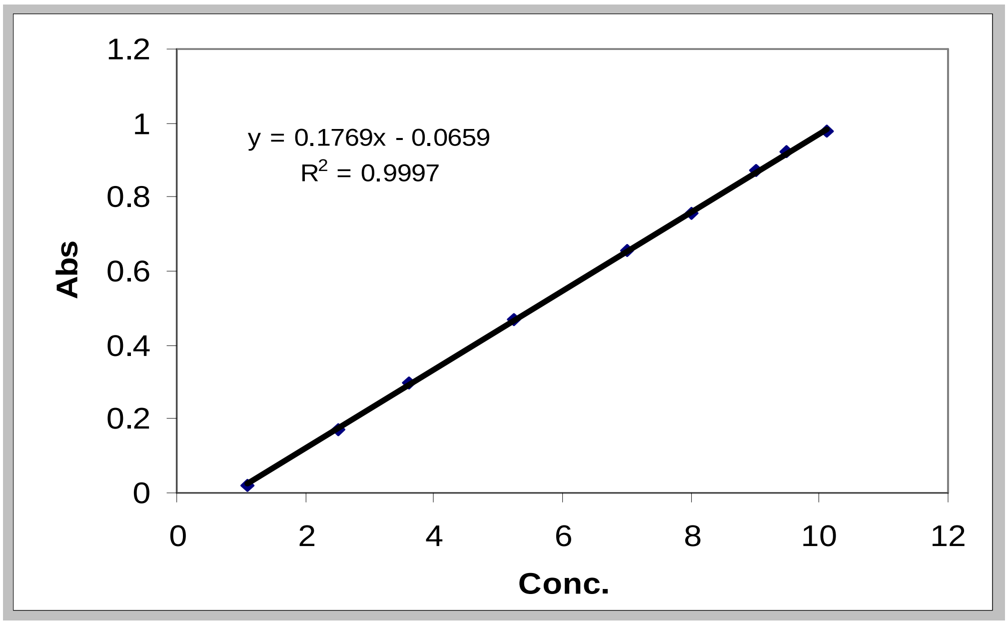


Figure 3.2 The calibration curve for lead using UV-Vis

The correlation coefficient for the above line was 0.9997 with a relative standard deviation of 0.0076%.

The above calibration curve was tested using prepared standard solution of lead to measure the recovery. The result obtained was listed in table 3.3:

Table 3.3 Lead recovery study

lead Concentration in ppm(mg/L) **prepared**	 **found**	**Recovery %**	**Relative error %**
15.00	**14.57**	**97.12**	**2.86**
25.00	**24.39**	**97.56**	**2.44**
50.00	**48.68**	**97.35**	**2.65**

The relative error was found less than 5%, which an accepted values for oil samples analysis. The relative error values was found to decrease with increased of lead concentration .While the recovery had the highest value 97.56% for 25.00 ppm because it had high value of absorbance that cause to decrease the error and give more accurate results.

Two types of crude oil were measured, the concentration of lead was found fewer than other metals found in samples, the results obtained are listed in table 3.4

Table 3.4 Pb concentration in Basra and Kirkuk crude oils

Lead concentration* in ppm (mg/L). ±SD				
Crude oil type	Dry ashing with HNO_3	Dry ashing with HCl	Wet digestion with HNO_3	Wet digestion with HCl
Basra crude oil	**0.469 ± 0.005**	**0.234 ± 0.003**	**0.532 ± 0.006**	**0.364 ± 0.004**
Kirkuk crude oil	**0.571 ± 0.004**	**0.267 ± 0.027**	**0.615 ± 0.007**	**0.331 ± 0.016**

*** Each concentration represents an average of at least three measurements**

The amounts of lead in Kirkuk crude oil digested with HCl were found more than in Basra crude oil; also high concentration of lead was found in Kirkuk oil using ashing methods. The standard deviation of 0.027 in Kirkuk crude oil dry ashing with HCl found highest value than other extracted methods, also the smallest standard deviation value of 0.003 measured for dry ashing with HCl in Basra crude oil. The concentration of lead was high value for dry ash and wet digestion with HNO_3 methods, in Kirkuk crude oil of 0.571ppm than Basra crude oil of 0.469 ppm; and the increment percentage was 17.86%.

The lead concentration for wet digestion with HCl in Kirkuk crude oil was 0.331 ppm, while for Basra digestion with HCl was found 0.364 ppm, and the increment percentage was 9.06%.

3.2.3. Vanadium

A calibration curve of vanadium standard solution commplexing with phosphotungstate. The vanadium range was from (1-10) ppm. These measurements were carried at λ max = 405 nm as the maximum absorption for the element.

A linear calibration curve was obtained as shown in figure (3.3). The line has the equation:

$$Y = 0.0511\ X - 0.0891 \qquad \text{---------------------------}\ (3.3)$$

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

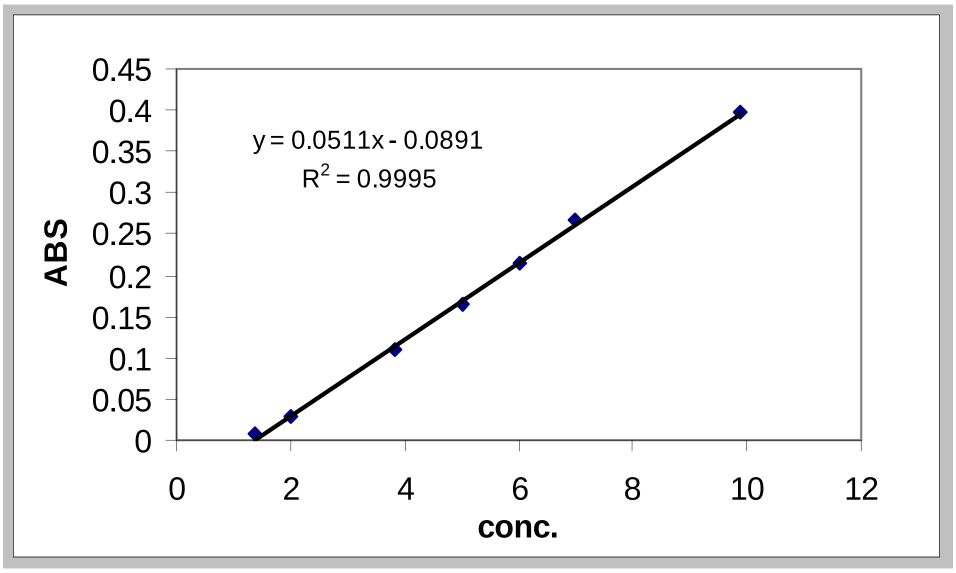


Figure 3.3 The calibration curve for vanadium using UV-Vis

The correlation coefficient for the above line was 0.9995. With a relative standard deviation 0.00811%.

The above spectrophotometric calibration curve was tested the recovery by preparation of vanadium standard solution; the study results obtained were listed in table (3.5):

Table 3.5 Vanadium recovery study

Concentration of vanadium in ppm(mg/L)		**Recovery %**	**Relative error %**
Prepared	**Found**		
30.00	**29.56**	**98.52**	**1.48**
45.00	**44.39**	**98.65**	**1.35**
70.00	**68.99**	**98.56**	**1.44**

The relative error for vanadium standard solution was found 1.48%; this value was accepted value for analysis intended amount of metals in crude oil samples. The above table was shown the recovery of vanadium standard for different concentration was 98.52%, 98.65% and 98.56% respectively for (30.00, 45.00 and 70.00) ppm.

The metals were determinate for wet digestion and dry ashing methods; the concentration of vanadium was appreciable amounts more than other metals in crude oil samples, the results obtained was tabulated in table (3.6):

Table 3.6 V concentration in Basra and Kirkuk crude oils

Vanadium concentration* in ppm (mg/L). ±SD				
Crude oil type	Dry ashing with HCl	Dry ashing with HNO_3	Wet digestion with HCl	Wet digestion with HNO_3
Basra Crude oil	**42.337 ± 0.029**	**42.817 ± 0.0478**	**42.129 ± 0.002**	**42.566 ± 0.001**
Kirkuk crude oil	**29.245 ± 0.005**	**29.239 ± 0.002**	**29.214 ± 0.002**	**29.226 ± 0.013**

*** Each concentration represents an average of at least three measurements**

The concentration range of vanadium for dry ashing with both HNO3 and HCl solution methods in Basra crude oils was found highest concentration than the wet digestion method. However, the amount of this metal in Basra crude oil appearance higher quantities than it's in Kirkuk crude oil. The result for wet digestion with HNO_3 in Basra crude oil was found less value of standard deviation of 0.001%; while the dry ashing had standard deviation value of 0.0478%.

3.2.4. Nickel

A calibration curve of nickel standard solution complexed with Dimethylglyoxime (DMG); which suitable method because it is possible to estimate large amount of Ni^{+2} with high accuracy; the maximum absorption of Ni^{+2} was measured at λ max = 440 nm. The nickel range was constructed from (1-15) ppm solution.

A linear calibration line was obtained as shown in figure (3.4). The line has the equation:

$$\mathbf{Y = 0.1814\ X + 0.0404} \text{---} \ \mathbf{(3.4)}$$

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

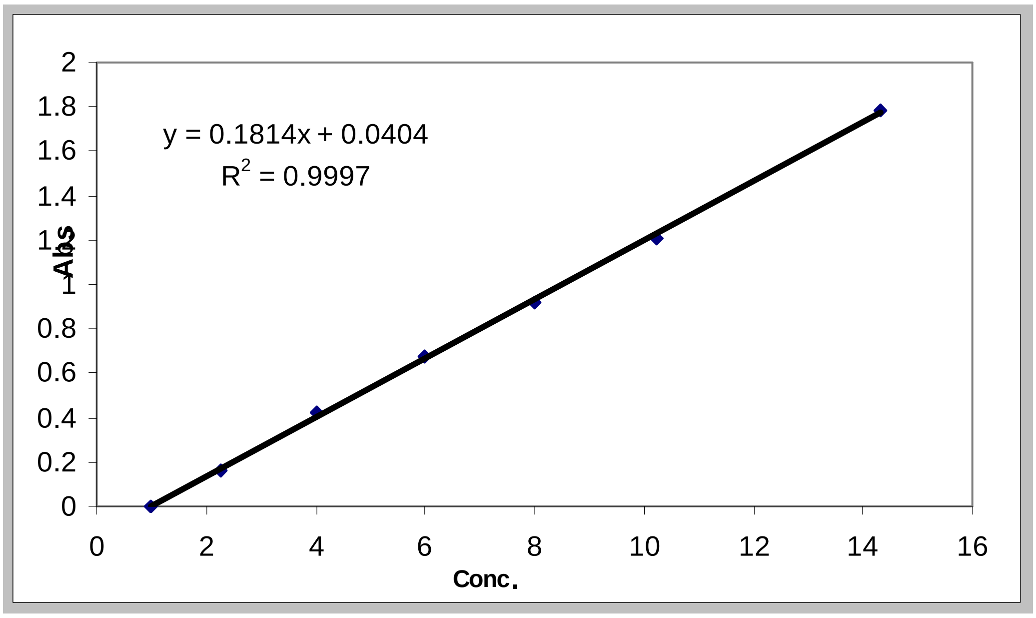


Figure 3.4 The calibration curve for nickel using UV-Vis

The correlation coefficient for the above line was 0.9997, with a relative standard deviation of 0.0069%.

The above calibration was tested using prepared standard solution of nickel to measure the recovery; the result obtained was listed in table 3.7:

Table 3.7 Nickel recovery study

Concentration of nickel in ppm(mg/L) Prepared	Found	Recovery %	Relative error %
12.00	**11.72**	**97.69**	**2.33**
22.00	**21.51**	**97.75**	**2.22**
40.00	**39.11**	**97.76**	**2.23**

The relative error range was from 2.33-2.22% .these values was accepted for analysis intended amount of metals in crude oil blends. While the errors range from (0.28-0.89), also the recovery was found 97.69% for 12ppm, and was 97.76% for 40.0 ppm.

The nickel concentration in crude oil samples for wet digestion and dry ashing methods were resulted and listed in table 3.8:

Table 3.8 Ni concentration in Basra and Kirkuk crude oils

Nickel concentration* in ppm (mg/L). ±SD				
Crude oil type	Dry ashing with HNO_3	Dry ashing with HCl	Wet digestion with HNO_3	Wet digestion with HCl
Basra crude oil	**15.238 ± 0.015**	**15.047 ± 0.022**	**15.421 ± 0.096**	**15.643 ± 0.015**
Kirkuk crude oil	**24.241 ±0.044**	**24.057 ± 0.026**	**24.461 ± 0.112**	**24.672 ± 0.010**

*** Each concentration represents an average of at least three measurements**

The concentrations range of nickel in Kirkuk crude oil was found higher 37.5% amounts than in Basra crude oil**;** however, the highest concentration was obtained form the dry ashing method. Also the above table showed the difference between dry ashing method and the wet digestion with HCl was very small. While the standard deviation of 0.01 for the nickel measurements found in Kirkuk crude oil digestion with HCl solution.

3.2.5. Iron:

A calibration curve of iron standard solution was prepared by complexing iron with 1, 10 phenonthroline reagent; which suitable method to estimate large amount of iron. The iron range was from (1-10) ppm. These measurements were carried at λ max = 505 nm as the maximum absorption for the element.

A linear calibration curve was obtained as shown in figure (3.5). The line has the equation:

Y = 0.0945 X -0.1023 -------------------------------------- (3.4)

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

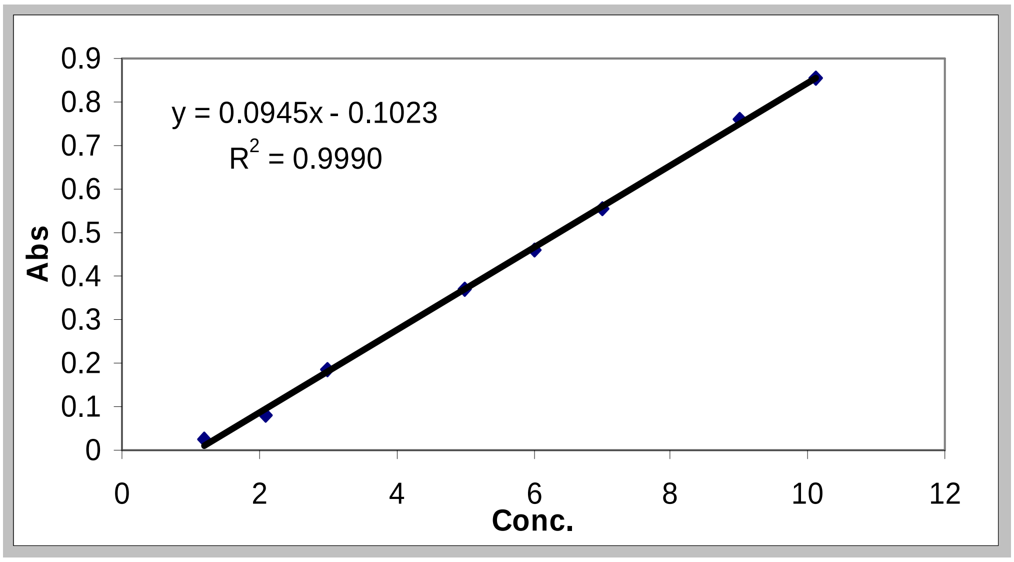


Figure 3.5 The calibration curve for iron using UV-Vis

The correlation coefficient for the above line was 0.9990, with a relative standard deviation of 0.0073%.

The above calibration curve was tested using prepared standard solution of iron to measure the recovery; the study result obtained was listed in table 3.9:

Table 3.9 Iron recovery study

Concentration of iron in ppm(mg/L)		Recovery %	Relative error %
Prepared	Found		
10.00	9.71	97.12	2.90
25.00	24.34	97.35	2.65
50.00	48.58	97.16	2.84

The accuracy of the iron standard concentrations was found 97.12 % for 10.00 ppm solution, with the relative error of 2.9 %. While the relative error for high concentration 50 ppm was 2.84 %, with the accuracy of 97.16%.

The table 3.10 showed iron concentrations were found in two crude oil samples:

Table 3.10 Fe concentration in Basra and Kirkuk crude oils

Iron concentration* in ppm (mg/L). ±SD				
Crude oil type	Dry ashing with HNO_3	Dry ashing with HCl	Wet digestion with HNO_3	Wet digestion with HCl
Basra crude oil	**10.521 ± 0.031**	**10.314 ± 0.021**	**10.419 ± 0.012**	**10.181 ± 0.065**
Kirkuk crude oil	**9.332 ± 0.034**	**9.170 ± 0.019**	**9.058 ± 0.047**	**9.126 ± 0.032**

*** Each concentration represents an average of at least three measurements**

The average amount of iron in Basra crude oil sample was found higher amount than in Kirkuk crude oil**.** For each crude oil samples, the iron concentration was found higher for dry ashing with HNO_3 than Wet digestion with HNO_3 method. The percentage increment of 11.30% iron concentration for dry ashing with HNO_3 (10.521, 9.332) ppm ; while the percent increment of dry ashing with HCl and wet digestion with HCl for Kirkuk crude oil **(**9.170, 9.126) was 0.47% these results were few differences between the two methods that gave good determinate of iron concentration for both extraction methods.

Atomic Absorption measurements

The metals in crude oil samples were measured in another technique using atomic absorption spectroscopy; the calibration curves of these metals found in crude oil were:

3.2.6. Nickel:

A calibration curve of nickel was constructed using the range 0.5 to 10 ppm standard solutions. These measurements were carried out at 232.0 nm as the absorption line for the element.

A linear calibration curve was obtained as showen in figure 3.6:

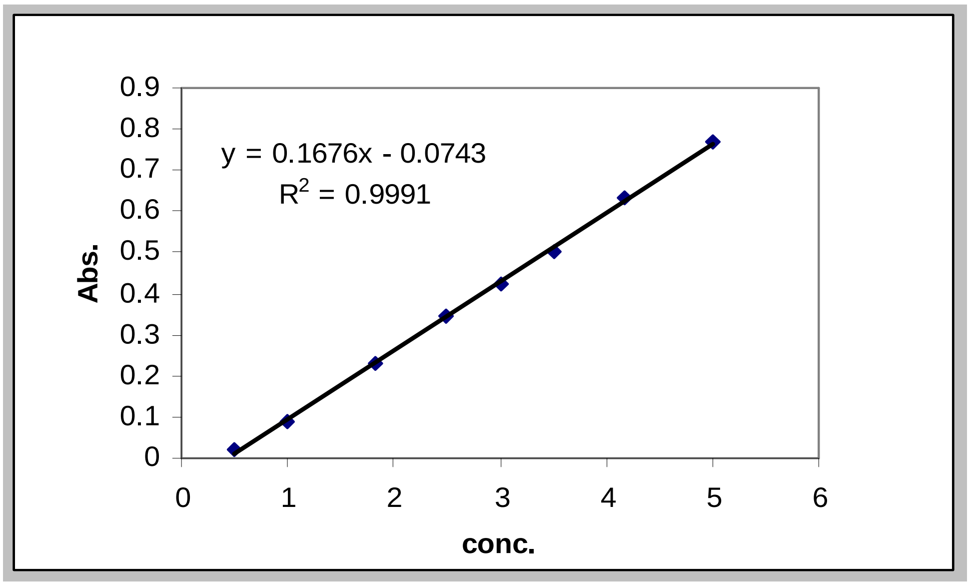


Figure 3.6 The calibration curve for nickel using AA spectroscopy

The line has the equation:

$$Y = 0.1676\,X - 0.0743 \text{---} (3.6)$$

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

The correlation coefficient for above calibration line was 0.9991, with a relative standard deviation of 0.0082%.

The above calibration was tested using prepared standard solution of nickel to measure the recovery .The results obtained were listed in table 3.11:

Table 3.11 Nickel recovery study

Concentration of nickel in ppm(mg/L)		Recovery %	Relative error %
Prepared	**Found**		
0.040	**0.039**	**98.89**	**2.5**
20.00	**19.77**	**98.84**	**1.16**
40.00	**39.51**	**98.76**	**1.24**

The relative error was 2.5% for 0.04ppm, while it was more for lead concentration of 40.00ppm with relative error of 1.24%. The recovery was 98.89% more accurate for low concentration, while the 20.00 ppm had 98.84 %, and the high concentration was 98.76%.

The nickel concentration in crude oil samples for wet digestion and dry ashing methods were measured and listed in table 3.12:

Table 3.12 Ni concentration in Basra and Kirkuk crude oils

Nickel concentration* in ppm (mg/L). ±SD				
Crude oil type	Dry ashing with HNO_3	Dry ashing with HCl	Wet digestion with HNO_3	Wet digestion with HCl
Basra crude oil	**15.409± 0.002**	**15.216± 0.023**	**15.594 ± 0.002**	**15.819 ± 0.001**
Kirkuk crude oil	**24.514 ± 0.015**	**24.328± 0.041**	**24.736± 0.005**	**24.949 ± 0.019**

*** Each concentration represents an average of at least three measurements**

The concentration ranges for Kirkuk and Basra crude oil using dry ashing method with HNO_3 was found 15.409- 24.514 ppm and with HCl 15.216-24.328 ppm; these measurements found significant differences; and the relative percent increment was 37.3%. While the concentration ranges of nickel was gave 24.514, 15.409 for Kirkuk and Basra crude oil digestion with HNO_3. However, the highest concentration ranges was obtained from dry ashing method. Here, also found the differences concentrations between dry ashing and wet digestion method was small.

The standard deviation for Basra crude oil digestion with HCl solution was 0.001 less value and the highest value was 0.005 for Kirkuk oil blends digestion with HNO_3.

3.2.7. Lead:

A calibration curve was constructed for lead; the range was from 0.1 to 10 ppm standard solutions. These measurements were carried out at 217 nm as the absorption line for lead.

A linear calibration curve was obtained as showed in figure 3.7. The line has the equation:

$$\mathbf{Y = 0.244\ X - 0.0117} \qquad \text{-----------------------} \ \mathbf{(3.7)}$$

Where Y represent the absorbance value and X represents the concentration of lead.

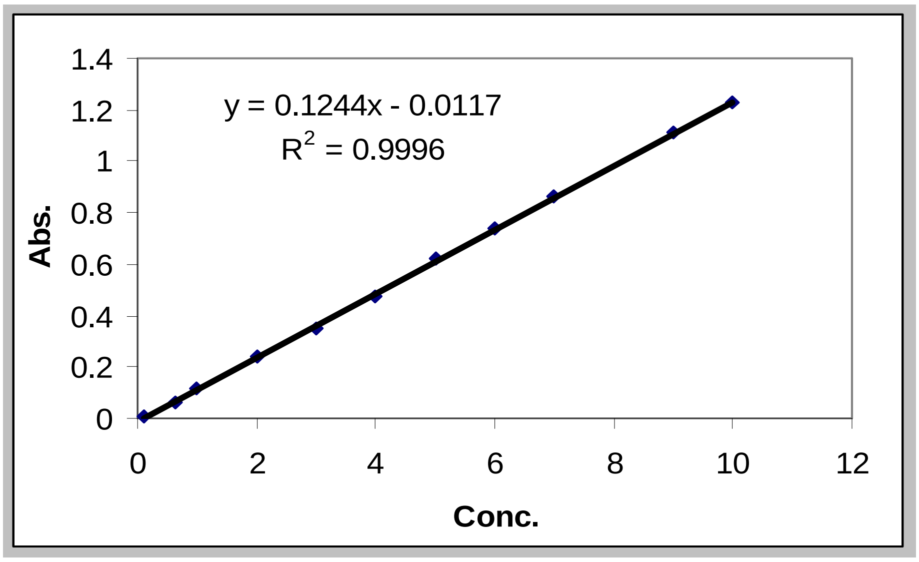


Figure 3.7 The calibration curve for lead using AA spectroscopy

The correlation coefficient for this calibration line was 0.9996; with a relative standard deviation of 0.0043%.

The above calibration curve was tested using prepared standard solution of lead to measure the recovery. The result obtained was listed in table 3.13:

Table 3.13 Lead recovery study

Concentration of lead in ppm(mg/L) **Prepared**	 **Found**	**Recovery %**	**Relative error %**
3.00	**2.95**	**98.28**	**1.7**
10.00	**9.82**	**98.26**	**1.8**
20.00	**19.64**	**98.24**	**1.7**

The recovery of the lead standard concentrations was found 98.26 % for 10.00 ppm; with a relative error of 1.8 % .While the value of relative error1.7% for high concentration 20 ppm, with recovery of 98.24%.

In two types of crude oil sample were measured few amounts of lead concentrations than other metals .The results obtained were tabulated in table 3.14:

Table 3.14 Pb concentration in Basra and Kirkuk crude oils

Lead concentration* in ppm (mg/L). ±SD				
Crude oil type	Dry ashing with HNO_3	Dry ashing with HCl	Wet digestion with HNO_3	Wet digestion with HCl
Basra crude oil	**0.473± 0.002**	**0.236 ± 0.001**	**0.538 ± 0.005**	**0.367± 0.003**
Kirkuk crude oil	**0.578 ± 0.017**	**0.269 ± 0.029**	**0.621 ± 0.019**	**0.334± 0.010**

*** Each concentration represents an average of at least three measurements**

The average concentration of lead, that listed in above table gave high amounts for Kirkuk crude oil using ashing method with HNO_3 than in Basra crude oil, with a relative increments percentage of 18.17 %. Also the Kirkuk crude oil wet digestion with HNO_3 method gave higher concentration than in Basra crude oil digestion with HNO_3, with a relative increments percentage of 13.36 %.While the standard deviation of 0.029 for Basra crude oil using dry ashing method with HCl had the high value, and the less value was 0.001 for Kirkuk crude oil using dry ashing method with HNO_3.

3.2.8. *Iron:*

A calibration curve for iron standard solutions was constructed with the range from 1 to 10 ppm. These measurements were carried at 248.3 nm as the absorption line for Fe metal.

A linear calibration line was obtained as showed in figure 3.8.

The line has the equation:

Y = 0.0661 X - 0.0551--- (3.8)

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

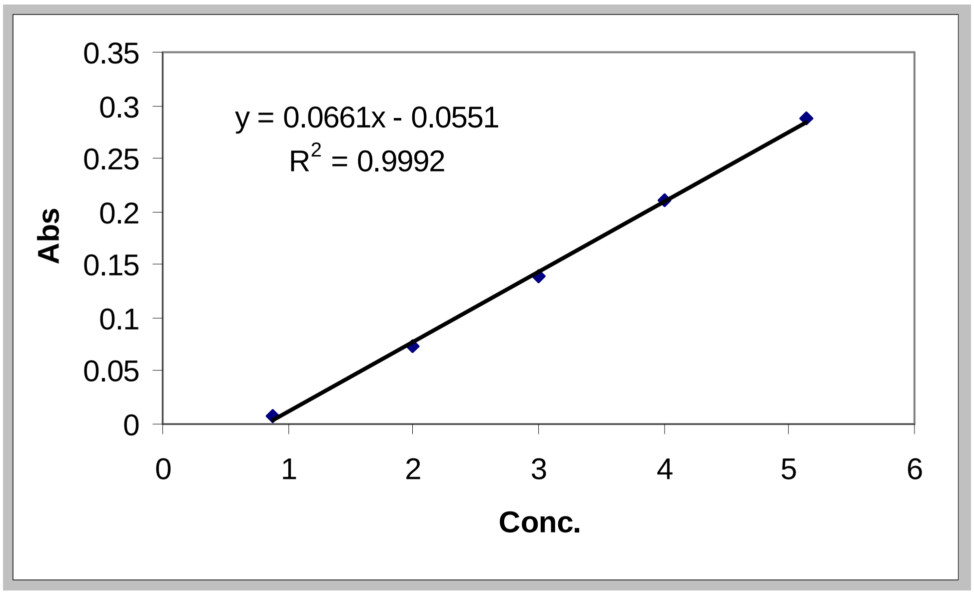


Figure 3.8 The calibration curve for iron using AA spectroscopy

The correlation coefficient for the above line was 0.9992 with a relative standard deviation of 0.0049%.

The above calibration curve was tested using prepared standard solution of iron to measure the recovery; the study result obtained was listed in table 3.15:

Table 3.15 iron recovery study

Concentration of iron in ppm(mg/L) **Prepared**	**found**	**Recovery %**	**Relative error %**
0.50	**0.49**	**98.04**	**1.96**
15.00	**14.76**	**98.43**	**1.57**
60.00	**59.15**	**98.58**	**1.42**

The recovery of the iron concentrations was found 98.04 % for the 0.50 ppm solution, and the relative error was 1.96 % .While the value of relative error of 1.42 % for high concentration 60.00 ppm; with the recovery of

98.58 %. Also the error was found small value for low concentration of iron standard solution 9.3 x10^{-3} ppm.

The concentrations of Iron measured in crude oil samples were found. And listed in table (3.16):

Table 3.16 Fe concentration in Basra and Kirkuk crude oils

Iron concentration* in ppm (mg/L). ±SD				
Crude oil type	Dry ashing with HNO_3	Dry ashing with HCl	Wet digestion with HNO_3	Wet digestion with HCl
Basra crude oil	**10.646 ± 0.004**	**10.435 ± 0.013**	**10.542 ± 0.0035**	**10.301 ± 0.001**
Kirkuk crude oil	**9.441 ± 0.004**	**9.278 ± 0.028**	**9.164 ± 0.006**	**9.231± 0.018**

*** Each concentration represents an average of at least three measurements**

The average concentration of iron in Basra and Kirkuk crude oil was found higher amount using dry ashing method with HNO_3 than wet digestion method. For iron concentration the percentage increment was 11.32% for dry ashing with HNO_3 (10.644, 9.441) ppm respectively in Basra and Kirkuk crude oil. The highest standard deviation was 0.006 for Kirkuk crude oil wet digestion with HNO_3, while the less value was 0.001 for Basra crude oil digestion with HCl solution.

3.2.9. Copper:

A calibration curve was constructed for copper with the range from 1 to 5 ppm standard solutions, employing 324.8 nm were the absorption line for the copper.

A calibration line was obtained as showed in figure 3.9. The line was having the equation:

$$Y = 0.3873\,X - 0.3753 \qquad \text{------------------}\ (3.9)$$

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

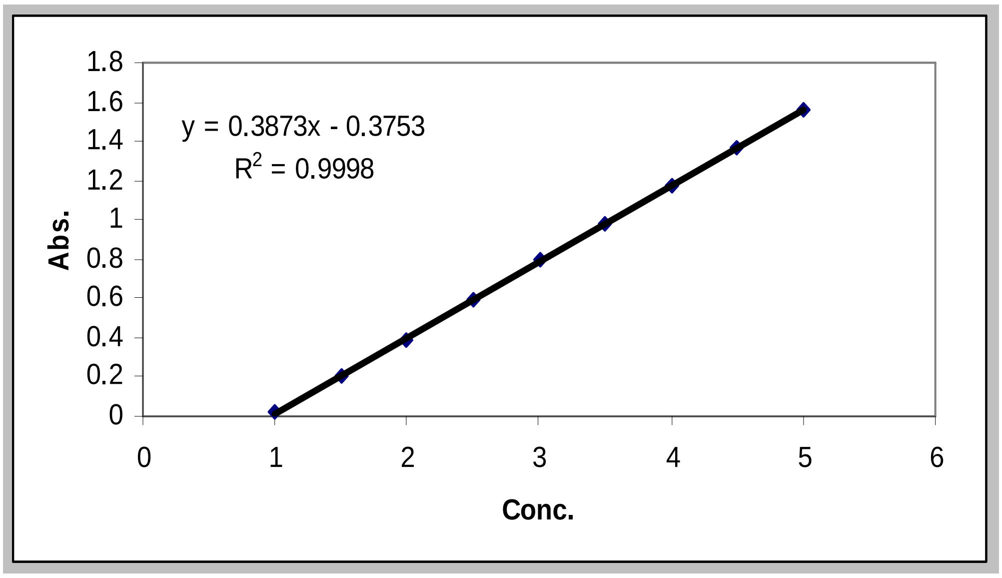


Figure (3.9) The calibration curve for copper

using AA spectroscopy

The correlation coefficient for the below line was 0.9998. With a relative standard deviation of 0.0039%.

The above calibration was tested using prepared standard solution of copper to measure the recovery; The results obtained were listed in table 3.17:

Table 3.17 Copper recovery study

Concentration of copper in ppm(mg/L) **Prepared**	**Found**	**Recovery %**	**Relative error %**
10.00	**9.88**	**98.75**	**1.24**
15.00	**14.82**	**98.78**	**1.22**
35.00	**34.56**	**98.74**	**1.26**

The standard copper preparation for 10.00, 15.00, 35.00 ppm were found 9.88, 14.82, 34.56 ppm respectively .While the error of these concentration were 0.44 for 35.00 ppm, the highest error. While the small relative error were found 1.22% for 15.00 ppm.

The concentrations of copper were found in crude oil samples for dry ashing and wet digestion methods were measured and the results listed in table 3.18:

Table 3.18 Cu concentration in Basra and Kirkuk crude oils

Copper concentration* in ppm (mg/L). ±SD				
Crude oil type	Dry ashing with HNO_3	Dry ashing with HCl	Wet digestion with HNO_3	Wet digestion with HCl
Basra crude oil	**0.619 ± 0.003**	**0.774± 0.018**	**0.633 ± 0.031**	**0.650 ± 0.028**
Kirkuk crude oil	**0.753 ± 0.001**	**0.790 ± 0.004**	**0.632 ± 0.025**	**0.724 ± 0.004**

*** Each concentration represents an average of at least three measurements**

The average concentrations of copper were found relatively low concentrations .For Basra crude oil was contain 0.619 ppm for dry ashing with HNO_3, while Kirkuk crude oil gave 0.753 ppm higher than it is in Basra crude oil sample. Also the concentration for copper in Basra and Kirkuk crude digestion with HCl was 0.650ppm and 0.724 ppm respectively. With a relative increment percentage of 10.22 %. However, the standard deviation for Kirkuk crude oil ashing with HNO_3 was 0.001, which less value, and for Basra crude oil wet digestion with HNO_3 gave high value of 0.031.

3.2.10. Vanadium:

A calibration curve for vanadium was constructed with the range from 0.5 to 5 ppm standard solutions, employing 318.5 nm was the absorption line for the vanadium.

A linear calibration line was obtained as shown in figure (3.10): The line has the equation:

$$\mathbf{Y = 0.3563\,X - 0.1692} \quad \text{------------------------------} \quad \mathbf{(3.10)}$$

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

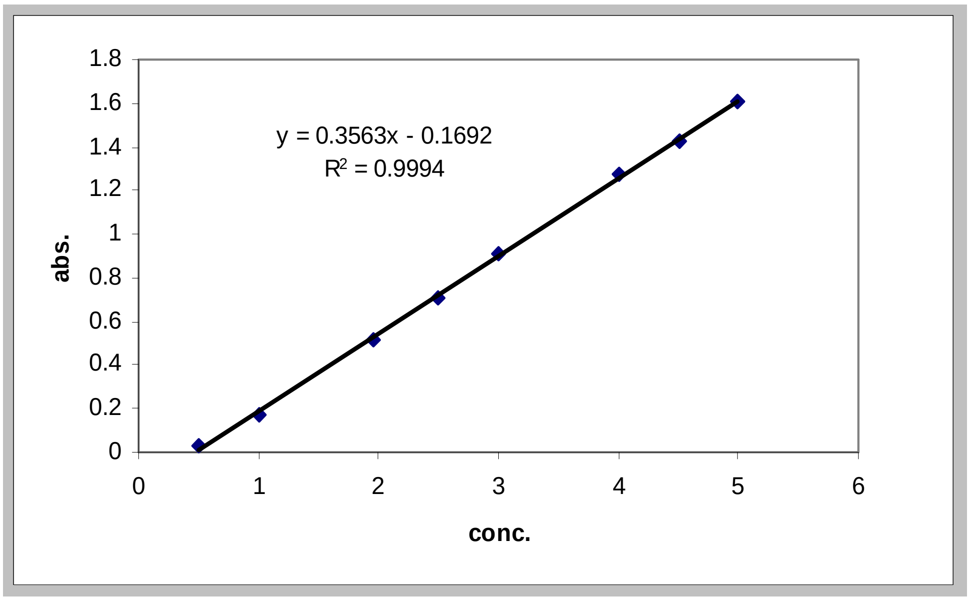


Figure (3. 10) The calibration curve for vanadium using AA spectroscopy

The correlation coefficient for the above line was 0.9994. With a relative standard deviate of 0.0531%.

The calibration curve was tested the recovery by preparation of vanadium standard solution; the results obtained were listed in table (3.19):

Table 3.19 vanadium recovery study

Concentration of vanadium in ppm(mg/L)		**Recovery %**	**Relative error %**
Prepared	**Found**		
10.00	**9.87**	**98.79**	**1.21**
25.00	**24.71**	**98.84**	**1.16**
50.00	**49.41**	**98.81**	**1.19**

The relative error for vanadium standard solution was found 1.21%; this value was accepted value for analysis intended amount of metals in crude oil sample. The above table shows the recovery of vanadium standard for different concentration were 98.79%, 98.84% and 98.81% ,and the error were found 0.12, 029 and 0.59 respectively for (10.00, 25.00 and 50.00) ppm.

The vanadium concentration was measured for wet digestion and dry ashing methods. The amounts of this metal was found high quantity than other metals in crude oil samples; the results were listed in table (3.20)

Table 3.20 V concentration in Basra and Kirkuk crude oils

Vanadium concentration* in ppm (mg/L). ±SD				
Crude oil type	Dry ashing with HCl	Dry ashing with HNO_3	Wet digestion with HCl	Wet digestion with HNO_3
Basra crude oil	**42.440 ± 0.021**	**42.921 ± 0.0163**	**42.231 ± 0.001**	**42.670 ± 0.005**
Kirkuk crude oil	**29.316 ± 0.003**	**29.310 ± 0.001**	**29.285 ± 0.004**	**29.297 ± 0.002**

*** Each concentration represents an average of at least three measurements**

The concentration range of vanadium using dry ashing method with HNO_3 was found highest concentration than wet digestion with HNO_3 method in both samples. However, the concentration of vanadium in Basra crud oil blends more 31% than Kirkuk crude oil blends for wet digestion and dry ashing methods.

3.2.11. Zinc

A calibration curve of zinc standard solution was constructed from 0.5 to 5 ppm solution. These measurements were carried at 213.9 nm as the absorption line for the zinc element.

A linear calibration line was obtained as shown in figure (3.11). The line has the equation:

$$\mathbf{Y = 0.1236X - 0.07} \text{--} \mathbf{(3.11)}$$

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

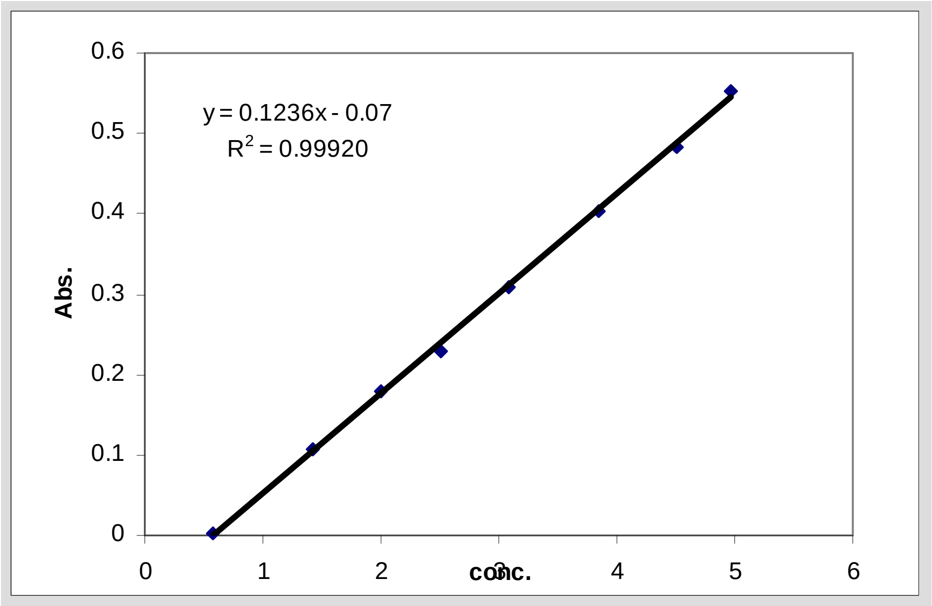


Figure 3.11The calibration curve for zinc *using AA spectroscopy*

The correlation coefficient for the below line was 0.99920 with a relative standard deviate of 0.00581%.

The calibration curve was tested the recovery by preparation of zinc standard solution; the results obtained was listed in table 3.21:

Table 3.21 Zinc recovery study

Concentration of zinc in ppm(mg/L)		**Recovery %**	**Relative error %**
Prepared	**Found**		
10.00	**9.84**	**98.45**	**1.60**
15.00	**14.77**	**98.49**	**1.51**
20.00	**19.71**	**98.54**	**1.46**

The relative error of high concentration standard solution was found 1.46%, with high recovery of 98.54%. While the relative error was found 1.6%, and the recovery was 98.45.The error range from 0.16 to 0.22; the range of these errors was accepted value to determinate the concentration of zinc in crude oil samples.

The table 3.22 shows zinc concentrations which found in two types of crude oil samples:

Table 3.22 Zn concentration in Basra and Kirkuk crude oils

Zinc concentration* in ppm (mg/L). ±SD				
Crude oil type	Dry ashing with HNO_3	Dry ashing with HCl	Wet digestion with HNO_3	Wet digestion with HCl
Basra crude oil	**1.820 ± 0.002**	**1.798 ± 0.013**	**1.808 ± 0.067**	**1.786± 0.001**
Kirkuk crude oil	**0.638 ± 0.004**	**0.609 ± 0.033**	**0.625 ± 0.010**	**0.589 ± 0.002**

*** Each concentration represents an average of at least three measurements**

The average concentration of zinc was found 0.638 and 1.820 for Kirkuk and Basra crude oil, with a relative increment percent of 64.94%. The standard deviation of 0.067 was high value for Basra crude oil wet digestion with HNO_3; while for Basra crude oil digestion with HCl solution had less value of 0.001.

The zinc concentration with atomic absorption spectroscopy was found to range from (0.638-1.82) ppm .However, it was not detected with U.V –Vis spectrophotometry in each crude oil samples because of the interferences with other metals.

Table 3.23 was listed the average concentration of metals that found in southern crud oil samples, and the significant differences between the two technique methods, U.V –Vis and atomic absorption spectrophotometry.

Table 3.23 comparison of metal concentrations in Basra crude oil

ions	Concentration of metals in Basra crude oil by UV-Vis in ppm (mg/L)				Concentration of metals in Basra crude oil by atomic absorption in ppm (mg/L)			
	Ash with HNO3	**Ash with HCl**	**Wet digestion With HNO_3**	**Wet digestion With HCl**	**Ash with HNO3**	**Ash with HCl**	**Wet digestion With HNO_3**	**Wet digestion With HCl**
pb	**0.469**	**0.234**	**0.532**	**0.364**	**0.473**	**0.236**	**0.538**	**0.367**
Cu	**0.621**	**0.761**	**0.624**	**0.608**	**0.619**	**0.774**	**0.633**	**0.650**
Fe	**10.521**	**10.314**	**10.419**	**10.181**	**10.646**	**10.435**	**10.542**	**10.301**
Ni	**15.238**	**15.047**	**15.421**	**15.643**	**15.409**	**15.216**	**15.594**	**15.819**
V	**42.817**	**42.337**	**42.566**	**42.129**	**42.921**	**42.440**	**42.670**	**42.231**
Zn	**	**	**	**	**1.820**	**1.798**	**1.808**	**1.786**

** Not detected

The different concentrations of metals were determinate by two techniques.

It was found that the concentration of metals analyzed by UV-Vis spectroscopy using both samples treatment method almost the same.

The atomic absorption measurements were also the same using both methods.

For the above table was listed, that the average concentration of lead was found higher detected using atomic absorption than UV-Vis spectroscopy.

The concentration of lead in Basra crude oil using dry ashing with HNO_3 measured by atomic and UV-Vis spectroscopy was 0.469ppm, 0.473ppm; the increment percentage was found 0.84%.while the low results of lead concentration using dry ashing and wet digested with HCl may be attributed to the formation of lead-chloride complexes which reduce the amount of free Pb.

But the average concentration found relatively large, with increment percentage of 37.2% for nickel concentration in Basra crude oil using ashing with HNO_3 15.421 ppm and 15.594 ppm.

Also the above table shows, that not detected of zinc for **UV-V**is spectroscopy, and found 1.808 ppm detected by atomic absorption in Basra crude oil using wet digestion with HNO_3.

The average concentration of metals that found in northern crud oil sample, which gave significant differences between the two technique methods, U.V –Vis and atomic absorption spectrophotometry; that the results were listed in table 3.24:

Table 3.24 comparison of metal concentrations in Kirkuk crude oil

ions	Concentration of metals in Kirkuk crude oil by UV-Vis in ppm (mg/L)				Concentration of metals in Kirkuk crude oil by atomic absorption in ppm (mg/L)			
	Ash with HNO3	Ash with HCl	Wet digestion with HNO_3	Wet digestion With HCl	Ash with HNO3	Ash with HCl	Wet digestion with HNO_3	Wet digestion With HCl
Pb	0.571	0.267	0.615	0.331	0.578	0.269	0.621	0.334
Cu	0.740	0.776	0.639	0.711	0.753	0.790	0.632	0.724
Fe	9.332	9.170	9.058	9.126	9.441	9.278	9.164	9.231
Ni	24.241	24.057	24.461	24.672	24.514	24.328	24.736	24.949
V	29.239	29.245	29.226	29.214	29.310	29.316	29.297	29.285
Zn	**	**	**	**	0.638	0.609	0.625	0.589

** Not detected

The different concentration of metals was determinate by two techniques. It was found that the concentration of metals analyzed by UV-Vis spectroscopy using both samples treatment method almost the same.

The atomic absorption measurements were also the same using both methods.

Table 3.24 lists the average concentration of lead, which have relatively small amount than other metals. However, the amount of lead concentration using ashing with HNO_3 in Kirkuk crude oil gave 0.578 ppm, 0.571ppm respectively detected by atomic and UV-Vis spectroscopy. While the low results of lead concentration using dry ashing and wet digested with HCl may also be attributed to the formation of lead-chloride complexes which reduce the amount of free Pb.

The average concentration of vanadium gave higher amounts than other metals using digestion with HCl in Kirkuk crude oil; it gave 29.214and 29.285 ppm respectively detected by atomic and UV-Vis spectroscopy.

While not detected of zinc concentration for UV-Vis spectroscopy, but found 0.589ppm detection of zinc by atomic absorption in Kirkuk crude oil using wet digestion with HCl.

The two analyzed technique were given almost the same results as shown in the table.

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Determination of some elements in Basra and Kirkuk crude oil blends

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University in Partial Fulfillment of the Requirements for the
Degree of Master of Science in Chemistry

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(B.Sc 2003)

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جمهورية العراق
وزارة التعليم العالي
والبحث علمي
جامعة النهرين
كليَّة العِلوْمِ
قسم الكيمياءِ

دراسة تقديرية لعناصرِ منتخبة في مزيجات نفطي البصرة وكركوك الخام

رسالة مقدمة إلى
كليَّةِ العلوم في جامعةِ النهرين كاستكمال جزئيٍ لمتطلباتِ نيل
درجةِ ماجستير علومِ في الكيمياءِ

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جمادي الاولى ١٤٢٧ **آيـــار ٢٠٠٦**

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الخُـلاصــة

يمثل هذا العمل أسهامه صغيرة لجلب الانتباه إلى كمية المعادن في مزيج النفط الخام في كل من البصرة وكركوك .وهذه المعـادن قد تؤثر على تحضير وتصفية النفط الخام.

ففي الفصل الأول لهذه الأطروحة ، أعطيت مقدمة حول النفط الخـام واصل تكوينه متضمنا كلتا النظريتين العضوية واللآعضوية وكذلك تركيبه وأنواع النفط الخـام وأهميتهُ والمشــاكل الخاصة بوجود المعـادن التي هي ذات أهمية .

الفصل الثاني يبحث في الجزء العملي والذي يتضمن الأجهزة و اربعة طرق مختلفة للنمذجة. إما النتائج ومناقشتها مقدمة في الفصل الثالث . وتضمنت النتائج حســاب تركيز المعادن،

Cu، Zn، Fe، Pb، Vوأخيرا Ni.

ووجدت هذه العناصر بتراكيز كبيرة نســبياً لعنصر الفنيديوم V بمعدل تركيز (٤٢,٩٢١ ، ٢٩,٣١٠) جزء بالمليون على التوالي بالترميد مع حامض النتريك المركز من نماذج النفط الخـام في البصرة وكركوك.

في حين ان كمية العناصر الأخرى وجدت (١٠,٦٤٦ ، ٩,٤٤١) جزء بالمليون، (٢٤,٥١٤ ، ١٠,٦٤٦) جزء بالمليون ، (٠,٧٤ ، ٠,٦٢١) جزء بالمليون (0.638, 1.820) ، جزء بالمليون للعناصر Fe ، Ni، Cu، Znعلى التوالي في كل من البصرة وكركوك بالترميد الجـاف مع حامض النريك المركزمن نماذج النفط الخـام ؛ تركيز الرصاص قد أعطى اقل واخفض نســبة بالمقارنة مع المعادن الأخرى (٠,٤٦٩ ، 0.571) جزء بالمليون في البصرة وكركوك من نماذج النفط الخـام.

في حين أن الهضم الرطب مع حامض النتريك أعطى (١٠,٥٤٢ و ٩,١٦٤) ، (15.594 و 24.736)،(0.624 و 0.639) ، (1.808 و 0.625) جزء بالمليون للعناصر Fe ، Ni، Cu، Znعلى التوالي للبصرة وكركوك لخليط النفط الخـام .

كما إن التراكيز لهذه العناصر تختلف أحيانا بشكل كبير تبعا لنوعية النفط و الطريقة المستخدمة للنمذجة.

Summary

This work represented a contribution to draw attention towards the amount of metals in Basra and Kirkuk crude oil blends. These metals may effect the processing refineries of crud oils.

In chapter one of this thesis, an introduction was given on the crude oil and it's origin including both inorganic and organic theories; also the composition and types of crude oil, the importance and the problems associated with the presence of the metals. Finally, the methods used for the determination of metals were given.

The second chapter was dealing with experimental part, which included instruments and four different methods of sample preparation before analysis.

The results and discussion was presented in chapter three. The results included the determinate concentrations of Cu, Zn, Fe, Pb, V, and Ni elements.

These elements were found to be relatively large concentrations in vanadium with an average of (42.921, 29.310) ppm in Basra and Kirkuk crude oil samples respectively using dry ashing with HNO_3. While the concentrations of elements Fe, Ni, Cu, and Zn were found to be relatively smallest (10.646, 9.441)ppm, (24.514, 10.646)ppm, (0.74, 0.621)ppm, (1.820,0.638)ppm respectively in Basra and Kirkuk crude oil samples too ; The lead concentration was much lower than other elements (0.469 and 0.571)ppm in Basra and Kirkuk crude oil samples.

Wet digestion with HNO_3 gave (10.542 and 9.164), (15.594 and 24.736), (0.624 and 0.639), (1.808 and 0.625) ppm for Fe, Ni, Cu, Zn, respectively,

in Basra and Kirkuk crude oil blends. The concentrations of these metals differ, some times, for certain metals in both types of the crude oil samples.