TÜRKİYE
FIRAT UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

# COMPARISON OF ELEMENT CONCENTRATIONS IN CRUDE OIL SAMPLES TAKEN FROM DIFFERENT SITES IN IRAQ AND TURKEY

**Ziyad Nawzad**

Master's Thesis

DEPARTMENT OF CHEMISTRY

Analytical Chemistry

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# THESIS APPROVAL

This thesis, which was prepared according to the thesis writing rules of the Graduate School of Natural and Applied Sciences, Fırat University, was evaluated by the committee members who have signed the following signatures and was unanimously approved after the defense exam made open to the academic audience.

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This thesis was approved by the Administrative Board of the Graduate School on

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# DECLARATION

I hereby declare that I wrote this Master's Thesis titled “Comparison of Element Concentrations in Crude Oil Samples Taken from Different Sites in Iraq and Turkey” in consistent with the thesis writing guide of the Graduate School of Natural and Applied Sciences, Firat University. I also declare that all information in it is correct, that I acted according to scientific ethics in producing and presenting the findings, cited all the references I used, express all institutions or organizations or persons who supported the thesis financially. I have never used the data and information I provide here in order to get a degree in any way.

1 February 2021

**Ziyad Nawzad**

# PREFACE

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# ABSTRACT

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The ability to accurately determine the metal contents of crude oils is necessary for reasons ranging from the need to identify the source of the oils (Ni and V) to the removal of components that might inhibit catalysis during refining or impact negatively on the environment during hydrocarbon combustion. Determination of the petroleum source is very important to prevent oil smuggling.

The aim of this thesis is a comparison of element concentrations in crude oil samples taken from different sites in Turkey and Iraq. For this purpose, the crude oil samples were collected from a few locations including Duhok, Zakho, and Erbil from Iraq, Batman, and Adiyaman from Turkey. Sample Digestion was performed by microwave (MW) oven-using HNO3 and polytetrafluoroethylene (PTFE™). After that, the digested samples were diluted for further analysis. The metal concentrations were determined by using Inductively coupled plasma-mass spectrometry (ICP-MS). For quantitative analysis, calibration graphs were obtained.

From the results obtained, it was found that Vanadium V concentrations are in ranges of (0.082 – 24.490) mg/L, while Nickle Ni concentrations are varying between (1.028 – 10.740) mg/L.

**Keywords:** Crude oil, Nickle, Vanadium, microwave, ICP-MS.

# ÖZET


## Irak ve Türkiye'deki Farklı Bölgelerden Alınan Ham Petrol Numunelerindeki Element Konsantrasyonlarının Karşılaştırılması

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Ham petrollerin metal içeriklerini doğru bir şekilde belirleyebilme yeteneği, yağların kaynağının (Ni ve V) belirlenmesi ihtiyacından, arıtma sırasında katalizi engelleyebilecek veya hidrokarbon sırasında çevreyi olumsuz etkileyebilecek bileşenlerin çıkarılmasına kadar değişen nedenlerden dolayı gereklidir. Petrol kaçakçılığının önlenmesi için petrol kaynağının tespiti çok önemlidir.

Bu tezin amacı, Türkiye ve Irak'taki farklı sahalardan alınan ham petrol numunelerindeki element konsantrasyonlarının karşılaştırılmaktır. Bu amaçla Irak'ın Duhok, Zaho, Erbil gibi birkaç lokasyonundan, Türkiye'den Batman ve Adıyaman'dan ham petrol örnekleri toplanmıştır. Numune çözünürleştirilmesi, HNO3 ve politetrafloroetilen (PTFE ™) kullanılarak mikrodalga (MW) fırında yapıldı. Bundan sonra, çözünürleştirilmiş örnekler daha fazla analiz için seyreltildi. Metal konsantrasyonları, Endüktif olarak eşleşmiş plazma-kütle spektrometresi (ICP-MS) kullanılarak belirlendi. Kantitatif analiz için kalibrasyon grafikleri elde edildi.

Elde edilen sonuçlardan Vanadyum konsantrasyonunun (0.082 - 24.490) mg/L aralığında olduğu, Nikel konsantrasyonunun ise (1.028 - 10.740) mg / L aralığında değiştiği bulunmuştur.



**Anahtar Kelimeler:** Ham petrol, Nikel, Vanadyum, mikrodalga, ICP-MS.


...

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# SYMBOLS AND ABBREVIATIONS

## Symbols

| | |
|---|---|
| S | : sulfur |
| V | : vanadium |
| Ni | : nickel |
| Cu | : copper |
| Fe | : iron |
| As | : arsenic |
| Cr | : Cromium |
| Pb | : lead |
| Mn | : manganese |
| Co | : Cobalt |
| Cd | : cadmium |

## Abbreviations

| | |
|---|---|
| API | : American petroleum institute |
| NCBN | : Naphtha Company Branoble |

# 1. INTRODUCTION

## 1.1. General Information

Pollution from various human activities like industry, agriculture, and wastewater in urban areas leads to a negative impact on the environment, health, and the economy. One of the most critical problems in the world is the pollution of soils with minerals, semi-minerals, and organic pollutants [1]. Fears arise when the contaminates are transported through underground water, sewerage, dust, and entering the food chain [2-4]. Heavy metals pollution is a probable danger to the environment [5]. The issues of oil and gas and their pollution in Iraq are very complex, particularly when it comes to the decision to raise the production of energy which may have different influences on the components of the ecosystem [6].

Accidental leakage of crude oil into the atmosphere due to operational accidents, equipment failure, and intentional weakness in the channels that transport crude oil are known as oil leaks. This phenomenon affects the soil environment and the entire aquatic ecosystem. Plant growth, micronutrients, and microorganisms in soils and the global environmental system are generally affected via the contamination of crude oil [7]. The activities of oil exploration and utilization in northern Iraq are the essential reason for the oil leaks, which always have an adverse effect on the ecosystem, especially in Duhok and Erbil. Thus, in the study area, food output, social-economic, and population health are negatively affected.

To comprehend the possible ecological effects that may happen through an oil spill and release, the molecular components of petroleum hydrocarbons, non-hydrocarbons, and their structures should be taken into consideration. The natural composition of petroleum is too complicated, and the difference somewhat between petroleum tanks. Generally, petroleum is a complex mixture of hydrocarbon molecules (consisting of only carbon C and hydrogen H) and non-hydrocarbon molecules (consisting of carbon C, hydrogen H, and a few other elements like sulfur S, nitrogen N, and oxygen O) that consist of the partial decomposition of biomaterials [8].

### 1.1.1. Aim and Objective of the Study

As a result of the environmental and ecotoxicological impacts of trace elements and heavy metals contamination, the present survey aims:

1. To assay the level of various trace elements/metals pollutants in crude oil samples. Furthermore, to determine their impact on northern Iraq and southeastern provinces of Turkey within the spill zone, including Erbil, Duhok, Zakho, Batman, and Adiyaman

2. To determine the American Petroleum Institute (API) level in each crude oil samples. additionally, the experimental procedures applied to the samples were also assessed by Inductively coupled plasma-mass spectrometry (ICP-MS).

## 1.2. Crude Oil and The Importance of Crude Oil

Crude oil is a good resource of transportation such as the land, sea, and air transport and these types of transportation usually rely on products refined from crude oil. As a result, refineries transform around 80% of crude oil into transportation fuels. Moreover, crude oil is a central part of modern life and the world's most important energy resources which is utilized to heat houses, commercial buildings, electricity generation, and also in the industry of medicines, cleaning products, waxes, plastics, artificial rubber, and asphalt. Respectively, the manufacturing of crude oil supplies hundreds of jobs in many different fields such as exploration, production, transportation, refining, and marketing. Besides, it cooperates with various research and technological development [9].

The origin of crude oil was the topic of much discussion, but it is currently acceptable that it is originally organic and that the raw materials were groups of marine creatures with the plant life deposited in water. Oil is a remnant of those living creatures and plants that have long-lived for in a nautical environment. Over time, the remnants were covered with a layer of clay. The heat and pressure of those layers associated the residue to convert it into crude oil [10].

Crude oil is essentially a complicated mixture of organic and inorganic materials, providing trace elements which can be gathered into categories of inorganic compounds [11]. The importance of identifying trace elements present in crude oils helps in obtaining more information about exploration, utilization, production, and refining process [12]. Both Hitchon and Filby mentioned that crude oils can be categorized based on the mineral-trace content present in identical litho-stratigraphic circumstances in families [13]. There are problems of marine contamination in various origins in which trace elements can be used to distinguish crude oils, according to an ecological site estimation, these sites contaminated with petroleum are an expansion of pollution [14]. Crude oils are categorized according to trace minerals as a heavy, medium, light, and remnant fraction [15]. Refining light crude oil requires a lower expense compared to heavy crude oil due to the low level of mineral content, adding hydrogen H or product waste because of the carbon C rejection may result in higher costs [16].

Alkanes, cycloalkanes, aromatic compounds, and a few other organic compounds that contain Sulfur, Oxygen, and Nitrogen are the main components of crude oils. Furthermore, the following minerals (Iron, Nickle, Copper, and Vanadium) are present in the crude oil at a minimum quantity. The ratio of the chemical elements of the crude oils is somewhat similar but the molecular components vary from each other [17]. Crude oils range in color from a light color to dark one, and

in intensity from liquid form to bitumen such as solid materials. Crude oils contain Carbon around 84 % to 87.4 %, Hydrogen about 10.9 % to 13.8 %, Sulfur from 0.05 % to 6.89 %, Oxygen 0.078 % to 1.80 %, Nitrogen 0.03 % to 1.20 %, metals, salts and others around 0.001 % to 0.15 % [17].

### 1.2.1. History of Crude Oil

Crude oils have been recognized for a long-term ago. Crude oil was reported by archeologists who have been using and extracting for almost 5,000 years before the era of Christ, the Kerch and Ephrata shore in China's Sichuan province are among the oldest known oil wells. Several centuries ago, crude oil had some civilian works and also a few applications for medical purposes. For instance, many prescriptions for medicines that involved petroleum has been illustrated by the Greek scientist Hippocrates. In one of the old manuscripts has written "patients should be rubbed with oil so that the disease is eliminated. White oil eliminates cough disease. Black oil removes the logic of coughing [18].

In addition, the ancient Egyptians used crude oil for many medical goals, supposedly as like as a covering of a wound, laxative, and ointment. After many centuries, crude oil in Peru, Cuba, Bolivia, and Mexico has been discovered by Spanish explorers. The demand for cheaper and appropriate energy sources increased due to the industrial revolution. Crude oil has been considered an easy way to transfer the energy source. The industrial revolution improved at the beginning of the twentieth century to the point the that industry of oil became the primary resource of energy, broadly due to the appearance of cars. The use of oil as the main energy supplier over the course of time in the history of mankind will be a matter for some centers, however, it will have a deep impact on the global industry [19].

So far, military service or construction work has been the main field of crude oil use. So it is therefore difficult to assume that what our life would be like without petroleum. Crude oil is utilized as lubrication for a different part of the machinery, and it also brings energy and heat to our homes and our machines. A barely modern device would work without depending on different crude oil products [18]. The actual production of petroleum may have started on August 25, 1860, as the first 22-meter-deep industrial crude oil was opened in Oil Creek, Pennsylvania. Despite that, crude oil can be dated back over 2,000 years. Subsequently, there was the beginning of quick progress in the production and processing of crude oil. A few years later, NCBN was launched by a Swedish businessman named Alfred B. Noble simultaneously with his brothers. The naphtha Co. transported the crude oil extracted in Baku, Russia to refineries through the pipelines [18]. In recent years, significant progress has been made in the production of crude oil and reserves all over the world. As shown in **Figure 1.1**. Production of crude oil all over the world 2018, source: U.S. Energy Information Administration the production of crude oil worldwide in 2018.

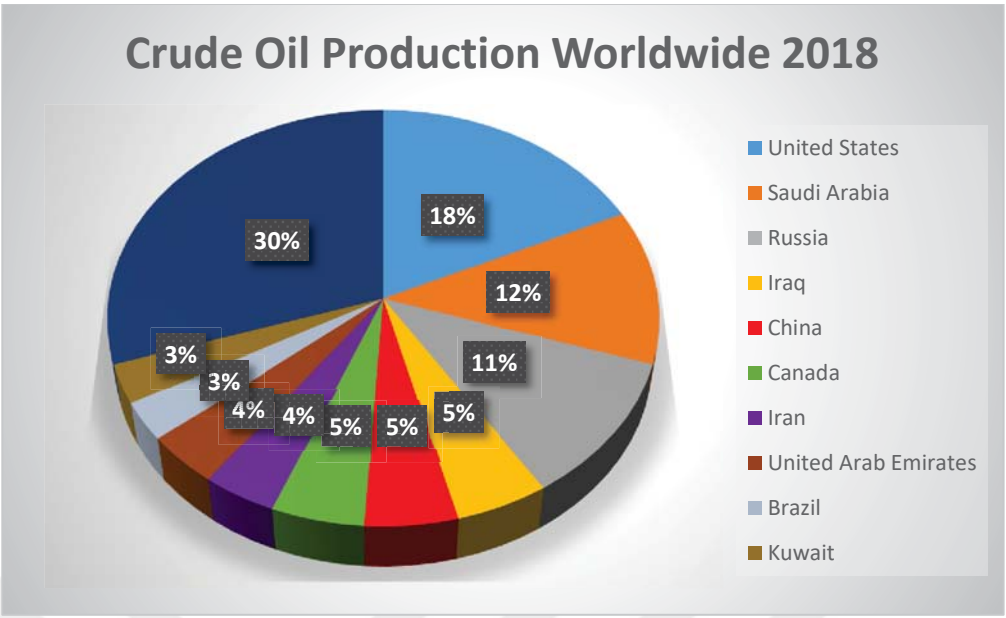


**Figure 1.1**. Production of crude oil all over the world 2018, source: U.S. Energy Information Administration

The economic field in Turkey has been experienced very rapid growth for 37 years ago. Since 1983, Turkey's demand for crude oil is expected to expand by 3.2 % annually, and its economy is expected to expand by 4.2 % annually, as a result, in 2001 produced 0.6 million bpd, and it is predicted to produce 1.4 million bpd in 2025 [20]. As can be seen from **Table 1.1.** Oil consumption and production in Turkey, 1990-2001 (thousands bpd), including crude oil, natural gas plant liquids, other liquids, and treatment refineries gain [20, 21].

**Table 1.1.** Oil consumption and production in Turkey, 1990-2001 (thousands bpd)

| **Year** | **1990** | **1991** | **1992** | **1993** | **1994** | **1995** | **1996** | **1997** | **1998** | **1999** | **2000** | **2001** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Production** | 77 | 92 | 88 | 80 | 76 | 71 | 71 | 72 | 69 | 63 | 57 | 52 |
| **consumption** | 476 | 468 | 492 | 564 | 540 | 601 | 633 | 634 | 627 | 626 | 663 | 619 |

The Middle East and Russia are the main resources of Turkish oil imports. While Iraqi supplies gradually arise, Turkey's imports from Saudi Arabia have lately descended. The Turkish Ceyhan port is the main way out for Iraqi oil exports [22]. Turkey possesses around 930 million tons of crude oil reserves [23]. In 2005, the proportion of domestic production to meet the demand for oil in Turkey was predicted to reach 2 percent, and in 2010 it was predicted to reach 1 percent [22]. As shown in **Figure 1.2.** Production of crude oil in Turkey from 1998 to 2002 [24]. The

extraction of oil is significant for refining, pipelines, and human activities, however, Turkey has quite little of its crude oil. The Kirkuk Ceyhan pipeline and the Baku-Tbilisi-Ceyhan pipeline are two long oil lines that cross eastern Turkey. Furthermore, cement, minerals, and stone are the other essential patriotic industries in Turkey [25].

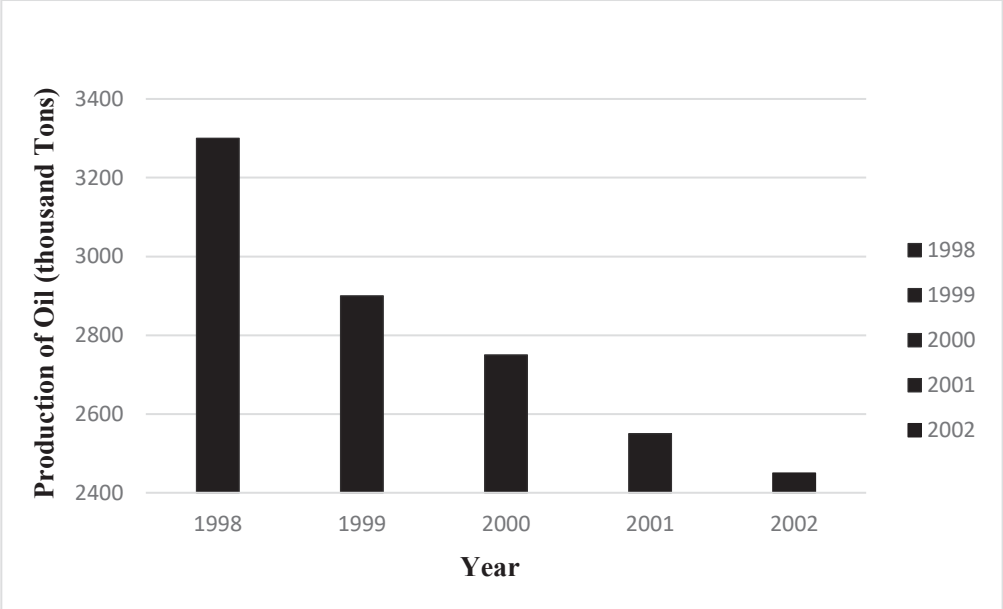


**Figure 1.2.** Production of crude oil in Turkey from 1998 to 2002 [24].

Historically and at the current time, Iraq occupies a significant site in improving policy and economical orientation of the global oil market. The confirmed reservoirs of Iraqi oil amounting to 116 billion barrels-and maybe to some extend overvalued while Saddam Hussein ruled-are in between the biggest in the world. The kingdom of Saudi Arabia is the first resource base in the world, and the second-largest base is Iraq, moreover, the important component in determining international oil supplies and pricing has been Iraq's policy of exporting for more than 30 years [26].

The current crude oil production in Iraq is about 2.50 percent of total global oil resources or 2.00 million bpd. The third-largest crude oil production in the world after Saudi Arabia and Iran is Iraq, whose crude oil reached 4 million bpd in 1979. Before the battle between Iraq and Kuwait in 1990, the production of crude oil was approximately 3.400 million bpd, started to descend in the nineties century as a result of the Gulf War and putting international sanctions on Bagdad. In 2003, as the U.S.A. military moved into Iraq, the capacity of oil production in Iraq was evaluated about 2.40 -2.60 million barrels per day. Average production was significantly lower than average in the latest years, reaching 1.50 million barrels per day in 2003, 2.0 million barrels per day in 2004, and in 2005 it has reached 1.80 million barrels per day [26]. As shown in **Figure 1.3.** Production of

crude oil in Iraq from 1993 to 2005 [24]. At the beginning of 2006, average oil production rates in Iraq were about 2.060 million barrels per day, which is much lower than the expected goal of the Iraqi government at 2.50 million barrels per day for 2006. Nevertheless, the Iraqi government was capable to achieve its budget profit goals because the oil prices were higher than expected [26].

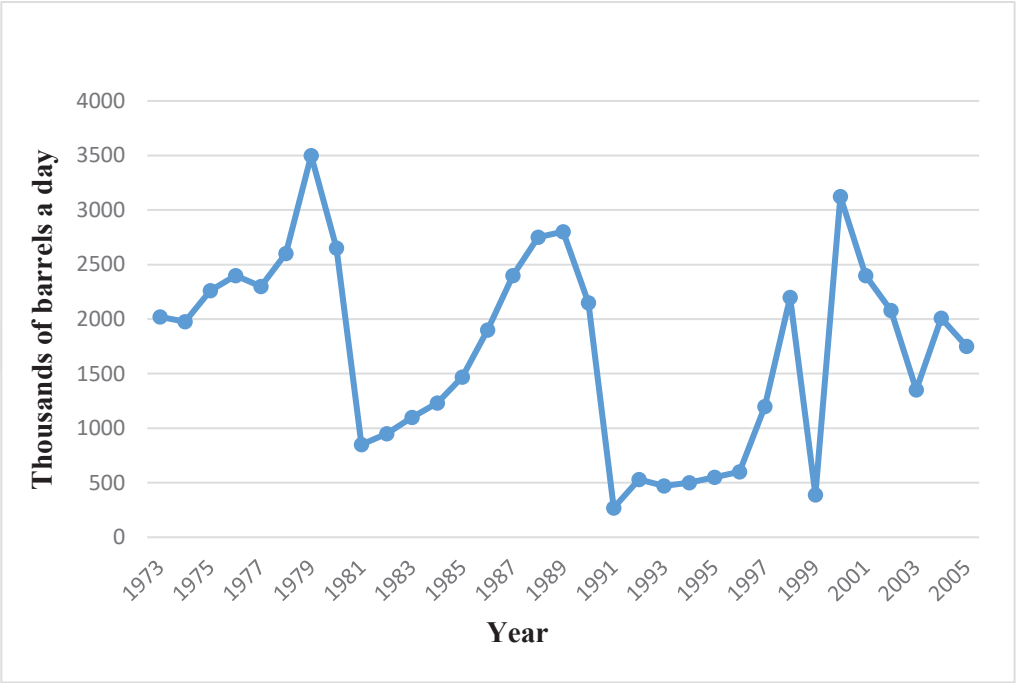


**Figure 1.3.** Production of crude oil in Iraq from 1993 to 2005 [24].

Recently, the Iraqi government has been unable to significantly raise its capability to produce crude oil due to economic sanctions, war, and civilian war. However, the oil scientists confirmed that the possibility of crude oil in Iraq is huge and can be the main agent affecting pricing tendencies and crude oil resources in the forward years [26]. Currently, southern Iraq in Basra and northern Iraq in Kirkuk are the two major geographical regions for the production of crude oil. The wide majority of crude oil production in northern Iraq is presented through the Kirkuk oil field [26]. In the last days of the Ottoman Empire, the search for oil in Iraq began by oil specialists, until they obtained privileges to explore for oil in Iraq. In 1927, the first vast crude oil field has been discovered in northern Iraq in and around the Kirkuk region [27]. The viscosity of the oil in the tank increases due to the oil being re-injected into the Kirkuk field, which makes the oil extraction harder, expensive, and respectively some damage to the field may always be. Most of the crude oil production in the second-largest field in northern Iraq is exported by Bay Hassan via the pipeline through Turkey [26].

In 1939, the Mosul Oil Firm discovered the Ain Zala field in the Mosul region. Ten years later, in 1949, the huge Zubair field in southern Iraq in and around the Basra region was discovered

by the Basra Oil Firm. Consequently, in 1991 the Shewashuk field in Koya was the first oil field to be excavated in the KRG, then fourteen years later, in December 2005 the Tawki field east of Zakho was excavated [27].

### 1.2.2. Classification of Crude Oil

Crude oil is a complicated mixture consisting of different hydrocarbons such as (paraffinic, naphthenic, olefinic, and aromatic compounds) that combine with changeable quantities of organic sulfur substances and a quite minimal amount of nitrogenous materials and oxygen [28, 29]. The most important saturated hydrocarbons contain only carbon-carbon single bonds in crude oil known as paraffines or (alkanes) which is named methane chain. The boiling point of paraffin is approximately between 40-200 °C which makes this compound liquid at room temperature. The most significant constituents of the production of refined liquids are naphthenes or (cycloalkanes), which are saturated cyclic hydrocarbon compounds [19]. Unsaturated hydrocarbon compounds contain carbon-carbon multiple bonds (double, triple, or both). These are unsaturated because they contain fewer hydrogens per carbon than paraffines. Unsaturated hydrocarbons are known as olefins. Those that contain carbon-carbon double bonds are called alkenes, while those that contain carbon-carbon triple bonds are known as alkynes. Moreover, the aromatics are generally unsaturated closed-loop chain, which makes up a tiny portion of all the oil raw materials. Consequently, Benzene is an almost common aromatic compound that exists in most crude oils [19].

Most of the crude oil contains approximately 84.0% to 87.4% C, and 10.9% to 13.8% H therefore crude oils mostly rely on Carbon and Hydrogen [30]. There are a few other elements present with a tiny portion of crude oil such as Sulfur, Oxygen, and Nitrogen. The presence of sulfur in crude oil is approximately less than 6.0%, and as a result, sulfur is measured as the third most available component of crude oil after Carbon and Hydrogen. In general, a high amount of Sulfur in crude oil means a high specific gravity that leads to heavy crude oil [19]. The other elements, such as Oxygen exist in most crude oils commonly not more than 2.0% (found in organic compounds such as carbon dioxide, phenols, ketones, and carboxylic acids) occurring in crude oils in different quantities. Subsequently, crude oils contain very low amounts of Nitrogen compounds, not more than 1.0%. The Nitrogen compounds in crude oils might be categorized as basic or non-basic. Basic Nitrogen compounds contain pyridines, and the non-basic Nitrogen compounds are a greater part of nitrogen in crude oils that usually content of pyrrole types. In addition, small amounts of metals such as Vanadium, Nickel, Iron, and Copper are also present in crude oil [19] as shown in Table 1.2.

**Table 1.2.** The chemical composition of some elements present in most of the crude oils.

| Elements | Composition (wt%) |
|---|---|
| **Carbon** | (84.0-87.4)% |
| **Hydrogen** | (10.9-13.8)% |
| **Sulfur** | (0.053-6.0)% |
| **Oxygen** | (0.06-2.0)% |
| **Nitrogen** | (0.03-1.0)% |
| **V, Ni, Cu and Fe** | (0.1-2000) ppm |

Crude oils have many properties. How crude oil is categorized hugely relies on how the classification is used. The characterization of oils can be slightly beneficial depending on their geographical exporter. The crude oils are categorized into 7 categories by Carpatica Classification based on the percentage of paraffines, naphthenes, and aromatic compounds [31]. These categories are divided into 12 groups specified by the content of wax, asphalt, and resin compound and sulfur content.

According to the Environmental Protection Agency (EPA) crude oil can be classified into 4 classes [32]:

1. First class, light volatile oil, this category is poisonous to humans and many other forms of life, therefore most of the light crude oil products are involved in this category.
2. Second class, non-viscous oil, contains medium-to-heavy paraffin-based oil and less poisonous than the first class.
3. Third class, viscous and heavy oil, low toxicity, and also contains medium-to-heavy crude oil with the remaining fuel.
4. Fourth class, non-liquid oil, is comparatively non-toxic and contains heavy crude oils, weathering oils, a few paraffin oils, and the remaining oils.

Another classification of crude oil is based on the level of Sulfur contents; crude oil is categorized as (sour or sweet). The high sulfur concentration in crude oil is referred to as high sulfur or “sour”. While the low concentration of sulfur in crude oil is referred to as low sulfur or “sweet”. The sweet crude oil is usually more required and desirable than the sour crude oil due to the high amount of Sulfur in sour oils which can be considered hard to refine, undesirable, unsafe for extraction, and difficult for transportation compared to sweet crude oil. Since sulfur is high in sour crude oil, it needs more refining, which includes both financial and environmental costs [33].

### 1.2.3. API Gravity

Crude oils are defined in terms of API (American Petroleum Institute) gravity. At the beginning of the crude oil industry, the American Petroleum Institute (API) measured the density of crude oil by API gravity [34]. The specific gravity of the API calculations is always set at 60 degrees Fahrenheit (15.6 °C). The API gravity is found as follows:

$$API\ Gravity\ = (141.5/(Specific\ Gravity)) - 131.5 \quad (1.1)$$

Crude oils are also classified into two types in terms of API gravity, light, and heavy crude oils. The lower the API gravity is, the greater the specific gravity and resulting in heavier (more dense) crude oils. Heavy crudes contain a higher amount of sulfur and some other elements, that makes crude oil harder and more cost in order to convert it into useable refined products. While the lighter (less dense) crude oils have low specific gravity and more useable and valuable when run through refinery products [35, 36]. In addition, one of the importance of API gravity is used to classify oils as light, medium, heavy and extra heavy. The API of crude oils varies typically between 10 and 50, with most crude oils falling in the range of 20 - 45. As the "weight" of an oil is the largest determinant of its market value, API gravity is exceptionally important [37]. The API values for each "weight" are illustrated in **Table 1.3**. Illustrates the classification of crude oils in terms of API gravity.

**Table 1.3**. Illustrates the classification of crude oils in terms of API gravity.

| Description | API gravity |
|---|---|
| **Light** | API > 31.1 |
| **Medium** | Between 22.3 and 31.1 |
| **Heavy** | API < 22.3 |
| **Extra heavy** | API < 10.0 |

These are only approximate valuations as the exact demarcation in API gravity between light and heavy oil changes depending on the region from which oil came. However, the specific gravity is the density comparison of two substances that can be used as a standard reference, mostly water. Despite that, the relationship between API standard and the specific gravity of oils is inversely proportional, which means that the lower API standard for oils is a high specific gravity. As shown in **Figure 1.4.** Illustrates the relationship between API standard and Specific gravity.

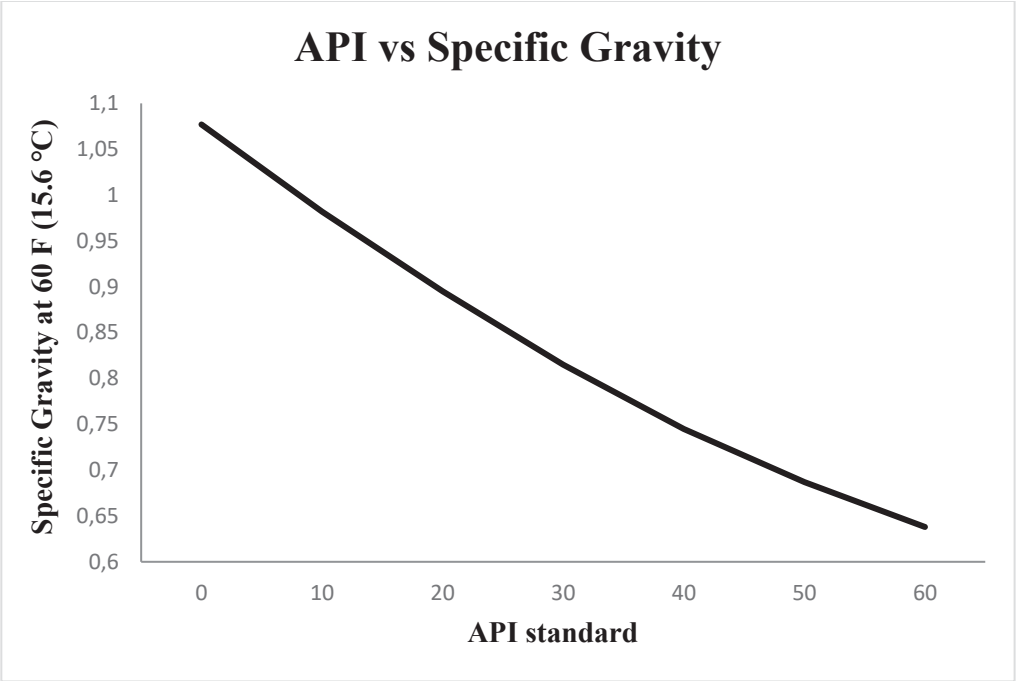


**Figure 1.4.** Illustrates the relationship between API standard and Specific gravity.

## 1.3. Trace Elements for Heavy Metals

A trace element is a chemical element whose concentration is very low a "trace amount". In analytical chemistry, a trace element is one whose average concentration is less than 100 parts per million (ppm) measured in the atomic count or less than 100 µg/g. Trace elements can be categorized into heavy and light based on their density. Elements with a density greater than 5.0 g/cm$^3$ are classified as "heavy" elements, whereas the elements that contain a smaller density than 5.0 g/cm$^3$ are classified as "light" elements [38].

The main source of man-made for heavy metals or contamination with trace elements in this environment are mining and refining area, agriculture waste, dumping of partially treated and untreated industrialization waste, burning of fossil fuels, exploration of crude oils, random use fertilizers that make up heavy metals, pesticides, agriculture and oil leaks [39-41].

The most abundant trace elements in crude oils are typically Vanadium, Nickle (and Iron for some types of oils), their concentration relies on the source of crude oil and may range less than 1 parts per billion (ppb) in light condensate oils to larger than 2000 parts per million (ppm) Vanadium and 200 ppm Nickle in asphaltic. Nevertheless, other metal ions reported from crude oils, include (Ca, Ba, As, Cu, Cr, Pb, Mn, Mg, Na, Zn, Co, Al, Ti, Ag, etc.) with a very small quantity in crude oils along with Sulfur, Oxygen, and Nitrogen [42]. In general, the abundance of other trace elements in crude oils are much lower than the presence of Vanadium and Nickle (or Iron) and significant differences occur in the concentration of a particular elements (and from element to element), even

between the oils from the specific sedimentation basin [43]. These differences in the concentration of particular trace elements between oils are illustrated in **Table 1.4.** Concentration and ranges (ppm) of selected trace elements in crude oils from the West Canada Basin.

Generally, Nickle (II) and Vanadium (II) porphyrins and non-porphyrins are the most abundant minerals in crude oils. The first compounds identified as belonging to a biological origin are known as Metalloporphyrins [44]. The Metalloporphyrins in crude oils are considered of essential importance from the geochemical context to better comprehend the geochemical origin of the oil source. The existence of Nickle and Vanadium Metalloporphyrins in heavy crude oils in vast quantities causes numerous problems because these minerals have a detrimental impact on the hydrogenation catalysts utilized in the upgrading processes [42]. The determination of trace elements is necessary in crude oils due to their significance in the geochemical categorization of the source and origin. Inorganic trace elements or organic minerals species might be utilized as biomarkers to provide information on the sedimentation environment of the source rocks, determine the type of organic source material, estimate sediment or oil maturity, or to correlate crude oils with other oils or possible source rocks [42, 45].

**Table 1.4.** Concentration and ranges (ppm) of selected trace elements in crude oils from the West Canada Basin.

| Elements | Concentration (ppm) | Range (ppm) |
|---|---|---|
| **V** | 13.6 | 0.1-177 |
| **Ni** | 9.38 | 0.1-74.1 |
| **Fe** | 10.8 | 0.1-254 |
| **Co** | 0.054 | 0.0002-2.0 |
| **Cr** | 0.093 | 0.005-1.68 |
| **Mn** | 0.010 | 0.003-3.85 |
| **Zn** | 0.459 | 0.025-5.92 |
| **As** | 0.111 | 0.002-1.99 |
| **Sb** | 0.006 | 0.0001-0.035 |
| **Se** | 0.052 | 0.003-0.511 |
| **Hg** | 0.051 | 0.002-0.399 |
| **Na** | 3.62 | 0.01-64.7 |
| **Cl** | 39.3 | 0.1-1010 |
| **Br** | 0.491 | 0.002-12.5 |
| I | 0.719 | 0.01-9.0 |

## 1.4. Literature Review

The information available in the literature about the concentration of trace elements present in crude oil from diverse origins is limited, and various analytical techniques have been used in several studies to determine the quantity of some elements (major, minor, and trace elements) in different types of crude oils throughout the world. There are several techniques to determine the concentration of trace elements in crude oil samples, and the most commonly used are inductively coupled plasma-mass spectrometry (ICP-MS) [46], inductively coupled plasma-optical emission spectrometry (ICP-OES) [47], and atomic absorption spectrometry (AAS) [48]. The analysis of crude oil samples via either ICP-MS or ICP-OES directly is quite hard due to its flammability, high viscosity, and various derivatives as well. As a consequence, the suction of plasma organic fluids requires additional equipment or pre-treatment sample in order to maintain plasma stability, minimize carbon accumulation, and background interferences [9].

### 1.4.1. Determination of Trace Elements in Crude Oil

In the early 1980s, Polo-Dies et al. [49] suggested a method through the use of emulsion to determine the concentration of Pb in gasoline by Flame Atomic Absorption Spectrometry FAAS. They prepared the sample from 1.00 mL of benzene, 20.0 mL of $H_2O_2$ and 5 drops of emulsifier with HLB 13.5 and stirring forcefully to produce an emulsion that is then instantly displayed into the instrument. As a consequence, the capacity of the procedure and the sensitivity of the absorption signals was about 15 times higher than those from aqueous solution. Fabec, J.L et al. [47] promoted a method by using ash with sulfuric acid to determine the concentration of Ni and V in crude oils via FAAS.

Aucelio and Curtius [50] used two sample preparation procedures to identify the concentration of Arsenic, Selenium, and also Antimony in kerosene and gasoline by using Electro-Thermal Atomic Absorption Spectrometry ETAAS. Silva et al. [51] proposed a method to determine the concentration of Pb and Cu in kerosene using ETAAS. They prepared a solution from three ingredients ranging from 5.0 mL of kerosene with 11.00 mL of $CH_3CH_2CH_2OH$ and 2.0 mL of 0.2% $HNO_3$. This solution provides appropriate stability for 24 hours which made it possible to identify the concentration of Pb and Cu in the presence of Pb as a modifier. Matos Reyes and Campos [52] described a method for determining the concentration of Pb and Ni in gasoline and diesel fuel stabilized as a micro-emulsion utilizing GFAAS. They prepared a solution from three components which consist of an oil sample, $CH_3CH_2CH_2OH$, and 50% of nitric acid as well (3.3.: 6.5: 0.1) mL respectively.

Recently, ICP-OES has been developed to determine the concentration of trace elements particularly in crude oil and its derivatives. Souza et al. [53] proposed a method for the

determination of Nickle, Molybdenum, Chromium, Vanadium, and Titanium using ICP-OES. They prepared the sample from 0.50 mL of concentrated nitric acid to acidify the sample, then 0.50 mL of xylene as a co-emulsifying solvent, and ultimately 0.60 mL of Triton X-100 as a surfactant. Furthermore, the determination of various trace elements in crude oil and heavy crudes fraction was carried out by [47, 54, 55].

Over thirty years, ICP-MS has been used to determine the concentration of trace elements at a very low concentration which becomes a typical alternative, due to its elevated sensitivity and many elements can be detected quickly and easily at the same time. Lord [46] described a method for the determination of trace elements in crude oil using ICP-MS by forming a micro emulsion solution. The sample was prepared by mixing 0.50 g of crude oil with an equivalent amount of Tetralin until a homogenous mixture was obtained. Finally, 1.0 g of Triton X-100 with graduate addition of de-ionized water was added until a final mass of 50.0 g was formed. The results that were achieved were well in agreement with the approved values.

Al-Swaidan [56] used an emulsion of crude oil to propose a new technique for analyzing trace elements which is sequential injection analysis / ICP-MS. The sample was prepared from mixing 0.50 g of oil with 1.50 mL of Tetralin, 0.50 mL of Triton X-100 and 5.0 mL of 40% $HNO_3$ with 50.0 mL of de-ionized water was gradually add until a homogenized mixture was attained. The results of this technique were good for Lead and Nickle, whereas a low V concentration was formed because of its background interferences. Moreover, V and Ni were determined in some crude oil and petroleum products in the Kingdom of Saudi Arabia by Al-Swaidan [57] via ICP-MS using the previous method described by lord [46].

Duyck, C. et al. [58] promoted a method to determine the following trace elements such as: Mn, Cu, Cd, Ba, Fe, Co, Mg, Al, Mo, Ag, and La in crude oil. They diluted the sample in toluene and then presented it into the ICP-MS for analysis. Precise and accurate results were obtained from the experimental work. Wondimu et al. [59] used ICP-MS to analyze some trace elements such as: Hg, Fe, Cu, Cr, Cd, Ca, Bi, Ba, Al, and Ag in residual fuel after microwave acid decomposition. Then $H_2O_2$ is added to complete the oxidation. Pereira et al. [60] used ICP-MS after microwave-induced combustion in a closed vessel to analyze light and heavy crude oil for the identification of several trace elements.

## 1.5. Heavy Metal Pollution

The “Heavy metals” expression indicates each metallic element which is toxic even at a low level of exposure and contains a comparatively large density [61]. “Heavy metals” are defined as a general collective term, applicable to a band of minerals and semimetals (metalloids) that have a higher specific density than water 5 g/cm$^3$ and adversely impacts the environment and living things [62]. Nevertheless, the fact that the heavy metal has little to do with density but is more related to

chemical properties. The most important toxic heavy metals and environmental pollutants include Lead (Pb), Cadmium (Cd), Zinc (Zn), Mercury (Hg), Arsenic (As), Silver (Ag), Chromium (Cr), Copper (Cu), Iron (Fe) and Platinum (Pt). These elements are generally present in the ores as well as somewhat in most soils. The environment is defined as the total situation of all surroundings of a living organism, including natural forces and other living things, which provide conditions for development and growth as well as of danger and damage [63].

Pollution is the entrance of detrimental substances into the environment. These detrimental substances are called pollutants. Pollutants can be natural, such as volcanic ash, it can also be created by human activity, such as garbage or runoff produced by factories. Pollutants damage the quality of air, water, and land may eventually lead to death. Subsequently, environmental pollution is the existence of pollutants in the atmosphere and might be toxic and can cause detrimental effects on living organisms [64]. The major sources of environmental pollution with heavy metals are manufacturing, agriculture activities, exhaust gases from factories and industries, mining operation, crude oils refinery, and others [65]. Environmental pollution with heavy metals is quite eminent in mining areas, and as a distance from mining areas increases, pollution decreases [66].

There are other important sources of environmental pollution named "Anthropogenic activities" or "Human activities" such as human reproduction, overconsumption, overexploitation, pollution, etc. these activities take place because of the advancement of technological civilization, science, and several decades of manufacturing evolution [67]. Hence, the most harmful pollutants to the environment pollution resulting from anthropogenic activities are heavy metals due to their extremely high toxicity and long residence in the environment [67, 68]. Continuous exposure to a high concentration of heavy metals from oil is one of the biggest problems associated with oil pollution [69].

Heavy metals can take place as a natural component of the Earth's crust and are permanent environmental pollutants that might not be deteriorated or become damaged. Somewhat, via water, food, and air they get into the human body and thereafter because of their non-biodegradable nature, and long biological half-lives to get rid of it heavy metal can typically accumulate in the body system over a period of time [61, 64]. There are several heavy metals in urban soil, and they may have many adverse impacts on the human body, particularly in children, the most dangerous of which are toxic impacts [70]. For instance, Lead is a toxic metal, and as a result, exposure to a high level of Lead may influence human intelligence, and exposure to a low level of Lead may be detrimental to the systems of enzymes participatory in the production of blood [71, 72].

Over the past fifty years, pollution of the biosphere with heavy metals and chemicals such as Lead, Zinc, Nickle, Copper, etc. has largely been raised due to manufacturing waste, industrialization, dumping materials, mining, municipal waste, and traffic discharges. Environmental pollution with heavy metals is concerned with major metropolises that have a giant

manufacturing area [73]. However, Geographical accumulation, Bioaccumulation, and Bio-magnification may occur because of the introduction of heavy metals into the environment.

The oil spillage is a main contributor to the environmental pollution, which indicates the accidental leakage of crude oil or refined products onto land or water, as a result of the process of the production and distribution of crude oil. The demand for crude oil as a source of energy has caused a dramatic increase in its production, transportation, and refinery process, resulting in environmental pollution. The oil spills take a place in various parts of the world, which leads to critical risks and problems for the environment [74]. However, oil production, exploration, and transportation activities may cause the risk of incidental oil spillage with possible environmental impacts [75]. Pollution of crude oil leads to the negative impacts on plants by making toxic metals in the soil and also damages the soil structure, loss of organic matter contents, and loss of minerals and nutrients in the soil [76]. Iraq is an important source of crude oil, and as a result, the country has experienced numerous oil spills that have influenced agriculture lands as well as plant growth and advancement in the impacted zones [77].

The spillage of crude oil, in general, can significantly increase the number of heavy metals in the soil [78]. Heavy metals pollution may occur due to various metals, especially Cu, Ni, Hg, Cd, Pb, Zn, and Cr [79]. Thus, it has been noticed that the pollution caused by heavy metals leads to negative impacts on different standards related to plant quality and yield [80]. The results of the effects of crude oil pollution on the heavy metals content of soil were implemented by [81]. The concentrations of heavy metals in the soil samples near the crude oil sites in Iraq were reported by [77]. This survey was conducted to determine the total concentration of trace elements in crude oil in various locations. The result can then be used as a basis to improve conditions in the region and guide environmental planners and the government in reducing pollution in northern Iraq and the southeastern provinces of Turkey.

Another source of environmental problems is the pollution of petroleum hydrocarbon, not only due to the large quantities emitted from it but likewise because of its toxicity [82]. Various components of petroleum and crude oil for instance polycyclic aromatic hydrocarbons (PAHs) have been found in watercourse due to contamination of industrial liquid waste and petrochemical products [83]. The main categories of hydrocarbon present in diesel fuel [84] are normal alkanes (rapid degradation), branched alkanes and cycloalkanes (hard to determine), the isoprenoids (highly resistant to biodegradation), the aromatics (somewhat determined and more soluble than other hydrocarbons), and eventually, the polar compounds consisting mostly Sulfur, Oxygen and Nitrogen compounds. **Table 1.5.** Some distillation components of Nigerian Brass crude oil.

**Table 1.5.** Some distillation components of Nigerian Brass crude oil

| Distillation Fraction | Composition % | Chain Length |
|---|---|---|
| **Gasoline** | 11.2 | C4 – C10 |
| **Naphtha** | 18.1 | C4 – C10 |
| **Kerosene** | 16.9 | C10 – C20 |
| **Gas oil** | 15.7 | C15 – C40 |
| **Heavy gas** | 25.8 | C40 and above |

### 1.5.1. Human Exposure to Heavy Metals

The fact that humans utilized heavy metals several centuries ago. Despite many of the negative health impacts of heavy metals have been identified for a large amount of time. Exposure to heavy metals continues in various parts of the world and even increases in a few parts, especially in the least developed countries, although the decrease in emissions in many developed countries over the past hundred years [85]. For instance, Arsenic is commonly used in wood preservatives. Hg is still used in various regions of Latin America for the mining of Gold, and Tetraethyl Lead is still used as an additive in petroleum. However, the utilizes of these heavy metals in developed countries has extensively descended [86].

Heavy metals are found naturally in the Earth's crust because of air emissions and some industrial facilities, and their compositions differ among various regions, which leads to spatial differences in surrounding concentration. Metals in the environment can be distributed according to the effects of ecological factors and metals properties. However, one of the common problems is the existence of toxic heavy metals in water, air, and soil, which poses an increasing threat to the ecosystem [87]. Natural and anthropogenic sources are the main ways for heavy metals to enter the environment. Twenty-five out of thirty-five metals that matter to humans due to residential and occupational circumstances are heavy metals and generally found in the environment and diet, such as (Mn, U, Ni, As, Cr, Cu, Co, Ce, Cd, Pt, Thallium Ti, V, Zn, Ag, Sb, Sn, Se, Ga, Fe, Pb, Au, Hg, Te, and Bi). These metals are potentially toxic to humans in large quantities but they are not known harmful and toxic in small quantities except (As, Pb, Hg, Cd, Cr, Cu, Co, Ni, Zn, and Se) are highly toxic even at in minor quantities [88]. Human exposure to these heavy metals has been extensively recognized from a variety of sources. Which includes industrial and medical waste, pesticides, petroleum by-products, drinks, snacks, sweets, food, and others [89].

In recent times, human exposure to heavy metals through food, air, and water has been a concern of many studies. The main exposure methods to heavy metals are through food, air, and water. Workers and other people in the workplace are essentially exposed to these pollutants. The chain of contamination of heavy metals usually follows a cyclical arrangement: industry, atmosphere, soil, water, food, and people. Thus, it is recognized that long-term exposure to heavy metals and semimetals (metalloids) with a relatively low concentration may lead to adverse effects [90, 91]. Inhalation, ingestion, and skin absorption are the other three major methods of human exposure to heavy metals. exposure to a high level of heavy metals leads to their accumulation in the human body and probably causes some negative health effects, and this is what was reported in previous researches [92, 93]. As shown in **Figure 1.5.** The health effects of heavy metals [94].

Heavy metals contamination of surface and groundwater sources leads to a significant increase in soil pollution and an increase in pollution when mined materials are thrown to the surface of the earth for manual dressing [64, 95]. Surface dumping displays the metals to air and rain which generates plenty of Acid Mine Drainage (AMD). When the soil is polluted, these metals are absorbed by the plants and thus buildup in their tissues [96]. Animals that eat polluted plants and drink from contaminated water, and also marine organisms which polluted with heavy metals are buildup these metals in their tissues [66, 95, 97, 98]. One of the serious routes for human exposure to heavy metals is by consuming polluted animals and plants which will lead to many biochemical disturbances. In general, all organisms within a particular environmental system are polluted differently along with the food chain cycles [64]. Respectively, it has been reported in previous researches that a number of these pollutants might be carcinogenic, therefore human exposure to environmental pollutants or heavy metals is a major cause of concern [99].

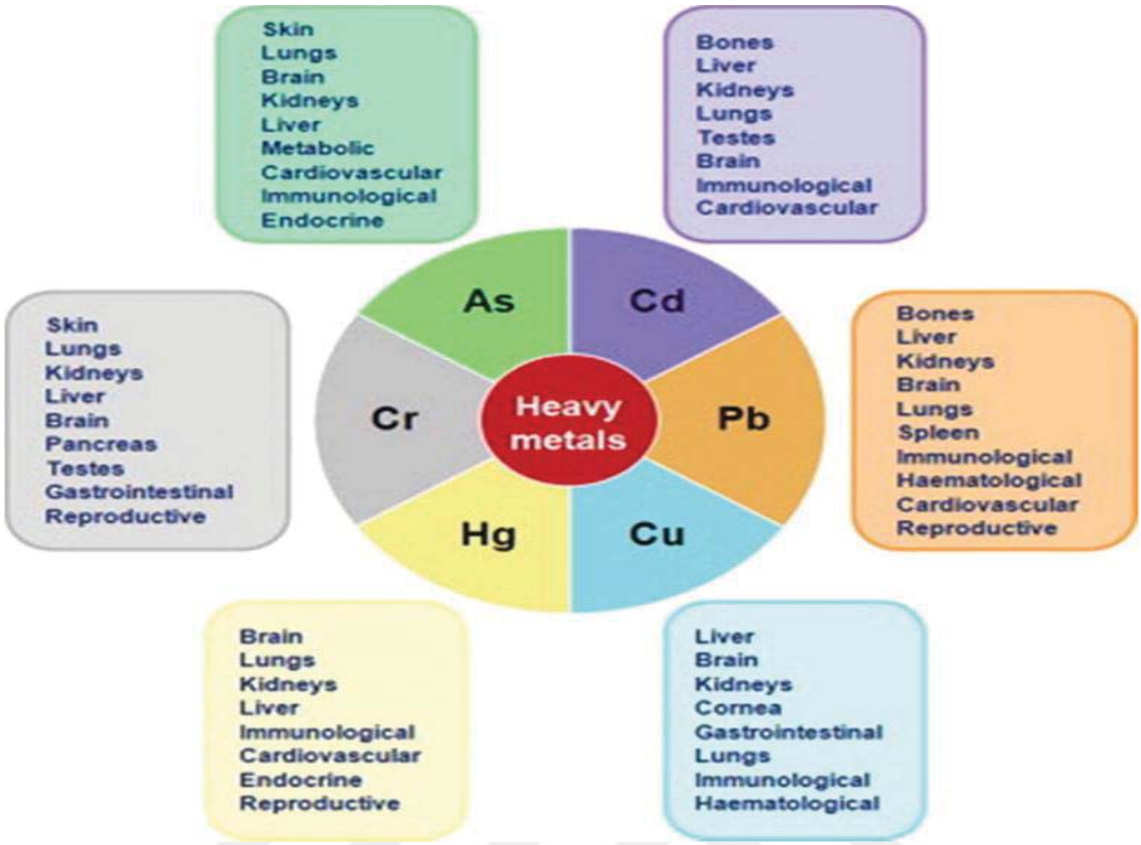


**Figure 1.5.** The health effects of heavy metals

Many researchers have studied the industrial use of heavy metals and their impact on the environment and human health lately. Industrial products utilized in houses that were produced with heavy metals are the main sources of human exposure to such metals. exposure to Hg is via antiseptics, creams, toiletries, etc. [100]. Exposure to Cd is via artist paints and Ni-Cd batteries are the most effective one. Exposure to Pb is via wine bottle rolls, mirror polish, batteries, and others. Children are oversensitive to the influences of heavy metals exposure [64]. One of the anthropogenic emissions of heavy metals sources is Metallurgical processes. Heavy metals evaporate from the ore matrix during the smelting operations, and without controlling the pollution technology, heavy metals potentially transfer into the atmosphere [101]. When street dust appears in civilized regions, it indicates heavy metals pollution from the sedimentation of the atmosphere. Ferreira-Baptista and De Miguel [102] reported that heavy metals in street dust may buildup from sedimentation of the atmosphere and could impact human health if they become toxic contaminants.

Human exposure to heavy metals is largely caused by occupational circumstances. Employees in the workplace have been exposed to heavy metals during mining and producing Cd, Cr, Pb, Hg, Au, and Ag. The residents of industrial areas are also exposed to mining heavy metals through the air with suspended particles [64]. Industrial use of heavy metals and their impacts on

the workplace and the environment has been reported by [103]. A comparison of heavy metals concentrations in industrial zones all over the world was carried out from recent studies [103].

Industrial wastewater pollutes the environment and severely impacts human health because it contains several heavy metals (like Cr, Cu, Cd, Ni, and Zn). As a result, environmental pollution prevention has been carried out by [104-106]. It has been implemented in [64] that a few heavy metals such as (Iron, Zinc, Calcium, and magnesium) are of biological importance to humans and their medical and nutritional allowances. However, it has been reported that other heavy metals such as (Arsenic, Cadmium, Lead, and Mercury) have no biological importance known to human health and they can be toxic even at quite low concentrations [64].

It has long been known that chronic exposure to heavy metals increases cancer cases such as Oral and Pharyngeal cancer, which are the sixth-largest cancers and cause problems all over the world. The maximum incidence of Oral cancer is about 275,000 cases and Pharyngeal cancer is around 130,300 cases. In summary, continuous exposure to heavy metals probably leads to cancer disease [107]. The major threats to human health from heavy metals are associated with exposure to the most toxic metals such as As, Pb, Hg, Cd, and Cr (Arsenic is a semimetal, but is always categorized as heavy metals).

## 1.6. Toxic Heavy Metals

Toxic heavy metals are usually found in the environments due to the anthropogenic activities, production of crude oil, agriculture fields, and other industries. The existence of toxic heavy metals in an environment probably results in negative health impacts [108]. The toxicity of heavy metals causes environmental pollutants with an important problem for nutritional, developmental, and ecological reasons [109, 110]. In general, toxic heavy metals can be dangerous to human and aquatic ecosystems resulting from some sources such as (industrial, municipal, and urban runoff). Serious health effects may occur on humans due to the heavy metals inside the water supply like decreased growth and development, organ damage, spoil of the nervous system, cancers, as well as sometimes death. In some cases, exposure to toxic metals like (Hg) and (Pb) can improve autoimmunity, as a person's immune system attacks their cells. This may result in disease of joint and kidney disease and nervous system [85]. In previous studies [111-113] the influences of toxic heavy metals on human health and ecological system were reported. Some of those toxic heavy metals with low concentration damage the internal organs of humans and animals. Diverse forms of mammalian carcinomas, respiratory diseases, organ failures, and intellect retardation are returned to metal toxicity [114-116].

Heavy metals can get into the human body via water, food, air, and skin absorption when they meet humans in manufacturing, agriculture, and residential environments. And when they are not metabolized by the body and buildup in delicate tissues, in this case, they become toxic metals

[94]. Energy levels potentially decrease and functions of the brain, kidneys, lungs, blood formation, liver, and other significant organs can be damaged due to the toxicity of heavy metals. continuous exposure may progressively cause physical and muscular improvements and neurological degenerative processes. Continuous exposure to some toxic metals can even lead to cancer [86]. Some heavy metals can be found naturally in the environment in which their toxicity level may be slightly higher than the surrounding concentrations. Thus, accurate recognition of heavy metals is somewhat significant to allow adequate defensive measures versus excessive contact [117].

In the early 19$^{th}$ century, several negative health effects of heavy metals were recognized. Workers who have been exposed to toxic heavy metals can cause cancers. Increased widespread consumption of non-ferrous metals due to the enormous development of manufacturing industries and other economic activities on the main industrialized countries, some of which have not been identified as human carcinogens. Exposure to the following toxic metals such as Arsenic (As), Lead (Pb), Mercury (Hg), Cadmium (Cd), and Chromium (Cr) occurs through natural sources with anthropogenic activities and manufacturing sources. At high exposure levels, these metals become toxic, and increasing evidence indicates adverse health impacts from low-level accumulative exposure [118]. Moreover, these metals Arsenic (As), Lead (Pb), Mercury (Hg), Cadmium (Cd), and Chromium (Cr) are xenobiotics which means they are useless in human physiology and are toxic even at very low concentrations [87].

Arsenic (As), Lead (Pb), Mercury (Hg), Cadmium (Cd), and Chromium (Cr) are the most toxic heavy metals and environmental contaminations. These toxic metals are naturally present in ores as well as somewhat in many soils [68]. These toxic metals are ranked as priority metals because of their high degree of toxicity which they become a major public health concern [119].

### 1.6.1. Arsenic (As)

Arsenic is one of the significant heavy metals that extensively occur in water, air, rock, and soil. Arsenic is a metalloid that has semimetallic properties, it is eminently carcinogenic to some organs of the body, and is rarely found as a free element in the environment, which is widely abundant in the form of sulfides, oxides, and as a salt of Na, Fe, Ca, Cu, etc. [120]. There are two main forms of Arsenic, the inorganic Arsenic, and organic Arsenic. Trivalent (Arsenite +3), and Pentavalent (Arsenate +5) are inorganic forms, and the organic forms include (MMA, DMA, and Trimethylarsine). Inorganic forms of Arsenic are present in groundwater used for drinking in many countries throughout the world, particularly in Bangladesh, Uruguay, Mexico, Taiwan, Chile, and China. While the organic forms of Arsenic are present in seafood and formed when Arsenic ions combined with Carbon and Hydrogen [120]. All oxidation forms of Arsenic whether (+3 or +5) are toxic and exposure to a high level of Arsenic can lead to death [121]. In general, most cases of

human exposure to Arsenic toxicity are related to the inorganic form of As. The inorganic Arsenic is much more toxic than organic Arsenic [120].

Exposure to Arsenic commonly occurs through eating food and drinking water. Food is a significant source in many areas. However, long-term exposure to Arsenic in drinking water is primarily associated with an increased risk of various types of cancer. Contaminated soil is also a possible source of Arsenic exposure [120]. Other important sources of environmental pollution caused by Arsenic are human-activities and natural phenomena like a volcanic eruption and soil erosion [122]. Exposure to high levels of Arsenic is of concern due to Arsenic can cause a number of impacts on human health.

The two major industrial processes that result in Arsenic contamination of air, water, and soil are the smelting of non-ferrous metals and energy production from the burning of fossil fuels. Smelting activities are the greatest unique source of atmospheric contamination. Other sources of Arsenic contamination are the manufacture and use of Arsenic pesticides and wood preservatives [86, 120]. Many compounds that contain Arsenic are industrially produced and utilized in manufacturing to produce agricultural applications. And they also have an important role in veterinary medicine to eliminate tapeworm in sheep and livestock [123].

In various parts of the world where the groundwater is polluted with high concentrations of Arsenic has been estimated that millions of people are significantly exposed to Arsenic, therefore the polluted groundwater with Arsenic has become a serious health problem. In the literature, it has been reported that 1 out of 10 people who drink water consisting of 500 g/L of As may eventually die due to the presence of As that leads to cancer [124]. Whereas the WHO has set 0.01 milligrams per liter of total As in drinking water as a guideline level for As. Recently, the World Health Organization estimates that exposure to Arsenic via drinking water may eventually lead to several types of cancer [125].

Due to the formation of crude oil and natural gas during the geological periods of marine and plant organisms, Arsenic is absorbed and accumulated generally from plants that grow in the soil or in the water that contains Arsenic. Thus, the crude oil that consists widely of plant and marine organisms, contains As and diverse heavy metals [126]. The average As concentration in 110 crude oils from the US was determined (0.042 milligrams per kilogram). In Alberta, Canada was determined (0.011 milligrams per kilogram) with a maximum of (2.0 milligrams per kilogram) [127]. The determination of As in crude oil has been well documented in [128, 129]. Very little information is reported in the literature about total As concentrations in crude oil and natural gas.

### 1.6.2. Lead (Pb)

It is a bluish-gray metal that occurred naturally and exists in tiny quantities in the crust of the earth. Human activities like mining, burning of fossil fuels, and industrial processes contribute

to the discharge of great levels of Pb even though it naturally occurs in the environment. It has several agricultural, industrial, and local utilization. Presently, Pb is utilized in the manufacturing of lead-acid batteries, ammunition, metal products, and shield X-rays devices. In 2004, in the US one and a half million metric tons of Pb were utilized for various manufacturing utilization. The production of lead-acid batteries accounted for 83 percent of that quantity. Additionally, the remaining utilization included some diverse products like ammunition oxides for paint, glasses, pigments, and chemicals with different quantities [130, 131]. Pb is a highly toxic metal that has been used in diverse products like gasoline, paints, and others. Therefore, the presence of Pb in the environment has caused massive health problems and environmental pollution in many years [132]. The EPA indicated that Pb is a human carcinogen that has several impacts on various parts of the body.

Inhalation of Pb polluted particles, ingestion of Pb contaminated food, water, and paints are major routes of Pb exposure [133]. Drinking water is likely poisonous from Pb when the pipes which carry the water made of Pb and its compounds that contaminated water [134]. The absorption of Pb is affected by factors like age and physiological conditions. As a result, the rate of Pb absorption via drinking water in young children exceeds 50 percent, and adults absorb around (35 to 50) percent. The largest percentage of Pb in the human body is transferred to the kidneys, then the liver and followed by the other tissues like the brain and heart [135]. However, the nervous system is the major vulnerable target of Pb toxicity.

It has been determined that people who are exposed to Pb in the workplace had a greater concentration of Pb in the blood than the general population. Various surveys have examined the relationship between Pb exposure and lung cancer. As a result, some of these surveys found a slight increase in the risk of lung cancer. Nevertheless, other surveys have determined some other factors that may influence the risk of lung cancer, like Arsenic exposure, smoking cigarette, and other heavy metals [136]. The toxic effect of Pb and exposure to Pb are both considered a serious health problem, and it is hazardous to all infants, children, adults, and particularly pregnant women [137]. Pb primarily gets into the body via two major pathways such as oral ingestion or inhalation of Pb dust. Consequently, the highest level of Pb is absorbed by children younger than six years old and pregnant women, and even exposure to a low level of Pb is harmful to pregnant women [138]. However, it has been reported by WHO that exposure of pregnant women to a high level of Pb may cause several damage effects.

In general, Pb exposure in the general population is either caused by drinking water or food. Car Exhaust emits an enormous amount of tons of Pb annually in several areas, most of which is absorbed by plants, the remaining are stabilized in soil and flowed into water bodies [139]. Pb has been utilized mostly in industry. It is clear that the use of Pb organic compounds such as (Tetraethyl Lead and Tetramethyl Lead) as antiknock motor automobile additives is a predominant source of

Pb prevalent throughout the for humans and the environment over the past fifty years [140]. At the beginning of 1922, Tetraethyl Lead was first added to gasoline to improve engine performance. The main source of Pb exposure worldwide is Leaded gasoline. Through polluting air, soil, drinking water, dust, and food crops, it has caused adverse health effects in humans, particularly in children. Therefore, the use of Pb as gasoline additives has become a public health disaster. Pb is added to gasoline because it is the cheapest route to increase gasoline antiknock properties. Which is still extensively used in most parts of the world [141]. In the literature, there are some specific studies in the determination of Pb in crude oil and one of those studies has been well carried out by [142].

### 1.6.3. Mercury (Hg)

Mercury (Hg) is a highly toxic heavy metal in nature, which is ubiquitous and can exist almost everywhere. Nevertheless, it is a naturally occurring metal which is a glossy white silver, odorless liquid and turns into colorless and odorless gas when heated. The existence of Hg in nature negatively impacts on marine organisms. Human activities are considered the most important source of Hg [143]. Both humans and animals are exposed to diverse chemical forms of Hg in the environment. These include (elemental, inorganic, and organic) with each having its own toxic profile. These three forms of Hg are extensively found in a marine environment like oceans, lakes, dams, and rivers where they are absorbed by microorganisms and converted to Me-Hg which is the most common compound of the organic form within microorganisms, that ultimately leads to bio-magnification causing a major disruption in aquatic life [144]. Due to the toxicity and health impacts from environmental exposure, Me-Hg is considered the most significant organic form of Hg. There are three oxidation states of Hg at room temperature, the most abundant being zero-oxidation state $Hg^0$ which indicates elemental Hg. The other oxidation states of Hg that are inorganic salt which include, Mercurous with a loss of one electron $Hg^{+}$ and Mercuric with a loss of two electrons $Hg^{+2}$ [145].

Hg is widely utilized in barometers, thermometers, and measuring blood pressure instruments, the main use of Hg is in the electrochemical process where Hg is used as an electrode [146]. Approximately 2000 metric tons is the total amount of Hg released into the environment per year [147]. Hg is well known as harmful heavy metal in the environment and it is released into the environment by several activities of diverse industries like paper and pulp preservatives, pharmaceuticals, agriculture, etc. [148].

The main source of human exposure in terms of Me-Hg which potentially carcinogenic by IRAC is dietary ingestion particularly for seafood and fish [136]. The other source of human exposure to Hg are environmental and food contamination, agricultural and industrial processes, dental care, and others [149]. The general population is exposed to Hg through two main sources which include: the emission of elemental Hg from the dental amalgam and eating fishes and marine

mammals as well [150]. At the beginning of 1970, thousands of people in Iraq were exposed to Hg through eating baked bread from grain contaminated with Hg, and most of them were poisoned and died as a result of poisoning. Nevertheless, people with higher fish consumption have a greater chance of the adverse effects of Me-Hg exposure than the general population [86]. Hg is capable to bind with some other elements and produce inorganic and organic Hg. High levels of Hg exposure might be harmful to several organs such as kidneys, brain, and also fetus in pregnant women. The brain remains the most vulnerable organ of Hg exposure [151].

The total concentration of Hg in crude oil is nearly around 0.1 to 20,000 micrograms per kilogram according to the surveys of Hg in crude oil where published before 1999 [152]. The concentration of Hg in crude oil has been implemented by [153]. Crude oil and coal are two major sources of Hg in combustible fuels. The concentration of Hg in crude oil significantly relies on the biological location and ranges from 0.01 ppb to 10 ppm by weight [154].

### 1.6.4. Cadmium (Cd)

Cadmium (Cd) is a heavy metal that occurs naturally in the earth's crust together with (Zn), (Pb), and (Cu) ores. The highest level of Cd compounds in the environment is found in sedimentary rocks and marine phosphates consist of about fifteen milligrams of Cd per Kilogram. This metal was first used in World War I as a replacement for Tin and in paint industries as a pigment. Nowadays, it is also being used in re-chargeable Nickle-Cadmium batteries, metal coatings, plastics (as a stabilizer), and plantings as well [155]. Due to the environmental concerns, the commercial use of Cd in batteries has descended in some developed countries, whereas the manufacturing of Cd in batteries has shown significant progress in recent years [156].

Cd is a by-product of Zn production. Humans or animals may get exposed to Cd during the working hours or in the surrounding environment, and it will accumulate inside the body throughout life after being absorbed by it [157]. Tobacco smoke is one of the largest unique sources of Cd exposure in humans and it has been well reported by [87]. It was determined that workers in the workplace were exposed to Cd at much greater levels than in public places. Epidemiological surveys indicated a relationship between exposure to Cd and several types of cancer such as prostate, lung, and sinus cancer, despite other surveys indicated a weak link relationship exposure to Cd and cancer [158, 159].

In general, human exposure to Cd occurs mostly via two routes. The first is the oral route via food and water polluted with Cd. Food and water are the two most critical sources of Cd exposure in the non-smoking population in many countries [160]. Cd is found in several food materials with significantly different concentrations. Due to the lower energy consumption than men, women frequently get less daily Cd [161]. The second route of Cd exposure is via inhaling Cd molecules that are consumed from industries and human activities. For instance, Cd with oxidation number

+2 from cigarette smoke must be taken very harmfully due to the readily absorption of Cd by the lungs [162, 163]. Biological monitoring of Cd indicated that smoking of cigarettes potentially leads to an extensive increase in Cd level in the blood, where the smoker's concentrations are on average approximately four to five times greater than those in non-smokers [164]. After inhalation Cd may buildup in the human body which impacts adversely many organs such as, kidneys, liver, bones, lungs, etc. [90]. Cd is unnecessary for biological function in humans. In both the general population and occupationally exposed, the kidneys are the major vulnerable organ impacted by Cd exposure. Tobacco smokers are at specific danger like a person with a low level of Iron [136].

Cd is the seventh most toxic heavy metals according to ATSDR [165]. Cd and its compounds are categorized as Group I carcinogens for humans by the IRAC [159]. However, the toxicity mechanism of Cd has not been determined so far, because of the weak evidence for Cd as a human carcinogen, especially after oral exposure [87]. In the US, nearly 500,000 workers may have been exposed to the toxicity of Cd annually according to [165]. In China and Japan, exposure to Cd is relatively greater than in other countries, due to the various industries and vast work areas [166]. Some studies assessed that 30,000 tons of Cd enter the environment annually, with along 4,000 to 13,000 tons resulting from anthropogenic activities [90]. Certain studies were found in the literature on Cd determination in crude oil and some of those studies were performed by [128, 129].

### 1.6.5. Chromium (Cr)

Chromium (Cr) is the six most abundant elements that occur naturally and presents in the crust of the earth, with several oxidation states varies from ($Cr^{+2}$) to ($Cr^{+6}$). However, elemental ($Cr^{0}$) does not occur naturally [167]. Cr compounds commonly occur in nature in the form of ($Cr^{+3}$) due to its stability, and the second-main stable form of Chromium is ($Cr^{+6}$). Both states are highly toxic to living organisms. Nevertheless, the occurrence of ($Cr^{+6}$) is rare in nature whereas it is almost produced from human activities [168]. Metal speciation is quite significant to identify the activities of metal ions in the environment. Where Hexavalent ($Cr^{+6}$) is highly soluble in water in its oxidized form while Trivalent ($Cr^{+3}$) is insoluble in water in its reduced state [169]. Through stimulating the activity of insulin, ($Cr^{+3}$) is considered to have a critical role in protein, sugars, and lipid metabolism in living organisms [170]. $Cr^{+3}$ is oxidized to $Cr^{+6}$ due to the existence of high levels of $O_2$ in the environment. As a consequence, the environmental pollution caused by Hexavalent $Cr^{+6}$ has been the biggest concern lately, and it is very toxic with extremely soluble in water which is classified as a human carcinogen by many agencies [171].

Cr can be emitted into the environment from the burning of natural gas, oil, and coal, as well as anthropogenic activities. Which is almost deposited in soil and water [172]. Cr can be utilized in several industries such as the industries involved in electroplating, leather tanning, mining, production of textiles, and others. Which they have a crucial role in Cr contamination and negative

impacts on living organisms in the environment [172]. It is assessed that hundreds of thousands of workers might be exposed to Cr and its compounds in the working area each year. However, it is evaluated around 34 tons of Cr are emitted into the environment per year, which might be toxic and harmful for the general population [170]. Cr is present in crude oil as a natural element linked with the formation process. Moreover, during the extraction process, Cr can be introduced into petroleum as a result of the corrosion of steel pipes [173]. The estimation of Cr in crude oil is likewise significant to assess the corrosion process due to the uses of Cr in the steel pipes industry. The determination of Cr in crude oil was carried out by [174].

## 1.7. Clean Up of Crude Oil-Contaminated Environment

Exploration of crude oil is the main problem of environmental pollution. Crude oil pollution is a worldwide event that impacts most parts of the ecosystem. The crude oil is spread into the environment through various methods such as natural and man-made oil spills via intentional or casual spills and leaks, for instance, the intended or casual explosion of pipelines [175, 176]. The impacts of crude oil spills differ from one source to another. Nevertheless, the possible biological damage details rely on the environment in which the oil spills take place. Because of many factors, environmental pollution with crude oil remains a major concern throughout the world. One of the difficult factors includes that crude oil is a complicated mixture of thousands of hydrocarbons and some other unspecified structures and additives [83].

In recent centuries, many routes have been innovated to clean-up the contaminated environment by crude oil utilizing diverse treatments such as chemical, physical, thermal and biological treatments. In general, the crude oil contamination of the environment particularly in soil was carried out by [83, 177].

# 2. TECHNIQUES USED FOR DETERMINING TRACE ELEMENTS

## 2.1. Different Techniques Used to Determine Trace Elements in Crude oil

Before using any analytical method for the determination of trace elements in crude oil, it is important to detect the information regarding the concentration of trace elements in crude oil. Different techniques have been used to identify trace elements in crude oil. However, each technique has its selectivity and sensitivity. A very sensitive analytical methods such as flame atomic absorption spectroscopy (FAAS) are required for the analysis of heavy metals due to the relatively small amount of heavy metals in crude oil [47, 178, 179]. Optical spectrometry, mass spectrometry, and X-ray spectrometry are three major techniques of spectroscopy to determine the elements in the material samples and to measure their concentration [180]. There are several techniques for the determination of trace elements in crude oil samples, which include: atomic absorption spectrometry (AAS) with graphite furnace technique (GFT) [181], Electro-thermal atomic absorption spectroscopy (ET-AAS) [182, 183], Inductively coupled plasma-optical emission spectrometry (ICP-OES) [47], Inductively coupled plasma-mass spectrometry (ICP-MS) [46], hybrid methods such as High performance liquid chromatography (HPLC)-ICP-MS, and others [184].

Another important method for the determination of metal ions in crude oil samples is combined Chromatographic-spectroscopic [185]. It described the differentiation of volatile Ni, V, and Fe metalloporphyrins in crude oils. Gas chromatography has been associated with many highly sensitive techniques such as it has been linked to an atomic emission detector, gas chromatography inductively coupled plasma mass spectroscopy (GC-ICP-MS) [186], and high-performance liquid chromatography inductively coupled plasma mass spectroscopy (HPLC-ICP-MS) [187] have been utilized as well. Two other techniques have been used as a sensitive analytical instrument for the analysis of metal ions in crude oil samples which includes: laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) [188], and neutron activation analysis [189]. Direct examination through the X-ray fluorescence technique has been used to determine metal and non-metal ions in petroleum and petroleum products, particularly for V, Ni, and S [190].

Inductively coupled plasma-mass spectrometry (ICP-MS) is considered to be an attractive method for determining the concentration of trace elements in many organic materials in the crude oil industry, due to its multi-element ability and low detection limits. Despite its high cost and spectral interferences. Detection limits for (ICP-MS) are in the subdivisions of ppb range [46] and its capability to measure isotopes ration us particularly interest [191, 192].

## 2.2. Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

Three closely related analytical methods include atomic emission, atomic absorption, and atomic fluorescence spectrometry produced from the interaction of energy with matter. Compared to these methods, there are many advantages of ICP-MS such as: multi-element capability, large analytical range, low detection limit, low sample volume, high sample throughput, etc. And some of the disadvantages of this technique include: equipment cost, operating cost (argon), multiple high purity gases required, high level of staff expertise, etc. [193]. ICP-MS allows the researchers to measure many elements in one analysis at the same time, thus, the multi-element ability is considered to be the most important advantage of ICP-MS. Otherwise, some other techniques such as Flame and GFAAS where the lamp is limited to a finite number of elements, so one (or a few) of them can be measured simultaneously. Furthermore, ICP-MS can provide simple sample preparation and a short time for analysis [193].

In general, ICP-MS is a technique use to determine low concentrations (parts per billion ppb = µg/L) and ultra-low concentration of elements (parts per trillion ppt = ng/L). almost all the elements in the periodic table can be analyzed by ICP-MS due to its speed of analysis, precision, and also multi-element analytical methods to determine the elements in liquid samples [9]. The main components of ICP-MS include: sample introduction system, excitation source, ion transport system, mass separation device, detector, and data processing. As shown in **Figure 2.1.** The basic instrumental components that make up the ICP-MS system [9].

### 2.2.1. Principle and Instrumentation

Nowadays, many of the various ICP-MS designs are commercially available, and each has its own strengths and limitations. They all have identical components including (nebulizers, spray chambers, plasma torch, interface, and detector). However, they can vary greatly in the design of the mass spectrometer and especially the mass separator [194]. Here's an overview of the ICP-MS principle, the sample which must be in a liquid form is pumped into a nebulizer, where it is transformed into a fine aerosol with argon gas at about 1 L/min. the fine droplets of the aerosol, which represent only (1 – 2) % of the sample, are separated from larger droplets using a spray chamber. The fine aerosol then comes out from the exit tube of the spray chamber and is transported into the plasma torch via a sample injector [194]. **Figure 2.1.** The basic instrumental components that make up the ICP-MS system.

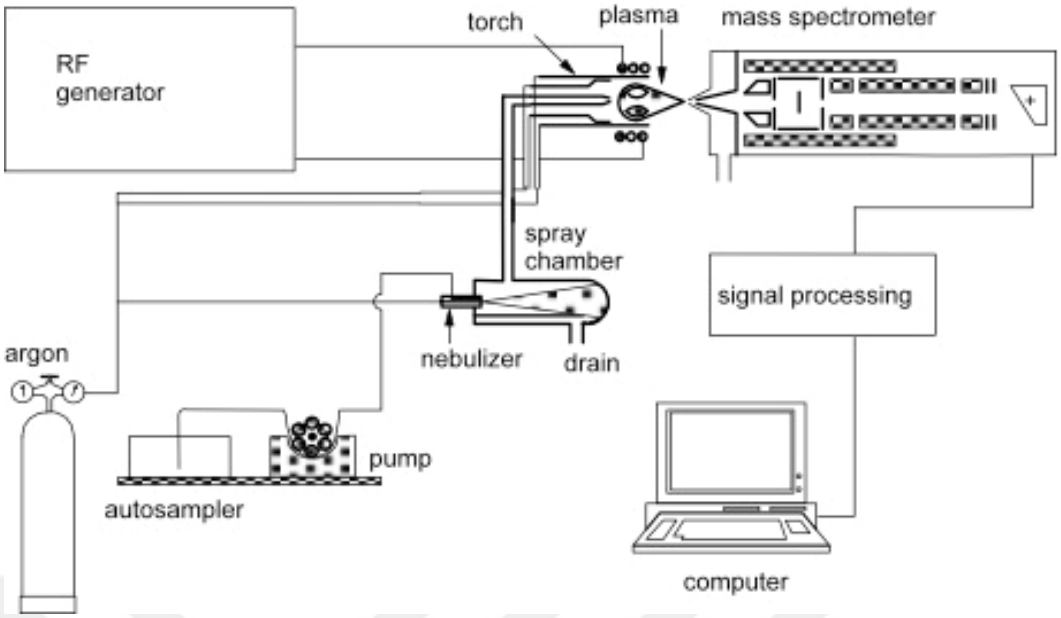


**Figure 2.1.** The basic instrumental components that make up the ICP-MS system

The temperature of argon plasma is above 8000 K. then inside the plasma torch solution is removed from the sample and also atomization and ionization occur. Only a small amount of ions produced in the plasma further penetrate the mass spectrometer part [194]. Eventually, the separated ions pass through the mass spectrometer to the detector to be measured. Ion signals are measured by the electron multiplier (EM), whose inner walls are covered with a metal oxide [9].

### 2.2.2. Sample Introduction

Solid samples can be analyzed directly using electro-thermal vaporization or laser-ablation. However, liquid samples are the most common form to be analyzed by the ICP-MS system and are often introduced with a nebulizer and spray chamber combination, similar to those used in FAAS. An aerosol is formed and introduced into the plasma by a nebulizer gas stream through the injector tube [195, 196].

### 2.2.3. Nebulizers

Nebulizers are important parts of the ICP-MS technique as a nebulization procedure is one of the most important stages in the sensitive technique. The liquid samples are transformed into the aerosol by a nebulizer and then transported into plasma. Commercial instruments use various types of nebulizers such as pneumatic, desolvating, and ultrasonic nebulizers [193]. The nebulizer used in this study was the Pneumatic nebulizer which is the most common type of nebulizer for clinical applications and can use gas flow to generate aerosol [197]. The desolvating nebulizer system uses

a heated spray chamber to desolvate the sample before it reaches the plasma. Nevertheless, an ultrasonic nebulizer uses sound energy (from a piezoelectric transducer) to produce an aerosol.

### 2.2.4. Detector

The detectors and their related electronics are used to measure the intensity of the emission line when the appropriate emission line is separated by a spectrometer. The electron multiplier (EM) is the most common detector utilized for ICP-MS. (EM) has an inner wall covered with a metal oxide. A negative voltage is applied to the multiplier to attract positive ions. When the ions get into contact with the metal oxide wall, other electrons will be released [193].

### 2.2.5. Interferences

A few interferences occur in the ICP-MS system, but are generally expected and can usually be corrected or minimized by improving device operating conditions. Three common types of interferences can occur during ICP-MS measurements (Isobaric Interferences, Molecular (or Polyatomic) Interferences, and Doubly-Charged Ion Interferences) [9].

# 3. MATERIAL AND METHOD

## 3.1. Characterization of Iraqi and Turkish Crude Oil

In this survey, the samples were taken from seven sites in different locations of Iraq and Turkey (Erbil, Duhok, Zakho, Batman, and Adiyaman) to determine the concentration of trace elements utilizing micro-emulsion as a sample introduction technique into the plasma, for ICP-MS analysis. The main characterizations of the selected oils are shown in **Table 3.1.** The main characteristics of both Iraqi and Turkish crude oil in 2020.

**Table 3.1.** The main characteristics of both Iraqi and Turkish crude oil in 2020

| Crude Oil Samples | Hkn | DNO Fishkhabour Export | Hunt oil | DNO Tawke Export | Rosneft | Tuprash Batman Oil | TPIC Adiyaman Oil |
|---|---|---|---|---|---|---|---|
| **Specific Gravity at 15.56 °C (60F)** | 0.8384 | 0.8888 | 0.9373 | 0.8931 | 0.9416 | 0.9250 | 0.9210 |
| **API Gravity** | 37.27 | 27.70 | 19.46 | 26.93 | 18.77 | 21.50 | 22.10 |
| **Total Sulfur, wt%** | 1.2285 | 3.0116 | 4.9326 | 3.1159 | 4.7425 | 2.6069 | 2.2054 |
| **BS&W %** | 0.13 | 0.74 | 0.17 | 0.21 | 0.20 | 0.18 | 0.22 |

This survey was carried out through three stages, including field (sampling process), laboratory (crude oil analysis) and, office works (data analysis). The current research was conducted out (Erbil, Duhok, Zakho, Batman, and Adiyaman) cities of northern Iraq and southeastern Turkey. **Figure 3.1.** Northern Iraq and southeastern Turkey on the world map. The sampling points of both sites are shown in **Figure 3.2.** Sampling points in Iraq and Turkey

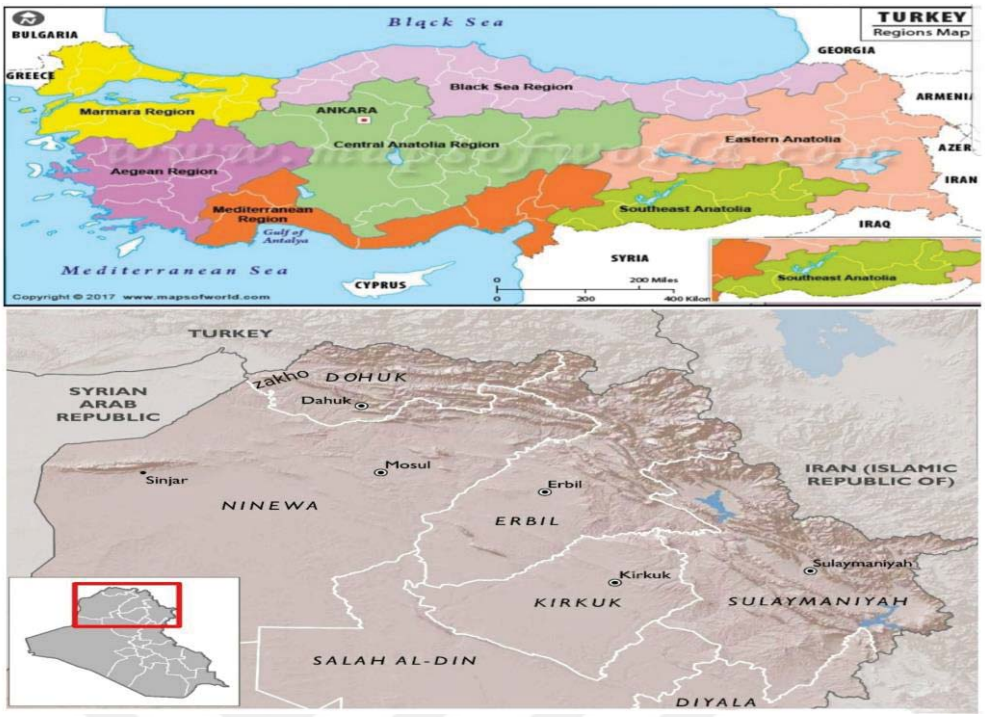


**Figure 3.1.** Northern Iraq and southeastern Turkey on the world map

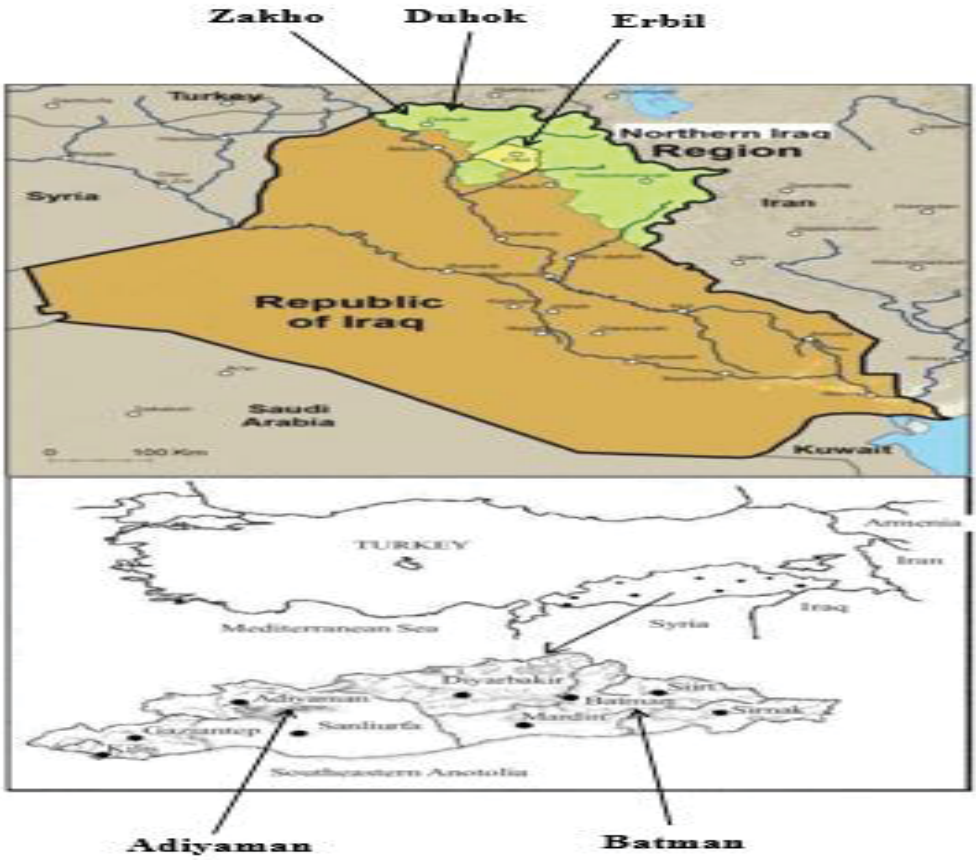


**Figure 3.2.** Sampling points in Iraq and Turkey

## 3.2. Crude Oil Samples

Seven samples of crude oil are shown in **Figure 3.3.** Samples of crude oil used for analysis were collected from seven different fields in either both northern Iraq and southeastern Turkey to determine the trace element concentrations. A detailed description of each sample and their ID is given in **Table 3.2.** Crude oil samples and their sample ID

**Figure 3.3.** Samples of crude oil used for analysis

**Table 3.2.** Crude oil samples and their sample ID

| Number | Sample | Sample ID |
|---|---|---|
| **1** | Harken Energy Scandal Crude Oil | HKN |
| **2** | Export Fishkhabour Crude Oil | CFK |
| **3** | Hunt Crude Oil | CH |
| **4** | Export Tawke Crude Oil | CT |
| **5** | Rosneft Crude Oil | CR |
| **6** | Tuprash Batman Crude Oil | CTB |
| **7** | Adiyaman Crude Oil | TPIC |

## 3.3. ICP-MS Operating Conditions and Analytical Parameters

ICP-MS technique (Perkin Elmer ELAN 9000 ICP-MS, Yildiz Technical University, Istanbul Research Lab) equipped with a pneumatic nebulizer was implemented to investigate this study project. The operating conditions for the ICP-MS element analysis technique in sample studies are summarized in **Table 3.3.** Operating conditions for ICP-MS instrument and a photographic picture of the instrument is shown in **Figure 3.4.** Photographic picture of ICP-MS**.**

**Table 3.3.** Operating conditions for ICP-MS instrument

| Parameters | Descriptions |
|---|---|
| **Nebulizers** | Crossflow |
| **Spray chamber** | Ryton, double-pass |
| **RF power** | 1000 W |
| **Plasma gas flow rate** | 15 L $min^{-1}$ |
| **Auxiliary gas flow rate** | 1.0 L $min^{-1}$ |
| **Carrier gas flow rate** | 0.9 L $min^{-1}$ |
| **Sample uptake rate** | 1.0 mL $min^{-1}$ |
| **Detector mode** | Auto |
| **Integration time** | Element-dependent |
| **Internal standard** | Ir |

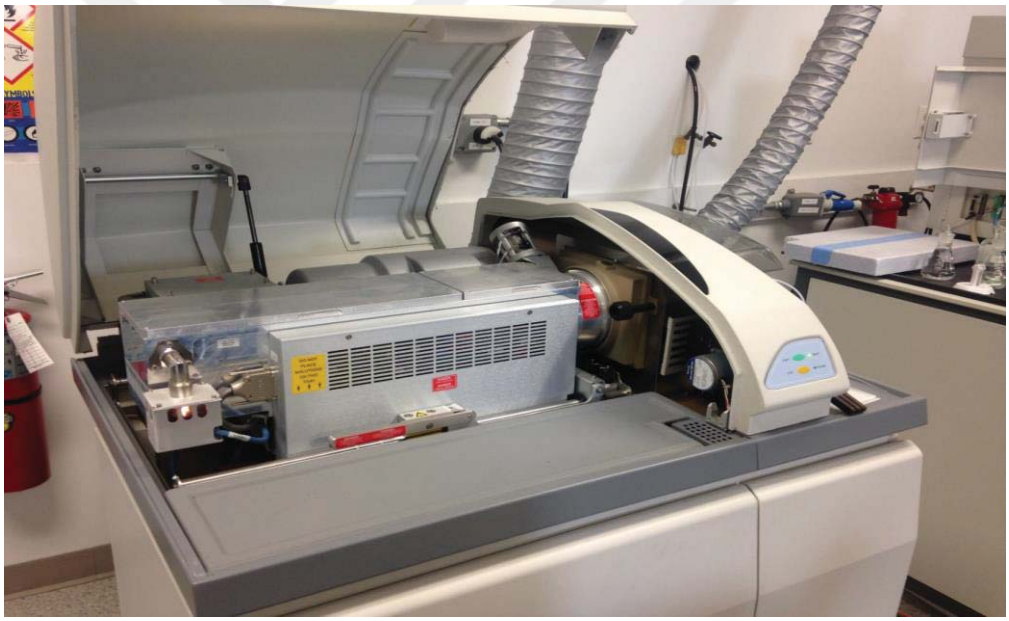

**Figure 3.4.** Photographic picture of ICP-MS

## 3.4. Crude Oil Sample Preparation methods

In general, sample preparation is performed for the specific purpose of the modification of the sample to make it amenable for particular chemical analysis. Crude oil is not a typical matrix for analysis due to its complexity, high viscosity, and mixed phases. To determine the concentration of trace elements in crude oil samples, sample pre-treatment is required before displaying a sample on the device. This is the stage at which most errors occur and takes a long time.

To prepare crude oil samples, various procedures can be used including open digestion and closed digestion system such as: (i) Dry Ashing (DA) digestion, (ii) Wet Ashing (WA) digestion, (iii) Microwave digestion. In this study, we used the Microwave digestion method to prepare the sample for analysis.

The results obtained proved that the open digestion systems are sensitive, simple, and cheap method but are simultaneously slow and insecure. However, the biggest advantages of using closed systems (microwave digestions) are time savings, heating 8 – 12 samples at the same time is possible and reaction times are typically less than 1 hour in comparison to 5 – 12 hours or even more for open systems. Open digestions are limited to boiling points of acids used while closed digestion systems can be operated at a higher temperature of 200 – 300 °C due to their ability to tolerate high pressure. Moreover, Acid consumption is lower in microwave digestion.

### 3.4.1. Microwave Digestion Method

The microwave oven used to digest samples was Model CEM MARS 5 with 2450 MHz microwave power system, as well as a selectable operator output from 0 to 1600 Watts. The MARS 5 model instructions of sample studies are described in **Table 3.4.** The Furthermore, the photographic picture of the MARS 5 model is shown in **Figure 3.5.** The photographic picture of MW-MARS 5 model.

**Table 3.4.** The MW-MARS 5 model instructions of sample studies

| Steps | Descriptions |
|---|---|
| **Edit / Create Method** | User Directory > ”New Method” |
| **Vessel Type** | X-Press |
| **Sample Type** | Organic |
| **Control Type** | Ramp to Temperature |
| **Power** | “1600 W” <Select> |
| **Right arrow, type** | “100” > “15:00” Ramp |
| **Temperature** | 80/115/150 > “15:00” Hold |
| **<Next>** | |
| **Method Name** | <Next> |
| **Method Info.** | <Next> |


**Figure 3.5.** The photographic picture of MW-MARS 5 model

In the present study, a closed vessel microwave digestion method was performed under elevated temperature to quantify the concentration of some trace elements such as (Al, Sb, As, Cu, Ba, Be, B, Zn, Fe, Cd, Co, Pb, Mn, Ni, Se, Cr, V) by using inductively coupled plasma-mass spectrometry (ICP-MS). Nevertheless, concentrated Nitric acid $HNO_3$, which is suitable acid for microwave digestion systems were used due to its strong oxidizing agent whose ability to oxidize is increased at high temperatures. In addition, Hydrogen peroxide $H_2O_2$ was added to the process to complete the oxidation of all organic substances that exist in the sample.

Digestion of crude oil samples was implemented as follows: around 0.250 g of each crude oil samples were weighted in Teflon vessels and 6 mL of concentrated $HNO_3$ with 2 mL of 30% (v/v) $H_2O_2$ were added. The operating conditions of the microwave device and the heating and time program were implemented as the following digestion methods:

- Digestion method 1: Petroleum program 1 followed by 1600 W, 80 °C for 30 min.
- Digestion method 2: Petroleum program 2 followed by 1600 W, 115 °C for 30 min.
- Digestion method 3: Petroleum program 3 followed by 1600 W, 150 °C for 30 min.

After the petroleum program 3 temperature was raised to 150 °C within 30 minutes by application of 1600 Watts, and then cooled for extra 15 minutes, yellowish homogenous solutions were obtained as shown in **Figure 3.6.** Crude oil sample before filtration. Eventually, the samples were filtrated to get rid of any large particles and transformed them into a cylinder and diluted them up to 30 mL with de-ionized water. **Figure 3.7.** Solutions of crude oil samples after digestion by a closed MW system.

**Figure 3.6.** Crude oil sample before filtration


**Figure 3.7.** Solutions of crude oil samples after digestion by a closed MW system

## 3.5. Calibration Curve

The calibration curve in analytical chemistry is a linear relationship between concentration and signals using the least-squares method. The researchers use this relationship to measure the concentration of unknown in a complex matrix. The unknown samples could be from various

sources such as: crude oil, medicine, agriculture, food, etc. This study is more focused on the analytical techniques by which analyte is measured in crude oil samples.

The obtained calibration curve for the studied elements is given in **Figure 3.8.** Calibration curve for Cu. **Figure 3.9.** Calibration curve for Ni. **Figure 3.10.** Calibration curve for Pb. **Figure 3.11.** Calibration curve for Cr. **Figure 3.12.** Calibration curve for V. **Figure 3.13.** Calibration curve for Fe. **Figure 3.14.** Calibration curve for Al.

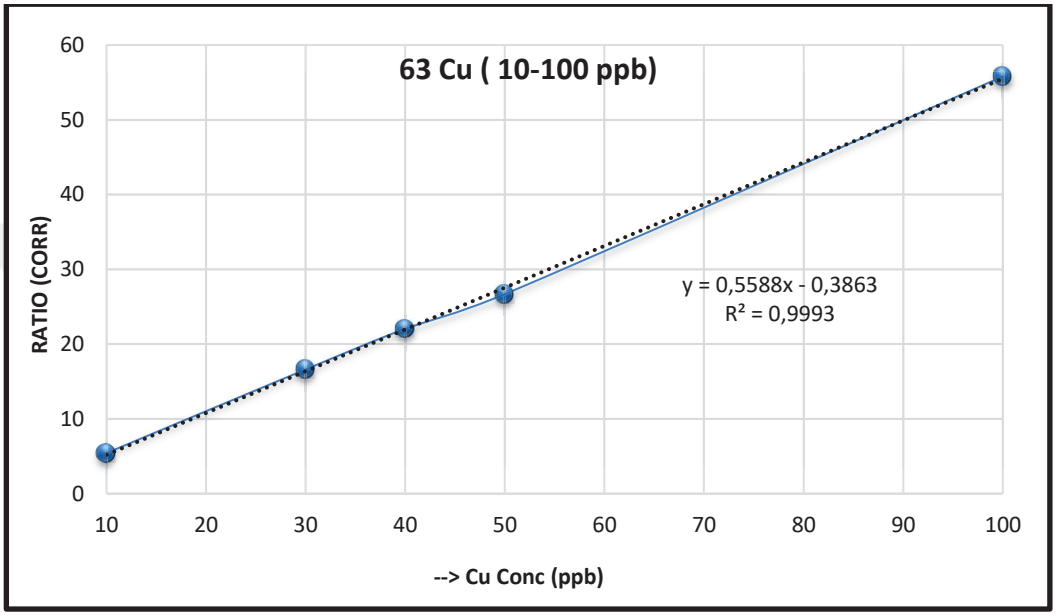


**Figure 3.8.** Calibration curve for Cu

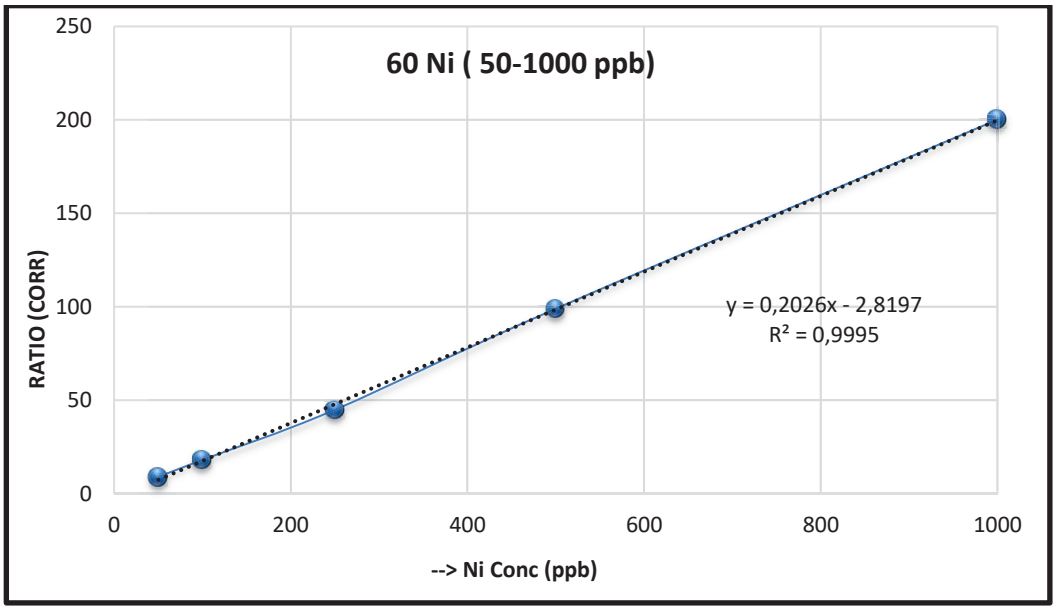


**Figure 3.9.** Calibration curve for Ni

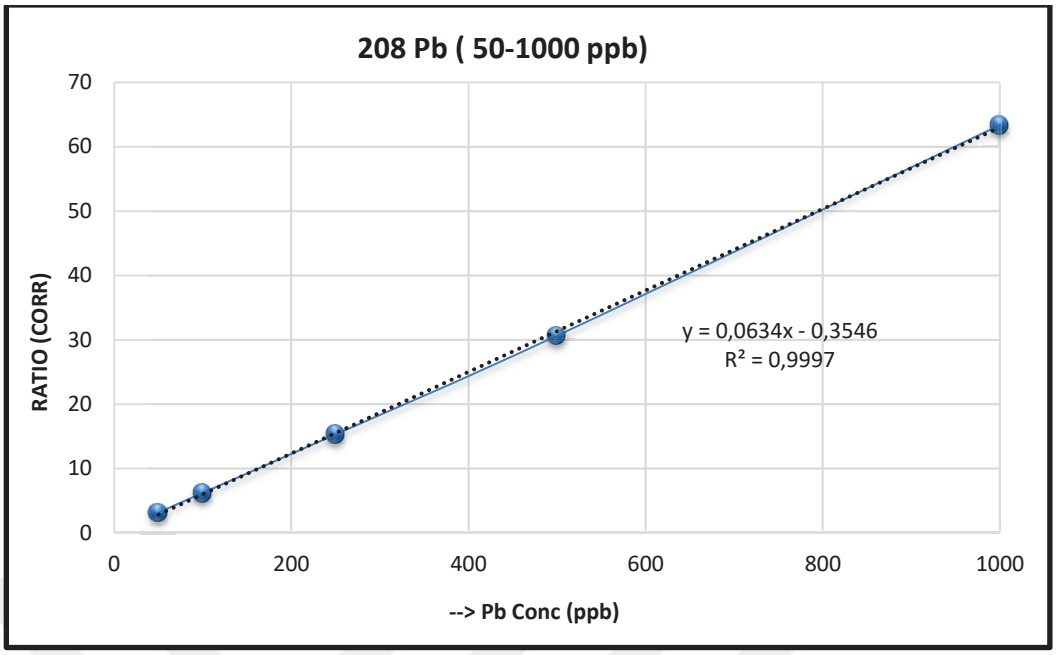


**Figure 3.10.** Calibration curve for Pb

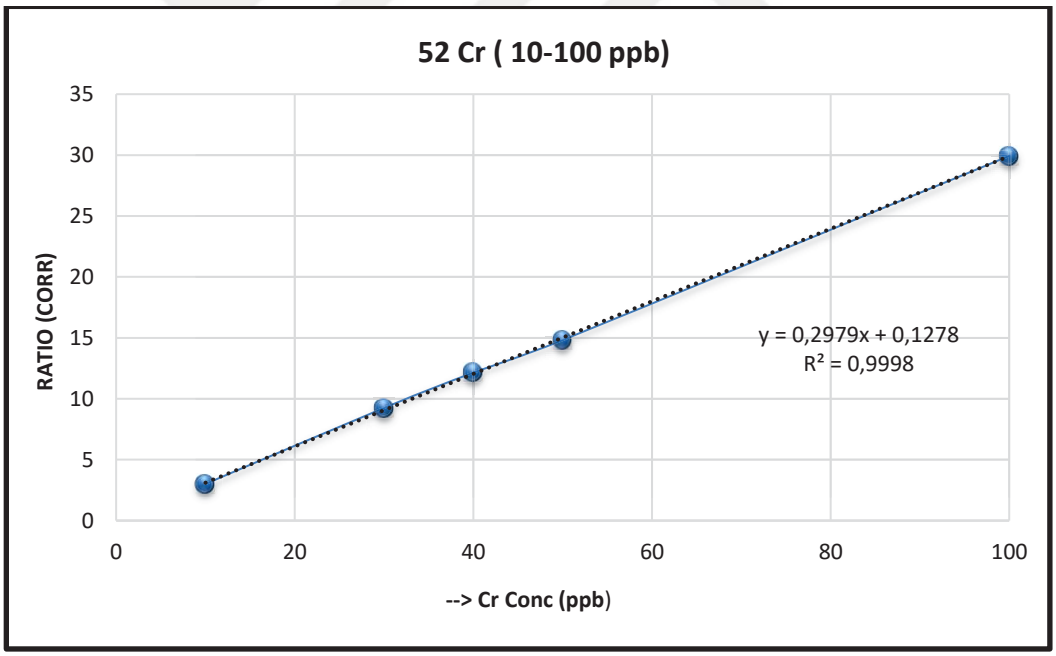


**Figure 3.11.** Calibration curve for Cr

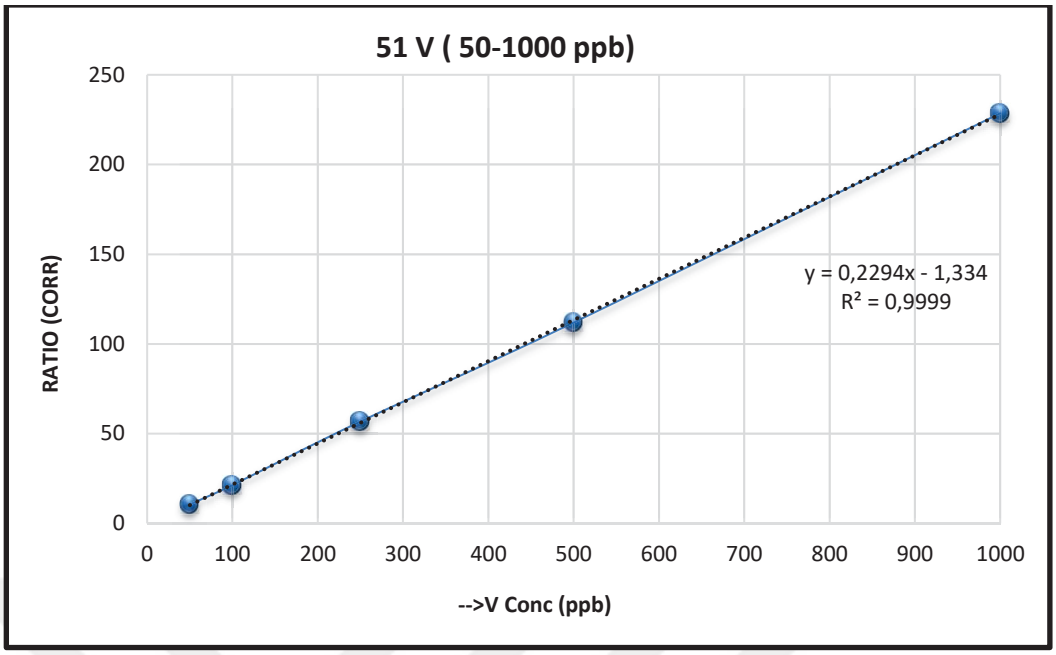


**Figure 3.12.** Calibration curve for V

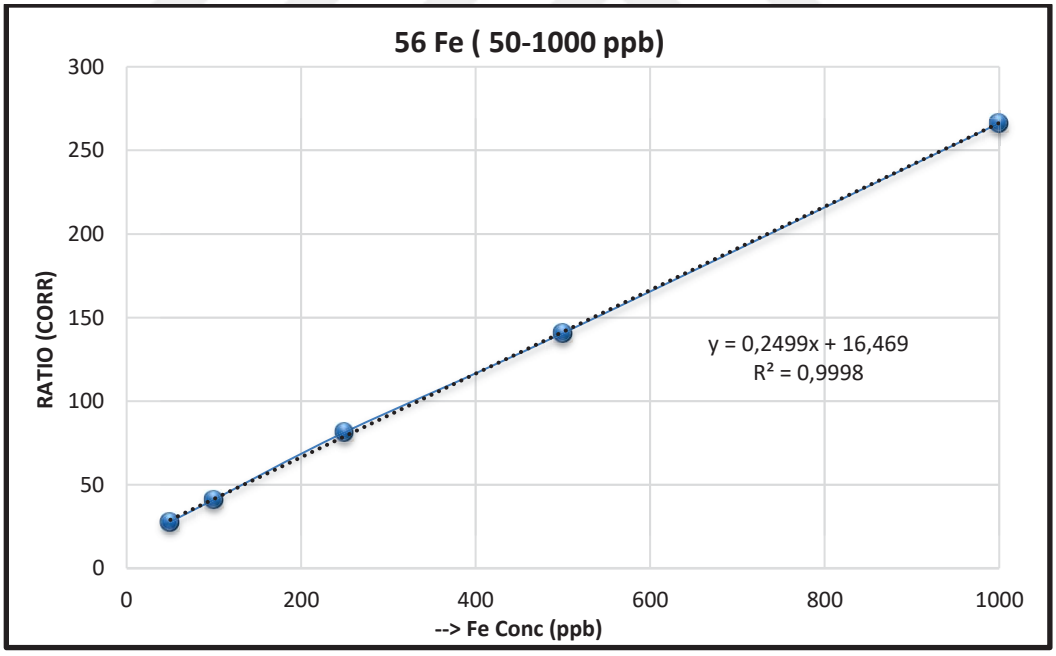


**Figure 3.13.** Calibration curve for Fe

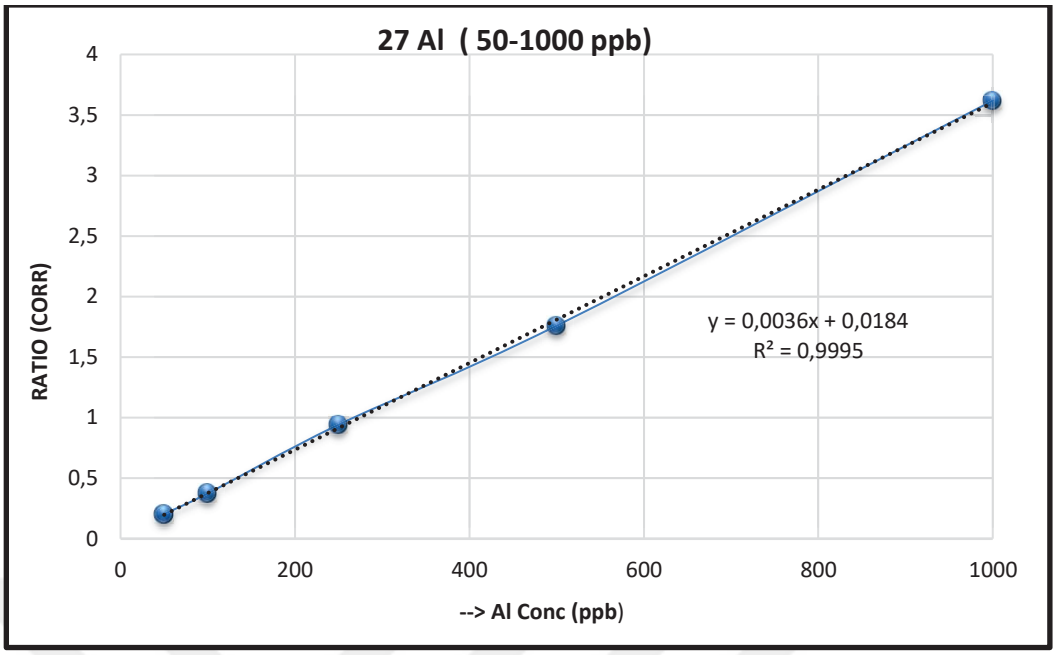


**Figure 3.14.** Calibration curve for Al

# 4. RESULTS AND DISCUSSION

An important characteristic of atomic spectroscopic techniques is the improvement of a suitable sample preparation procedure, which should be simple and capable to convert the sample into a compatible sample with the sample input system and spray chamber. Another purpose in choosing an appropriate sample preparation procedure is to reduce the interferences in signal analysis. Several procedures have been applied to determine the concentration of trace elements in crude oil samples due to the high organic and high viscosity of crude oil. In the present study, a closed Microwave system was used to digest crude oil samples and then diluted and transferred to an ICP-MS to analyze the concentration of trace elements in each sample.

## 4.1. The Concentration of Trace Elements in Analyzed Crude Oil Samples

In this study, the total concentration of 11 elements were determined, including: (Aluminum Al, Arsenic As, Copper Cu, Zinc Zn, Iron Fe, Cadmium Cd, Cobalt Co, Lead Pb, Nickel Ni, Chromium Cr, and Vanadium V) in crude oil samples by using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) technique as a result, achieved accurate and precise results related to each crude oil samples. As shown in **Table 4.1.** The elemental concentration level for all crude oil samples. The concentration level of each crude oil samples according to their location is described in **Figure 4.1.** Elements concentration of HKN crude oil. **Figure 4.2.** Elements concentration of DNO Fishkhabour crude oil. **Figure 4.3.** Elements concentration of Hunt crude oil. **Figure 4.4.** Elements concentration of DNO Tawke crude oil. **Figure 4.5**. Elements concentration of Rosneft crude oil. **Figure 4.6.** Elements concentration of Tuprash Batman crude oil. **Figure 4.7.** Elements concentration of TPIC Adiyaman crude oil. **Figure 4.8.** Elements concentration of all crude oil samples.

**Table 4.1.** The elemental concentration level for all crude oil samples

| Location | Elements Concentration (mg/L) | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Al (mg/L) | As (mg/L) | Cu (mg/L) | Zn (mg/L) | Fe (mg/L) | Cd (mg/L) | Co (mg/L) | Pb (mg/L) | Ni (mg/L) | Cr (mg/L) | V (mg/L) |
| **Z1 – HKN** | 2.008 | 0.261 | 1.805 | 15.747 | 6.213 | 0.407 | 0.016 | 2.974 | 1.028 | 0.108 | 0.082 |
| **Z2 – DNO Fishkhabour Export** | 2.669 | 0.115 | 1.750 | 10.300 | 6.879 | 0.436 | 0.035 | 3.268 | 7.235 | 0.157 | 16.287 |
| **Z3 – Hunt Oil** | 1.345 | 0.079 | 1.325 | 2.303 | 5.025 | 0.293 | 0.025 | 2.712 | 8.061 | 0.091 | 24.490 |
| **Z4 – DNO Tawke Export** | 1.880 | 0.087 | 1.296 | 5.177 | 11.550 | 0.269 | 0.027 | 2.162 | 9.660 | 0.101 | 20.650 |
| **Z5 – Rosneft Oil** | 1.180 | 0.096 | 1.250 | 3.824 | 5.369 | 0.263 | 0.017 | 2.111 | 5.477 | 0.076 | 17.710 |
| **Z6 – Tuprash Batman Oil** | 2.896 | 3.415 | 1.376 | 3.629 | 12.110 | 0.090 | 0.027 | 2.064 | 10.740 | 0.243 | 19.210 |
| **Z7 – TPIC Adiyaman Oil** | 2.365 | 2.764 | 1.290 | 3.843 | 1.054 | 0.086 | 0.025 | 1.989 | 9.876 | 0.207 | 18.423 |

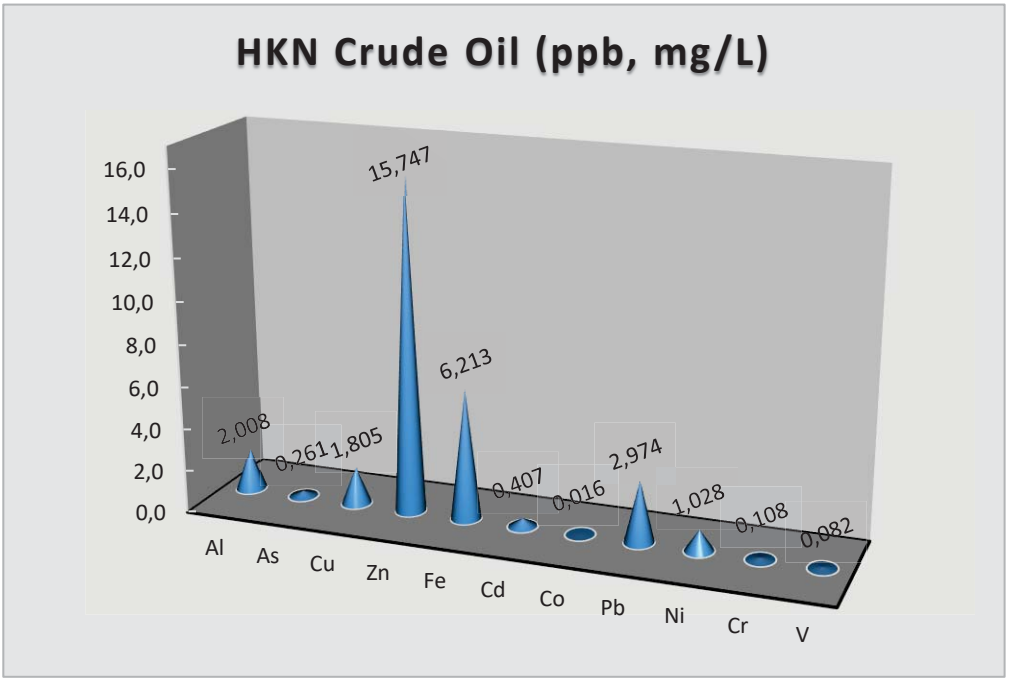


**Figure 4.1.** Elements concentration of HKN crude oil

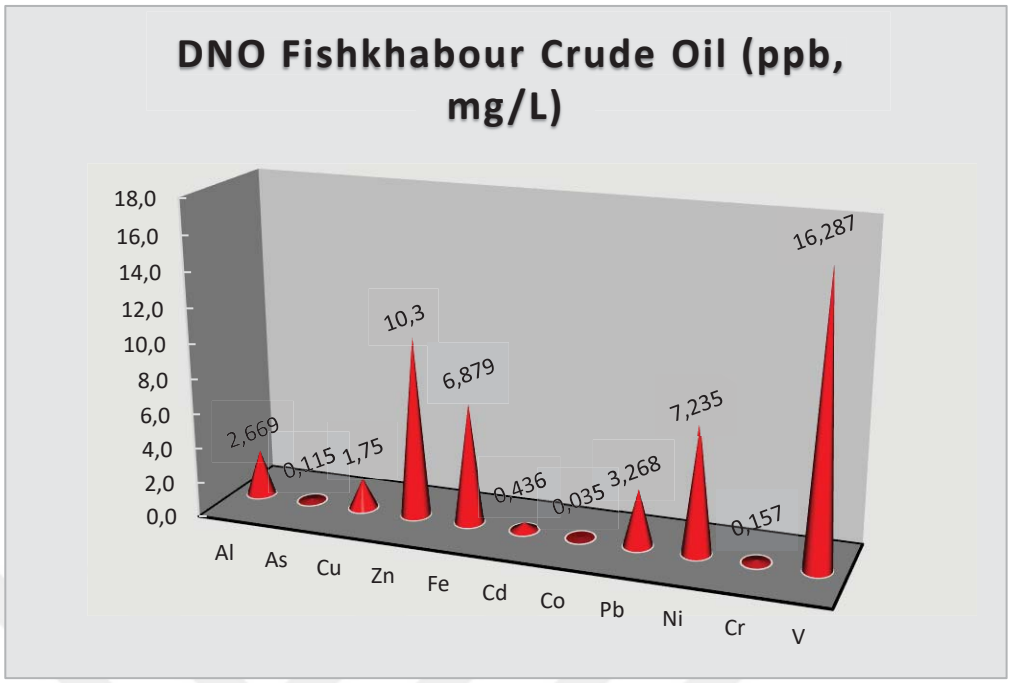


**Figure 4.2.** Elements concentration of DNO Fishkhabour crude oil

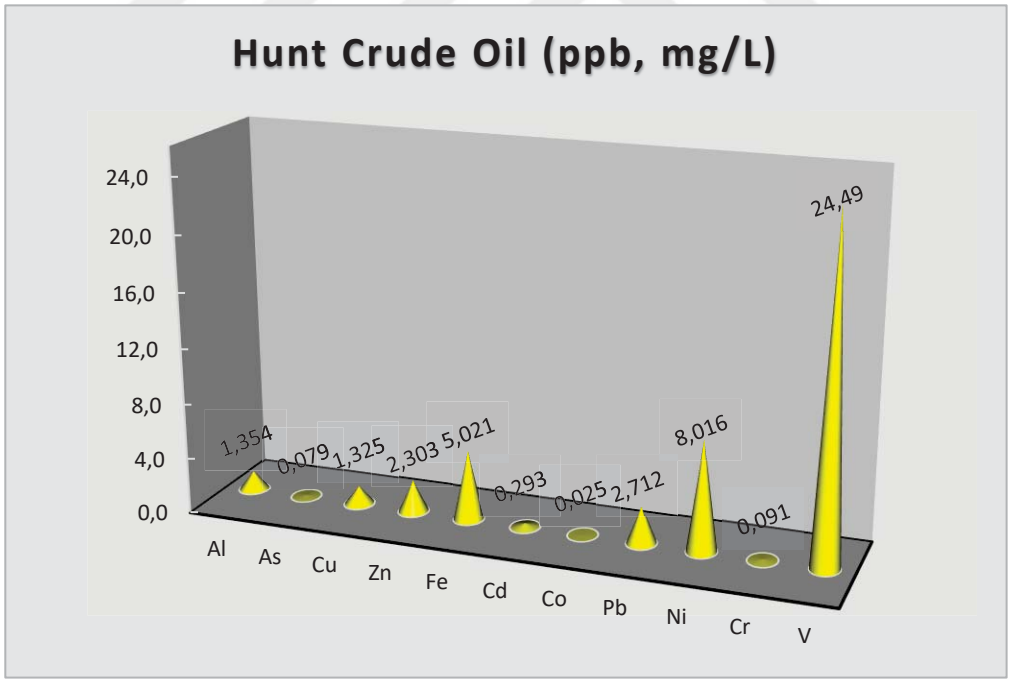


**Figure 4.3.** Elements concentration of Hunt crude oil

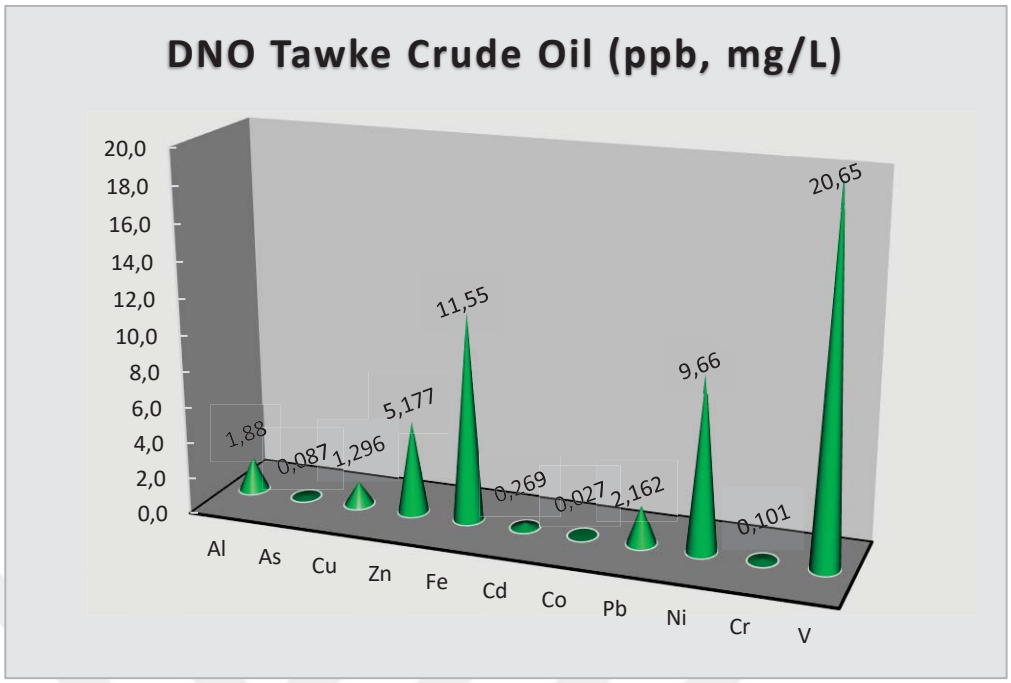


**Figure 4.4.** Elements concentration of DNO Tawke crude oil

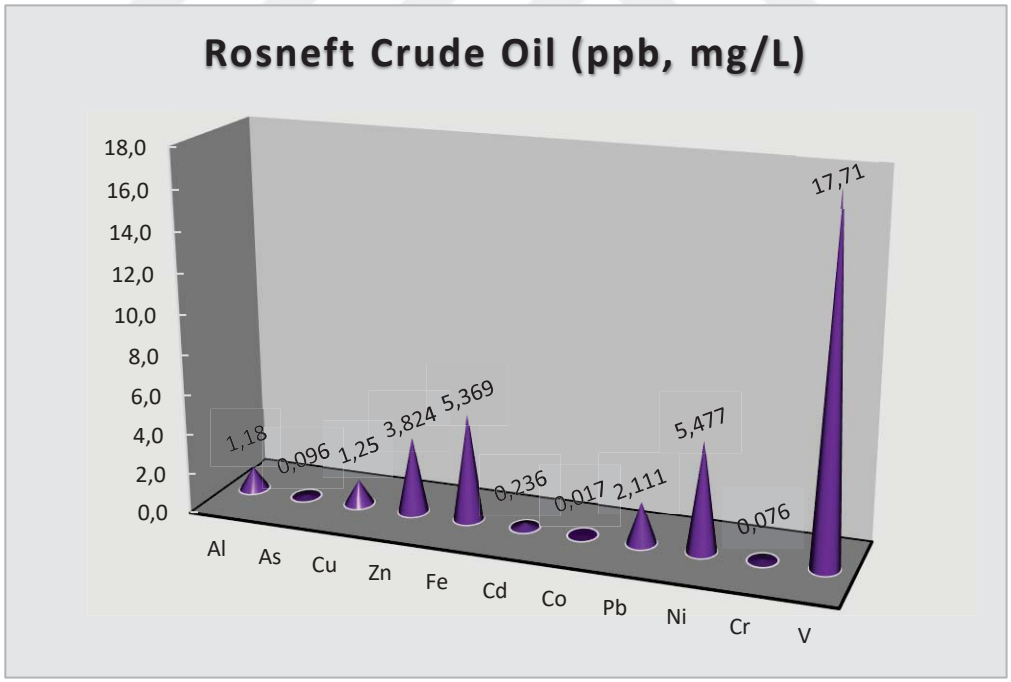


**Figure 4.5**. Elements concentration of Rosneft crude oil

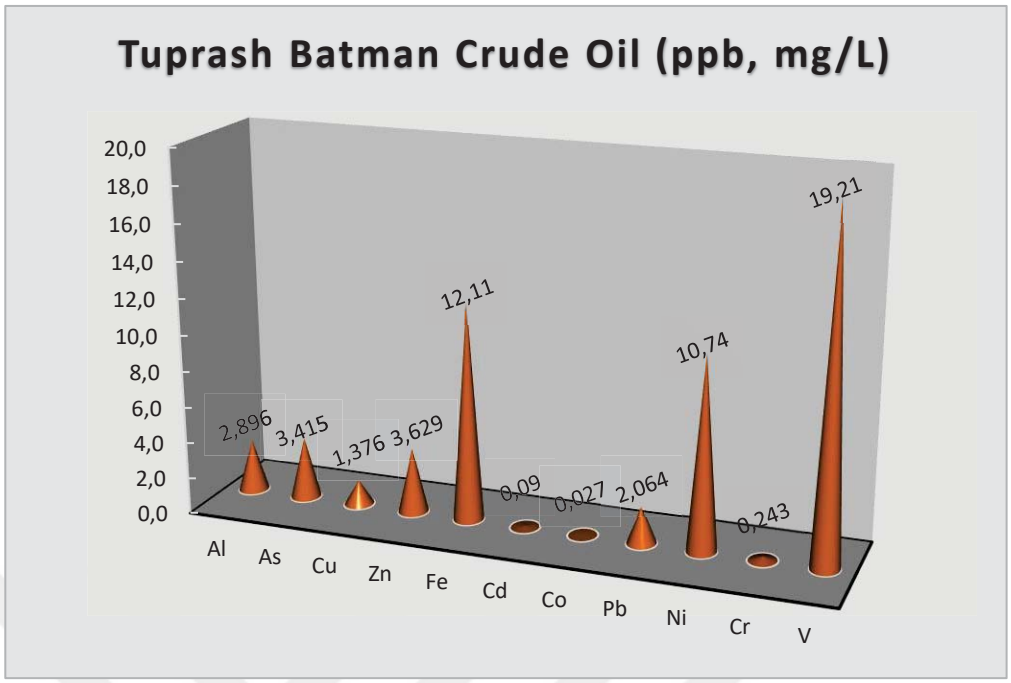


**Figure 4.6.** Elements concentration of Tuprash Batman crude oil

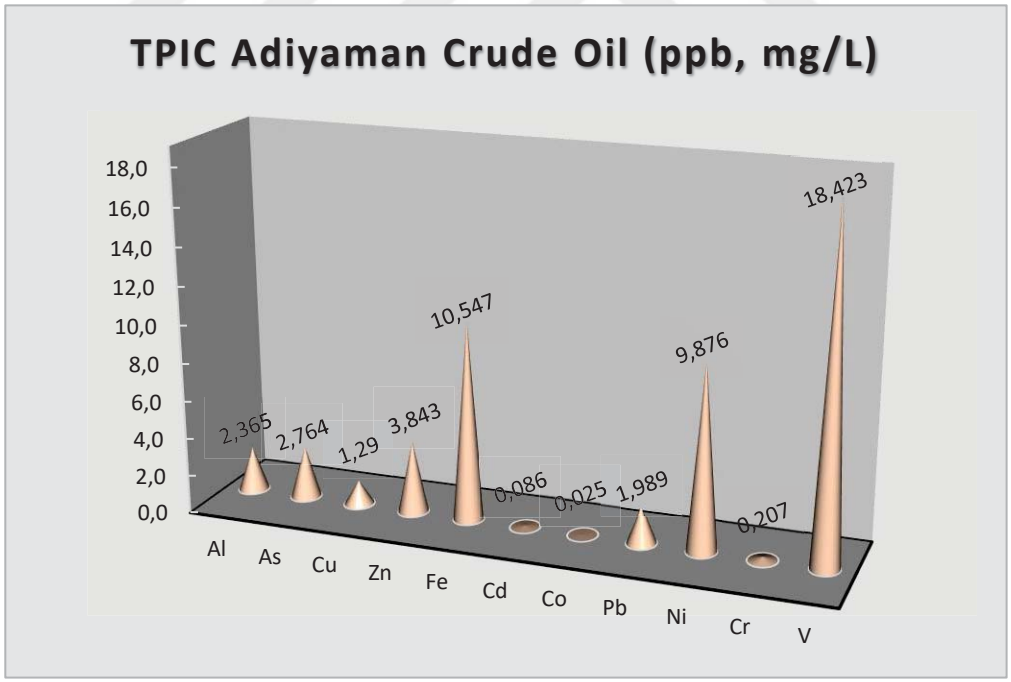


**Figure 4.7.** Elements concentration of TPIC Adiyaman crude oil

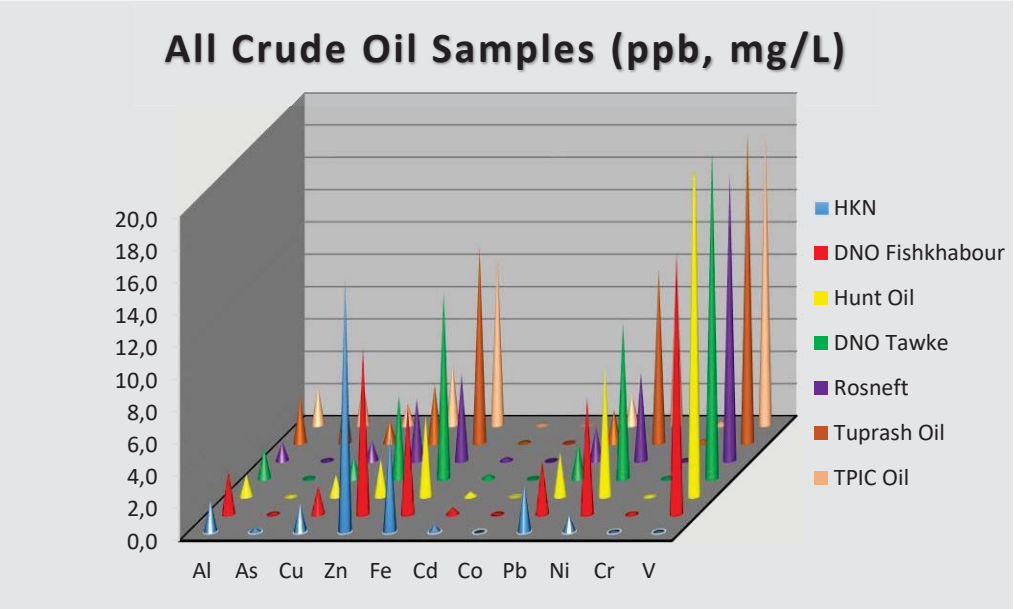


**Figure 4.8.** Elements concentration of all crude oil samples

## 4.2. API Measurements in All Crude Oil Samples

In this study, the API gravity of each crude oil sample was measured by taking 4 mL from each sample with various masses as can be seen from **Table 4.2.** API measurements related to mass and volume in all crude oil samples, and obtained the following results. Furthermore, these results were compared with the results of each crude oil location and accomplished accurate and precise results related to crude oil samples. As shown in **Figure 4.9.** Comparison between all crude oil samples according to their API measurements.

**Table 4.2.** API measurements related to mass and volume in all crude oil samples

| location | Mass (g) | Volume (mL) | API |
|---|---|---|---|
| **HKN** | 3.1690 | 4 | 37.27 |
| **DNO Fishkhabour** | 3.1917 | 4 | 27.70 |
| **Hunt Oil** | 3.3374 | 4 | 19.46 |
| **DNO Tawke** | 3.3661 | 4 | 26.93 |
| **Rosneft** | 3.6210 | 4 | 18.77 |
| **Tuprash Batman Oil** | 3.7010 | 4 | 21.50 |
| **TPIC Adiyaman Oil** | 3.6848 | 4 | 22.10 |

From the results obtained, the sample of HKN crude oil has the highest API value, which means that is a light crude oil with low specific gravity and more useable and valuable for refinery products. As can been seen from **Table 1.3**. Illustrates the classification of crude oils in terms of API gravity. Meanwhile, Rosnift crude oil sample shows the lowest API value compared to the other samples, which leads to heavy crude oil with high specific gravity and potentially due to the high amount of Sulfur and other elements in the oil that makes crude oil harder and more cost for refinery products.

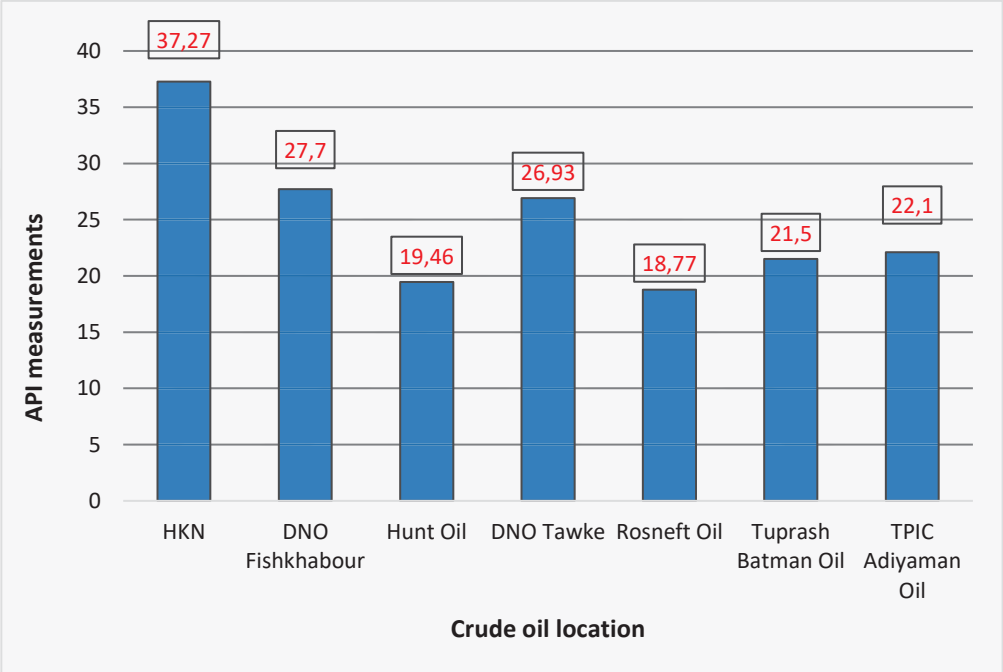


**Figure 4.9.** Comparison between all crude oil samples according to their API measurements

## 4.3. Comparison and Correlation for Crude Oil Samples

Ni and V concentrations in sample no-Z1 were found clearly lower than in the other samples studied while Zn in this sample was significantly higher.

On the other hand, Fe concentrations in two samples (number Z4 and Z6) were two times higher than in the other samples. Moreover, from the results obtained, Co contains the lowest concentration of elements in all samples of crude oil compared to other elements.

In the literature, Hamad (2018) found similar results for Ni, Pb, Zn and Cu in the crude oil taken from Iraq while the results were higher for Cd and Co [198]. These differences may be attribute to their measurement method (ICP-AES) due to its lower sensitivity.

Further, Al-Swaidan et al. (1996) found similar V and Ni levels in Saudi petroleum samples [56].

# 5. CONCLUSION

Crude oil exists as a liquid form in earth and is a complex mixture of hydrocarbons as important components of the primary fossil fuel. Nowadays, crude oil plays an important social and economic role. It is one of the most extensively consumed beverages worldwide. The essential components of human survival is soil and it has been described by different definitions. In the present thesis, the total concentration of 11 elements were determined from seven different samples of crude oils out of various sites in northern Iraq and southeastern Turkey by using Inductively coupled plasma – mass spectrometry (ICP – MS) instruments, samples were prepared based on partial decomposition. Various organic solvents were utilized and compared to find the reliable solvent to obtain the accurate results for determination the total concentration of the following elements including: Aluminum Al, Arsenic As, Copper Cu, Zinc Zn, Iron Fe, Cadmium Cd, Cobalt Co, Lead Pb, Nickle Ni, Chromium Cr, and Vanadium V. the experimental parameters were optimized to enable the sensitive, accurate and precise determination of these elements in crude oil samples. Nevertheless, the calibration curves were also performed for some elements such as: Cu, Ni, Cr, Pb, V, Fe, and Al to obtain good and accurate results. The results obtained in this thesis were compared with those obtained from dry ash, wet digestion, and microwave digestion and found to be satisfactory. Eventually, the present results showed that there is a huge difference between the initial content of the different crude oil samples due to their location and the organic solvent.

## RECOMMENDATIONS

Recently, huge progress has been accomplished in the Republic of Iraq and specially in the Kurdistan region and this results in the nation being dependent only on oil. Dealing with oil, whether exported or imported to any country, is the most effective way to pollute the environment. This wealthy place possesses large quantities of natural gas and crude oils. The oil industry has indicated a series of operations from exploration to marketing through pipelines and tankers. These oil industries are a source of toxic gases and some other toxic elements that are the main factor of causing cancer and other diseases. Certainly, the environmental issues must be taken into careful consideration. Social awareness has enabled people to keep themselves away from those areas in which oil companies are busy with oil operations, particularly those companies that refine crude oil into their products. For this reason, new technology has invented modern equipment and paid greater attention to the determination of trace elements in crude oils. Nevertheless, we highly recommend the oil companies that currently operating in the Republic of Iraq and Turkey to import and use those equipment that is least harmful to the environment because the excessive oil industries staying in one place seriously affects civilians. Both Iraq and Turkey must provide oil companies an outline regarding oil operation and the way that could be acceptable for people.

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# CURRICULUM VITAE

**Ziyad Nawzad**

## PERSONAL INFORMATIONS

**Researcher Information**

**Student Orcid ID : 0000 0002 9192 5169**

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## EDUCATION

**Master Degree:** "Comparison of Element Concentrations in Crude Oil Samples Taken from Different Sites in Iraq and Turkey"
Firat University, Graduate School of natural and applied sciences, Department of chemistry, Year 2020
Supervisor: Prof. Dr. Mehmet Yaman

**Bachelor :** Duhok University, Science Faculty, Department of Chemistry, Year 2014 – 2017

**High School:** Science school, Duhok City, Year 2012 – 2014

## RESEARCH EXPERIENCES

- ✓ Laboratory Instruments you use, such as test systems etc. you know
- ✓ Computer Programming languages available (C-C++, MATLAP, LABVIEW, vb.)
- ✓ Computer programs you can use (CAT/CAM, PROTEUS, CALCULUS, vb.)

## WORK EXPERIENCE

**2016 – 2017:** Worked at burn hospital as a lab assistant, Biochemistry Diagnostic Tests.
**2017 – 2018:** Worked at Judy Medical Complex, Biochemistry, Clinical Biochemistry.
**2017 – 2019:** Worked at **Shekhan Polytechnic University,** Satisfactory analyzes department.
**2018 – 2019:** Worked at **Duhok Polytechnic University,** pharmaceutical department.
**2019-** Participated in the international congress on preventive medicine hold in Turkey.
**From 2018:** Working in an English high school as a teacher (Cihan private School-Duhok).

## ACADEMIC ACTIVITIES

**Projects:**

**1.** BSc. Graduation Project **(Hydrogel in Drug Delivery)** Chemistry department, faculty of science.

**2.** Worked on project about **(Rare earth elements)** chemistry department.