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OIL-OIL CORRELATION USING TRACE METALS FROM SELECTED OIL FIELDS, NORTH IRAQ

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ABSTRACT

A collection of 11 crude oil samples from 11 oil exploratory wells in 5 oilfields in northern Mesopotamian basin were subjected for geochemical analysis of trace metals and sulfur. The crude oil samples were collected from Guwear, Kirkuk, Tawke, Khurmala, and Taq Taq oil fields. The mean values of vanadium and nickel were 20 and 15 ppm, respectively. Trace metals configurations and constraints helped to explore the depositional environments and used in the geochemical grouping the oils. Based on nickel to vanadium ratio, the crude oils were differentiated into five groups: **1)** Tawke-3, Tawke-4, Guwear-2, Shiwashok, and Taq Taq-6; **2)** Khurmala-1 and Kirkuk-247; **3)** Khurmala-2 and Kirkuk-331; **4)** Guwear-3; and **5)** Guwear-1. The low ratio of nickel to vanadium (Ni/V<1) in the crude oils of Guwear-2; Shiwashok; Tawke-3; Kirkuk-331; Khurmala-2; Guwear-3; Kirkuk-247; and Khurmala-1 oils indicates oil source of marine environment, whereas, the crude oil source of Guwear-1; Tawke-4; and Taq Taq-6 is non-marine and probably deposited in lacustrine or land. The oils can be arranged from older and more mature to younger and less mature based on V/Ni as Guwear-2, Shiwashok, Tawke-3, Guwear-1, Tawke-4, Taq Taq-6, Kirkuk-331, Khurmala-2, and Guwear-3.

مقارنة النفوط في حقول نفط مختارة من شمال العراق باستخدام العناصر النزرة

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المستخلص

تم تحليل مجموعة من 11 عينة من النفط الخام من 11 بئرا استكشافيا للنفط في 5 حقول نفطية في شمال حوض ما بين النهرين للعناصر النزره والكبريت. جمعت العينات النفطية الخام من حقول گوير، كركوك، طاوكي، خورملة، وطق طق. كان الناتج المتوسط لقيم عناصر الفناديوم والنيكل 20 و 15 جزءا من المليون على التوالي. وقد ساعدت تراكيب العناصر في أستكشاف البيئة الترسيبية القديمة وتصنيف النفوط جيوكيميائيا. استنادا الى نسبة النيكل الى الفناديوم، أمكن تقسيم النفوط الخام الى خمس مجموعات هي: **1)** طاوكي-3، طاوكي-4، گوير-2، شيواشوك، وطق طق-6؛ **2)** خورملة-1 وكركوك-247؛ **3)** خورملة-2، وكركوك-247 **4)** گوير-3؛ و **5)** گوير-1. ان نسبة النيكل إلى الفاناديوم المنخفضة (نيكل/فناديوم<1) تشير إلى ان مصدر النفوط الخام في حقول گوير-2، شيواشوك، طاوكي-3؛ كركوك-331. خورملة-2، گوير-3، كركوك-247، وخورملة-1 هي البيئة البحرية، بينما مصدر النفوط الخام في حقول گوير-1؛ طاوكي-4؛ وطق طق-6 هي بيئة غير بحرية وقد تكون قد ترسبت في بيئة لاكوسترين أوبيئة قارية. أمكن ترتيب النفوط الخام من الأقدم والأكثر نضجا الى الأحدث والأقل نضجا على أساس نسبة الفناديوم الى النيكل وهي گوير-2، شيواشوك، طاوكي-3، گوير-1، طاوكي-4، طق طق-6، كركوك-331، خورملة-2، وگوير-3.

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INTRODUCTION

Hodgson (1954) studied the oils of Western Canada and measured vanadium (V) and nickel (Ni), and concluded that the V/Ni ratio decreases with increasing maturation. Hyden (1956) and Ball *et al*. (1960), however, presented data to show that the V/Ni ratio increased with the age of the host rock. Similar conclusions were used by Al-Shahristani and Al-Atyia (1972) to suggest that the V/Ni ratio of less than one indicates oil of a younger age, while the ratio more than one is an indicator to older aged oils. Abu-Elgheit *et al*. (1979) studied the total V and Ni contents in petroleum residues from different oil fields in Egypt and concluded that the V/Ni index decreases with the age of oil. Other authors (Demekova *et al*., 1958 and Gilmanshi *et al*., 1971) have concluded that the V/Ni ratio does not correlate with age.

Lewan (1984) concluded that the ratio of vanadium to nickel in crude oils is more or less fixed and may be attributed to the Eh, pH, and sulfide activity within the depositional environment of their source rocks and defined three basic Eh-pH regimes. Nicolás and Leo (2011) used trace elements to classify oils into families. Akinlua *et al*. (2007) stated that metals of proven association with organic matter may be used as reliable correlation tools. Nickel, vanadium, and cobalt (usually referred to as biophile elements) are such examples. Thus, trace metals can be very useful tool for correlating oil-oil and oil-source rock. Abdula (2010; 2015) used V and Ni besides other parameters to correlate oils and determine depositional environment for the oil source.

The studied area is located in northern Iraq within the Unstable Shelf of the Foreland Basin. The structural phenomenon of the region is favorable for hydrocarbon preservation. The region of north Iraq is divided into 53 licensed blocks and 27 of them are producible blocks. Based on the distribution of oil fields, the crude oil samples were collected from producing oil wells and refinery laboratories. The crude oil was selectively sampled from across the region, to obtain reasonable spatial coverage for the analysis for trace elements. The crude oil samples were collected from Tawke, Khurmala, Guwear, Shiwashok and Kirkuk oil fields (Fig.1).

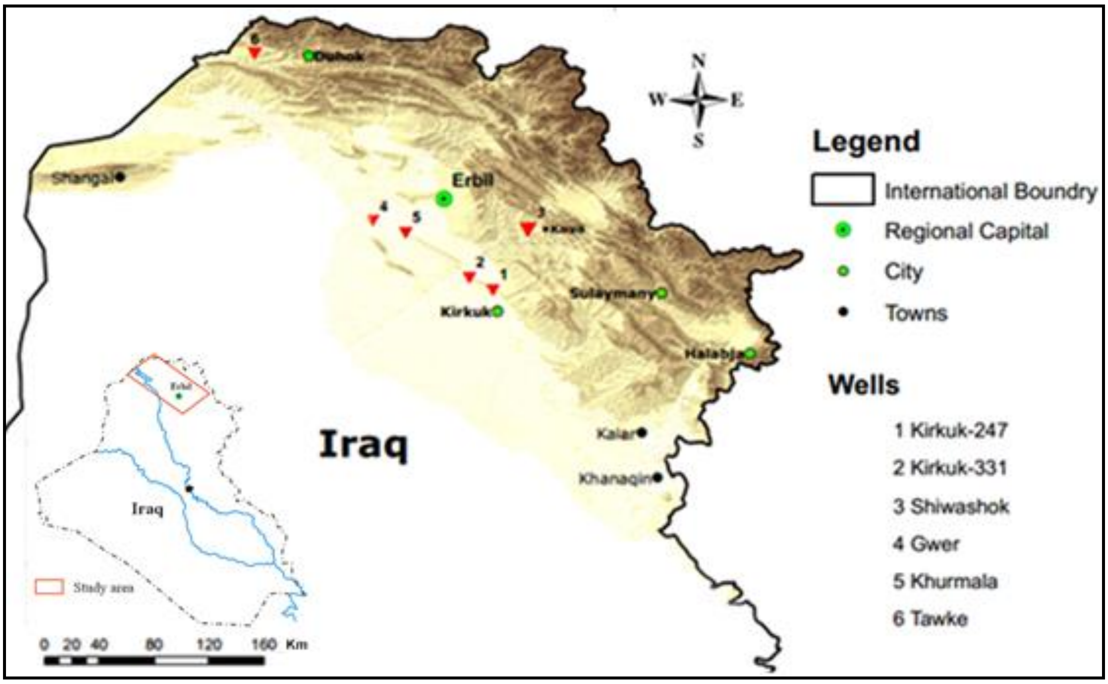

Fig.1: Map shows location of the sampled oil fields in northern Iraq

The studied crude oils contain trace elements in concentrations that differ with different formations and locations. Crude oils from Guwear and Khurmala fields contain noticeable concentrations of trace metals which need to be removed during refinery processes in order to have acceptable petroleum products. The existence and form of trace metals in crude oil must be defined in all oil fields in order to determine the method of refining and compiling material balance for some of the processes. The main purpose of this work is to exploit the potential of some trace metals in oil-oil correlation and determination of depositional environment of source rock.

MATERIALS AND METHODS

Crude oil samples were collected in the winter of 2016 from the Khurmala, Guwear, and Shiwashok oil fields, for geochemical analyses. Trace metal data were obtained from previous studies which covered five wells in three oil fields: Tawke, Kirkuk, and Taq Taq. The quality of the samples were highly considered; therefore, all the samples were kept in dry and clean glass bottles and perfectly sealed to prevent contamination, vaporizing of volatile elements and sample weathering. Representative samples of crude oils were analysed in the Ministry of Natural Resources (MNR) Laboratories in Erbil, Kurdistan Region, Iraq for geochemical analysis of trace metals using optical emission spectroscopy (OES) (Spectroil M/F Spectrometer).

TRACE METALS IN PETROLEUM

Petroleum "Hydrocarbon", as most of other things in nature is not "Pure"; beside carbon and hydrogen; there are trace metals that have been detected. Examples of trace elements include: U, Zn, Zr, V, Sr, Sn, Pb, Ni, Nd, Mo, Li, Ga, Cu, Cr, Co, Ce, Ba, B, As, Ag, Mn, Ti, Fe, and Al. The occurrence of trace metals in petroleum is well established, but the question remarkably demands the "Origin" of these metals. There are several scientifically reasonable explanations for metals being bound to the organic matrix of crude oil. Metal parts in the oils are in the form of salts of organic acids and chelates in which the metal atom is located in the center of the porphyrin ring or as a condensed aromatic moieties voids and bulk in complex form polydentate complexes (Abdula, 2008). Many such complexes may be ion-exchanged with metals that are present in solution or on the surface of rocks in contact with the oil. The greatest amount of metals is contained in the asphalt-resinous substances.

Porphyrins are tetrapyrrolic compounds occur naturally as metal complexes (e.g. nickel, vanadium, and iron) or as free-base species. Organometallic porphyrins account for much of the vanadium and nickel in petroleum (Peters *et al*., 2005). Vanadium is fully concentrated in the asphalt-resinous substances. Nickel is also the most concentrated in the high molecular weight of the hydrocarbon (Barwise, 1990). There are two different ideas about trace metals origin: **1)** biotic source through incorporation and diagenesis of metal complexes of the original biological material into the organic matrix in the source rocks, and **(2)** abiotic origin through uptake from an aqueous phase or mineral phases during primary or secondary migration from formation waters or from reservoir rock minerals.

APPLICATION OF TRACE METALS

- **Oil-Oil Correlation**

Trace metals concentration in crude oils such as vanadium and nickel can be used to classify crude oils into groups (Table 1). Since the proportionality of vanadium to nickel is stable for crude oils from particular rock unit, stratigraphic section, or area within a basin which provides a reliable tool for crude oil analysis (Lewan, 1984). Each crude oil within a certain field has come from specific source and definite depositional environment and each crude oil has different trace elements concentration which infuses the environment in which they were derived from (Mudiaga *et al*., 2011).

Some oils can be grouped together because of their close relationship and common properties. Based on nickel to vanadium proportionality, the analysed crude oils were differentiated into five groups (Fig.2 and Table 2). Guwear-1 and Guwear-3 can be grouped into two different families (groups), because they may have come from different pay zones and different depths. Samples from Kirkuk and Khurmala are also grouped differently regardless of their close geological relation, they are both extracted from Kirkuk anticline, but they are not sharing the same genetic characteristics.

Table 1: Trace metals concentration in crude oils from northern Mesopotamian basin, Iraq

Se.	Well Name	Formation	Depth (m)	Trace Metals (ppm)											Wt.%	
				V	Ni	Li	Pb	Zn	Si	Cr	Cu	Al	Fe	Mn	C	S
1	Guwear-1	Avanah	900	2.8	64.9	109.2	1411.0	23.5	49.0	0.0	5.7	32.6	36.8	25.3	1.2	0.7
2	Guwear-2	Qamchuqa	1050	0.3	0.0	53.7	0.9	0.0	9.7	0.3	0.0	0.7	1.2	1.9	2.2	0.7
3	Guwear-3	Qamchuqa	1610	75.9	28.7	58.9	0.0	0.0	0.0	0.2	0.0	1.2	0.0	1.4	2.1	3.6
4	Khurmala-1	Shiranish	1725	23.3	13.3	72.2	50.7	2.8	2.4	0.4	0.1	2.2	7.5	1.9	2.0	1.6
5	Khurmala-2	Shiranish	1746	45.1	17.7	71.9	0. 8	0.0	0.0	0.2	0.0	0.3	0.0	0.9	1.9	0.6
6	Shiwashok	Kometan	1825	0.0	0.0	82.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.7	1.4	0.5
7	Taq Taq-6	Kometan	1952	6.0	9.0											0.9
8	Tawke-3	Qamchuqa	2545	5.6	0.0											3.1
9	Tawke-4	Jeribe	315	1.2	4.6											3.5
10	Kirkuk-247	Jeribe	740	23.6	5.9											2.8
11	Kirkuk-331	Qamchuqa	1174	38.0	15.2											3.5

Table 2: Grouping of crude oils in northern Mesopotamian basin, Iraq

Group 1	Group 2	Group 3	Group 4	Group 5
Tawke-3	Khurmala-1	Khurmala-2	Guwear-3	Guwear-1
Tawke-4	Kirkuk-247	Kirkuk-331		
Guwear-2				
Shiwashok				
Taq Taq-6				

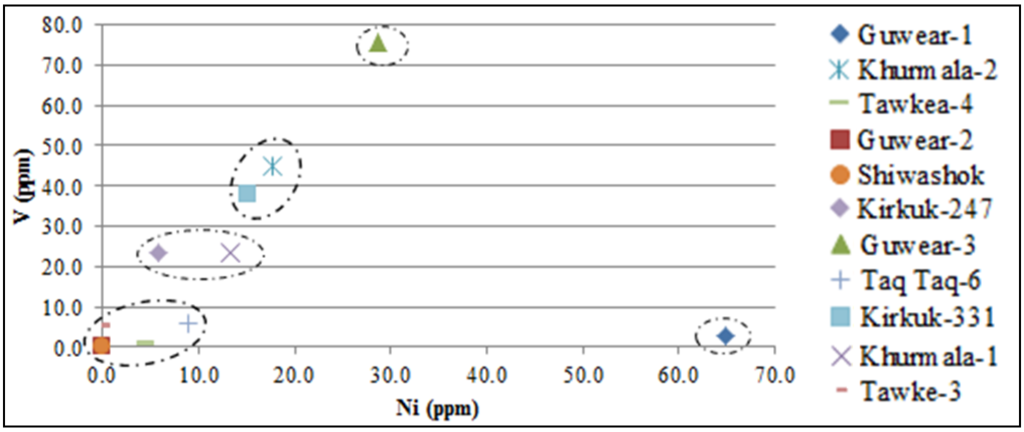

Fig.2: Vanadium (V) versus nickle (Ni) plot showing different crude oil groups

- **Depositional Environment**

Based on environmental classification, oils from marine origin have low nickel to vanadium ratio (Ni/V<1) and moderate to high sulfur content, but lacustrine source rocks have Ni/V ratio greater than one and low sulfur content (Barwise, 1990; Peters and Moldowan, 1993). Figure 3 shows that the samples of Guwear-1, Tawke-4, and Taq Taq-6 oils appear to have deposited in non-marine environment, while the other samples were deposited in marine environment. Lewan (1984) identified three depositional systems for vanadium, nickel, and sulfur. Accordingly, the crude oils from the studied wells belong to the following systems (Fig.4):

– **System I:** Represents conditions under which nickelous cations are available for bonding, but vanadium is not available because of its occurrence as a quinquivalent anion. Crude oils, such as Shiwashok and Guwear-1, were expelled from source rocks that were deposited in this regime and will have low vanadium – nickel fractions (less than 0.10) and low sulfur contents.

– **System II:** Represents conditions under which nickelous and vanadyl cations are available, but the presence of sulfide or hydroxide ions may hinder their availability for bonding. Source rocks deposited in this regime are expected to expel crude oils, such as Kurmala-2 and Taq Taq-6, with a wide range of vanadium – nickel fractions (0.10 – 0.90) and low sulfur contents (<1 weight percent).

– **System III:** Represents conditions under which vanadyl or trivalent vanadium cations are available with the availability of nickelous cations being hindered by the presence of sulfide ions. Crude oils, such as Khurmala-1, Guwear-3, Tawke-3, Kirkuk-247, and Kirkuk-331, expelled from source rocks deposited in this regime, are expected to have high vanadium – nickel fractions (>0.50) and high sulfur contents (>1 weight percent) (Lewan, 1984). The Guwear-2 and Tawke-4 do not appear to belong to any system.

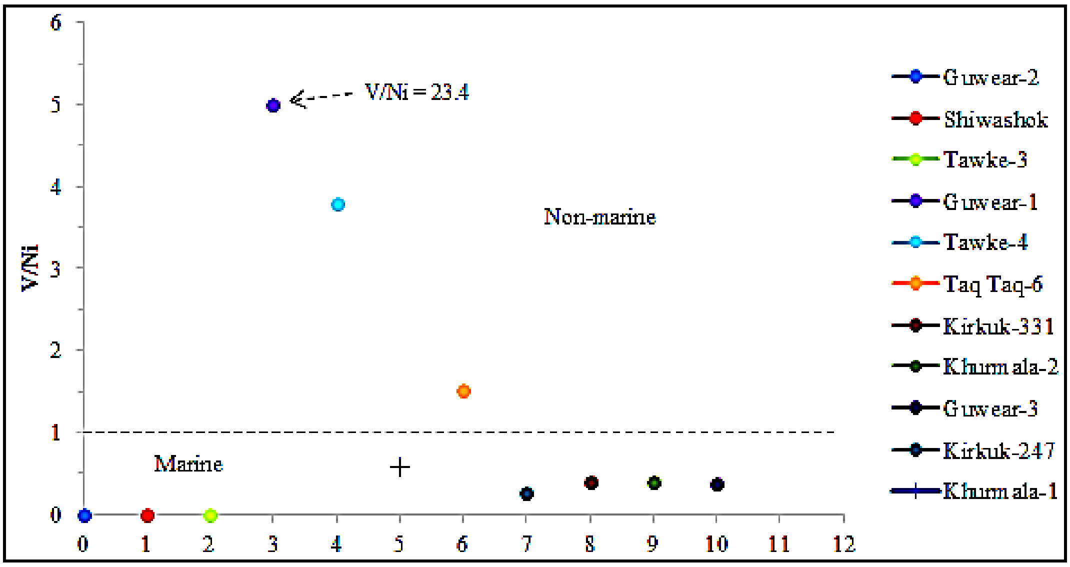

Fig.3: Plot of V/Ni ratio for each of the crude oil samples showing the Guwear-1, Tawke-4, and Taq Taq-6 plot in the field of non-marine environment, while the other samples plot in the marine environment field. One sample from Guwear-1 well is off scale (purple circle)

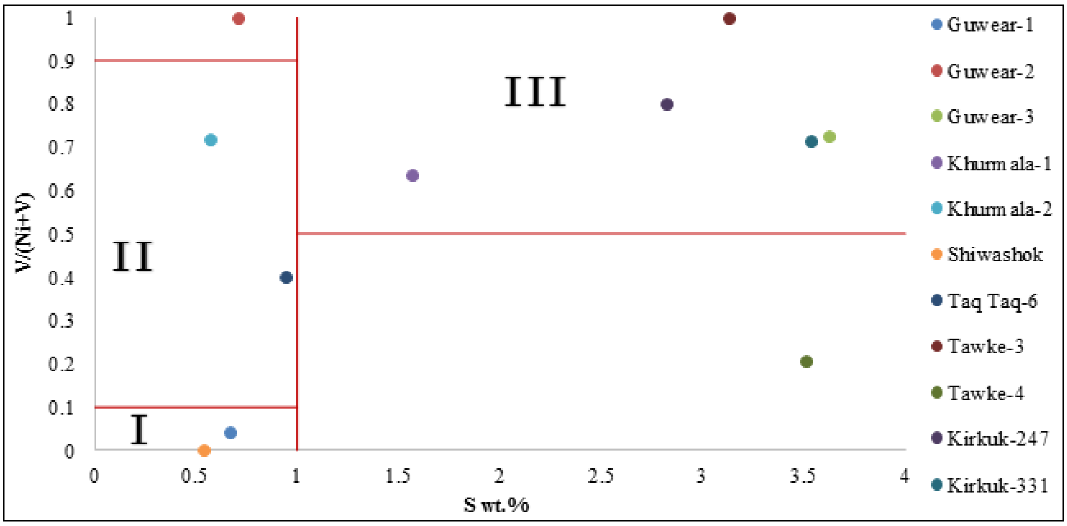

Fig.4: Crude oil distribution within Lewan's (1984) classification diagram

- **Age Relationships**

An index of 1.00 – 1.44 for V/Ni was reported for the Lower Cretaceous oils and an index of 3.25 – 3.53 for the Miocene oils. However, Demekova *et al*. (1958) and Gilmanshi *et al*. (1971) have concluded that the V/Ni ratio does not correlate with age based on their study, but this conclusion conflicts with the instability of vanadium compounds which is less stable than nickel compounds (Ali *et al*., 1983). There are many factors that may change trace metals concentration in organic matter beneath the earth such as adding up or subtracting a portion of trace metals through the formation water or minerals. Based on V/Ni ratio crude oils from the studied wells can be arranged from older to younger as shown in Table 3.

Table 3: Sorting samples from older and more mature to younger and less mature based on V/Ni ratio

Well Name	V	Ni	V/Ni	Relative Age
Guwear-2	0.30	n.d.		Older and more mature ↓
Shiwashok	n.d.	n.d.		
Tawke-3	5.60	n.d.		
Guwear-1	2.80	64.90	0.04	
Tawke-4	1.20	4.60	0.26	
Taq Taq-6	6.00	9.00	0.67	
Khurmala-1	23.30	13.30	1.75	
Kirkuk-331	38.00	15.20	2.51	
Khurmala-2	45.10	17.70	2.55	
Guwear-3	75.90	28.70	2.64	

n.d. = not detected

- **Maturation**

The V/Ni ratio decreases with increasing maturation (Hodgson, 1954; Udo *et al*., 1992; Akinlua *et al*., 2007). But there is no relevance between maturation and trace metals concentration in crude oil, even if high temperature is to be considered, where energy breaks the bonds of porphyrin and the concentration decreases, but this does not prove the relation, because the metal concentration is still traced in organic matter. Although maturation could relatively be compared with V/Ni ratio and consider the difference for a certain field, but that does not apply for other fields and could not provide reliable maturation measurement. Based on V/Ni ratio, the crude oils from the studied wells can be arranged from more mature to less mature as shown in Table 3.

EFFECTS OF TRACE METALS ON API GRAVITY AND VISCOSITY

Trace metals increase viscosity of crude oil and will decrease API gravity. Figure 5 shows the relations between API and trace metals (Pb, Ni, Cu, and Fe) concentrations. Samples with higher trace metals concentration give higher viscosity and consequently lower API and *vice versa* (Hess *et al.*, 1959) (Fig.6). The sulfur content (Fig.7) does not show any relation to trace metals occurrence.

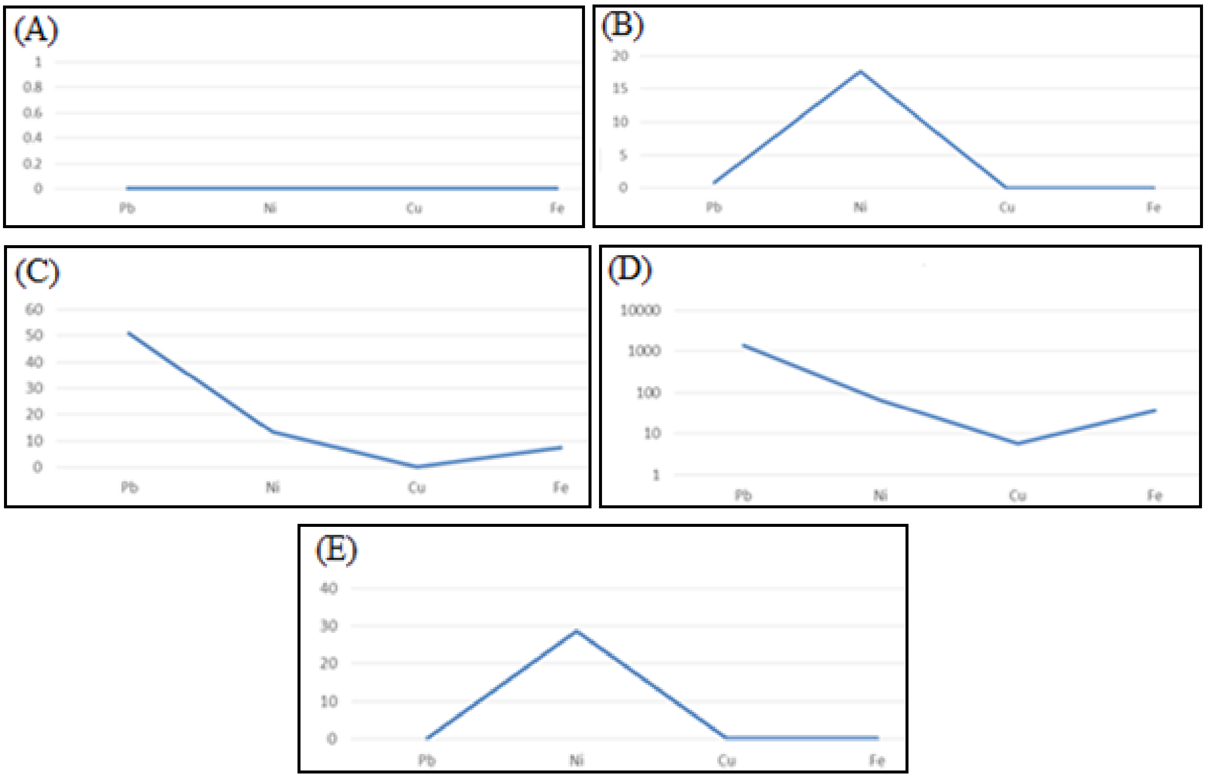

Fig.5: **A)** Shiwashok oil has high API (45.43) and low concentration of trace metals; **B)** Khurmala-2 has moderate concentration of trace metals and marginally moderate API (35.83); **C)** Khurmala-1 has API (27.75) and high trace metals concentration; **D)** Guwear-1 has very low API (22.4) and very high concentration of trace metals; and **E)** Guwear-3 has low API (27.39) and high trace metal concentrations

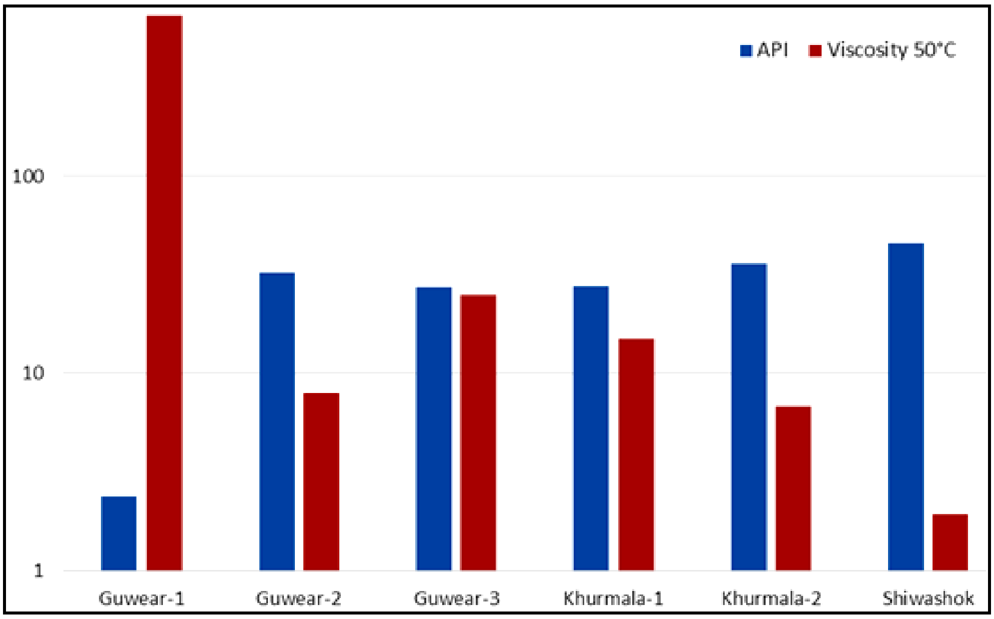

Fig.6: The relation between API gravity and viscosity. Samples with higher trace metals concentration give higher viscosity and consequently lower API and *vice versa*. The samples with moderate trace concentration give moderate viscosity and moderate API (Hess *et al*., 1959).

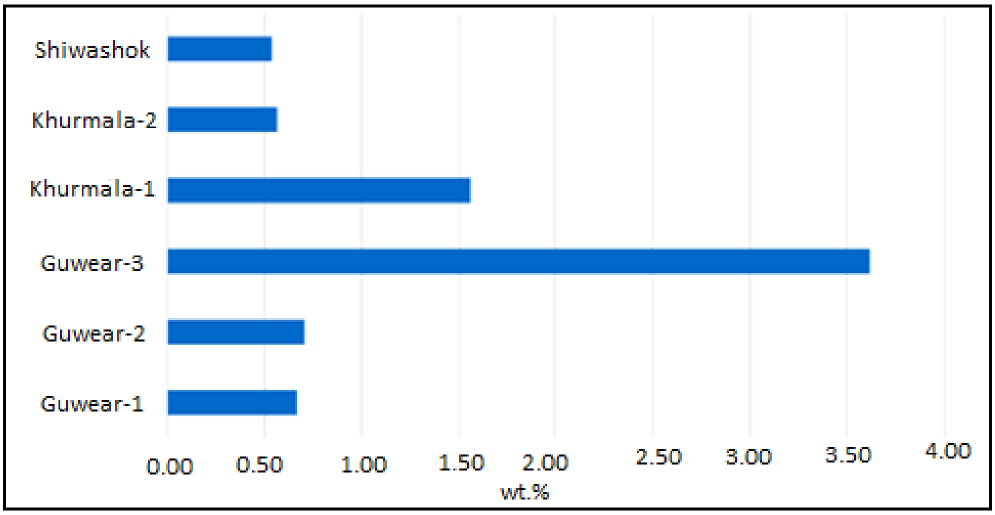

Fig.7: Various portions of sulfur in the analyzed samples

CONCLUSIONS

- Based on nickel to vanadium proportionality, the studied crude oils can be differentiated into five groups: **1)** Tawke-3, Tawke-4, Guwear-2, Shiwashok, and Taq Taq-6; **2)** Khurmala-1 and Kirkuk-247; **3)** Khurmala-2 and Kirkuk-331; **4)** Guwear-3; and **(5)** Guwear-1.
- The low ratio of nickel to vanadium (Ni/V<1) indicates that the oil source of Guwear-2; Shiwashok; Tawke-3; Kirkuk-331; Khurmala-2; Guwear-3; Kirkuk-247; and Khurmala-1 oils was deposited in marine environment, while the oil source of Guwear-1; Tawke-4; and

Taq Taq-6 was deposited in non-marine environment and probably deposited in lacustrine or land.

- The oils can be arranged from older and more mature to younger and less mature based on V/Ni ratio as Guwear-2, Shiwashok, Tawke-3, Guwear-1, Tawke-4, Taq Taq-6, Kirkuk-331, Khurmala-2, and Guwear-3.

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