

Comparative Evaluation of Metals and Heavy Metals in Some Yemeni Crude and Fuel Oil

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ABSTRACT---- *Due to high importance of the crude oil to the modern society as a source of energy and as raw material for a wide chemical and petro chemical industries.*

In this study we made assessment of metals and heavy metals in some Yemeni crude, and fuel oils namely Mareb crude oil blend, Masila crude oil blend plus two samples from Sounah and Hijah oil fields in Masila basin.

Fifteen metals and heavy metals were determined in above samples, but the most indicated were (Na, K, Mg,) and (V, Co, Ni) using ICP technique and atomic absorption spectroscopy .

The order of concentration of metals in Yemeni crude oils were as shown in figures:

Na > K > Co > Mg > V > Ni > Ca > Fe > Cd > Al > Zn > Cr > Cu > Pb > Mn.

In Fuel oil: Na > Co > V > Mg > K > Ni > Ca > Fe > Al > Cd > Zn > Cr > Pb > Mn > Cu.

Comparing concentrations of metals in studied sample, in general were less than in crude oil and fuel oil in many countries. That mean Yemeni crude and fuel oil are the best in quality.

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Keywords---- crude, fuel oil, Mareb, Masila oil Sounah, Hijah, heavy metals

1. INTRODUCTION

The environmental pollution with oil organic compounds and heavy metals, which are very toxic and relatively accessible, has become a global phenomenon. Contaminated soils from oil extraction activities include a lot of complex organic compounds such as alkanes, benzene, methylbenzene etc, and heavy metals as well. These contaminants are dangerous to the health of all life forms, including humans because usually are categorized as carcinogenic substances. They can not be easily eliminated from soils and frequently these contaminants will leach into the groundwater systems.

Therefore the soil is the most precious capital of which the humans dispose to satisfy all needs and ambitions. Hence, at least to the invention of artificial photosynthesis, all depending by thin and fertile layer of the Earth's surface, where the resources are extracted whole life [8,14,19,17,13].

These metals dissociates in the pore water of these rocks, which in turn is absorbed into the crude oil. These heavy metals may possibly play an important role as catalyst in conversion of organic matter to petroleum[12] Therefore many trace metals found in crude oil are simply a reflection of those picked up during migration of the source rock to the reservoir rock [12]. Another possible source of heavy metals in crude oil is the introduction of drilling mud fluids into the oil well during crude oil extraction. These chemicals are added directly to the crude oil and invariably act as contaminants in the soil [18]. This explains the reason why fuels used by drilling rigs may be the source of heavy metals found in oil producing countries [11]. The heavy metals in the crude distributes themselves into the petroleum fractions after fractionation and refining thus accounting for the presence of heavy metals in petroleum products.

This study therefore tends to examine the presence and distribution of heavy metals in crude oil and fuel oil of Yemeni oil in the area of Mareb-Shabwa basin and Masilla basin with a view to comparatively evaluate the concentration levels of these metals so as to see if they meet desirable standards or otherwise.

The significance of determining trace elements that exist in crude oils is helpful for further information about exploration, production and the refining process. Heterogeneous distribution of trace metals in crude oils could be applied to further explain the geochemical characterization of the basin and source rocks [1]. Hitchon and Filby stated that crude oils can be classified based on the trace metal content which exists in similar litho-stratigraphic situations into families [10]. Crude oils can be classified in terms of trace metals as heavy, medium, light and residual fraction [4,5]. Refining heavy crude oil requires more expenditure in comparison to light crude oil because of the high level of metal content, the high cost is related to either hydrogen addition or yield loss due to carbon rejection [15]. Selecting a reliable method for this process is a vital step.

2. SITE DESCRIPTION

Masila Basin is one of the onshore basins in Yemen, which is located in the east part of Yemen (Fig. 1). The Masila Basin is classified as large hydrocarbon basins in the Yemen and contains several, well known hydrocarbon oilfields (Fig. 1A). However, the area of interest of this study is the Masilla, Hajjah and Sunah oilfield. These oilfield is one of the most productive oil fields in the Masila Basin, located in the N/W sector from the Masila Basin (Fig.1A). These oilfield is also boarded with several successful producing oilfields such as WadiTaribah, Kharir and Tasour oilfields (Fig. 1B).

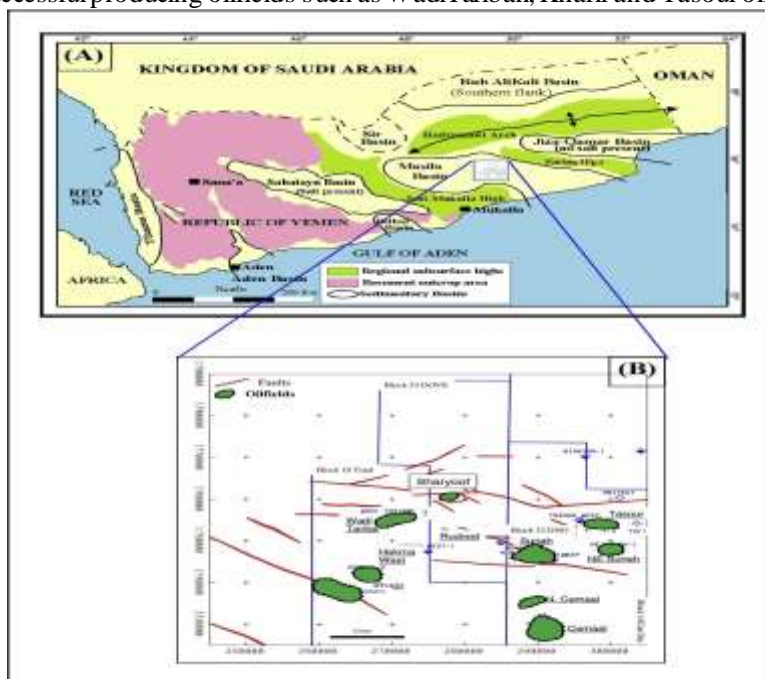


Figure 1 (A) Main sedimentary basins in Republic of Yemen (modified after Beydoun et al. [6] and (B) location map of some Masila Basin's Blocks including Sharyoof oilfield (Block 53), Hadramawt region of the Republic of Yemen.



Figure 2. Mareb and Hijah location map.

The Masila fields are associated with the Upper Jurassic to Lower Cretaceous Say'un Masila rift graben basin. Almost 90% of the oil reserves discovered are in the Lower Cretaceous upper Qishn sandstones, Qishn Formation, Tawilah Group. Oil also is found in seven other reservoirs consisting of Lower Cretaceous and Middle to Upper Jurassic elastics and carbonates as well as fractured granitic basement. The uppermost marine sandstones are more homogeneous because they are texturally more mature. The major field accumulations are tilted, normal-fault block structures located over basement paleohighs and dependent on cross-fault juxtaposition against overlying Qishn Carbonates Member top seal.

The another area of interest in this study is the section in the Marib - Shabwa.

The stratigraphic section in the Marib-Shabwa Basin is dominated by a thick Mesozoic succession and ranges in age from Jurassic to Cretaceous.

Hydrocarbon exploration activity became extensive after 1990 and provided considerable amount of subsurface data, which allowed revised synthesis of basin evolution in Yemen, such as the work done by [16], [9], and [6]. The petroleum geology was summarized in [7]. Two major tectonic periods occurred that formed the tectonic evolution of Yemen.

The first events took place in the Late Jurassic – Early Cretaceous, when three basins developed within Gondwanaland: the Marib-Shabwa, the Sir-Sayun, and the Jeza-Qamar basin. The second major tectonic activity in the Cenozoic was related to the opening of the Gulf of Aden and the Red Sea and the collision of the Arabian Peninsula with Eurasia, respectively.

3. OBJECTIVES

Determination of (Na, K, Ca, Mg) from alkali and earth alkali group, as well as (Al) from IIIA group and determination of heavy metals: (V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb) in crude oils and fuel oil of (Mareb, Masila, Sunah and Hijah) wells.

4. MATERIAL AND METHOD

Crude oils from Masila, Hijah Sunah and Marib-Shabwa were collected and taken from Aden Refinery Company. And prepared for analysis such as characterization to determine 15 inorganic metals such as (Al, Ca, V, Mg, Cd, Co, Cr, Cu, Fe, K, Mn, Na, Ni, Pb and Zn). Using modern technique An Inductively Coupled Plasma (ICP), further determination for some metals were done using AAS in the laboratory of Ibb and Hadramout Universities.

Metal content

An iCAP 6000 series Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES), featuring a 27.12 MHz RF generator. Analytical signals are measured using the RACID86 Charge Injection Device (CID), the detector of choice for ICP emission spectroscopy. The analytical wavelength range is a no compromise 166.25- 847.0 nm allowing full access to all elements that can be determined by ICP. For optimum operation, the nebulizer pressure was set at 160 kPa which compares to 170 kPa while running aqueous solution. The nebulizer pressure varies depending on the solvent type and to minimize any potential carbon build up on the rims of two inner tubes and injector tip of the torch, the auxiliary gas flow was set to 1.0 L/min. Metal content in studied samples were determined using the above ICP apparatus and all these tests had been done in laboratory of Aden Refinery Company.

10 ml of each product was digested with a mixture of 20 ml HNO₃ and H₂SO₄ (ratio 4:1) and heated 4 hours daily slightly in a water bath at a temperature of 80°C for 9 days to ensure complete digestion. The digestion method was adopted to avoid inflammation due to the volatility of the samples. The digested samples were then taken for A.A.S analysis. Samples were analyzed at a laboratory of Ibb University using (Analytik Jena) Nova300, in addition to laboratories of Hadramout University using Buk Model 210/211 VGP, at appropriate wavelengths of 324.8 nm, 283.3 nm, 357.9 nm, 213.9 nm and 228.8 nm for Cu, Pb, Cr, Zn and Cd respectively. Their concentrations were obtained from the absorbances read.

Quality Control and Assurance- Replicate analyses were performed on samples to yield a mean which was used to determine trueness and also standard deviation of the mean to measure precision [20,21].

Procedural blanks and standard solutions were also included for analytical quality control to assure the accuracy and reproducibility of the results.

Trace metal contents were determined by the calibration curve method (CC Method) and achieved accurate and precise results. This method is applied only when there is a linear relationship between absorbance (y) and concentration (x). Finally, the unknown concentration of the element is calculated from the calibration curve by interpolation.

Statistical analysis All statistical analyses were performed using SPSS software Using origin programme (One way ANOVA) and the data were expressed as mean ± standard deviation (SD). We compared the metal contents of unrefined and refined salts using Mann-Whitney U-test. Significance level was set at $p < 0.05$.

5. RESULTS AND DISCUSSION

Fifteen metals and heavy metals were determined in above samples, but the most indicated were (Na, K, Mg,) and (V, Co, Ni).

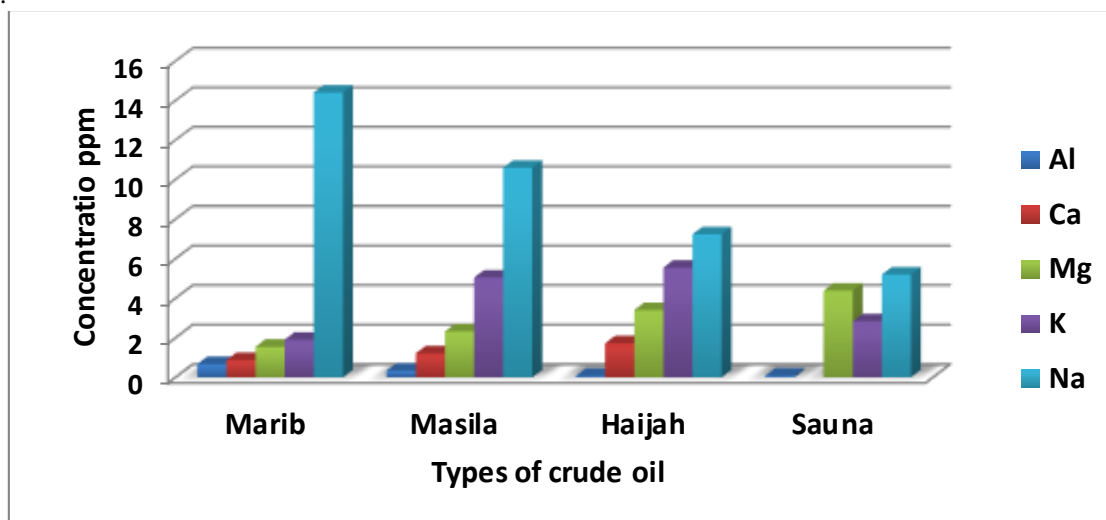


Figure (1) Determination of metals in Yemeni crude oil

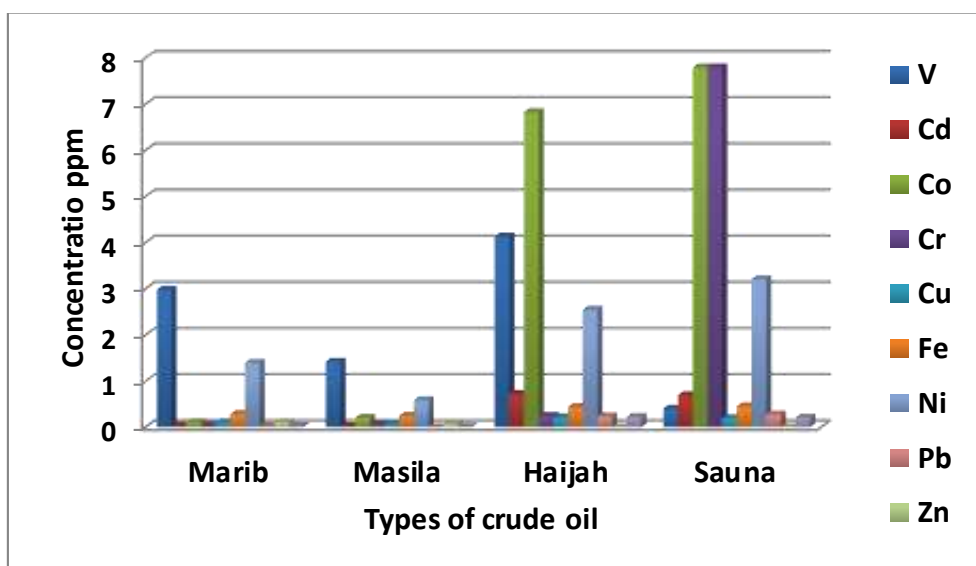


Figure (2) Determination of heavy metals in Yemeni crude oil

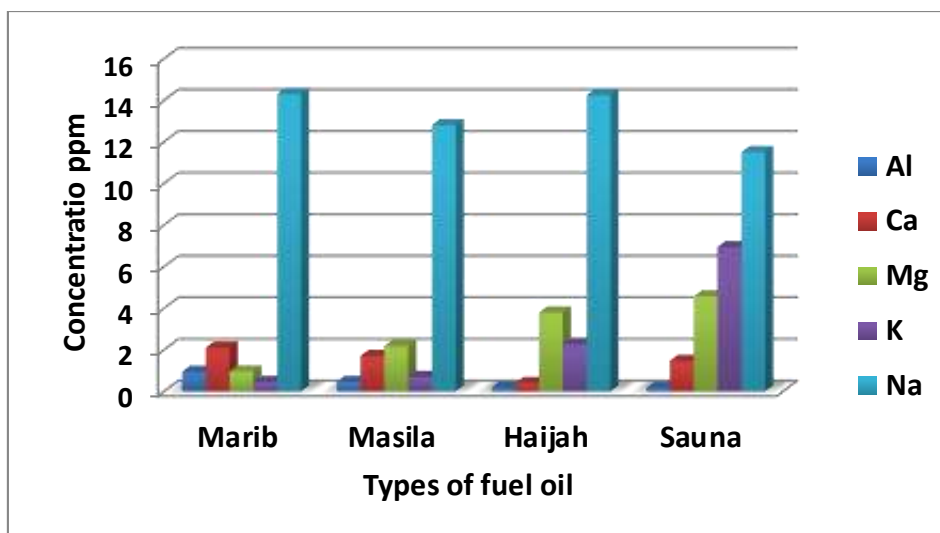


Figure (3) Determination of metals in Yemeni fuel oil

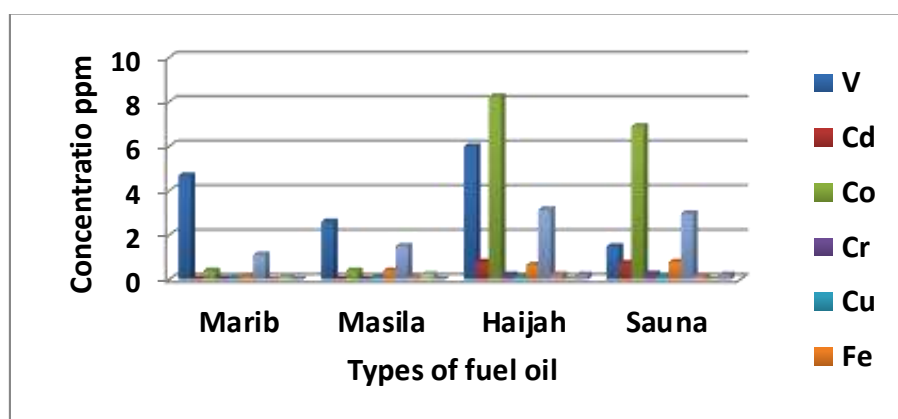


Figure (4) Determination of metals in Yemeni fuel oil

Figure (1) show that the high concentration of alkali metals is (Na) which were (14.40±0.05, 10.60±0.1, 7.23±0.06, 5.20±0.1) for Mareb, Masila, Hijah and Sounah crude oil respectively. The statistical analysis showed (Na) values for every sample were significantly different at $p < 0.05$, and comparing with Syrian crude oil we found that (Na) in Sounah crude oil equal to

Syrian sample, but the other samples are higher than in Syrian sample. [2] see(table 1)

Regarding (K) as shown in figure 1 the values were (1.9±0.05, 5.05±0.05, 5.55±0.08, 2.83±0.06) for Mareb, Masila, Hijah and Sounah crude oil respectively. This indicate that concentration of (K) in Hijah crude oil was the highest and in Mareb crude oil was the lowest. All concentration of (K) in Yemeni samples were higher than in Syrian crude oil as shown in table (1). [2] .In all samples were significantly different at $p < 0.05$,

Concerning (Mg) concentrations as shown in (figure 1), the values were (1.547±0.005, 2.325±0.002, 3.398±0, 4.39±0.02) for Mareb, Masila, Hijah and Sounah crude oil respectively.

crude oil Metal ppm	Mareb	Masila	Hijah	Sounah	Syria	Kuwait	Morocco	West Texas	East Texas
Na	14.40	10.60	7.23	5.20	5.67				
Mg	1.55	2.33	3.398	4.387					
Al	0.675	0.34	0.082	0.095	0.285				
K	1.9	5.05	5.55	2.83	0.51				
Ca	0.874	1.22	1.72		0.97				
V	2.972	1.413	4.127	0.398	15.04	22.5	0.6	7.9	1.2
Cr	0.04	0.06	0.24	0.26	48.43				
Mn	0.02	0.01	0.22	0.20	38.46				
Fe	0.28	0.24	0.43	0.54	0.79	0.7		5.1	3.2
Co	0.1	0.2	6.82	7.79	0.36				
Ni	1.39	0.58	2.54	3.20	6.67	6	0.8	4.8	1.7
Cu	0.1	0.062	0.21	0.19	26.90	0.1	0.1	0.4	0.4
cd	0.03	0.02	0.717	0.69	29.49				
Zn	0.10	0.07			0.74				
pb	0.02	0.001	0.23	0.27	1.53				

Table 1. Reported contents of metals and heavy metal of Yemeni and some International crude oil

The highest concentration of (Mg) was in Sounah crude oil, the lowest concentration was in Mareb crude oil. In all samples were significantly different at $p < 0.05$.

The highest concentrations of heavy meals in Yemeni crude oils studied were in (V, Co, and Ni) as shown in figure 2. The concentrations of (V) were $(2.972 \pm 0.001, 1.413 \pm 0.001, 4.127 \pm 0.001, 0.398 \pm 0.001)$ for Mareb, Masila, Hijah and Sounah crude oil respectively. The highest value of (V) was in Hijah crude oil, and the lowest was in Sounah crude oil. In all samples were significantly different at $p < 0.05$. We found the concentration of (V) in all studied samples were lowest than in Syrian and Kuwait crude oils as shown in (table 1). The concentration of (V) in all studied sample were under the normal values which is (5-1500 ppm). [3]

Figure (1) indicates that the concentrations of (Co) were $(0.1 \pm 0.023, 0.2 \pm 0.014, 6.82 \pm 0.004, 7.79 \pm 0)$ for Mareb, Masila, Hijah and Sounah crude oil respectively. The highest concentration of (Co) was in Sounah crude oil, and the lowest was in Mareb crude oil. We found that the concentration of (Co) in Mareb and Masila crude oil were less than in Syrian crude oil while it was higher in Sounah and Hijah crude oil than in Syrian crude oil. (table 1).

The concentration of (Co) in all studied sample were under the normal values which is (0.001-12.00 ppm). [3]

Figure (1) showed that the concentrations of (Ni) in studied samples were $(1.39 \pm 0.01, 0.58 \pm 0.002, 2.54 \pm 0.01, 3.20 \pm 0.004)$ for Mareb, Masila, Hijah and Sounah crude oil respectively.

The highest concentration of (Ni) was in Sounah crude oil, the lowest was in Masila crude oil.

In addition we found that the concentrations of (Ni) in all studied samples were less than in Syrian and Kuwait crude oil as shown in (table 1). The concentrations of (Ni) in all studied samples were under the normal value which is (3.0 – 12.0 ppm).

In all samples were significantly different at $p < 0.05$.

The concentration of alkali metals such as (Na, K, Mg) in fuel oil of studied samples were shown in figure (3).

The concentrations of (Na) in fuel oil were $(14.30 \pm 0.06, 12.80 \pm 0.03, 14.24 \pm 0.25, 11.50 \pm 0.25)$ for Mareb, Masila, Hijah and Sounah fuel oil respectively.

Figure (3) shows that the highest concentration of (Na) in fuel oil of Mareb and low was in Sounah fuel oil.

There were no significantly different at $p < 0.05$ between concentrations of (Na) in fuel oil of Mareb and Hijah, while there were significantly different at $p < 0.05$ between all samples. We found that Concentration of (Na) I studied samples were less than in fuel oil of Syria. [2].

Figure (3) indicate that the concentration of (K) in fuel oil in studied samples were $(0.45 \pm 0.04, 0.69 \pm 0.07, 2.27 \pm 0.03, 6.93 \pm 0.03)$ for Mareb, Masila, Hijah and Sounah fuel oil respectively. As shown in figure (3) the highest concentration of (K) was in fuel oil of Sounah, and lowest in Mareb fuel oil, there were significantly different at $p < 0.05$ between all samples.

From figure (3) , the concentration of (Mg) in studied fuel oil were (0.946±0.002, 2.172±0.002, 3.79±0.05, 4.57±0.01) for Mareb, Masila, Hijah and Sounah fuel oil respectively.

The highest concentration was in Sounah fuel oil, the lowest was in Mareb fuel oil, there were significantly different at p<0.05 between all samples.

Figure (4) indicated the concentration of heavy metals (V, Co, Ni) in fuel oil of Mareb, Masila, Hijah and Sounah, the concentration of (V) in fuel oil of mentioned samples were (4.68±0.001, 2.6±0.1, 5.989±0.001, 1.492±0.001) respectively. The highest concentration of (V) was in Hijah fuel oil, and lowest Sounah fuel oil. Comparing concentration of (V) fuel oil of Syria, we found that in all samples were less than Syrian fuel oil. (table 2) . there were significantly different at p<0.05 between all samples.

Concentrations of (Co) in all studied samples were shown in (figure 4) these concentration were (0.40±0.006, 0.40±0.009, 8.24±0.0133, 6.90±0.001) respectively.

Fuel oil / Metal ppm	Mareb	Masila	Hijah	Sounah	Syria
Na	14.30	12.80	14.24	11.50	28.49
Mg	0.95	2.172	3.79	4.57	
Al	0.935	0.45	0.169	0.152	3.80
K	0.45	0.69	2.27	6.93	1.04
Ca	2.105	1.7	0.39	1.466	3.28
V	4.68	2.6	5.989	1.492	255.45
Cr	0.03	0.01	0.22	0.25	665.95
Mn	0.01	0.01	0.21	0.21	117.51
Fe	0.14	0.4	0.65	0.79	3.91
Co	0.40	0.40	8.24	6.90	1.16
Ni	1.11	1.50	3.15	2.97	38.51
Cu	0.03	0.1	0.13	0.17	
cd	0.03	0.01	0.794	0.73	
Zn	0.07	0.23	No analysis	No analysis	0.47
Pb	0.003	0.1	0.22	0.16	

Table 2. Reported contents of metals and heavy metal of Yemeni and Syrian fuel oil

The highest concentration of (Co) was in Hijah fuel oil, and less was in Mareb and Masila fuel oils. It was found the concentration of (Co) in Hijah and Sounah fuel oils were highest than in Syrian fuel oil.

Concentrations of (Ni) in studied fuel oil were (1.11±0.002, 1.50±0.004, 3.15±0.008, 2.97±0.005) respectively. The highest concentration of (Ni) was in Hijah fuel oil, and less was in Mareb fuel oil, there were significantly different at p<0.05 between all samples.

These concentrations were less than in Syrian fuel oil(table 2). [2].

6. CONCLUSION

Crude oil extraction activity brings serious heavy metal contamination of soil. The heavy metals accumulation in the soil is due to various factors such as: the nature of soils, the relief, and the litology, the hydrology, the climate, the dominant winds, the soil reaction, the cationic exchange capacity, the use of the land, and not least the source of contamination, which is various depending by oil extraction, The risk associated with the presence of metals in soil depends by their ability to transfer in water or plants. The higher concentrations of V, Co, Ni were found in all contaminated soil samples

The order of concentration of metals in **Yemeni crude oils** were as shown in figures:

Na > K > Co > Mg > V > Ni > Ca > Fe > Cd > Al > Zn > Cr > Cu > Pb > Mn.

In Fuel oil: Na > Co > V > Mg > K > Ni > Ca > Fe > Al > Cd > Zn > Cr > Pb > Mn > Cu.

Comparing concentrations of metals in studied sample, in general were less than in crude oil and fuel oil in many countries. That mean Yemeni crude and fuel oil are the best in quality.

7. ACKNOWLEDGMENT

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