



Investigation of Heavy and Trace Metals in Some Kurdistan Region Crude Oils by Spectroscan MAX-G

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Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

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ABSTRACT

Four types of Kurdistan crude oils have been studied to determine the heavy and trace metals. The significance of determining trace elements that exist in crude oils is helpful for further information about exploration, production and the refining process. In this work crude oil can be separated into products such as (gasoline, kerosene, diesel, and atmospheric distillation residue +350°C) by using atmospheric distillation unit and vacuum distillation unit. The trace metals can be determined with acceptable accuracy and precision by spectroscan MAX-G. However, the values of Ni concentration were the best in accuracy among the group of metals of interest. The average values of the results will be employed as reference values of the trace metal content in the coming discussion and using Ni and V as test elements. The crude oil samples are characterized by with a dominance of V over Ni with a V/Ni ratio of 3.7 to 2.5. Trace element analysis of the five metals in crude oils and atmospheric distillation residues +350°C, for each crude oils and atmospheric distillation residues +350°C is investigated, samples of these areas has not been previously examined for trace element contents. In this study to find the relation between metals in crude oils and atmospheric distillation residue of samples. To detect the concentration of trace elements by using this instrument.

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1. INTRODUCTION

Crude oil is a naturally occurring mixture; it consists predominantly of hydrocarbons with other elements such as sulfur, oxygen, nitrogen. Appearing in the form of organic compounds which some cases form complexes with metal [1,2]. Metal and Metalloid constituents could be naturally found in crude oil or they could be added during transportation and storage. In general, these elements are present in crude oil as inorganic salts (mainly as chloride and sulfates of Na, K, Mg and Ca), or as organometallic compounds of Ca, Cu, Cr, Mg, Fe, Ni, Ti, V and Zn [3]. The type composition of crude oil is known to vary depending on several characteristics including type of geological formation, location, age of the oil field and depth. These factors can cause the metal concentration to change appreciably [4,5]. The quantities of individual metals differ significantly in different crude oils and asphalts and even in the same type of crude oil field from different localities [6]. Crudes origination from different oil fields may vary markedly in trace –metal content [7].

There are several methods for the determination of trace elements in crude oil by such neutron activation, pulse polarography, proton induced X-ray emission, high performance liquid chromatography, atomic absorption spectrophotometry, ASS and Induced coupled plasma emission (ICP). The ICP is not being available in many laboratories due to the requirements and cost. Furthermore, most of the methods for overcoming these problems come with an organic injection by the nebulization system, Electro thermal vaporization and improving of sample treatments.

The aim of this research investigations trace element and evaluation of physicochemical properties and measuring the distillation cuts to fine the percentage of products and residue in each type of crude oils samples from Tawke T-21A (located in Tawke region Zakho, Dohuk city) and Shekhan PF2 (located in Shekhan region Dohuk city).

2. EXPERIMENT

2.1 Crude Oil Samples

The study was carried out on Four Iraqi-Kurdistan region crude oil samples which are

collected from the fields of Tawke well No. (T-21A and T-5), and Shekhan well No. (PF1 and PF2).

2.2 Physical and Chemical Properties of Crude Oils

The study of physicochemical characterizations of the four crude oils (T-21A, T-5, PF1, and PF2) was carried out using the standard test methods of analysis, ASTM and GOST. Physical and chemical properties of crude oils were determined and measured at Ufa state petroleum technological university, Faculty of Technology, department of oil and gas technology. Laboratory 531, and at university of zakho, Faculty of Science, Department of Chemistry, Research laboratory.

2.3 Atmospheric Distillation Unit

The method covers the determination of the percentages and distillation range of the fractions in crude petroleum. According in GOST 2177-99; 100 ml for each T-21A, T-5A, PF1, and PF2 were placed in 250 ml distillation flask, by using the atmospheric distillation unit as shown in Fig. 1. The distillation was carried out under atmospheric pressure [8,9].

2.4 Spectroscan MAX-G

SPECTROSCAN MAKC-G, Wavelength Dispersive X-Ray Fluorescence (WDXRF) spectrometer determines the elements from Ca (Calcium) to U (Uranium) in solids, liquids or powders, in solutions and thin films, deposits on filters.

The spectrometer operation is based on irradiation of the sample with primary X-rays generated by X-ray tube, registration of the secondary fluorescence from the sample elements, preliminary diffracted on a crystal, and calculation of the element's concentration with the help of calibration equation, which is a relation between the element concentration and intensity of the registered secondary emission from the element. The spectrometer has high resolution of spectral lines and therefore provides accurate determination of elements in complicated multicomponent substances [10].

Four samples T-21A, T-5, PF1, and PF2 crude oil from various oil field of Kurdistan region were

collected and analyzed for zinc, nickel, vanadium, lead, iron and manganese. Using SPECTROSCAN MAKC-G.

3. RESULTS AND DISCUSSION

3.1 Physicochemical Properties of Crude Oils and Products

The physical and chemical characteristics of crude oil vary widely from one production field to another and even within the same field. Colloquial terms like light and heavy are used to characterize crude oil in terms of its boiling range, composition and sulfur content [11]. It is important to discuss crude oil properties because refining technology has been developed in response to the differences between crude oil properties and final product specifications.

Table 1 shows some of the important tests used to determine the properties of T-21A, T-5, PF1 and PF2 crude oils. Each of these properties gives a certain value to the crude oil. The density of T-21A and T-5 crude oil is lower than PF2 and PF1 crude oil, while the API gravity of T-21A and T-5 crude oil is higher than PF1 and PF2 crude oil.

Determining the sulfur content in crude is important because the amount of sulfur indicates; the type of treatment required for the distillates, that sulfur has the most important effects on refining. It has the greatest influence on the value of the crude oil. Crude oil with higher sulfur content, generally requires more expensive processing than those with lower sulfur content. Table 1 shows that the Shikhan PF1 and PF2 crude oil are higher sulfur content than Tawke T-21A and T-5 crude oils. Trace metals vanadium and nickel contents directly increase with sulfur content [12,13]. The correlation between sulfur content and vanadium and nickel shown in Fig. 2.

Ash contents, this test indicates the amount of metallic constituents in a crude oil. The ash is left after completely burning an oil sample which usually consists of stable metallic salts, metal oxides, and silicon oxide [14]. Table 1 shows that the Tawke T-21A and T-5 crude oils have a lower percentage of ash content than Shikhan crude oils PF1 and PF2.

The carbon residue is a property that can be correlated with several other properties of petroleum; hence, it also presents an indication of the volatility of the crude oil and the coke-forming (or gasoline-producing) propensity. However, tests for carbon residue are sometimes used to evaluate the carbonaceous depositing characteristics of fuels used in certain types of oil-burning equipment and internal combustion engines. Table 1 shows that the Tawke T21A crude oil and Shikhan PF1 have approximately the same value of carbon residue. Whereas, Shikhan PF2 crude oil has a higher carbon residue than T-21A, T-5 and PF1 crude oil. Trace metal vanadium and nickel contents directly increase with carbon residue [12], the correlation between carbon residue and vanadium and nickel is shown in Fig. 3.

3.2 Evaluation Atmospheric Distillation of Four Crude Oil Samples

For the evaluation and determination of distillation characteristics of small amounts of crude oil, atmospheric distillation was carried out according to GOST 2177 to give a rough indication of the boiling range of the crude oils and to control the operation products through the percent light and heavy compounds. The GOST distillation data for crude oils gives some idea about the fraction that could be collected below (350°C), to avoid the thermal decomposition of remaining petroleum constituents [15].

Table 1. Physical and chemical properties of four crude oils

Value	Unit	Crude oils			
		T-21A	T-5	PF1	PF2
Density at 20°C	g/cm ³	0.8943	0.8943	0.939	0.9441
API gravity at 15.6°C	° API	26.7	26.7	19.1	18.3
Sulfur	% Mass	2.8	2.96	5.0598	5.15
Ash Content	% Wt.	0.1762	0.1825	2.978	3.563
Carbon Residue	%Wt.	5.65	3.89	5.84	9.39

According to the results from atmospheric distillation the volume percentage of the product for Shikhan (PF1 and PF2) crude oils is higher than in Tawke (T-21A and T-5) crude oils, as show in Fig. 3. the remaining hydrocarbon in Shekhan (PF1, PF2) crude oil may be heavier than in Tawke (T-21A, T-5) crude oil, then the amount of Shekhan residue $+350^{\circ}\text{C}$ products by atmospheric distillation (PF1 37% and PF2 38%) is lower than Tawke residue $+350^{\circ}\text{C}$ (40%).

Material balance of atmospheric distillation for T-21A, T-5, PF1 and PF2 Crude Oil in different volume percentage of distillation products between IBP and FBP were obtained from the distillation of the four different well crude oils with the residue are shown in Table 2. As the results, the equal ratio of liquid derivatives such as gasoline and diesel is obtained by atmospheric distillation, and this indicates that the work carried out according to the standard specifications of the distillation process, which was done according to the standard GOST of work method.

As mentioned before, from the Table 2, it is clear that the percentage of residue is close for all oil samples, and even heavy ones have a lower percentage, which is not reasonable. Although gasoline and diesel are derivatives of economic benefit and are required for use as fuel, these derivatives obtained in this study contain a high percentage of sulfur, which means that they must be sent for further refinement to the unit of hydrotreatment before using it as fuel.

3.3 Physical and Chemical Properties of Residue $+350^{\circ}\text{C}$

Tawke T-21A and T-5 residues, Shekhan PF1 and PF2 residues were obtained from their crude oils by removing distillates boiling point up to 350°C using the atmospheric distillation unit.

Table 3 shows that the density of T-21A and T-5 residue is lower than PF1 and PF2 residue. This

indicated that the PF1 and PF2 residue contained more aromatic compound than T-21A and T-5 residue $+350^{\circ}\text{C}$, while T-21A and T-5 residue $+350^{\circ}\text{C}$ contained more paraffinic compound than PF1 and PF2 residue. As a result, Shikhan (PF1 and PF2) residues $+350^{\circ}\text{C}$ are higher sulfur content than Tawke (T-21A and T-5) residues $+350^{\circ}\text{C}$. Trace metals vanadium and nickel contents directly increase with sulfur content of residues. Tawke T-21A and T-5 residues $+350^{\circ}\text{C}$ have a lower percentage of ash content than Shikhan residues $+350^{\circ}\text{C}$ PF1 and PF2. Shikhan PF1 and PF2 residues $+350^{\circ}\text{C}$ have higher carbon residues than T-21A, T-5 residues $+350^{\circ}\text{C}$. Trace metal vanadium and nickel contents directly increase with carbon residues $+350^{\circ}\text{C}$.

3.4 Determination of Trace Metals in Crude Oils and Residue $+350^{\circ}\text{C}$

Trace element analysis of five metals in crude oils and residues $+350^{\circ}\text{C}$ from four producing fields are given in Table 4. For each crude oils and residue $+350^{\circ}\text{C}$ is investigated by using spectroscan MAX-G as in Fig. 2. Samples of these areas has not been previously examined for trace element contents. The API value of crude oils is inversely proportional to specific gravities and might be considered as a primary estimation for hydrocarbon contents. The relationship between trace metals and specific gravities of the samples are inversely proportional where the increasing specific gravities of crude oil and residue $+350^{\circ}\text{C}$ samples mean an increase in the metal contents of the samples [16].

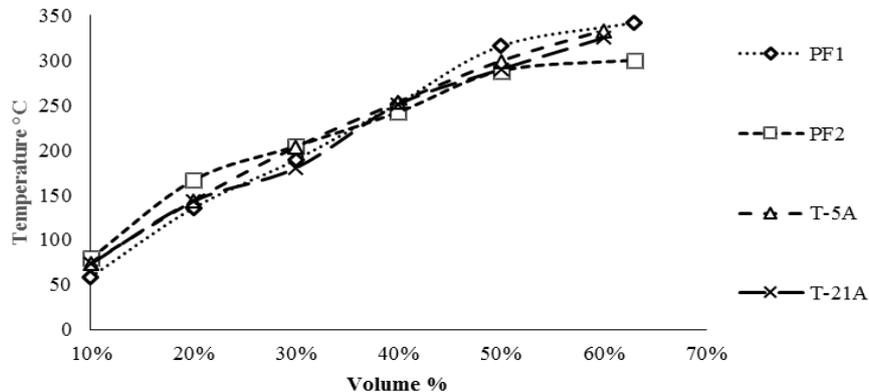
According to the results of determining the concentration of trace element in Table 4, the amount of lead, iron and manganese of PF1 and PF2 crude oils and residues $+350^{\circ}\text{C}$ is higher than T-21A and T-5 crude oils and residues $+350^{\circ}\text{C}$ due to the different chemical composition the sample, confirming trends observed by other investigators [17-19].

Table 2. Material balance of atmospheric distillation for four crude oils

Results	Crude oils			
	T-21A	T-5A	PF1	PF2
Volume %	100	100	100	100
Gasoline	20	20	20	20
Diesel	40	40	43	42
Residue	40	40	37	38
Total	100	100	100	100

Table 3. Physicochemical properties of residue +350°C

Value	Unit	Residue +350°C			
		T-21A	T-5	PF1	PF2
Density at 20°C	g/cm ³	1.0122	1.0122	1.0182	1.0255
Sulfur content	% wt.	4.39	4.09	6.86	6.70
Ash Content	% wt.	2.384	2.013	4.264	5.968
Carbon Residue	%wt.	8.59	7.61	9.16	17.93

**Fig. 1. Distillation Curves of T-21A, T-5, PF1 and PF2 crude oils****Table 4. Elemental determination in crude oils and residues +350°C**

Metals (ppm)	Crude oil				Residue +350 °C			
	T-21A	T-5	PF1	PF2	T-21A	T-5	PF1	PF2
Pb	5	7	2	7	9	6	11	16
Ni	7	8	40	43	18	18	87	86
Fe	1	0	4	6	2	0	5	7
Mn	1	<Range	<Range	1	0	1	1	2
V	26	22	88	114	51	50	222	252

In Table 4 vanadium concentration ranged from 22 to 252 ppm and nickel concentration ranged from 7 to 86 ppm of crude oils and residues +350°C. Other metals, i.e., lead and iron were observed at the 0-16 ppm level of crude oils and residues +350°C. Manganese is present in very low level (0-2 ppm) of crude oils and residues +350°C. Metals in crude oil as deposits depend to a large extent on the geological location of oil formation as well as the source rock and reservoir rock. Other sources may be included divided between clays and related minerals as well as dissolved metals from corroded pipelines or containers [20]. For this reason, the metal content of crude oil and residues +350°C is different in composition and the concentration of trace metal [17].

Vanadium and nickel have been studied more thoroughly than any other metallic element found in petroleum. One of the reasons is that these elements occur, in part as nitrogen complexes

(porphyrins) closely related to chlorophyll and hemoglobin, thus suggesting a biogenic origin for petroleum. Many correlations based on vanadium and nickel content have been made in attempts to obtain information on the geological origin of petroleum.

In Table 5 the crude oil samples are characterized with a dominance of V over Ni with a V/Ni ratio of 3.7 to 2.5 which is indicative of typical of the sapropelic-type organic matter generating oil. The V and Ni contents were correlated with the API gravity values for the studied crude oils Fig. 2. The ratio V/Ni is decreasing with decrease API gravity, in Fig. 3 the ratio V/Ni decrease with increase the percentage of sulfur, also in Fig. 4 both metal V over Ni was decreased with increase carbon residue.

Correlations between API gravity, sulfur content and carbon residue with trace metals content

(vanadium and nickel) are shown in Figs. 2, 3 and 4, respectively. According to the results, increase in metal content with an increase in API

gravity, sulfur content and carbon residue (%wt), confirming trends observed by other investigators [12].

Table 5. Correlations between API gravity, sulfur content and carbon residue with V/Ni ratio

Metals	V/Ni	API	Sulfur	Carbon Residue
T-21A Crude oil	3.7143	26.72	2.8	5.65
T-5 Crude oil	2.75	26.72	2.96	3.89
PF1 Crude oil	2.2	19.19	5.059	5.84
PF2 Crude oil	2.6512	18.38	5.15	9.39
T-21A Residue +350 °C	2.8333	8.29	4.39	8.59
T-5 Residue +350 °C	2.7778	8.29	4.09	7.61
PF1 Residue +350 °C	2.5517	7.47	6.86	9.16
PF2 Residue +350 °C	2.9302	6.48	6.7	17.93

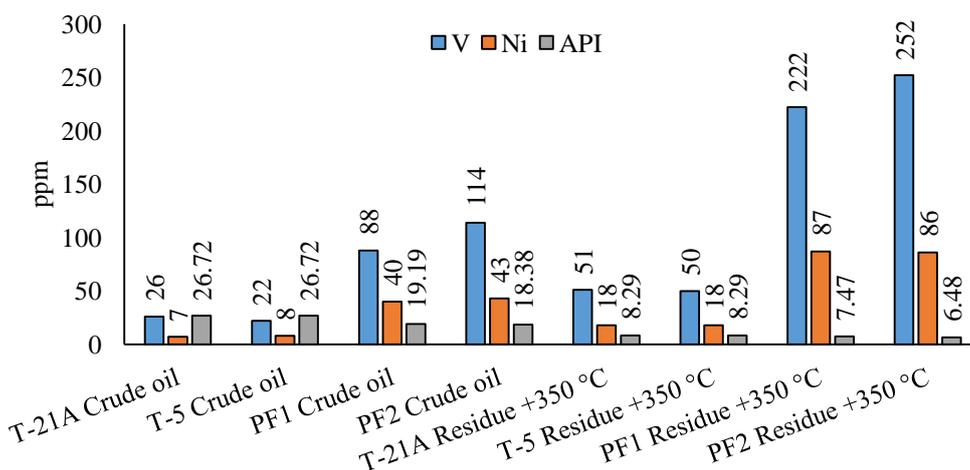


Fig. 2. Correlation of API gravity with Vanadium and Nickel content of Crude oils and Residues +350°C

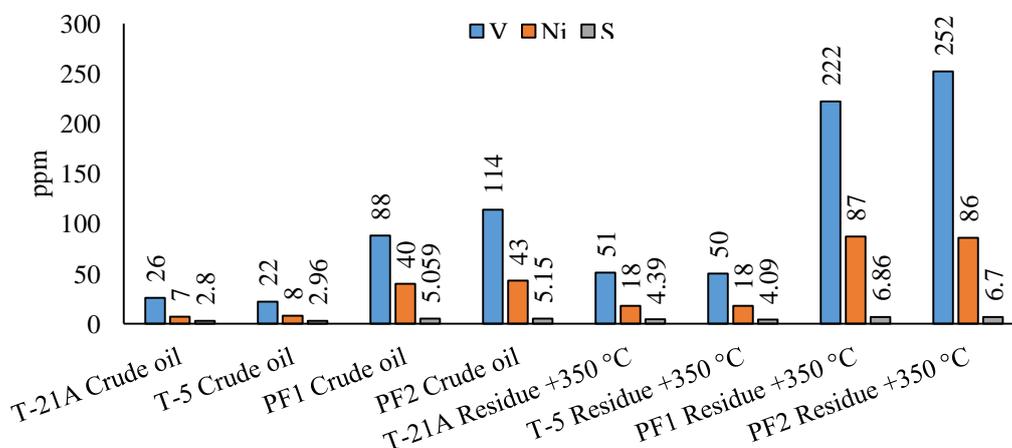


Fig. 3. Correlation of Sulfur content with Vanadium and Nickel content of Crude oils and Residues +350°C

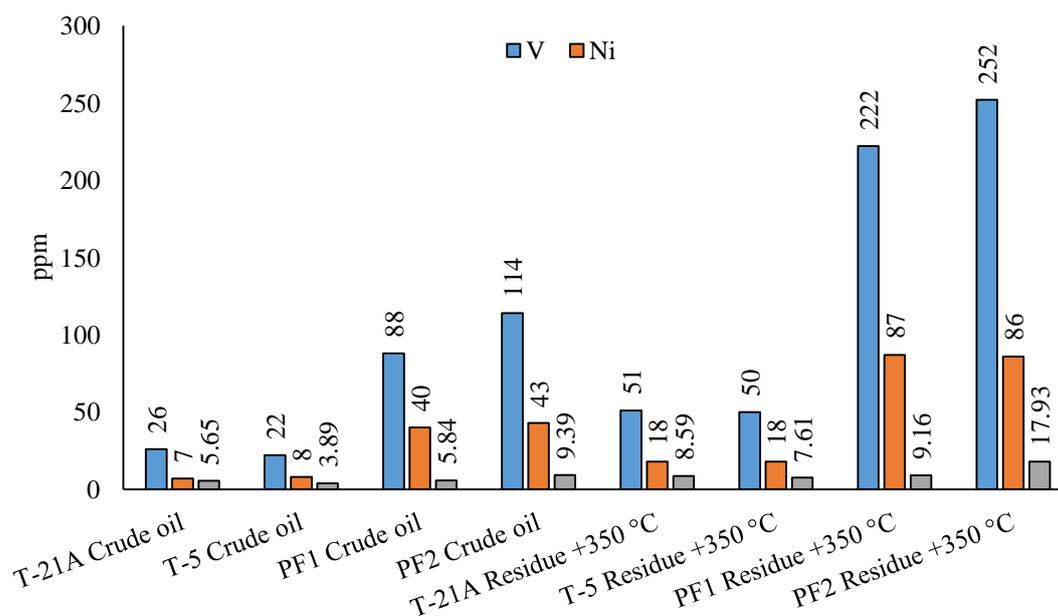


Fig. 4. Correlation of Carbon Residue with Vanadium and Nickel content of Crude oils and Residues +350°C

4. CONCLUSION

In this study, many methods have been suggested to evaluate the crude oil and petroleum residue. A series of experiments were designed and carried out in order to investigate the possible formation of petroleum residue. The results of these experiments showed that the formation of such components is possible. Evaluation of physical properties and measuring the distillation cuts of four crude oil and residue samples of (Tawke well No. T-21A, T-5 and Shekhan well No. PF1, PF2) Crude oils have been studied. The result shows that the determination some metals it's more in some crude oil well than the other crude oil well. Our study shows that some metals have relation with API, Sulfur and carbon residue like V, and Ni, but for other elements are difficult to correlate with those parameters, they were found in very low concentration in crude oil.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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