



**ELEMENTAL ANALYSIS FOR
CRUDE OIL & OILFIELD AREA
“SOIL” USING ICP-OES TECHNIQUE**

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Masters Thesis

Chemistry of Science

Supervisor: Prof. Dr. Habibe ÖZMEN

AUGUST-2018

**REPUBLIC OF TURKEY
FIRAT UNIVERSITY
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES**

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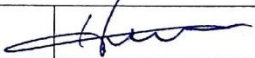
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MASTERS THESIS

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DECLARATION

I declare that the Master Thesis entitled (**Elemental Analysis For Crude Oil & Oilfield Area “Soil” Using ICP-OES Technique**) is my own research and prepared by myself, and hereby certify that unless stated, all work contained within this thesis is my own independent research and It is being submitted for the Degree of Master of Science (in analytical chemistry) at the Firat University. It has not been submitted for the award of any other degree at any institution.

Sincerely

Dalaho Dhahir HAMAD

ELAZIĞ - 2018

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ABSTRACT

Elemental Analysis For Crude Oil & Oilfield Area “Soil” Using Icp-Oes Technique

The objective of this research was to determine the concentrations of some major, minor and trace elements in nine crude oil samples from five different field (Oryx, Sarqala, TTOPCO, Tawke, Xurmala) and fourteen soil samples from eight different locations (Oryx, Sarqala, TTOPCO, Tawke, Xurmala, Kawrgosk, Erbil, Mergasor) in north Iraq. The crude oil and soil samples were analyzed for ten elements (As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn) by using inductively coupled plasma optical emission spectroscopy (ICP-OES). Prior to the analysis by ICP-OES, all crude oil samples were completely digested by extraction induced emulsion breaking and all soil samples were completely digested in dry and wet digestion.

According our results, the determined elements for Crude oil we got a minimum value for (As) was zero in TTOPCO feild and maximum value was 6.968 mg/l for (Ni) in Sarqala oil feild and for Soil samples also we gent a mininmum value for (As) was zero and maximum value is 1972.13 mg/L for (Fe) in mergasore soil field.

Statistical analysis of the results showed significant differences in the level of each element in different coffee samples of different origins, ($P < 0.05$).

Keywords: Crude Oil, Soil, Elements, Analysis, Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES).

ÖZET

ICP-OES Tekniđi Kullanılarak Ham Petrol Ve Petrol Alanlarındaki Topraklarda Element Analizleri

Bu araştırmanın amacı, Kuzey Irak bölgesinde sekiz farklı bölgeden ((Oryx, Sarqala, TTOPCO, Tawke, Xurmala, Kawrgosk, Erbil, Mergasor) temin edilen on dört toprak örneklerinde ve beş farklı alandan (Oryx, Sarqala, TTOPCO, Tawke, Xurmala) alınan dokuz ham petrol örneklerinde bazı major, minor ve eser elementlerin konsantrasyonlarını belirlenmiştir. Ham petrol ve toprak örneklerinde, indüktif eşleşmiş plazma optik emisyon spektroskopisi (ICP-OES) kullanılarak on element (As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb ve Zn) analiz edilmiştir. ICP-OES tarafından yapılan analizden önce, tüm ham petrol örnekleri indüklenmiş ekstraksiyon emülsiyon kırılması ile, tüm toprak örnekleri ise yaş ve kuru yakma medodu ile tamamen parçalanmıştır.

Elde ettiğimiz sonuçlara göre, ham petrolde belirlenen minimum değer, (As) için TTOPCO'da en düşük, en yüksek değer ise Sarqala petrolde (Ni) için 6.968 mg /L olarak, toprak numuneleri için de (As) için en düşük değer, Mergasor alanındaki topraklarda (Fe) için maksimum değer 1972.13 mg /L olarak belirlenmiştir.

Sonuçların istatistiksel analizi, farklı bölgelerdeki farklı örneklerde her bir elementin değeri önemli farklılıklar göstermiştir, ($P<0.05$).

Anahtar Kelimeler: Ham Petrol, Toprak, Elementler, Analiz, İndüktif Eşleşmiş Plazma Optik Emisyon Spektroskopisi (ICP-OES).

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LIST OF ABBREVIATIONS

AAS : Atomic absorption spectroscopy

FAAS : Flame atomic absorption spectroscopy

GFAAS : Graphite furnace atomic absorption spectroscopy

ICP-OES : Inductively coupled plasma optical emission spectrometry

ICP-MS : Inductively coupled plasma mass spectrometry

XRF : X-Ray Fluorescence

D1: Wet Digestion

D2: Dry Digestion

N.D: Not Ditection

EIEB: Extraction induced emulsion breaking

r: correlation coefficient

ID: Identification

1. INTRODUCTION

1.1. General Information

The resulting pollutions from different human activities such as industrials, agricultures and urban wastewater lead to environmental, health and economic problems. Soil contamination with metals, semi-metals and organic pollutants is one of the serious global problems [1]. Concerns intensify when the pollutants are moved by groundwater, drainage, dust and enter into the food chain [2-3-4]. Pollution with heavy metals is certainly considered as a potential ecological risk [5]. Oil and gas issues and their pollutions in Iraq are very complicated, especially when it is decided to increase the energy productions that can have various impacts on the environment components [6].

Environmental metal contaminations are increasing eco-toxicological problems because as they are non-biodegradable, irreversible nature contamination and accumulated in food [7].

The crude oils incidental release into the atmosphere due to the operational mishap, the failure of the equipments and intentional impairment to channels transferring the crude oil is recognized as oil leakage. This phenomena impacts the soil's ecosystem and totally aquatic environment. The growth of plant, micronutrients and microorganism in the soil and the global ecosystem in general are impacted by the crude oil contamination[8].

The activities of oil exploration and exploitation occurring in the North of Iraq are the main cause of oil leakage, which usually have negative impact on the ecosystem, particularly Erbil. Consequently, in the study zone, the food productivity, socio-economic and inhabitants health are adversely impacted.

Because of the ecotoxicological and environmental effect of the pollution by trace metal, the current studies is intended to examine the level of several trace elements/metals contaminations in Erbil, Sulaymanniyha and Duhok oil spill impacted sites and identify their effect on the North of Iraq within the spillage area.

1.2. Trace Elements or Heavy Metals

Trace element can be described as an element with occurring about 1000 mg/Kg or less in the crust of the earth. These elements are classified into light and heavy elements based on their densities. Elements with densities smaller than 5g/cm^3 are considered as 'light' elements, while densities of elements bigger than 5g/cm^3 are considered as 'heavy' elements. [9]. The major man-made sources of heavy metals or trace element pollution in this surroundings are mining, wastes of agricultur, dumping of partly treated and untreated manufacturing wastes, fossil fuels, exploration crude oil, indiscriminating utilization of heavy metal-comprising fertilizer, pesticides, agricultural fields and oil leakage [10-11-9]. Contamination with trace elements is concerned because of their impending hazards to human health and the surroundings once their level get to particular intensities. It has been discovered that the contamination of soil is caused by the existence of heavy metals and residues from oil leakage, waste from town and industrial activities. [12-13-14].

1.3. Crude Oil

Naturally, it is occurred in the formations of the rock and consists of a multifaceted combinations of hydrocarbons of different molecular weights, and other organic mixtures. the major components of crude oils are alkanes, cycloalkanes, aromatic compounds and some other organic compounds that comprise S, O₂ and N. In addition, a trace amount of the following metals exist in crude oils such as Fe, Ni, Cu and V. The molecular components of crude oils are various from each other but the chemical elements proportions are fairly the same. The major components of crude oils are alkanes, cycloalkanes, aromatic compounds and some other organic mixtures that encompass oxygen, nitrogen and sulfur. In addition, a trace amount of the following metals exist in crude oils such as Fe, Ni, Cu and V. The molecular components of crude oils are various from each other but the chemical elements proportions are fairly the same narrow limit as follows: C from 83 to 87%, H from 10 to 14%, and N from 0.1 to 2%, S from 0.5 to 6%, O₂ from 0.1 to 1.5% , Metals less than 1000 part per million[15].

Archeologists have reported that, crude oil has been recognized by human for long time ago and has been extracted and used for about 6000 BC. The oldest known oil wells from human kind history are located at Ephrata and Kerch coast in China. [16].

Crude oil exists as a liquid form in the earth and it's a complicated mixture of hydrocarbons as important components of primary of fossil fuels. Crude oils were used by ancient Egyptians for several medical purposes such as a liniment, wound covering and laxatives. The demand of convenient and cheap sources of energy is increased after the industrial revolution. The industrial revolution was developed at the beginning 20th century to extent that the oil production became the main energy supplier, as a crude oil was transportable to the other source of energy in a different concentrated and flexible form of fuels. The world economy now days mainly depend on the oil productions as oil become the most important sources of energy.

Paraffins, naphthenes and aromatic compounds are three main composite of crude oils. The chemical compositions of crude oils form various sources may not be completely the same.[17].

The most components hydrocarbons of crude oil are paraffins which are called methane series. Paraffins are usually liquid at room temperature and their boiling point is varied from 40 to 200 °C. Naphthenes are saturated cyclic hydrocarbon compounds and they are the most important components of all refinery liquid productions. Aromatics are unsaturated cyclic hydrocarbon compounds and exist as a tiny portion of all types of crude oils. The most well-known aromatic compound is benzene and it is found in the most of crude oils.

There are some elements present in crude oil but in a small fractions such as sulfur, oxygen and nitrogen. The third most abundant crude oil component is sulfur and the total sulfur contain of crude oil varies from 0.05% to 5%. Usually, the crude oil with high specific gravity contains a large fraction of sulfur. Crude oil contains oxygen but usually not more than 2% and nitrogen also exist in the most of crude oil with a quantity not more than 0.1%. [18].

Crude oils are classified as a “sweet” or a “sour”, based on the low and high sulphur contents of the crude respectively. When the concentration of sulphur is low in the crude oil, it is categorized as a “sweet”. However, when the content of sulphur is high in the crude oil, it is categorized as a “sour”. In general, the content of sulphur is regarded as unwanted

characteristics regarding processing and the quality of end product, thus sweet crudes are usually more demanded and valued compared to sour crudes [19]. Crude oils are classified into two types light and heavy according to the API gravity. Light crude oils are described as their API gravity is more than 10 and it will float on water, while the API gravity of heavy crude oils is smaller than 10 and it will sink on water. [20-21]. With respect to production, lighter crudes are easier and cheaper. In general, lighter crudes have a greater proportion of light hydrocarbons that can be recuperated by a simple distillation at the refinery. In contrast, because heavy crudes have high sulphur content of and some other metals, they cannot be produced, conveyed and refined by conventional approach. The density of heavy crudes are approaching or even above that of water [22].

Furthermore, aromatics, saturates and mixtures bearing heteroatoms (S, O₂ and N) are the three classes of compounds that can describe the molecular composition of petroleum. The followings are some families of related compounds in every class:

1. Saturated elements comprise normal alkanes, branched alkanes, and cycloalkanes (paraffins, iso-paraffins, and naphthenes, in petroleum terms).
2. Alkene elements (olefins) are occasional to the degree of being regarded an oddity.
3. Monoaromatic elements varied between benzene and multiple fused ring analogs (naphthalene, phenanthrene, etc.).
4. Thiol (mercaptan) elements include sulphur as do thioethers and thiophenes forms.
5. Nitrogen-comprising and oxygen-comprising elements are highly possibly to be present in polar forms (pyridines, pyrroles, phenols, carboxylic acids, amides, etc.) compare to in nonpolar forms (like ethers). The characteristics and distribution of these molecular types constitute the rich diversity of petroleum [24].

The Arabian Gulf oil fields (onshore and offshore) provide more than half of the total oil production from overall the world [23].

In 347 CE in China, the first oil well was recognized. The well was drilled 240 meter deep by utilizing by bits attached to bamboo shafts. Close to Baku, Azerbaijan, a well was dug by hand to a depth of 35 meter in 1594. Until the 1850s, these kinds of well continued to be utilized in Azerbaijan to recover crude oil. From 1846, once Abraham Gesner established a procedure to

extract what he named “keroselain” from coal, the modern history of petroleum has possibly started [16].

Start searching for oil in Iraq since the late days of the Ottoman Empire, so they get concessions for oil exploration in Iraq, The first oil discovery in Iraq, a huge Kirkuk field, in 1927. So twelve years later, in 1939, was Ain Zala field in the Mosul area discovered by the Mosul oil company, after ten years, in 1949, was the giant Zubair field in the Basra area discovered by the Basra oil company [25].

The first field drilled oil in the Kurdistan Regional Government at 1991 in Shewashok in Koya, then some other field was discovered, and Tawki field drilled at December 2005 in Tawki well east of Zakho [26]. And [25].

1.4. Soil

The key element of human survival is soil and it has been defined by different definitions. that, soil has been describe as a compound of medium of heterogen that comprise solid forms comprising minerals and organic substance. The solution of soil has been described as liquid form at which soil adsorption, transportation and reaction happen in plants utilized in phytoremediation have the ability for self-engineering or exerting specific control upon the rhizosphere, local biogeochemistry (soil and water pH, redox conditions, organic content), water and nutrient obtainability, producing a hydraulic blockade for capturing pollutant plumes and the indigenous microclimate [27].

For entire terrestrial ecosystems, soil is the most important constituent. Firstly, soil supplies the nutrient-bearing environment for the life of plant. Secondly, it is vital for the degradation and biomass transfer. It is highly multifaceted heterogeneous medium, which is composed of two phases. The first phase is fluid in which interaction occur between the soil, water and the soil, air and ions entering the soil system. The second phase is solid (the soil matrix) including organic substance minerals [28].

Soil is complex mixture of organic matter, minerals, air, water, and limitless organisms that are the decomposing leftovers of living organism after death. Soil is known as the earth's skin because it forms at the surface of land. It is able to support life of plants and is a imperative to

life on earth. In virtually any ecosystems (marsh, farm, prairie, forest, or suburban watershed), it performs numerous important functions.

Soils have seven general roles:

- 1 For growing of all types of plants, they serves like a media.
- 2 Through discharging and absorbing gases such as methane, carbon dioxide and water vapor and dust, soil amend the atmosphere.
- 3 For animals that live in the soil like mice and groundhogs and organisms like fungi and bacteria, that account for most of the living things on Earth, soil provide habitat.
- 4 The majority of the water in terrestrial systems is held, absorbed, released, altered, and purified by soils
- 5 Recycling of nutrients, such as carbon, is performed by soils. Thus, living things can use the kind of nutrients over and over again.
- 6 For constructing roadbeds, foundations, dams and buildings and preserving or destroying artifacts of human endeavors, soil function like an engineering media.
- 7 For cleaning water prior it moves into an aquifer, soil perform as a living filter.

Sets of microorganisms that utilize the soil as its natural territory are called Soil microbes. Mainly they comprise of both eukaryotes such as microscopic algae, fungi and protozoans, and prokaryotes such as blue- green algae, bacteria and actino-mycetes. In the process of noxious chemicals detoxification, the recycling of plant nutrients and soil structure maintenance, The activity and diversity of soil microbes have an imperative role [29].

1.5. Literature Reviews

The available information in the literature about the quantity of the trace elements that exist in the petroleum from different origins is limited, different analytical techniques in a number of studies have been used for determination the amount of some elements (major, minor and trace element) in different types of crude oils and soils in different countries around the world.

1.5.1. Heavy metal Determination in Crude Oil

Subsequent ashing with H_2SO_4 , the FAAS was utilized for determining Nickel (Ni), Vanadium and Iron in crude oils and residual fuels [30-31]. However, determination of Nickel and Vanadium in crudes and heavy crude fractions by FAAS subsequent diluting in xylene has been reported. Determination of Vanadium by nitrous oxide, acetylene flame AAS has been reported [31]. It is reported that after the solubilization in MIBK, FAAS was applied for analyzing of Cadmium, Lead and Nickel in petroleum and its burning remains [32]. In addition, analyzing of Arsenic, Cadmium, Chrome, Copper, Magnesium, Nickel, Lead and Vanadium in heavy oils by ET-AAS subsequent acid digestion with HNO_3 - H_2SO_4 combination has been published [33].

It is illustrated that Se, Sb and As in oily water was determined by hydride generation AAS, subsequent oxidation completely of the organic matrix utilizing microwave-assisted digestion in the closed system [34].

The same study reported the metal determination by ICP-OES in crude oil subsequent diluting with organic diluters. In crude oil, The Ti, Fe, Zn, Ni, V, Mn, Mo, Co, Cr and Cd was determined by ICP-OES utilizing emulsions without detergent including acidified water for constituent solubilization and propan-1-ol like a cosolvent with the O_2 supplementation to the nebulizer gas flow [35]. [37] have utilized ICP-OES for determining Nickel and Vanadium in petroleum and heavy crude fractions subsequent diluting in xylene. The S, V and Ni determination in petroleum distillation residues by ICP-OES subsequent sample digestion by microwave induced burning was studied in [39].

In addition, [34] have utilized ICP-OES in determining Ti, Mo, Cr and V in diesel and in crude oils. The evaluation of detergentless and detergent emulsion sample preparation procedures were conducted. Superior outcomes were gained for detergent emulsions in comparison to detergentless emulsion with recoveries between 90.1 and 106.5%. Furthermore, decent precision for the determinations of La, Ag, Mo, Al, Mg, Co, Fe, Ba, Cd, Cu, and Mn in crude oils and residual fuel oil by applying ICP-MS subsequent diluting the sample in toluene was reported [41].

The Fe, Al, Co, Zn, Li, Ti, V, Ni, Cu, Mn, Sr, Mo, Sn, Ag, Sb, Cd, Pb and Ba in petroleum by utilizing ICP-MS with a micro-emulsion sample introduction was reported [43].

The high performance liquid chromatography (HPLC) and high temperature gas chromatography (HTGC) coupled to ICP-MS for the determination of geoporphyrins from crude oil was examined in [44]. For identifying Co, Cr, Fe, Ni, Ti, V and Zn metalloporphyrin rapidly, the HTGC-ICP-MS was utilized [44].

1.5.2. Determination of Heavy metals in Soil

Worked on farming soils of Suszec commune affected by the main industrial central of Poland. They determined that Cd, Pb, As, Sb and Hg concentration increased in the soil caused by local contamination sources [45]. the heavy metal contamination in roadside fields of Van as function of intensive motorized traffic was studied. The study stated the escalation of Cadmium and Lead level at the roadside in comparison to inside positions were happened because of intensive traffic [38].

For evaluating the possible dangers to residents and tourists, working on Beijing urban parks is vital. samples were gathered from thirty urban parks situated in the city of Beijing for identifying the level and sources of heavy metals, and for assessing the soil environmental quality. After that, the level of Ni, Zn, Pb and Cu in the samples were analyzed. It was determined that while Cu, Pb and, in part, Zn were comprise mostly by anthropogenic activities, the concentrations of Ni and Zn were controlled by parent material in the soils. The results indicated that the age and the site of the park are significant aspects in determining the amount of heavy metal, mainly Cu and Pb, contamination. Furthermore, Zn accumulation did not seem to reach the level of contamination, and no clear contamination by Ni was monitor in the soils of the parks in Beijing [46].

Have reported that lead concentration of urban soils increased in industrial area because of battery manufactory dominated in Baoji city-China [47].

Collected soil samples randomly in the agricultural, industrial and a highway soils in the northren Iran (Amol-Babol). They have examined level of Lead, Cadmium and Zinc. An oven was utilized for drying the samples of the of soil. Then, the sapmles were passed through a 2

mm polyethylene sieve. For extracting the metals present in samples a mixture of HCL and HNO₃ was used. The Cd, Pb and Zn measurement was conducted by Perkin-Elmer Atomic Absorption Spectrometer (AAS), subsequent filtrating by number 42 Whatman paper. The concentration of metals that gathered in industrial, agricultural, and highway soils, were correspondingly as the following: Pb 213 – 132 mg/L, 19.70 – 9.5 mg/L, 84 – 38 mg/L, Cd 4.90 – 3.80 mg/L, 1.9 – 1.2 mg/L, 0.95 – 0.40 mg/L, Zn 214 – 111.50 mg/L, 112 – 47 mg/L, and 107 – 39.50 mg/L. The biggest levels of these metals were monitored in industrial zone soils in accordance to acquired outcomes, concentration of Zn in all the investigated zones was less compared to the permissible limit (400 mg/kg) and level of Lead and Cadmium in the industrial zones of Amol and Babol was higher than the standard limits [49].

Worked on industrial soil just Erbil city. Thirty five elements were analyzed in these soil samples. These site positions are North Industrial, South Industrial, Erbil Citadel and three sites outside the city as background. Fe, K, Al, Na, P, Li, Be, B, Sc, V, Cr, Ga, As, Se, Rb, Sr, Y, Zr, Mo, Sn, Cd, Cs, Ba, La, Ce, Th, and U have higher concentrations than those of the local background but still have not reached the pollutant levels when compared with the international standards. The level of Nickle, Copper, and Zinc have exceeded pollutant levels but still cannot be considered as a toxic or hazardous because of their immobile nature under the current oxidizing environmental conditions. Meanwhile, Co, Mn and Pb have reached critical levels in the industrial areas; while Ni, Cu, Co, and Mn have critical values in the Citadel soils. The concentration of Ca in all studied areas is higher than those of international soil standards, while Mg is lower. According to his results there are high concentrations of P in the Erbil Citadel soil samples which are considered pollutant [50].

1.6. Pollution

The most dangerous pollutant of anthropogenic environmental pollution is heavy metals because of their highly toxicities and long residence in the environment [48-51].

previous researches have exposed that high level of heavy metals exposure will result in their buildup in the body of human being [52]. Human exposure to heavy metal happen via three main routes such as ingestion, inhalation and skin absorption. low environmental mobility of heavy metals, even under elevated precipitation and long-term persistence of these substances

in the surroundings aggravate risk to human and animal health [53]. Increasing the level of heavy metals in soil is critical and present fear for regulatory and governmental bodies for environmental and human hazard assessments [54].

This research conducted to determine the total level of heavy metal in soil near oilfield site. The result can then be utilized as a foundation to improve the circumstances in the region and for guiding environmental planners and government in decreasing contamination in North of Iraq.

Throughout the last fifty years, the pollution of the biosphere by heavy metals and chemicals like Ni, Cu, Z and Pb increased in great extent because of industrial waste, manufacturing, mining, material dumping, traffic discharges, municipal wastes, manufacturing effluents and industrial chemicals. The environmental pollutions by poisonous heavy metals is concerned in the major big cities that have giant industrial zones [55]. The introduction of the heavy metal into the environment might cause a bioaccumulation, geoaccumulation and bio magnification [56]. Phytoremediation gets benefits of the statement that a living plant are regarded a solar energy driven system, which have the ability for extracting and accumulating certain elements from the soil. Due to the reproductive interdisciplinary cooperation of plant biochemists, molecular biologists, agronomists, soil chemists and eco engineers, it is becoming more probable [57].

Since it is a primary raw material for industries and the main source of energy, the demand on crude oil has escalated. Thus, its production, transportation and refinery has increased. This caused environmental contamination issues[58]. oil spillage is the main contributor to this environmental contamination. It denotes to the unintentional of crude oil's or refined product's leakage in water or on land throughout the distribution or transportation procedure cuasing contamination of the environmen. In various regions of the globe, The oil spillage incidence happens resulting in severe hazards and problems to the environment. Iraqi nation has experienced numerous oil spills that impacted agricultural lands, growth and development of the plants in the affected regions because Iraq is one of the main producer and exporter of crude oil [59].

Generally, crude oil spillage is the main cause for increasing the heavy metal content in the soil [60]. Different heavy metals like Ca, Co, Z, Ni, Pb and Cr are main cause of heavy metal

contamination of the soil [61]. the heavy metal contamination caused negative impact on different parameters associated with the quality and yield plant. In addition, this kind of pollution also causes alteration in the composition, activity and volume of the microbial activities [62]. where there is pollution, the root of plants can absorb heavy metals in the soil [63]. Weak growth of plant, chlorosis, crop reduction, reduction in nutrient uptake, plant metabolism disorders and decreased capability for fixing molecular nitrogen in leguminous plants are produced when these heavy metals are absorbed by plant roots [64]. Severe danger to both animal and human health are posed when of these heavy metals uptaken by plants and gathered in the food chain [65]. In human body, the existence of these heavy metals is poisonous they amass in the soft tissues. The intake of high concentration of poisonous metals has adverse impact on humans which only appear after long term of exposure [66]. The main aims of this research were to identify the impact of crude oil contamination on heavy metal contents in the soil.

1.7. Metals and Human Health

Naturally, metals found in the crust of the earth. Nevertheless, the contents these metals can differ in the environment between various zones leading to spatial differences of background level. In the environment, metals dispersal is administered by the possessions of the metals and impacts of environmental elements [67]. Thirty out of ninety two naturally happening metals and metalloids are possibly poisonous to humans. The examples of these poisonous elements are Mn, Co, Ni, Be, B, Li, Cu, As, Al, Ti, V, W, Pt, Cr, Mo, Se, Pd, Ba, Ag, Sn, Sb, Te, Cd, Sr, Cs, Pb, Au, Hg and Bi. For metallic elements that have an atomic weight bigger than 40.04 (the atomic mass of Ca), heavy metals is the generic term [68]. Via man-made and natural means; like mining, soil erosion, natural weathering of the crust of the earth, industrial release, city or town runoff, sewage waste, disease or pest control agents utilized for plant and air contamination fallout [68]. For the majority most individuals the chief exposure route to these poisonous substances is via water and food, some people are mainly exposed to these pollutants in the workplace. The heavy metals' pollution chain is usually follows a cyclic order: industry, atmosphere, soil, water, foods and human. Even though poisonousness and the causing health

risk to human of any pollutant are concentration, it is acknowledges that long term exposure to heavy metals and metalloids at comparatively low concentration can result in negative impacts (Agency for Toxic Substance and Disease Registry [ATSDR], 108-109-110-107-69]. Thus, primarily in the developed countries, there has been escalating fear on exposures, consumptions and absorption of these substances by humans. Generally, People are progressively cleaner a surroundings, and decreases in the quantities of pollutants reaching people due to escalating human activities. In the developed regions, a practical utilization of this trend are imposing novel and more constricting rules [70-111].

Regarding the significance of this topic, provides an outline of the key characteristics of heavy metals and their impact on human health. Mercury, lead, arsenic and cadmium are the most poisonous heavy metals.

1.8. Toxic Metals

The widely distributed elements in the environment are Cadmium (Cd), Lead (Pb), Arsenic (As) and Chromium (Cr). There are no advantageous impacts for these elements in humans, and they do not have a recognized homeostasis mechanism [75-76]. in general, these elements are regarded the most poisonous to animals and humans. Their negative impacts on human health related exposure, even at low level, are not limited to neurotoxic and carcinogenic actions [108-109-110-107-69-77-71].

1.8.1. Lead

It is a bluish-gray metal that occurred naturally and discovered in tiny quantities in the crust of the earth. Man made 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 utilizations. Presently, lead is utilized in the manufacturing of lead-acid batteries, ammunitions, metal products (solder and pipes), and devices to shield X-rays. In 2004, in the United States an projected one and a half million metric tons of Pb were utilized for different manufacturing utilizations. The production lead-acid batteries comprised 83% of that quantity. Moreover, the remaining utilization included a variety of products like ammunitions oxides for paint, glass, pigments and chemicals

and sheet lead by 3.5%, 2.6%, 1.7% respectively [72, 73]. Industrial production of lead begun more than 5000 years ago. Recently, the manufacturing utilizations of lead has been considerably decreased from ceramic and paints products, pipe solder and caulking [74]. In spite of this advancement, it has been stated that amongst more than 16 million homes in the USA that have at least one child aged less than six years/household, twenty five percent of homes still had substantial quantities of Pb-polluted worsened paint, dust, or nearby bare soil [79]. Cleaned houses are usually re-polluted lead in soil and dust [89]. Thus, it contributes to escalating concentrations of lead in blood in kids who play on bare, polluted soil [90]. In children, the biggest source of Pb contamination originates from chips and dust from worsening Pb paint on wall or other surfaces [91]. The concentrations of lead in blood can reach to 20 μ g/dL or higher in children who live in homes with worsening Pb paint [92].

1.8.2 Cadmium

This heavy metal of significant occupational and environmental concern. Cadmium is extensively dispersed in the crust of earth at an average level of about 0.1 milligram per kilogram. The biggest concentration of Cd in the environment is accumulated in sedimentary rocks, and marine phosphates comprise about fifteen milligram of Cd per kilogram [93].

In numerous industrial activities, Cadmium is commonly utilized. The pigments, alloys and batteries production are the main industrial utilizations of Cd [94]. Even though using Cd in batteries has exposed substantial escalation, in reaction to environmental concerns its commercial utilization has decreased in developed regions. For instance, in the USA, the daily intake of cadmium is around 0.4 μ g/kg/day, it is 50% less compared to the United States EPA's oral reference dosage [95]. The introducing strict effluent restrictions from plating industry and the introducing general limitations on Cd intake in some states are associated to this decrease.

1.8.3 Chromium

It is a substance that occurred naturally and exist in the crust of earth, with oxidation states (or valence states) varying between Cr (II) and Cr (VI) [96]. Elemental Chromium [Cr(0)] does not occur naturally. In the form of trivalent [Cr(III)], the Cr composites are stable, in addition it

occurs in nature in this state in ores, for example ferrochromite. The second-major stable state is the form of hexavalent [Cr(VI)] [98]. From a broad diversity of man-made and natural sources, Cr goes into soil, water and air with the biggest discharge happening from industrial activities. The production of chromate, tannery facilities, metal processing, stainless steel welding, and ferrochrome and the production of Cr pigment have the biggest contribution to chromium discharge. Via potentiating the act of insulin, Chromium (III) has a crucial nutrient role in glucose, fat and protein metabolism in animals and humans [100]. Numerous non-regulatory and regulatory agencies have classified Cr(VI) as a poisonous manufacturing contaminant and is human carcinogen [101-103]. The oxidation state of chromium is highly associated with the health hazard. It is varying between the low poisonousness of the metal to the elevated poisonousness of the hexavalent form. In the past, it was believed that all Chromium (VI)-containing composites are anthropogenic, with merely Chromium (III) ubiquitous naturally in soil, water, air and biological constituents. Lately, nevertheless, in ground and surface waters the occurring naturally Cr(VI) has been found at values above the limit of (WHO) for drinking water of 50 µg of Cr(VI) per liter [133]. The Cr is a pollutant of several environmental systems because it is extensively utilized in various industrial processes [106]. In chrome plating, industrial welding, dyes and pigments, tanning of leather and preservation of wood, the commercially Cr composites are utilized. In addition, in the boilers and cooking systems, Cr is utilized as anticorrosive in cooking systems [113, 114].

1.8.4 Arsenic

It is a ubiquitous constituent that is found at low level in water, air and soil [144]. The chief non-organic formulation of arsenic are the pentavalent arsenate and trivalent arsenite. The methylated metabolites – monomethylarsonic acid (MMA), dimethylarsinic acid (DMA) and trimethylarsine oxide are the organic forms of arsenic. Man-made activities and natural phenomena such as volcanic eruptions and erosion of soil are the main causes of environmental pollution by arsenic [144]. Numerous arsenic-comprising composites are manufactured commercially, and have been utilized to produce products with agricultural utilization like fungicides, algicides, sheep dips, insecticides, wood preservatives, herbicides and dye-stuffs.

To eradicate of tapeworms in sheep and cattle, arsenic-comprising compounds have also been utilized in veterinary medicine [145]. For treating amoebic dysentery, syphilis, yaws and trypanosomiasis, this element has been utilized for at least a century in the medical field [145,146]. In the treatment of some tropical illnesses like African sleeping illness and amoebic dysentery, and parasitic illnesses, comprising filariasis in dogs and black head in turkeys and chickens Arsenic-based drugs are still in use [80]. Lately, the Food and Drug Administration has declared arsenic trioxide as an agent for anticancer in treating severe promyelocytic leukemia [104]. The healing characteristic of arsenic is caused by inducing programmed cell death (apoptosis) in leukemia cells [112].

1.9. ASSESSMENT OF EXPOSURE TO HEAVY METALS

According to World Health Organization, human exposure is the quantity of a substance that contacts human body throughout specific period of time and in specific area [102]. There are two main approaches for measuring the human exposure to pollutant chemicals in the environment. Every single approach is grounded on various data profiles, therefore allowing the validation and verification of the information. The first method, the environmental observations such as identifying the chemical level scenario. However, throughout the utilization of biomarkers, the second method is grounded on exposure estimates [115].

In human health research, Biomarkers are important indices. According to National Institute of Health (NIH), these Biomarkers are defined as a characteristic that is accurately calculated and assessed as a gauge of a ordinary biological procedures, pathogenic processes, or pharmacologic reactions to a therapeutic interference [97]. Biomarkers might be utilized at any concentration in biological organization (for example, cellular, molecular, or organ concentration). For identifying exposed persons or groups, amount to the exposure, evaluate the health danger, or help in diagnosing the occupational or environmental illnesses, these biomarkers could be utilized [116].

For assessing the exposure to dangerous substances, like those from waste locations, a vital measure is assessed of the possibly exposed inhabitants. In addition, in this phase, routes of the potential exposure, the degree and occurrence extent are included. To evaluate exposure to

dangerous chemicals in possibly exposed inhabitants, an important direction method is determining chemicals or their metabolic products on several biological liquids like urine or blood. In this case, the concentration the metal exposure is accurate and reliable.

Nevertheless, long-term storage of several poisonous metals occur in hard tissues like bones and teeth. Furthermore, for routine clinical diagnosis and screening of the chronic exposure of metals examples of keratinous tissue constituents like hair and nails are frequently utilized. For instance, lead concentration in teeth, hair and bones escalates with age. This indicates that lead is accumulated gradually in the body. Thus, food pollution with lead and the probability of long-lasting Pb poisoning via the food or water required continuous observations [117]. Furthermore, lead and cadmium might persist within the matrix throughout teeth mineralization [118].

1.10. CLEAN UP OF CRUDE OIL CONTAMINATED SOIL

The major problem associated with crude oil exploration is the pollution contamination of the environment. Crude oil contamination is a global phenomenon affecting on all aspects of the environment. Cases of crude oil contamination of the soil have been documented [119-120]. Contamination of soils by crude oil has remained as an emerging issue. Costly damages have been reported on coastal lines in different parts of the world by offshore oil spills [121-122-123]. Crude oil comes into contact with the soil naturally through a natural oil seeps or man-made through accidental or deliberate spills and leakages such as intentional or accidental bursting of pipelines [124-125-126-127]. Over past decades, several methods have been devised for the clean-up of crude oil contaminated soil using a physical, chemical, thermal and biological treatments.

1.10.1. Types Of Soil Treatment

There are four steps involved in the remediation of any contaminated site. These include:

1. A preliminary assessment: This involves the identification of those conditions at the site that pose an imminent threat to the human health and the environment.
2. Selection and implementation of the appropriate interim remedial measures: It addresses

any imminent hazards that may exist at the site.

3. A site investigation and remediation technology feasibility study: In this stage the nature and extent of contamination are defined, and potential final remedial methods are identified and evaluated.
4. Selection of final remedial methods: Selection processes are taken into account based on results of the site investigation, including effectiveness of different remedial methods, the time necessary to complete a clean-up and the overall treatment cost [128-129-130].

There are two major types of soil treatment: the first is, In situ where the soil is treated at the site of contamination. The second is, ex situ in which case the soil is excavated and transported to another site for treatment purpose.

2. TECHNIQUES UTILIZED FOR DETERMINING TRACE ELEMENTS

2.1. Different techniques utilized to determine trace elements in soil and crude oil.

Various instruments have been applied to determine trace elements in petroleum and soil.

Nevertheless, the sensitivity and selectivity of instruments changes from one to another.

An extremely sensitive analytical methods are necessitated for heavy metal analysis because the quantity of heavy metals in soil and fuel is usually small. Flame atomic absorption spectroscopy is commonly utilized for heavy metal determination [131-132-133].

Atomic absorption spectroscopy has been utilized to determine cadmium and lead concentration and accompanied by the following techniques such as, Graphite Furnace technique. [83]. electro thermal atomic absorption spectroscopy (ET-AAS) [134-135]. cloud vaporization atomic absorption spectroscopy (CV-AAS) [136]. inductive coupled plasma-optical emission spectroscopy (ICP-OES) wells [137-81-138-139]. inductive coupled plasma-mass spectroscopy (ICPMS) [139] and ultra-violet (UV-VIS) spectroscopy [42-140].

Chromatography is a separation method that is utilized to determine metal ions in crude oils [78]. It described the discriminating recognition of volatile Nickle, Vanadium and Iron metalloporphyrins in crude oil samples. Gas chromatography has been linked to various highly sensitive techniques such as, it has been associated with an atomic emission detector, gas chromatography inductively coupled plasma mass spectroscopies (GC-ICP-MS) [141] high performance liquid chromatography inductively coupled plasma (HPLC-ICP) [88] have been used as well.

Direct examination via laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) [87], Neutron activation analysis [86] are utilized as a sensitive analytical instrument for analyzing trace element in soil and crude oil samples. Utilising X-ray fluorescence technique previously has been reported for a direct examination of metal and non-metal in petroleum and its products especially for vanadium, nickel and sulfur [85].

2.2 Inductively coupled plasma –optical emission spectroscopy (ICP-OES)

For determining metals in a range of various matrix samples, Inductively coupled plasma/optical emission spectroscopy (ICP-OES) is a great device. In this procedure, one of different nebulizers or sample introduction techniques are utilized for injecting samples of fluid into a radiofrequency (RF) induced argon plasma. throughout accidental excitation at elevated temperature, the sample mist getting the plasma is rapidly energized, vaporized and dried. By a mirror or lens, the atomic discharge originating from the plasma is observed, gathered. Then it is imaged on the entering slit of a wavelength selection tool. By a combination of a modest monochromator /photomultiplier tube (PMT), a single element measurements can be carried out cost effectively. Furthermore, polychromator/ an array detector combination is utilized for determining multielement up to seventy elements simultaneously. With the majority of other inorganic analysis procedures, the analytical performance of these kind of systems is competitive particularly regarding the sample sensitivity and quantity [82].

2.2.1 Principle:

The principle used in the (ICP-OES) is that the atoms are motivated as an energy of plasma is supplied to an investigation samples from outdoor. Discharge rays (spectrum rays) are released and the emission rays that symbolize the wavelength of photon are calculated once the motivated atoms go back to the low energy position. Based upon the location of the photon rays, the kind of substance is identified. In addition, grounded upon the intensity of the ray, the concentration of every substance is identified. For generating plasma, the torch coil is supplied by electric current and argon gas, with elevated frequency is employed to the work coil at the tip of the torch tube. The plasma is generated and argon gas is ionized by utilizing the electromagnetic field produced in the torch tube by the current's elevated frequency. This plasma has high electron density and temperature approximately (8000 °K) and this energy is utilized in the excitation discharge of the sample. In an atomized state via the thin tube in the middle of the torch tube, solution samples are presented into the plasma [84].

2.2.2 Inductively Coupled Plasma Characteristics

The capability of ICP for the reproducible and efficient excitation, atomization, vaporization and ionization for a broad variety of substances in different sample matrices are the major analytical benefits of the ICP over other motivation origins. Primarily, this is caused by the elevated temperature, 7000 – 8000 K, in the ICP's monitoring areas. In comparison of the highest temperature of furnaces or flames (3300 K), this temperature is considerably higher. Capablility of ICP of exciting refractory elements is mainly due to its high temperature. Moreover, this high temperature makes it less vulnerable to the matrix interferences. in addition to the ICP, other electrical-discharge-based sources like the microwave-induced plasma (MIP), alternating current and direct current arcs and sparks have high temperatures for the ionization and excitation as well. Usually, The ICP have better capability in handling fluid samples and less noisy in comparison to other electrical-discharge-based sources. there is no pollution from the contaminants exsited in an electrode substances because the ICP is an electrodeless source. Moreover, in comparison to the several other sources, like a laser induced plasma (LIP), an ICP assembly is relatively easier to construct and also cheaper. Some of the major advantageous features of the ICP source are listed in the following.

- Elevated temperature ranging from 7000 to 8000.
- High density of electron varying bbetween 10^{14} and 10^{16} cm³
- Considerable ionization degree for various elements
- Instantaneous multi element capacity (more than 70 elements containing S and P)
- Comparatively low chemical interference and low background discharge
- Outstanding precision and accuracy because of high stability
- Outstanding detection boundaries for the majority of substances (0.1 to 100 ng mL⁻¹)
- Broad linear dynamic range (LDR) (four to six orders of magnitude)
- the refractory elements applicability [82].

2.2.3 Instrumentation

In the ICP-OES, regularly the samples are conveyed into the apparatus as a liquid stream sample. Inside the instrument, via a process called nebulization, the liquid is changed to an

aerosol. After that aerosol samples are conveyed to the plasma at which it is vaporized, atomized, desolvated, ionized and/or excited by the plasma. The characteristic radiation of excited atoms and ions which is gathered via an instrument that categories the radiation by the wavelength. The radiation is identified and turned into electronic indicators that are transformed into concentration information for the specialist [84]. Figure (1.4) represents the layout of a typical ICPOES device.

2.2.3.1 Sample introduction

Liquids are the most common form to be analyzed by the plasma emission. These are usually introduced with a nebulizer and spray chamber combination, similar that used for F-AAS. An Aerosol is formed and introduced into the plasma by nebulizer gas stream through the injector tube [84].

2.2.3.2 Nebulizers

Nebulizers are important parts of the ICP-OES technique as a nebulization procedure is one of the most important stages in this sensitive technique. The liquid samples are transformed into aerosol by a nebulizer and then transported into plasma. Commercial instruments uses only two type of nebulizers with an ICP: (i) pneumatic nebulizer and (ii) ultrasonic nebulizer [40].

2.2.3.3 Detector

The detectors and their related electronics are utilized for measuring the intensity of the emission line when the appropriate emission line has been separated by the spectrometer. The most commonly utilized detectors are [40]:

- Photo multiplier tube
- Array detectors
- Photodiode array
- Charge-injection device (CID)
- Charge-coupled device (CCD)

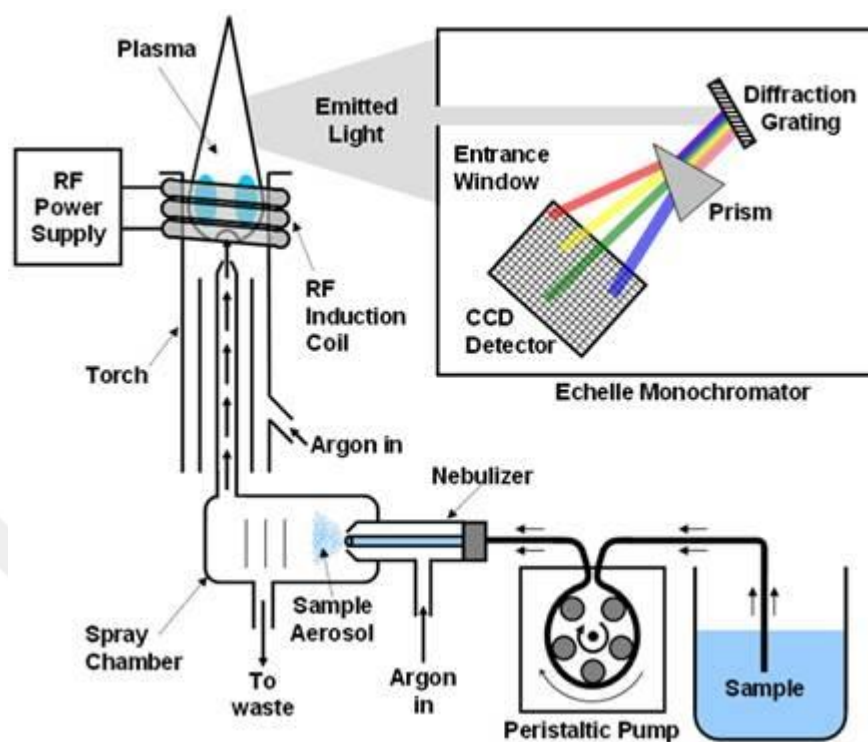


Fig. 2.1 indicates the main constituents and layout of a normal ICP-OES instrument [84].

3. MATERIAL AND METHODS

This study was carried out in three stages, including field (sampling process), laboratory (Crude oil and soil analyses) and office works (data analyzed). This research was conducted out (Erbil, Zaxo, Koye, Kalar) cities of North Iraq located between $43^{\circ}14'37''$ - $45^{\circ}37'41''$ E longitudes and $36^{\circ}46'18''$ - $35^{\circ}28'04''$ N latitudes. The North Iraq location was shown in the world map in (Figure 3.1). The sample points was shown in (Figure 3.2).



Fig. 3.1. North Iraq region location on the world map

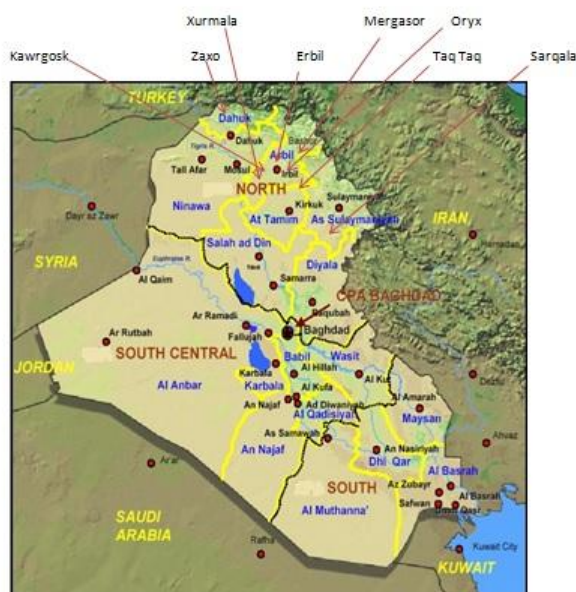


Fig. 3.2. Sampling points

3.1 Crude Oil Sample

Nine samples of crude oil (Figure 3.3) over five different oil fields were collected for the investigation. Detailed description for each samples and their ID are given (Table 3.1)



Figure 3.3. Crude oil sampling used for analysis

Table 3.1. Crude oil samples and their sample ID

No.	Sample	Sample ID
1	Oryx Crude Oil	COX
2	Sarqala Crude Oil	CSQ
3	TTOPCO crude oil	CTT
4	Tawke crude oil well 21	CT21
5	Tawke crude oil well 5	CT5
6	Tawke crude oil well 22	CT22
7	Xurmala crude oil well M9	CXM9
8	Xurmala crude oil well M23	CXM23
9	Xurmala crude oil well N2	CXN2

3.2 Soil Sample

Fourteen Soil samples (Figure 3.4). From eight different locations were selected for the analysis detailed description of soil samples and their sample ID are given in Table 3.1.

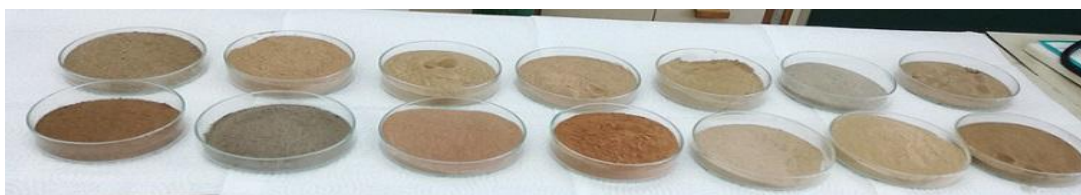


Figure 3.4. Soil samples used for analysis

Table 3.2. Soil samples and their sample ID

No.	Sample	Sample ID
1	Oryx Soil	SOX
2	Sarqala Soil	SSQ
3	TTOPCO Soil	STT
4	Tawke Soil well 21	ST21
5	Tawke Soil well 5	ST5
6	Tawke Soil well 22	ST22
7	Tawke Soil well Cump	STC
8	Xurmala Soil M9	SXM9
9	Xurmala Soil M23	SXM23
10	Xurmala Soil N2	SXN2
11	Xurmala Soil CPS	SXCPS
12	Kawrgosk Soil	SKG
13	Erbil City Soil	SEB
14	Mergasor Soil	SMR

3.3 Chemical and substances

All chemicals used were analytical reagent grade listed in the Table 3.3.

Table 3.3. Name of materials, purity and their companies

No.	Chemical substance	Purity	Supplier
1	Toluene	99.9%	Merck
2	N- Hexane	96%	Merck
3	IBMK	99%	Merck
4	Conc. Sulfuric acid H ₂ SO ₄	99%	Sigma-Aldrich
5	Nitric acid	69-71 %	
6	Triton X-100		BDH
7	DMSO	99.9%	Merck
8	Per chloric acid	99.9%	Sigma Aldrich
9	Arsenic standard 1000 ppm (µg/ml)		Avonchem.
10	Cadmium standard 1000 ppm (µg/ml)		Avonchem.
11	Cobalt standard 1000 ppm (µg/ml)		Avonchem.
12	Chromium standard 1000 ppm (µg/ml)		Avonchem.
13	Cobalt standard 1000 ppm (µg/ml)		Avonchem.
14	Iron standard 1000 ppm (µg/ml)		Avonchem.
15	Manganese standard 1000 ppm (µg/ml)		Avonchem.
16	Nickle standard 1000 ppm (µg/ml)		Avonchem.
17	Lead standard 1000 ppm (µg/ml)		Avonchem.
18	Zinc standard 1000 ppm (µg/ml)		Avonchem.
19	Multi-element standard solution for ICP		Standard
20	De ionized water		Standard

3.4. Operating Conditions for ICP – OES Instrument

ICP-OES (Perkin Elmer-USA “ OPTIMA 2100 DV ” Sreial No. : 080N6111403, Dicle Üniversitesi araştırma laboratuvar) technique has been used for investigation in this research project. The conditions of the operation of ICP-OES technique for analysis of elements in sample studies are described (Table 3.4) and a photographic picture of the instrument is shown (figure 3.5).

Table 3.4. Operating conditions for ICP – OES instrument

Parameters	Descriptions
Power	1400 Watts
Coolant flow	13 L/min
Auxiliary flow	1 L/min
Nebulizer flow	0.83 L/min
Plasma Torch	Quartz, demountable
Injector tube	2.0 mm
Spray chamber	Glass Cyclonic
Nebulizer	Concentric nebulizer
Sample uptake rate	1.2 ml/min



Figure 3.5. Photographic picture of ICP – OES

3.5. Sample Preparation

3.5.1. Sample Preparation For crude oil

For preparing crude oil samples, three different procedures are utilized: (i) dry ashing (DA), (ii) wet ashing (WA) digestion and (iii) extraction induced emulsion breaking (EIEB).

But we do it by third one extraction induced emulsion breaking (EIEB). The preparation of the samples is a iterative phase in the oil analysis. The process required pre-treatment of the

samples for destroying the organic matrix involving particular uses and following danger of sample pollution and/or analyst loss.

The results obtained proved that the DA and WA procedures are sensitive, simple and cheap method but they are slow and unsafe. While, EIEB is beneficial for routine examination and it can be regarded as a good alternative than DA and WA procedures.

The EIEB methodology was used to analyze trace elements for sample studies. The result indicated that this methodology could be very accurate to determine elements in petroleum samples and their products by ICO-OES technique. For extraction processes the diluted HNO_3 solution was used instead of using the concentrated acid which is usually used in WA and DA methodologies. [143]

3.5.1.1. Extraction induced emulsion breaking

The elements were removed from crude oil samples through the extraction induced by emulsion breaking. The procedure is grounded upon the creation of constant emulsions between an acid Triton X-100 and the samples. For improving the metal extractions, in the initial, 80% of the samples (approximately 5.2 g) and 20% of the 3% the acidic Triton X-100 solution was mixed and stable water-in-oil emulsions were attained via strong stirring of the samples. For half an hour, the emulsions were agitated on a mixer (auto vortex). To promote the emulsion breaking the mixed solution was putting in the centrifuge at 3000 RPM for 30 minutes. Two well-isolated phases were produced from the emulsion breaking. The first one was an upper phase comprising the organic part of the solution. However, the second phase was lower phase comprising the aqueous acid solution with the extracted elements. Then, the upper phase was removed and the lower aqueous phase was collected and transferred the calibrated flasks, then diluted to the mark with deionized water. All samples solution after EIEB digestion shown in (Figure 3.6.), also we used five different organic solvent shown in Table 3.5. Finally the solution was used to measure the elements of interest [142].

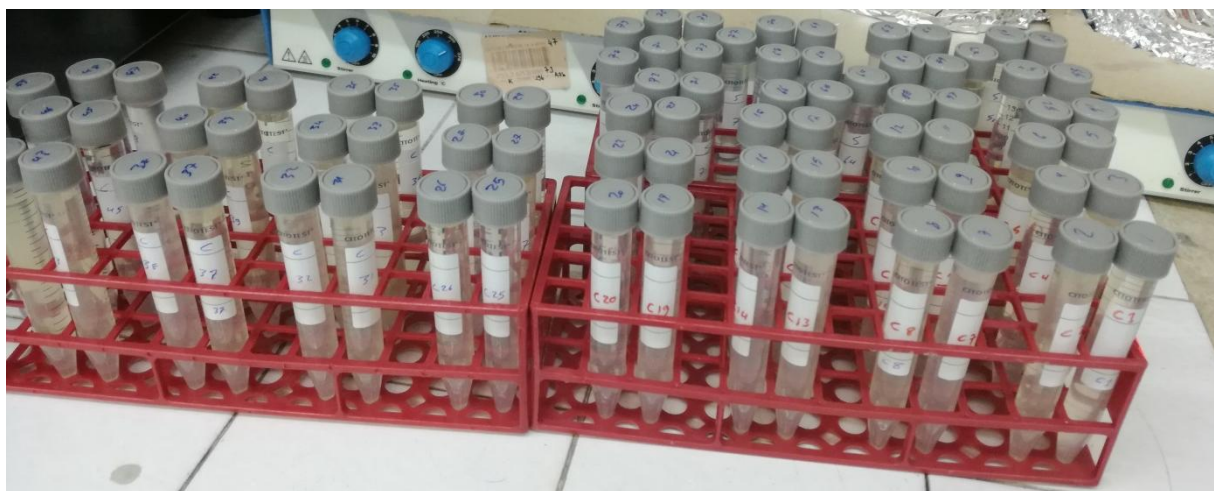


Figure 3.6. Crude oil Samples after Digestion

Table 3.5. Organic solvent and their solvent ID

No.	Sample	Sample ID
1	Toluene	T
2	N-Hexane	H
3	Dimethyl sulfoxide (DMSO)	D
4	Mixed Solvent	S
5	Isobutyl methyl ketone (IBMK)	I

3.5.2. Sample Preparation For Soil

Soil samples were stored in plastic bags after take; they were carried to the analytical laboratory belong Chemistry Department at Science Faculty at Firat University and air dried. Air dried soil samples will be crushed by wooden hammer and passed through a 2 mm sieve. Soil samples were extracted with (1:2 HNO₃: HClO₄) acid,

These research locations are in oilfield area and city center with one out of the city and oilfield area. Soil sampling procedures were realized in different positions in all locations. A total number of 14 surface soil samples (0-30 cm depth) of near and faraway from the pollution sources were taken from one sample in Oryx field, one sample in Sarqala field, one sample in

TTOPCO field, four samples in Tawke field, four samples in Xurmala field, one sample in Kawrgosk refinery, one sample in Erbil city center, one sample in Mergasor.

3.5.2.1. Digestion Of Soil Samples

We do digestion for all soil sample by two way as shown in Table 3.6

Table 3.6. Digestion ID

No.	Sample	Sample ID
1	Wet digestion	D1
2	Dry digestion	D2

3.5.2.1.1. Wet Digestion

By taking 2.0g of each Soil sample into a beaker and 2 ml of solvent (1:2 HNO_3 : HClO_4) was added then the resulting mixture were syndicated in an ultrasonic bath for 1 hour, after that 15.0 ml of deionized water were added, filtrated to remove any undissolved particle then diluted to 50 ml with deionized water. Figure 3.7 shows a soil sample after wet digestion.



Figure 3.7. Soil Samples After Wet Digestion

3.5.2.1.2.Dry Digestion

By taking 2.0g of each Soil sample into a Crucible, and heated at fans till 500°C for four hours and 2 ml of solvent (1:2 HNO₃: HClO₄) were added after that 15.0 ml of deionized water were added, filtrated to remove any undissolved particle then diluted to 50 ml with deionized water Figure 3.7 shows a soil sample after dry digestion.



Figure 3.8. Soil Samples After Dry Digestion

3.6. Statistical Analysis

The data of the study were examined statistically utilizing (SPSS, Version 16), which is a software package used for statistical analysis. The obtained data were expressed as (Mean $\pm$ St Dev). Differences in mean values of each element in all fourteen soil samples and nine samples of crude oil were examined by one-way ANOVA and T test and relationships between concentrations of the elements in analyzing crude oil and soil were assessed by using the Pearson's linear correlation coefficient. The probability level of P - value ($P < 0.05$) level of significance was regarded to be significant statistically.

4. RESULTS AND DISCUSSION

4.1. Concentration of Elements in Analyzed Crude Oil and Soil Samples

This research determined the concentration of 10 elements (Arsenic, Cadmium, Cobalt, Chromium, Copper, Iron, Manganese, Nickel, Lead and Zinc) in soil and crude oil samples by using inductively coupled plasma optical emission spectroscopy (ICP-OES) .

4.1.1. Elements for Crude oil Sample

According to collected crude samples can be classified into five main group with two sub group, for each sample in all groups used five different organic solvent (Toluene, N Hexane, DMSO, Mixed Organic Solvent and IBMK), Table 4.1 shown the P-Value test for all elements in crude oil to found the significant value and Table 4.2, shown Duncan test to choose a best organic solvent for significant value And (Figure 4.1, 4.2, 4.3, 4.4, 4.5 and 4.6) and table 4.3 shown each of elements in crude oil according to its locations.

Table 4.1. P- Value test for all groups in crude oil sample

Code			Sum of Squares	Df	Mean Square	F	P-Value
C	As (mg/L)	Between Groups	.317	4	.079	.250	.903
		Within Groups	3.176	10	.318		
	Cd (mg/L)	Between Groups	.002	4	.000	.362	.830
		Within Groups	.011	10	.001		
	Co (mg/L)	Between Groups	.007	4	.002	.632	.651
		Within Groups	.029	10	.003		
	Cr (mg/L)	Between Groups	.997	4	.249	1.019	.443
		Within Groups	2.445	10	.245		
	Cu (mg/L)	Between Groups	.002	4	.001	.213	.925
		Within Groups	.029	10	.003		
	Fe (mg/L)	Between Groups	21.633	4	5.408	.452	.769
		Within Groups	119.547	10	11.955		
	Mn (mg/L)	Between Groups	.006	4	.002	.288	.879
		Within Groups	.055	10	.006		
	Ni (mg/L)	Between Groups	3.485	4	.871	40.996	.000
		Within Groups	.213	10	.021		HS
	Pb (mg/L)	Between Groups	.209	4	.052	8.418	.003
		Within Groups	.062	10	.006		HS
Zn (mg/L)	Between Groups	4.459	4	1.115	.382	.817	
	Within Groups	29.206	10	2.921			

Table 4.2. Duncan Test For Crude oil Sample

Solvent	N	Subset for alpha = 0.05		
		1	2	3
D	3	1.4809600		
H	3	1.6293333		
T	3		1.8997333	
S	3		2.0536533	
I	3			2.8620800
Sig.		.241	.225	1.000

Solvent	N	Subset for alpha = 0.05	
		1	2
T	3	1.5905067	
H	3	1.6002133	
S	3	1.6293333	
D	3	1.7097600	
I	3		1.9080533

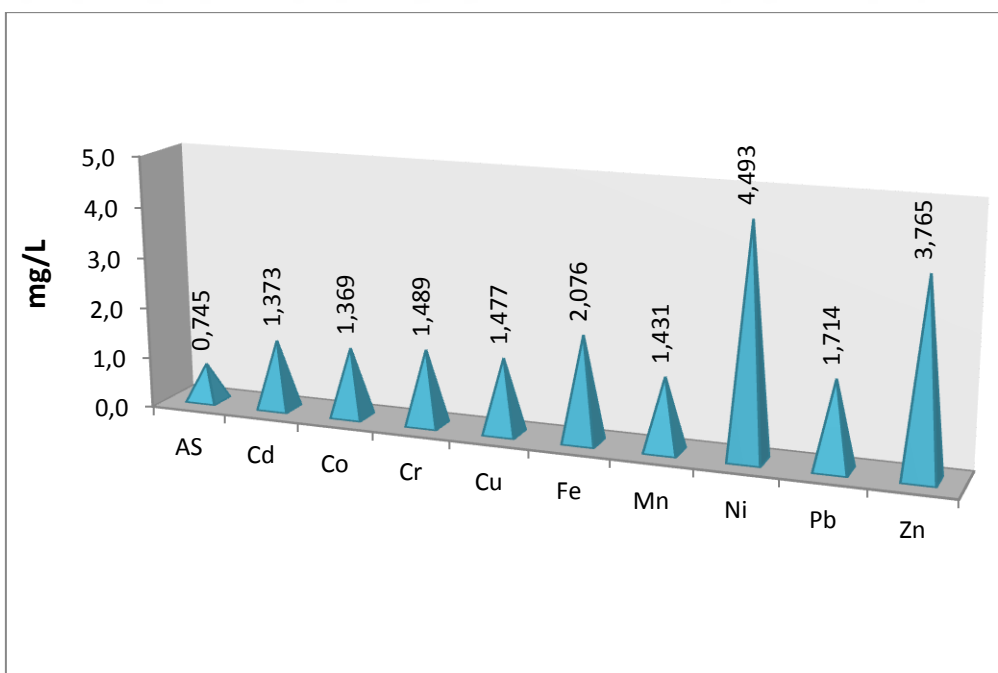


Figure 4.1. Elements in Oryx Oil well

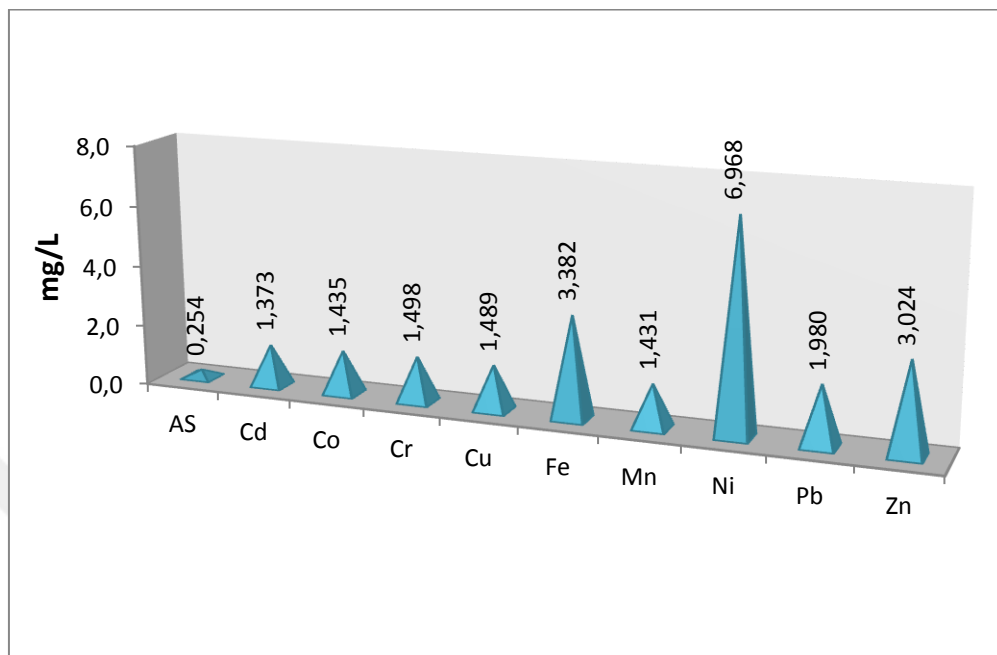


Figure 4.2. Elements in Sarqala Oil Well

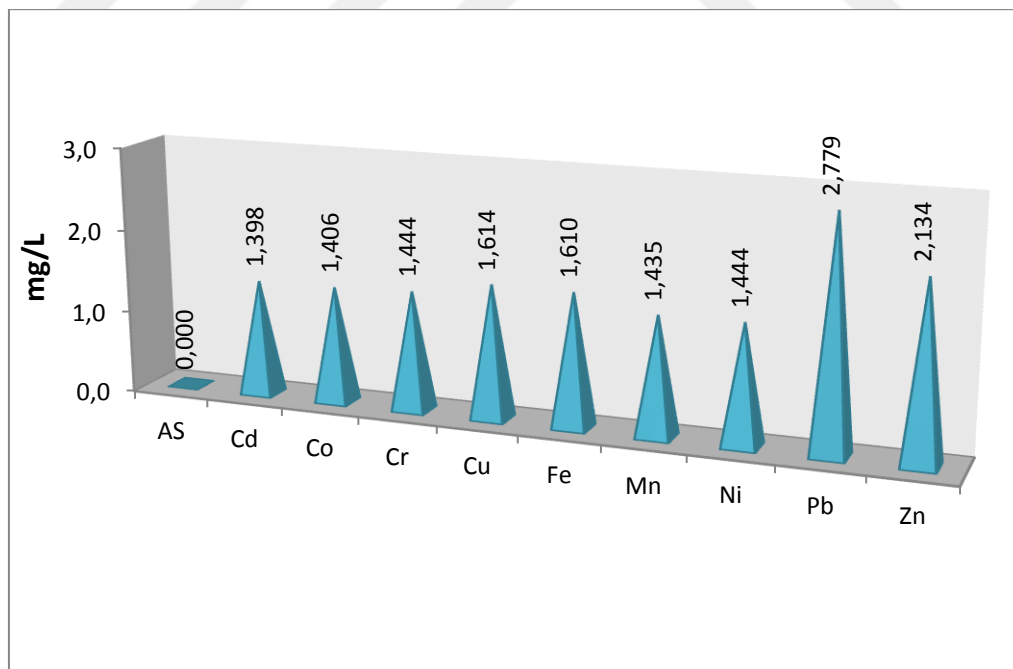


Figure 4.3. Elements in TTOPCO Oil Well

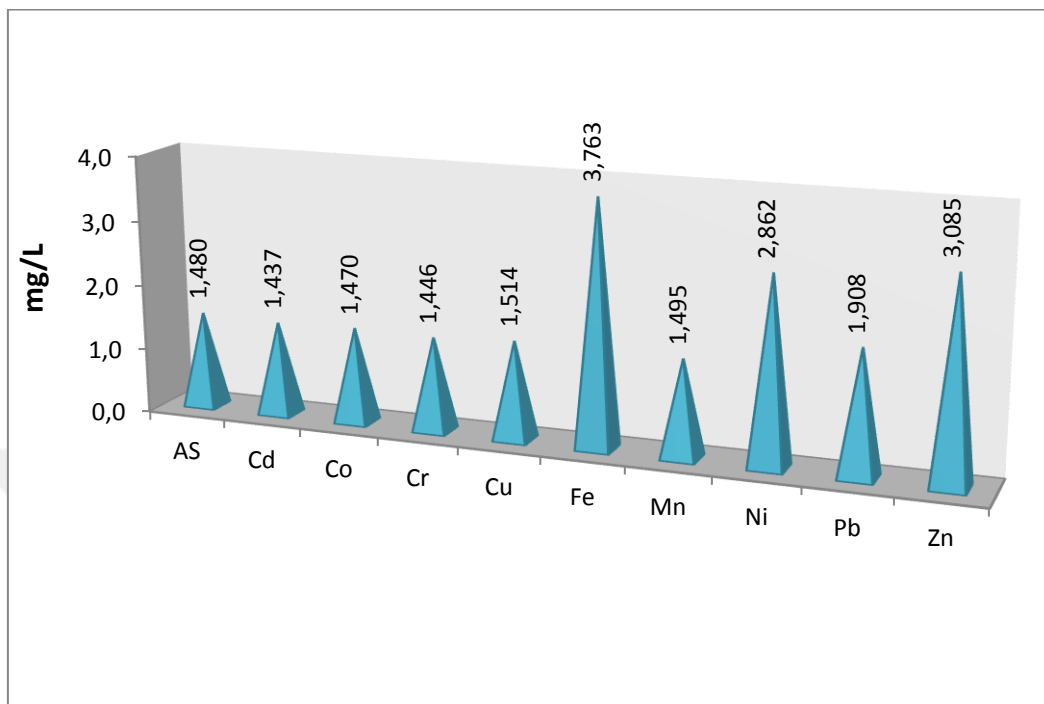


Figure 4.4. Elements in Tawke Oil Well

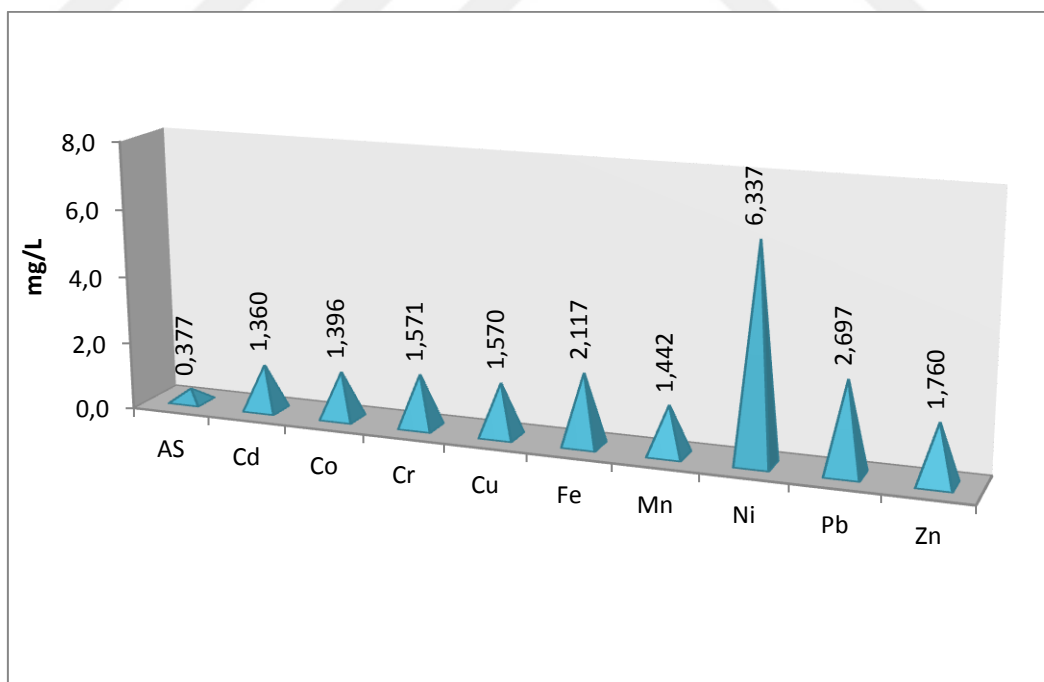


Figure 4.5. Elements in Xurmala Oil Well

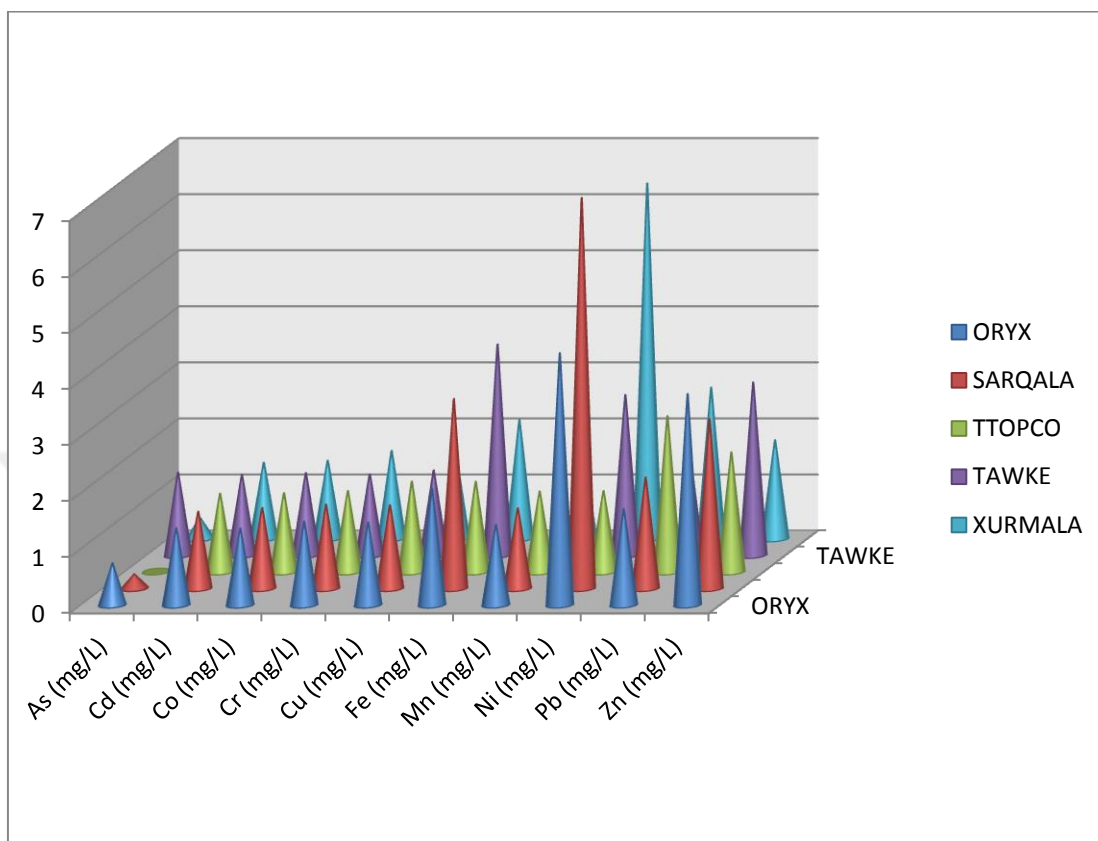


Figure 4.6. Elements Level For All Crude Oil Samples

Table 4.3. Elements Level For All Crude Oil Samples

		Location				
		ORYX	SARQALA	TTOPCO	TAWKE	XURMALA
Elements	As (mg/L)	0.745	0.254	N.D	1.480	0.377
	Cd (mg/L)	1.373	1.373	1.398	1.437	1.36
	Co (mg/L)	1.369	1.435	1.406	1.470	1.396
	Cr (mg/L)	1.489	1.498	1.444	1.446	1.571
	Cu (mg/L)	1.477	1.489	1.614	1.514	1.570
	Fe (mg/L)	2.076	3.382	1.610	3.763	2.117
	Mn (mg/L)	1.431	1.431	1.435	1.495	1.442
	Ni (mg/L)	4.493	6.968	1.444	2.862	6.337
	Pb (mg/L)	1.714	1.980	2.779	1.908	2.697
	Zn (mg/L)	3.765	3.024	2.134	3.085	1.760

4.1.2. Elements for Soil Sample

According to collected Soil samples can be classified into four main group with five sub group, First group include oil field production area and contain five sub group location, shown in (figure 4.6, 4.7, 4.8, 4.9, 4.10). Second group is Refinery area in the refinery used crude oil and produce crude oil product like benzene, diesel and gasoline ... etc., but crude don't have in it land, shown in (figure 4.12). Third group Erbil city center, (figure 4.11)., I think is polluted by oil products which is used by cars and industrial area. Fourth group the area is far from oilfield production, refinery area and city, so we used as a blank, (figure 4.13). For all of each soil sample we do two different ways for digestion is dry and wet digestion.

Table 4.8 comparison between D1 & D2. In Table 4.10 and figure 4.14 we shown all heavy metals level for all Soil location:

Table 4.4. Comparison Between D1 an D2 For Soil Samples:

Solvent		N	Mean	Std. Deviation	T	Df	P-Value
As (mg/L)	D1	4	56.256	5.811	0.745	6	0.485
	D2	4	50.363	14.726			
Cd (mg/L)	D1	4	7.975	0.124	0.735	6	0.490
	D2	4	7.900	0.162			
Co (mg/L)	D1	4	18.825	3.152	1.752	6	0.130
	D2	4	15.469	2.177			
Cr (mg/L)	D1	4	88.281	43.574	0.474	6	0.652
	D2	4	77.475	13.527			
Cu (mg/L)	D1	4	30.919	2.209	1.907	6	0.105
	D2	4	25.106	5.682			
Fe (mg/L)	D1	4	1544.188	434.381	0.630	6	0.552
	D2	4	1363.938	371.845			
Mn (mg/L)	D1	4	189.425	72.721	0.342	6	0.744
	D2	4	172.656	65.938			
Ni (mg/L)	D1	4	127.231	73.054	0.759	6	0.477
	D2	4	96.581	34.532			
Pb (mg/L)	D1	4	13.619	1.446	1.008	6	0.352
	D2	4	12.656	1.248			
Zn (mg/L)	D1	4	84.881	15.586	2.502	6	0.046 S
	D2	4	63.369	7.272			

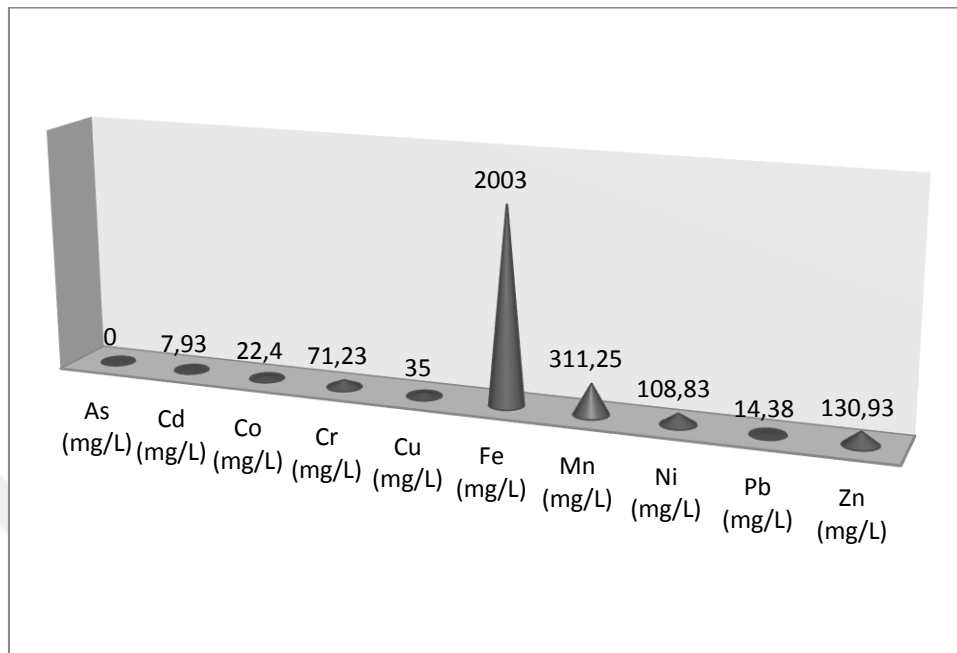


Figure 4.7. Elements Level in Oryx Soil

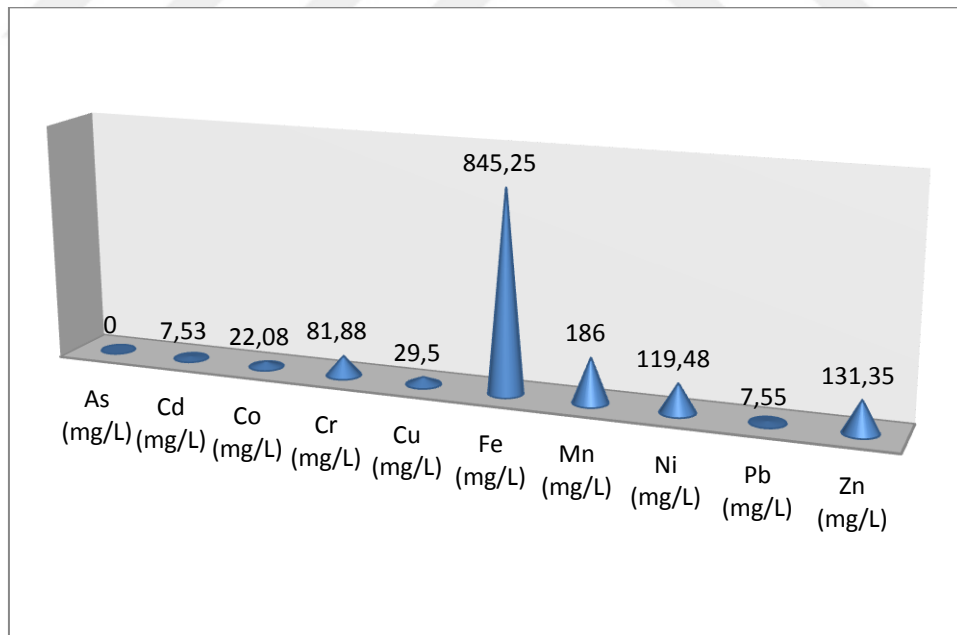


Figure 4.8. Elements Level in Sarqala Soil

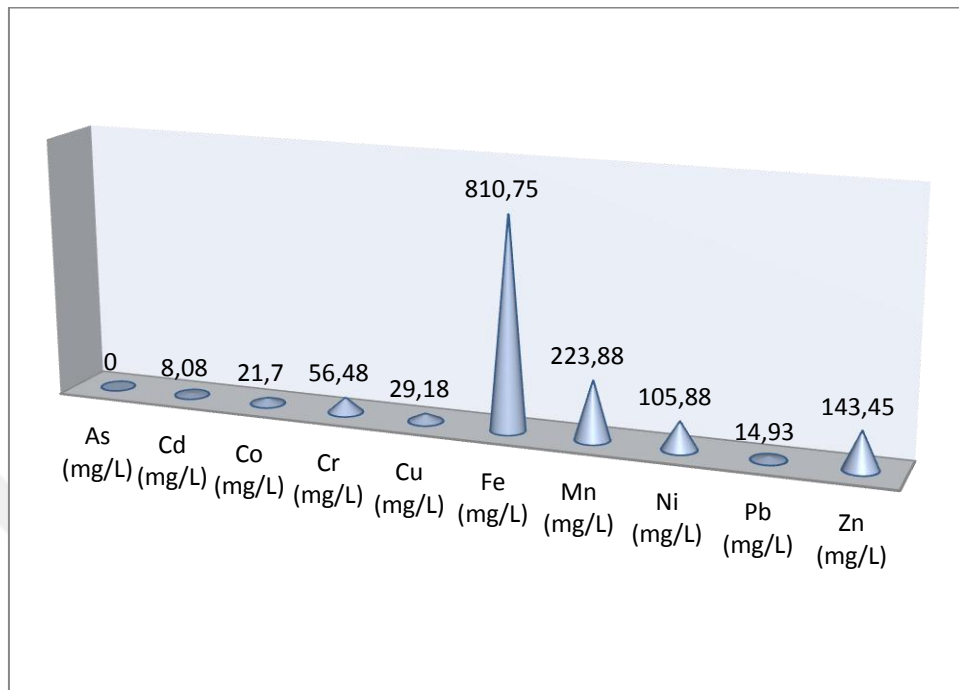


Figure 4.9. Elements Level in TTOPCO Soil

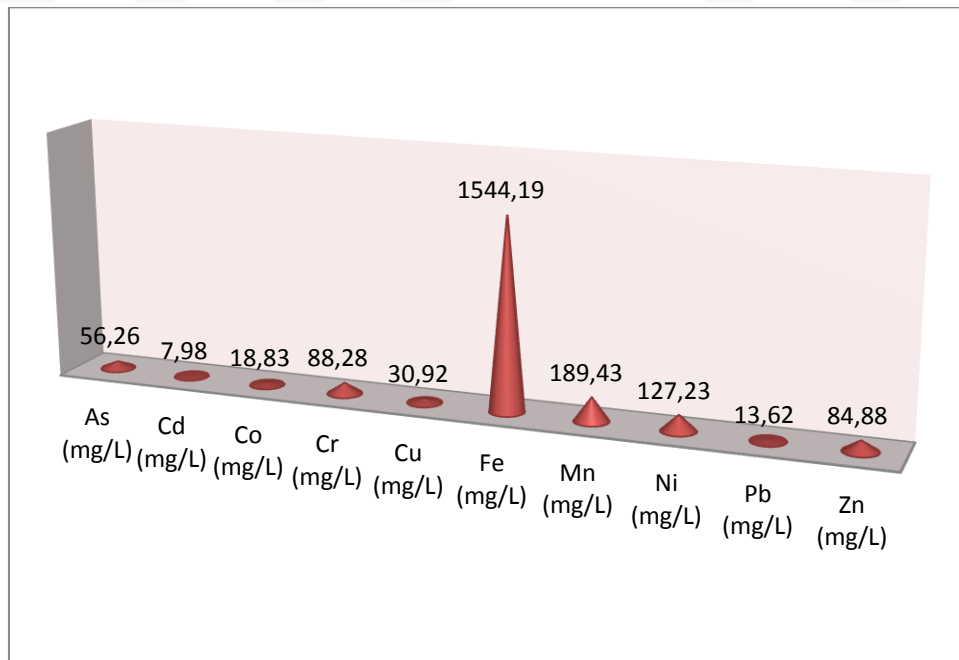


Figure 4.10. Elements Level in Tawke Soil

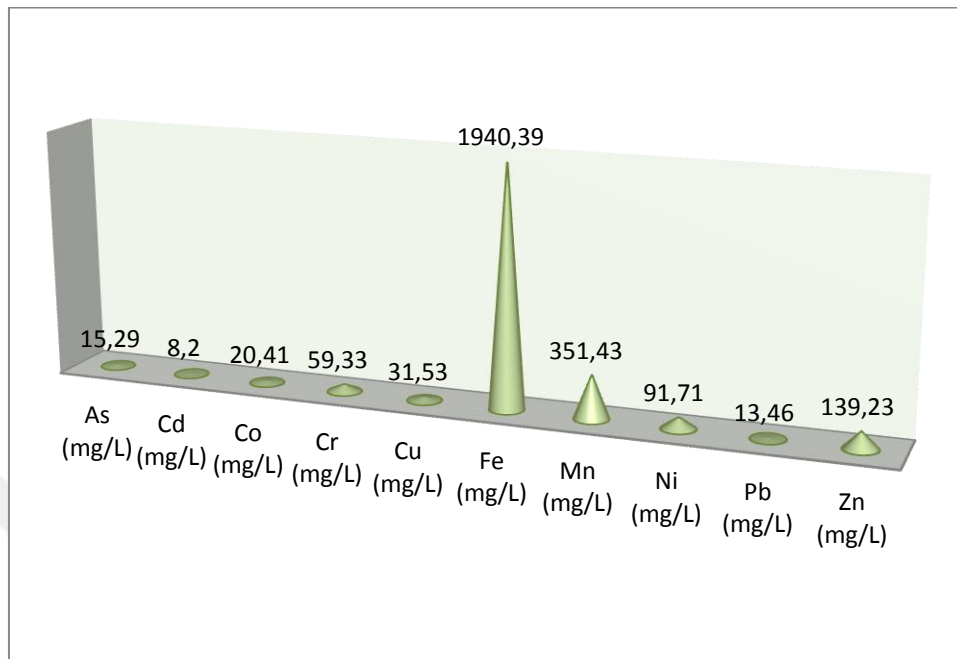


Figure 4.11. Elements Level in Xurmala Soil

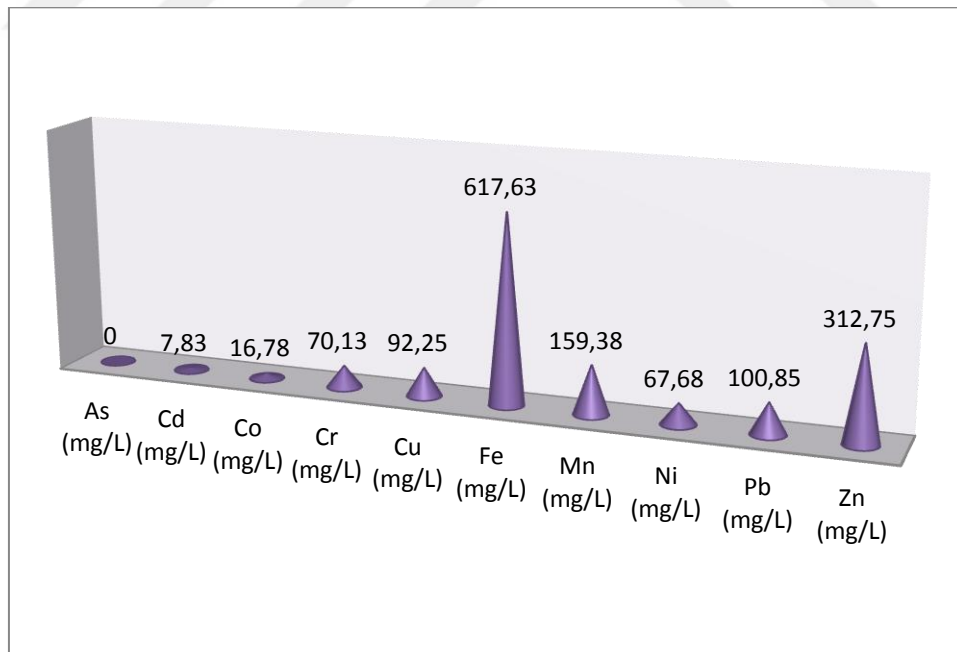


Figure 4.12. Elements Level in Soil Erbil City

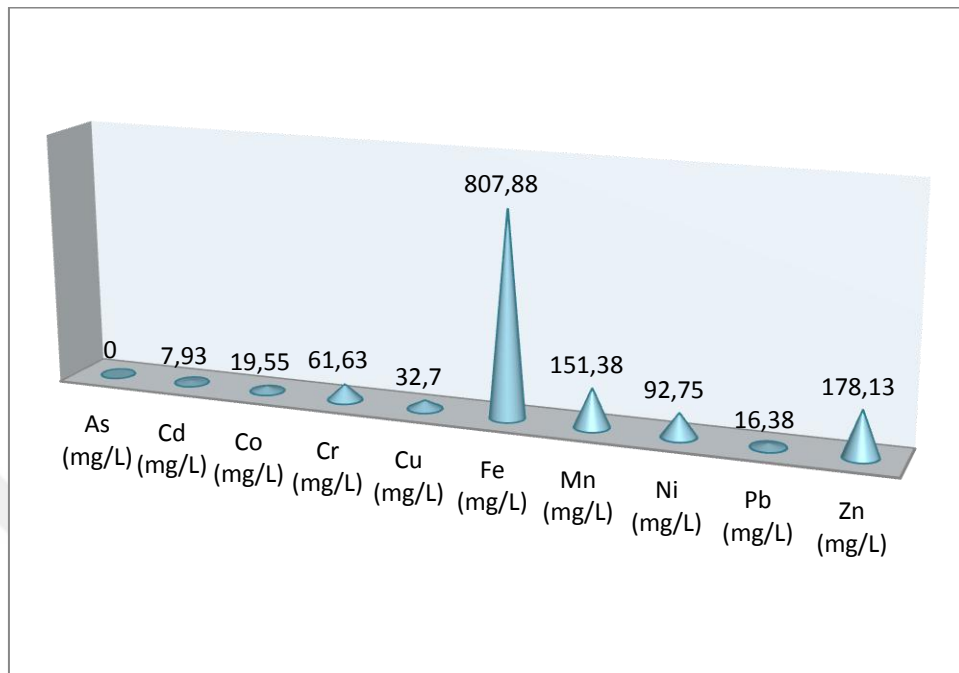


Figure 4.13. Elements Level in Soil of Kawrgosk

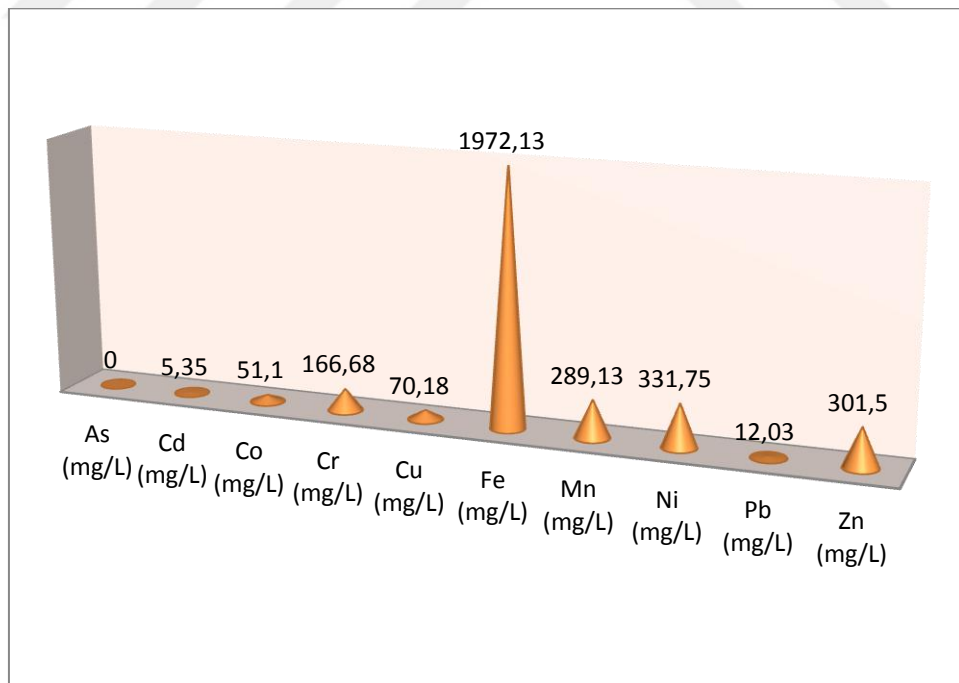


Figure 4.14. Elements Level in Soil Mergasor

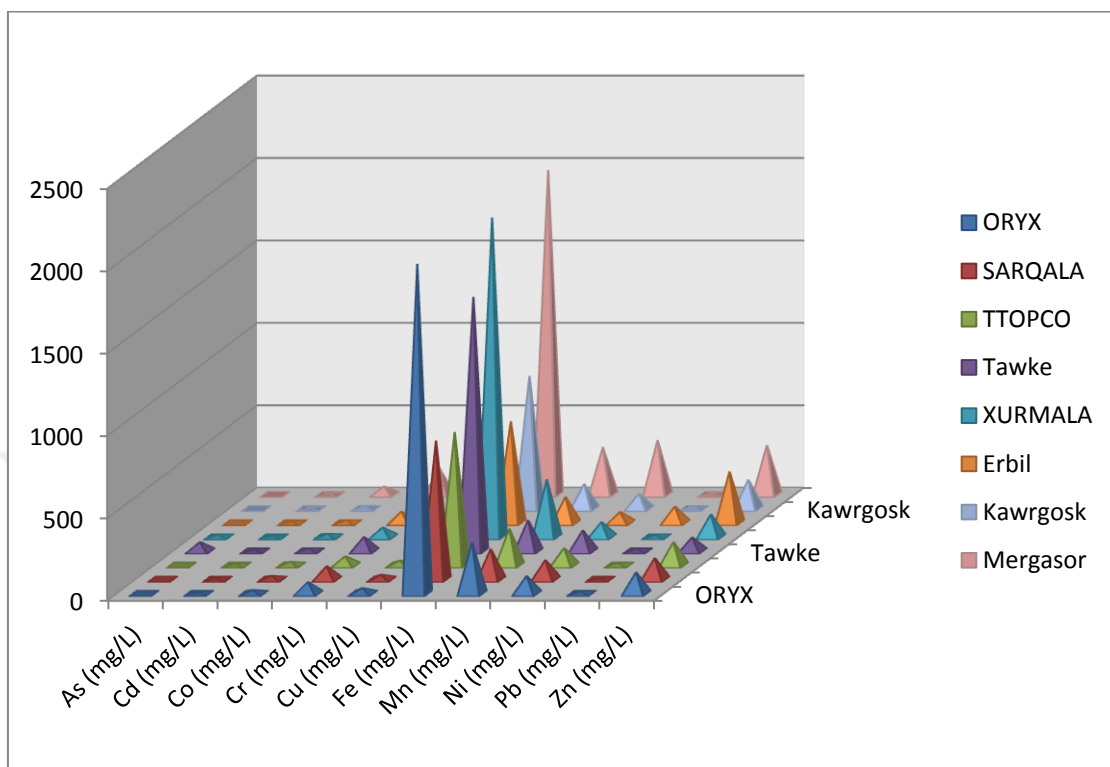


Figure 4.15. Elements Level For All Soil Samples

Table 4.5. Elements Level For All Soil Samples

		Soil Location							
		ORYX	SARQALA	TTOPCO	Tawke	XURMALA	Erbil	Kawrgosk	Mergasor
Elements	As (mg/L)	N.D	N.D	N.D	56.26	15.29	N.D	N.D	N.D
	Cd (mg/L)	7.93	7.53	8.08	7.98	8.20	7.83	7.93	5.35
	Co (mg/L)	22.40	22.08	21.70	18.83	20.41	16.78	19.55	51.10
	Cr (mg/L)	71.23	81.88	56.48	88.28	59.33	70.13	61.63	166.68
	Cu (mg/L)	35.00	29.50	29.18	30.92	31.53	92.25	32.70	70.18
	Fe (mg/L)	2003.00	845.25	810.75	1544.19	1940.39	617.63	807.88	1972.13
	Mn (mg/L)	311.25	186.00	223.88	189.43	351.43	159.38	151.38	289.13
	Ni (mg/L)	108.83	119.48	105.88	127.23	91.71	67.68	92.75	331.75
	Pb (mg/L)	14.38	7.55	14.93	13.62	13.46	100.85	16.38	12.03
	Zn (mg/L)	130.93	131.35	143.45	84.88	139.23	312.75	178.13	301.50

4.2. COMPARISON AND CORRELATION

To determine correlation between concentrations of elements in Crude oil and soil samples, Pearson's correlation coefficient were assessed.

4.2.1. Comparison And Correlation For Crude Oil Sample

Very high positive correlation ($r > 0.9$) is observed only for Fe-Mn, it means that Fe-Mn are strongly related to each other and by increasing or decreasing the concentration. Very high correlation exist between Fe-Mn with correlation coefficient of (0.954) which means by increasing or decreasing the concentration of Fe in Crude oil samples concentration of Mn will also increase or decrease and vice versa, High positive correlations ($0.7 < r < 0.9$) is observed for the following pairs of elements: As-Cd, Cd-Co, Fe-Zn, Mn-Zn., which means by increasing or decreasing concentration of one of these elements in Crude oil samples is either increase or decrease or vice versa. For other pairs of elements, either positive or negative correlation are established but they are moderate correlation with correlation coefficients of ± 0.4 to ± 0.7 , low correlation with correlation coefficients of ± 0.2 to ± 0.4 or almost negligible correlation with correlation coefficients from 0 to ± 0.2 . Correlations between all measured elements in Crude oil samples are shown in Table 4.4.

Table 4.6. Corelation Between All Crude Oil Samples

C		As (mg/L)	Cd (mg/L)	Co (mg/L)	Cr (mg/L)	Cu (mg/L)	Fe (mg/L)	Mn (mg/L)	Ni (mg/L)	Pb (mg/L)
Cd (mg/L)	Pearson Correlation	.815**								
	P-Value	.007								
Co (mg/L)	Pearson Correlation	.757*	.896**							
	P-Value	.018	.001							
Cr (mg/L)	Pearson Correlation	-.248	-.322	-.004						
	P-Value	.520	.398	.991						
Cu (mg/L)	Pearson Correlation	-.022	.014	.217	.371					
	P-Value	.955	.971	.575	.325					
Fe (mg/L)	Pearson Correlation	.394	.218	.388	.409	.340				
	P-Value	.294	.574	.302	.274	.370				
Mn (mg/L)	Pearson Correlation	.533	.387	.479	.343	.371	.954**			
	P-Value	.139	.304	.192	.367	.326	.000			
Ni (mg/L)	Pearson Correlation	-.288	-.410	-.043	.672*	-.014	-.050	-.209		
	P-Value	.452	.273	.913	.047	.971	.897	.590		
Pb (mg/L)	Pearson Correlation	-.673*	-.620	-.502	.431	.589	-.090	-.103	.132	
	P-Value	.047	.075	.168	.247	.095	.818	.792	.735	
Zn (mg/L)	Pearson Correlation	.555	.415	.528	.207	.229	.843**	.791*	-.093	-.452
	P-Value	.121	.266	.144	.593	.553	.004	.011	.811	.222

* $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$

4.2.2. Comparison And Correlation For Soil Sample

Very high positive correlation ($r > 0.9$) is observed only for Cr-Ni, pairs of elements, Very high correlation exist between Cr-Ni with correlation coefficient of (0.956) which means by increasing or decreasing the concentration of Cr in Crude oil samples concentration of Ni will also increase or decrease and vice versa,

High positive correlations ($0.7 < r < 0.9$) is observed for the following pairs of elements: Co-Cr, Fe-Mn, Co-Ni, Cu-Pb and Cu-Zn., which means by increasing or decreasing concentration of one of these elements in Crude oil samples is either increase or decrease or vice versa.

Significant adverse correlations is present between Cd-Co and high negative correlations exist between Cd-Ni and concentration of these two pairs of elements are inversely related to each other. which means that by increasing the concentration of Cd in the soil samples concentration of Co and Ni will decrease and vice versa, are shown in Table 4.5.

Table 4.7. Correlation Between All Soil Samples

S		As (mg/L)	Cd (mg/L)	Co (mg/L)	Cr (mg/L)	Cu (mg/L)	Fe (mg/L)	Mn (mg/L)	Ni (mg/L)	Pb (mg/L)
Cd (mg/L)	Pearson Correlation	.267								
	P-Value	.357								
Co (mg/L)	Pearson Correlation	-.308	-.909**							
	P-Value	.284	.000							
Cr (mg/L)	Pearson Correlation	.129	-.723**	.766**						
	P-Value	.659	.003	.001						
Cu (mg/L)	Pearson Correlation	-.354	-.532	.407	.380					
	P-Value	.215	.050	.148	.181					
Fe (mg/L)	Pearson Correlation	.205	-.057	.339	.322	-.209				
	P-Value	.483	.848	.236	.262	.474				
Mn (mg/L)	Pearson Correlation	-.241	.087	.266	.059	-.143	.820**			
	P-Value	.406	.768	.359	.841	.626	.000			
Ni (mg/L)	Pearson Correlation	.011	-.792**	.897**	.956**	.316	.384	.182		
	P-Value	.971	.001	.000	.000	.271	.175	.533		
Pb (mg/L)	Pearson Correlation	-.227	.040	-.193	-.075	.807**	-.440	-.272	-.217	
	P-Value	.434	.893	.509	.800	.000	.116	.346	.457	
Zn (mg/L)	Pearson Correlation	-.668**	-.602*	.557*	.310	.884**	-.172	.035	.349	.604*
	P-Value	.009	.023	.038	.280	.000	.556	.906	.221	.022

* p<0.05, ** p<0.01, *** p<0.001

4.2.3. Comparison And Correlation Between Soil and Crude Oil Sample

High positive correlations ($0.7 < r < 0.9$) is observed for the following pairs of elements: As-As, which means by increasing or decreasing As concentration in Crude oil samples is either As concentration in soil sample increase or decrease or vice versa. are shown in Table 4.5

Table 4.8. Correlation between Soil and Crude oil Sample

			S									
			As	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
C	As (mg/L)	Pearson Correlation	.779*									
		P-Value	.013									
	Cd (mg/L)	Pearson Correlation		.029								
		P-Value		.941								
	Co (mg/L)	Pearson Correlation			.024							
		P-Value			.952							
	Cr (mg/L)	Pearson Correlation				-.247						
		P-Value				.521						
	Cu (mg/L)	Pearson Correlation					-.260					
		P-Value					.499					
	Fe (mg/L)	Pearson Correlation						-.450				
		P-Value						.224				
	Mn (mg/L)	Pearson Correlation							-.598			
		P-Value							.089			
	Ni (mg/L)	Pearson Correlation								-.191		
		P-Value								.622		
	Pb (mg/L)	Pearson Correlation									.091	
		P-Value									.815	
	Zn (mg/L)	Pearson Correlation										-.126
		P-Value										.748

* $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$

4.3. Conclusion

Crude oil exists as a liquid form in the earth and it's a complicated mixture of hydrocarbons as important components of primary of fossil fuels.

Crude oil and soil plays a major social and economic role. It is one of the most widely consumed beverages throughout the world.

The key element of human survival is soil and it has been described by different definitions.

In this study, the total concentrations of ten elements were determined from nine different samples of crude oils over different locations in Northern Iraq by using ICP-OES instrument, Samples were prepared based on the partial decomposition. Five different organic solvents were used and comparing between each of them to find out the best reliable solvent to obtain

the best result for determination the total concentration of the following heavy elements such as Cd, As, Cu, Co, Fe, Cr, Zn, Pb and Mn.

The results obtained in this study showed there are significant differences between different elemental content of different Crude oil samples due to their location and organic solvent.

And determined in fourteen soil sample from northern Iraq Concentration of elements were determined by using inductively coupled plasma optical emission spectroscopy (ICP-OES), sample preparation procedure based on two different digestion method wet and dry decomposition to comparison between them for analysis the total amount of each the following elements such as Cd, As, Cu, Co, Fe, Cr, Zn, Pb and Mn.

The results obtained in this study showed there are significant differences between different elemental content of different Soil samples due to their location and digestion method.

And founded correlation between elements in crude oil and oilfield area soil.

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