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# DETERMINATION OF SELECTED ELEMENTS IN SHALE OIL LIQUID

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***Abstract***. *The result of quantitative determination of selected non-hydrocarbon elements present in shale oils produced by pyrolysis of oil shales from El-Lajjun, Attarat Umm Ghudran, Al-Wehda dam and Al-Sultani deposits is presented. Fischer Assay analysis of oil shales indicated their water content to range from 2.4 to 2.9 wt%, liquid shale oil amount to vary between 5.44 and 15 wt%, spent shale to be in the range 78–90.93 wt% and gaseous loss from 1.03 to 4.0 wt%. Distillation of shale oils showed comparable volume percent distilled with temperature. Seventeen non-hydrocarbon elements were quantified using inductively coupled plasma-optical emission spectroscopy (ICP-OES). The detected elements were: arsenic (As), barium (Ba), beryllium (Be), boron (B), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), iron (Fe), manganese (Mn), nickel (Ni), lead (Pb), selenium (Se), strontium (Sr), tin (Sn), vanadium (V) and zinc (Zn). The concentrations of these elements depended on oil shale deposit location. The elements concentration ranges determined were the following: As 2.11–2.59 ppm, B 0.57–0.58 ppm, Cd 5.00–6.13 ppm, Cr 1.78–2.47 ppm, Ni 8.91–11.10 ppm, V 2.29–0.887 ppm, antimony (Sb) 1.43–1.52 ppm, molybdenum (Mo) 0.42–0.78 ppm, Zn 10.5–12.93 ppm, Se 1.79–1.91 ppm and Sr 0.78–0.94 ppm.*

***Keywords***: *shale oil, distillation, inductively coupled plasma-optical emission spectroscopy, metals, Fischer Assay.*

## 1. Introduction

Jordanian oil shale was the subject of many investigations focused on the organic part of oil shale to utilize it as a substitute for oil. Al-Ayed [1] studied the thermal decomposition of oil shale under high temperature and found its adverse impact on the yield of the oil fraction to be the main

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concern. Investigations indicated that the yield of liquid oil fractions was around 10% wt% and the sulfur content in oil shale about 3 wt% as reported by Khraisha [2], whereas sulfur in shale oil was higher than 9.0 wt% as found by Al-Ayed and Matouq [3].

Jordanian shale oil is mainly aliphatic with a small concentration of aromatic and olefin compounds. The structural distribution of sulfur in the distillate fractions of the obtained oil was investigated, to identify that the sulfur containing compound was basically composed of naphthenic rings in different combinations with aliphatic alkyls [4, 5]. Several authors have studied Jordanian oil shale pyrolysis and some characteristics of the shale oil obtained were determined [6, 7].

Neto et al. [8] have developed a method for the determination of cadmium (Cd) and thallium (Tl) in oil shale pyrolysis by-products by using graphite furnace atomic absorption spectrometry (GFAAS) and direct analysis.

Metals present in the shale oil obtained by pyrolysis were due to its fractions as found by Mazur et al. [9]. The researchers also reported the presence of boron (B), molybdenum (Mo), nickel (Ni), selenium (Se) and zinc (Zn) in appreciable amounts and of gold (Au) and cesium (Cs) in very low concentrations. Hu et al. [10] analyzed the oil shale composition and established the presence of heavy metals in it. Al-Harahshesh et al. [11] studied Jordanian oil shales and reported the presence of metals in them. The migration of metals in oil shale to vapors and liquids produced was investigated by Bai et al. [12], who found that transfer of some elements was affected by pyrolysis temperature.

The determination of the above elements in oil shale is of importance for shale oil refining processes. These elements in complex or simple form of compounds damage equipment during refining. Metals migrated from oil shale rock to shale oil liquid during pyrolysis have a deleterious effect on both, catalyst and equipment. The removal of such metals requires their prior identification in shale oil.

For this study, oil shale samples were taken from different deposits in Jordan. The chemical analysis was carried on four samples. Some standard analyses were also performed on the produced shale oil. The oil content of the oil shale varied between 9 and 13 wt% with an average oil content of about 11 wt%. The sulfur content of the rock varied from 1.93 to 5.3 wt% and the moisture content ranged from 0.4 to 2.3 wt%.

## 2. Heavy metals in shale oil

The concentrations of metals in crude oil usually vary from a few ppm to more than 1000 ppm. Normally there can be found different metals such as potassium (K), lithium (Li), calcium (Ca), strontium (Sr), copper (Cu), vanadium (V), manganese (Mn), silver (Ag), tin (Sn), cobalt (Co), lead (Pb), titanium (Ti), gold, chromium (Cr) and nickel.

The metals are usually found in combination with naphthenic acid as soaps and in the form of complex organometallic compounds such as metalloporphyrins [13, 14].

The main non-organic elements of oil shale are calcium and silicon (Si); minor constituents are sulfur (S), aluminum (Al), iron (Fe), phosphorus (P), and traces of others. Silicon (Si) is derived from two sources: clastic sediments together with titanium, aluminum and iron, and sedimentary or early diagenetic solidification [15]. Molybdenum, chromium and tungsten (W) are significantly enriched in the bituminous marl, differently from limestone. Zinc, vanadium, nickel, copper, lanthanum (La) and cobalt are also enriched, whereas barium (Ba) is depleted. The contents of arsenic and lead (Pb) are low to moderate and do not pose any problem either for the technical processes or the environment. The uranium (U) content is relatively high, but it is clearly associated with the phosphorous and not with the bituminous organic matter. Significant positive correlations exist between the oil content and contents of sulfur, chromium, nickel, copper, zinc and molybdenum as well as clastic components like silicon, aluminum, titanium (Ti), iron and probably zirconium (Zr). There is a pronounced positive correlation between the contents of phosphorus, uranium, yttrium (Y), and vanadium.

Oil shale consisting of sedimentary rocks rich in hydrocarbon organic matter affords liquid oil when exposed to destructive distillations at temperatures up to 500–550 °C. Carbonates, chalk marl and shale, whose solid immature organic content is insoluble in organic solvents, formed during the Cambrian era to the Tri-cherry era in a variety of depositional environments. Oil shale is considered as a potential deposit for hydrocarbon generation upon artificial thermal maturation, at which stage shale oil and gas can be generated. It is characterized by a high sulfur content, up to 10%, and high concentrations of rare elements such as cobalt, chromium, nickel, vanadium, zinc, etc. [8].

This research focuses on the quantitative determination of elements in Jordanian shale oil obtained from oil shales from El-Lajjun, Attarat Umm Ghudran, Al-Wehda dam and Al-Sultani deposits by retorting oil shales in retort or Fischer Assay apparatus. Inductively coupled plasma-optical emission spectrometry (ICP-OES) was used to analyze and quantify the elements present in the shale oil obtained from Fischer Assay, or simple retorting. The elemental analysis was performed using a CHNS analyzer.

The evaluation of metals concentration levels in Jordanian shale oil is important for the geochemical characterization of its source and origin, in addition to any future usage of shale oil as fuel systems.

## 3. Experimental

The oil shales were subjected to pyrolysis in the Fisher Assay apparatus to obtain shale samples for elemental analysis. Samples from El-Lajjun, Al-Sultani, Attarat Umm Ghudran and Al-Wehda dam deposits were crushed and sieved to the desired size. A representative sample was selected, which was sieved to several particle size fractions. A size fraction of 125–250 μm was used in this study.

The samples were homogenized and weighed to the nearest 0.1–5 g in a porcelain dish. After drying on Bunsen burner, the sample was placed in the 550 °C oven and left to ash. Then 30 ml concentrated nitric acid was added, and the sample was heated on the sand bath with intermittent swirling until the contents were dissolved. Thereafter 20 ml deionized water was added and the sample was reheated gently on the sand bath until the solution became clear or colorless.

Then the solution was cooled to room temperature and diluted to the mark 100 volumetric flask using distilled water. Finally, the obtained solution was used to measure the concentration of elements using ICP.

All reagents used in this work were analytical grade reagents. 67% nitric acid ($HNO_3$) for trace analysis was purchased from Fluka Company (Switzerland). Distilled water was used for acid preparation and washing of acid treated shale. Standards of As, B, Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, Sn, Sr, Zn, Be, Mo and V used in the study were all with concentrations of 1000 μg/ml and were purchased from Fluka.

## 4. Results and discussion

### 4.1. Elemental analysis

The oil shale samples were subjected to elemental analysis using Leco CS-244 according to ASTM D 1551. The results are presented in Table 1. As can be seen from the table, the carbon weight percent of all samples was in the 74.61–77.48 wt% range. The contents of deleterious elements of nitrogen and sulfur were found to be between 0.84 and 1.13 wt%, and from 7.88 to 11.79 wt%, respectively. These high-concentration elements will be leached to shale oil during pyrolysis, lowering its economic value as a liquid fuel. The hydrogen content of the oil shale samples fluctuated between 9.24 and 9.7 wt%.

**Table 1. Elemental analysis of oil shale samples, wt%**

| Element / Location | Carbon | Nitrogen | Hydrogen | Sulfur | Oxygen (by difference) |
|---|---|---|---|---|---|
| El-Lajjun | 75.74 | 0.90 | 9.37 | 9.31 | 4.5 |
| Al-Sultani | 74.61 | 0.84 | 9.24 | 10.62 | 4.4 |
| Attarat Umm Ghudran | 75.75 | 0.86 | 9.30 | 11.79 | 2.5 |
| Al-Wehda dam | 77.48 | 1.13 | 9.70 | 7.88 | 3.7 |

### 4.2. Fischer Assay analysis

The oil shale samples were analyzed for oil, water and spent shale contents, and gas loss. As indicated in Table 2, the shale oil content of samples ranged between 5.44 for Al-Wehda dam and 15.1 wt% for El-Lajjun sample. These values give evidence of that the amount of shale oil generated depended upon the location of oil shale deposits. On the other hand, the amount of water produced during pyrolysis fluctuated between 2.4 and 2.9 wt%. These water weight percent values are reasonable since all the oil shale deposits in Jordan are located in arid areas. The gas loss varied between 4.01 and 1.03 wt%. It is clear from these data that there is a relationship between the amounts of shale oil generated and gas evolved. The higher the generated shale oil weight percent, the higher the reported gas loss weight percent.

**Table 2. Fischer Assay analysis of oil shale samples according to ISO 647, wt%**

| Component / Location | Shale oil | Water | Gas loss | Spent shale |
|---|---|---|---|---|
| El-Lajjun | 15.10 | 2.4 | 4.01 | 80.00 |
| Al-Sultani | 13.59 | 2.4 | 3.97 | 78.51 |
| Attarat Umm Ghudran | 10.36 | 2.9 | 3.7 | 83.04 |
| Al-Wehda dam | 5.44 | 2.6 | 1.03 | 90.93 |

### 4.3. Simple distillation curves

After the pyrolysis of oil shale samples shale oil was collected for simple distillation. The samples of shale oil collected from Ellajjun, Al-Sultani and Attarat Umm Ghudran oil shales were distilled and the results are depicted in Figure 1. It was not possible to generate enough shale oil from Al-Wehda dam oil shale sample due to its small size. Figure 1 displays that the shale oils volume percent distilled as a function of distillation temperature ranging from 50 °C to 360 °C. The amount of residue boiling above 360 °C was

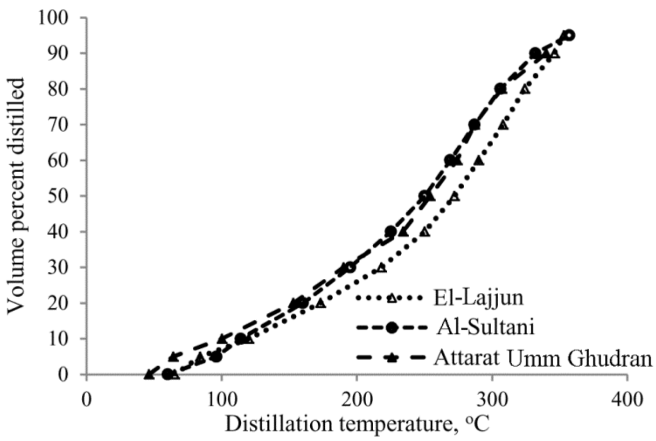


Fig. 1. Distilled shale oils volume percent as a function of distillation temperature.

estimated to be 6 wt%. These curves are similar to those of the simple ASTM distillation for crude oil. The overlapping of the distillation curves for Al-Sultani and Attarat Umm Ghudran shale oils may be related to the geographical location of the deposits. The quality of shale oils generated from different oil shales was different depending upon pyrolysis conditions such as heating rate, particle size, and inorganic content of oil shale.

### 4.4. Heavy metals concentrations in shale oil

Interest in shale oil metals content arises from several considerations and factors. Some metals are harmful to cracking catalysts in operations during the refining process, leading to the reduced yields of gasolines. Trace metals analysis may be useful for the identification of the source of oil and may ultimately give a clue to the mechanisms of petroleum formation.

The concentrations of the 20 metal elements detected in shale oil are presented in Table 3. As can be seen from the table, the concentrations of metals in the produced shale oils varied depending upon the location of the deposit. Table 3 reveals that the vanadium concentration, 2.29 ppm, is the highest in El-Lajjun and the lowest, 0.89 ppm, in Al-Sultani shale oil. Another metal that might have an effect on the yield and quality of oil during the processing is arsenic. Since an appreciable amount of retorted water is generated during the retorting process, it is important determine the percentage of harmful As in it, which was done by Al-Harahsheh et al. [16].

**Table 3. Concentrations of detected heavy metals in shale oils by location, ppm**

| Element \ Location | El-Lajjun | Al-Sultani | Attarat Umm Ghudran | Al-Wehda dam | Max | Min |
|---|---|---|---|---|---|---|
| V | 2.290 | 0.887 | 1.863 | 1.073 | 2.290 | 0.887 |
| As | 2.590 | 2.137 | 2.117 | 2.770 | 2.770 | 2.117 |
| B | 0.584 | 0.265 | 0.589 | 0.284 | 0.589 | 0.265 |
| Ba | 0.443 | 0.190 | 0.343 | 0.259 | 0.443 | 0.190 |
| Cd | 6.133 | 0.636 | 5.007 | 0.805 | 6.133 | 0.636 |
| Co | 0.005 | 0.021 | 0.007 | 0.033 | 0.033 | 0.005 |
| Cr | 2.470 | 0.519 | 1.787 | 0.572 | 2.470 | 0.519 |
| Cu | 2.540 | 0.827 | 2.160 | 0.842 | 2.540 | 0.827 |
| Fe | 23.600 | 9.520 | 22.400 | 9.813 | 23.600 | 9.520 |
| Mn | 0.577 | 0.207 | 0.531 | 0.367 | 0.577 | 0.207 |
| Ni | 11.100 | 3.140 | 8.910 | 3.760 | 11.100 | 3.140 |
| Pb | 0.175 | 0.073 | 0.230 | 0.116 | 0.230 | 0.073 |
| Sb | 1.520 | 0.693 | 1.430 | 0.971 | 1.520 | 0.693 |
| Se | 0.396 | 0.255 | 0.390 | 0.401 | 0.401 | 0.255 |
| Mo | 0.785 | 0.226 | 0.426 | 0.238 | 0.785 | 0.226 |
| Zn | 12.933 | 2.520 | 10.500 | 3.753 | 12.933 | 2.520 |
| Sn | 1.917 | 1.012 | 1.797 | 1.450 | 1.917 | 1.012 |
| Pd | 0.123 | 0.123 | 0.130 | 0.137 | 0.137 | 0.123 |
| Pt | 0.813 | 0.247 | 0.800 | 0.263 | 0.813 | 0.247 |
| Sr | 0.940 | 0.505 | 0.789 | 0.874 | 0.940 | 0.505 |

Zinc was found at a concentration of 12.9 ppm in El-Lajjun and 10.5 ppm in Attarat Umm Ghudran shale oil, whereas its quantity in Al-Sultani and Al-Wehda dam shale oils was lower. This trend of Zn concentration is similar to that of nickel's. The concentrations of Ni and Zn are similarly high in shale oils from El-Lajjun and Attarat Umm Ghudran oil shales. Iron is present in significantly higher concentrations compared with other elements, as Table 3 reveals. The concentration of Fe fluctuated between 23.6 ppm in El-Lajjun shale oil to 9.52 ppm in Al-Sultani shale oil. Concentrations of other elements are also given in Table 3 and can be compared.

As can be observed from Table 4, the concentrations and ratio of vanadium to nickel, the most harmful elements to catalyst, are comparable to those reported in crude oils. These heavy metals tend to accumulate in the heavy portion of crude oils, especially in the bottom residue. The calculated ratio is found to be higher than 3.5:1 and lower than 4.8:1 depending on the location of the deposit. As a result, it can be concluded that shale oil liquid is quite similar in composition to crude petroleum since these ratios are identical to those reported in crude oils. Considering the geological region and location of the crude oil and oil shale deposits, a similar trend is observed for the Ni:Fe ratio. It is almost constant and fluctuates between 1:2 and 1:3. These three metals, nickel, vanadium and iron, are the most deleterious to the catalyst used in hydrotreating and other operations during the petroleum refining process.

The concentrations of V, Ni, Zn and Fe that poison and destroy catalysts are shown in Figure 2. The concentrations of Fe are the highest among the

**Table 4. The concentration ratios of nickel to vanadium and iron in shale oils**

| Location / Ratio | El-Lajjun | Al-Sultani | Attarat Umm Ghudran | Al-Wehda dam |
|---|---|---|---|---|
| Ni:V | 4.8:1 | 3.5:1 | 4.8:1 | 3.5:1 |
| Ni:Fe | 1:2.1 | 1:3 | 1:2.5 | 1:2.6 |

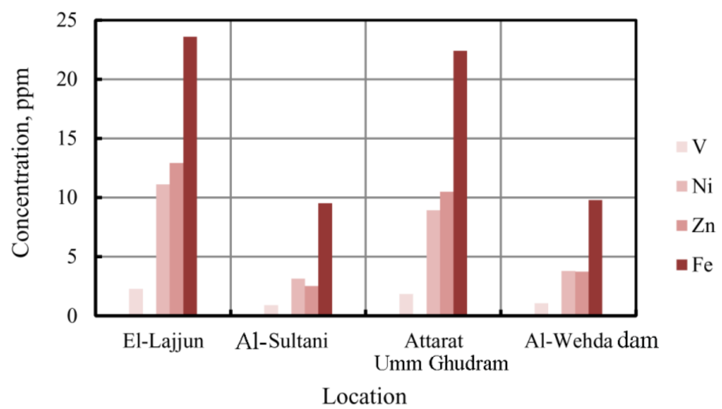


Fig. 2. Concentrations of V, Ni, Zn and Fe in shale oils by location.

four elements as indicated by the height of the column; its concentration is almost twice those of other elements. As the figure shows, the concentrations of the said elements in El-Lajjun and Attarat Umm Ghudran shale oils appear in the order Fe > Zn > Ni >V, whereas this order is slightly changed in Sultani and Al-Wehda dam shale oils.

## 5. Conclusions

In this research work, Fischer Assay and elements analysis were conducted on oil shale samples from different deposits in Jordan. Distillation curves for shale oils from three Jordanian oil shales were obtained, and these exhibited a similar behavior. Non-hydrocarbon elements present in shale oils were determined. Concentrations of metal elements As, B, Ba, Be, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, Sn, Sr, V and Zn were determined using inductively coupled plasma-optical emission spectrometry. The concentrations of metals in El-Lajjun, Attarat Umm Ghudran, Al-Wehda dam and Al-Sultani shale oils were as follows: As 2.11–2.59 ppm, B 0.57–0.58 ppm, Cd 5.00–6.13 ppm, Cr 1.78–2.47 ppm, Ni 8.91–11.10 ppm, Sb 1.43–1.52 ppm, Mo 0.42–0.78 ppm, Zn 10.5–12.93 ppm, Sn 1.79–1.91 ppm and Sr 0.78–0.94 ppm. Experimental results indicated the percentages of non-metallic elements in oil shale samples to be the following: carbon 74.61–77.48%, nitrogen 0.84–1.13%, hydrogen 9.24–9.70% and sulfur 7.88–11.79%.

Fischer Assay analysis confirmed that the water content of oil shale samples varied between 2.4 and 2.9 wt%. On the other hand, the oil content fluctuated between 5.44 and 15 wt%, whereas the spent shale was in the range of 78–90.93 wt%, and, finally, the calculated gas loss was 1.03–4.0 wt%.

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