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Determination of Trace Metals in Crude Oils by Atomic Absorption Spectrophotometry in Khurmala and Guwayar Oil Fields of Kurdistan Region, Iraq

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Abstract

Fifteen crude oil samples were collected from different oil fields of the Kurdistan region, Northern Iraq to determine four trace metals, Fe, Ni, Cr and Pb. The analytical technique is applied mainly by flame atomic absorption spectrophotometry (ASS). Samples of these areas has not been previously examined for trace elements contents. API value of crude oils are inversely proportional to specific gravities and might be considered as a primary estimation for hydrocarbon contents. The relationship between trace metals and American Petroleum Institute (API) values of the samples are inversely proportional where the increasing API value of crude oil samples means a decrease in the metal contents of the samples. The method of dry ashing-acid dissolution (DA) was implemented. The results concluded that crude oil samples of the Kurdistan region have a low metal content. Nevertheless, they could be seen as an essential health hazard for humans and the environment. In t-Test $t_{stat} < t_{crtical}$ for iron, chromium and lead, there is no relationship between these three heavy metals.

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Keywords: crude oil; API; Specific gravity; Atomic Absorption.

1. Introduction

Crude oils are basically a complex mixture of organic and inorganic matters, presenting trace elements that can be grouped under inorganic compound categories [1]. 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 [2]. 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 [3]. There is a marine pollution problem in different origins where trace elements can be used to differentiate between the crude oils, according to an environmental site assessment, those locations which have been contaminated by oil products are viewed as the extension of pollution [4]. Crude oils can be classified in terms of trace metals as heavy, medium, light and residual fraction [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 [6]. Selecting a reliable method for this process is a vital step.

There are several methods for the determination of trace elements in crude oil by such neutron activation [1,7], pulse polarography [3], proton induced X-ray emission [8], high performance liquid chromatography [9], atomic absorption spectrophotometry, ASS [10] and Induced coupled plasma emission (ICP) [11]. The ICP is not be available in many laboratories due to the requirements and cost. Furthermore, most of the methods for overcoming these problems come with organic injection by the nebulization system [12], Electro thermal vaporization [13] and Improving of sample treatments [14].

ASS is the analytical technique for this process regarding its availability, simplicity and cost of instrumentation requirements. Bettinelli and Tittarelli,[15], identified a comparison for the determination of trace elements in crude oil between flame atomic absorption and other instrumental techniques and achieved that accuracy, repeatability, reproducibility and precision of the flame direct method have progressed compared to other data given by the Institute of Petroleum (IP) 228 method. Procedures for the atomization system were clarified as the introductory for the crude oil samples [10,16,18].

Barbooti and his colleagues [20], stated that silica gel can be used for lubricating oils as a stabilizer during reference and acid digestion for determining trace metals. Udoh and his colleagues [21], recommended using the procedure of p-xylene sulphonic acid ashing for the purpose of mineralizing crude oil samples in order to analyze for Fe, Cu, Ca, Na, Ni, Mg, and Zn. The advantage of this method is the prevention of the loss of materials during ashing. Osuji & Onojake, [18], applied the method of dithionite citrate carbonate for the pre extraction of Pb, Fe, Ni, Cr, and V and analyzing all metals by ASS in order to solve the matrix problem. Kowalewska, [22] , discovered that chemical modifiers like Pd could be vital in determining Ni in crude oils by ASS while it is introduced to a muffle furnace as a sample. Dittert and his colleagues [23], said continuum source radiation has been applied for continuous determining Cr and Fe in crude oil samples continuously by

atomic absorption and preliminary treatment for samples involve homogenization in an ultrasonic bath. Sedykh and his colleagues [24], applied that autoclave digestion that consists of nitric acid and hydrogen peroxide and the procedure was applicable for V and Ni contents. Ortega and his colleagues [25], examined microwave digestion that works based a maximum temperature and pressure system (ranging from 220oC and 40 bar to ~1400˚C and 80 bar) by making a comparison with a digestion method in the High Pressure Asher (HPA-S) autoclave. They concluded that digestion improvement, increasing sample size and detection of a limit occurs, if pressure and temperature are increased.

The objective of this work is to determine Fe, Cr, Ni and Pb in some newly explored oil fields of the Kurdistan region in Northern Iraq. In addition the correlation of the results with other basic characteristics of crude oil such as API and specific gravities. Moreover, evaluating the experimental procedures that have been applied for the samples by ASS was reviewed.

2. Materials and Methods

2.1. Apparatus

This experiment was implemented on a Buck 210 VGP atomic absorption spectrophotometer and set at the conditions referred to in **Table 1**. The specific gravity, API, value which stands for American Petroleum Institute were found out by the hydrometer method (PM-B-4) and its values are shown in **Table 2.**

2.2. Materials

Muffle furnace12000oC 240V, hot plate stirrer and hood were provided by the KRG. AAS instrument and its standard solution, 1000 µg.mL-1 were provided by the University of Kurdistan-Hewler. Fifteen samples of crude oil were collected from different oil fields of the Kurdistan region, Iraq.

2.3. Procedures

2.3.1. Dry Ashing Acid Dissolution (DA Method)

Specific amount of crude oil samples 1-3g were weighed in a porcelain crucibles accurately and were heated the samples on a hot plate at ~130oC for 4-5 hours. After that sulfuric acid 1-3g was added into the crucibles then waited to perform the charring at 180oC. The samples became an ash in a muffle furnace at 550oC for 6 hours. Hydrochloric acid, 5ml was added into the ash and transferred into calibrated flask for the purpose of dilution with deionized water.

3. Results and Discussion

3.1. 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.

Table 1: Operating Parameter for Flame Atomic Absorption Spectrophotometer.

Elements / Parameter	Flame Type	Lamp Current, mA	Wavelength, nm	Background Correction
Fe	Air/Acetylene	7	248.3	yes
Pb	Air/Acetylene	2	283.3	yes
Ni	Air/Acetylene	4	232	yes
Cr	Air/Acetylene	4	357.9	yes

Table 2: API, Specific gravity of crude oil samples in different oil fields.

Sample No	Field Names	Sp.gr at room temp. ASTM D1298	Sp.gr at 15.56oC ASTM D1298	API, ASTM
1	Taqtaq	0.781	0.7835	49.09
2	Garmiyan	0.833	0.8353	37.89
3	Guwayer	0.855	0.8625	32.55
4	Khurmala	0.851	0.8535	34.2
5	Khurmala,1	0.898	0.9008	25.58

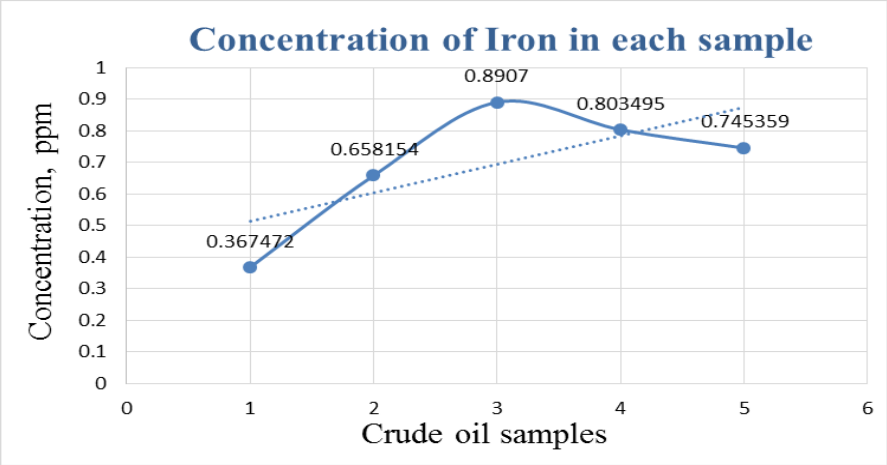

Figure 1: This graph shows the concentration of trace metals in each sample.

3.2. Discussion

API follows the American Petroleum Institute, which refers to set standards for petroleum products. One of the significance of API standard is the method of measuring the density of petroleum. Despite of classifying oils into light, medium, heavy and extra heavy.

- Light > 31
- Medium is between 22 and 31
- Heavy < 22
- Extra heavy < 10

However, specific gravity is the comparison of the density between one substance and another that is used as a standard reference, mostly water. Light oil “less dense” is much more preferable than dark oil “more dense” because it contains a huge amount of hydrocarbons which can be converted into gasoline. API gravity of oil is found by using this formula:

API gravity = (141.5/Specific Gravity) – 131.5 at 69 F◦.

The relationship between API gravity and relative density of the oils is inversely proportional, which means the higher API gravity of the oils the less density.

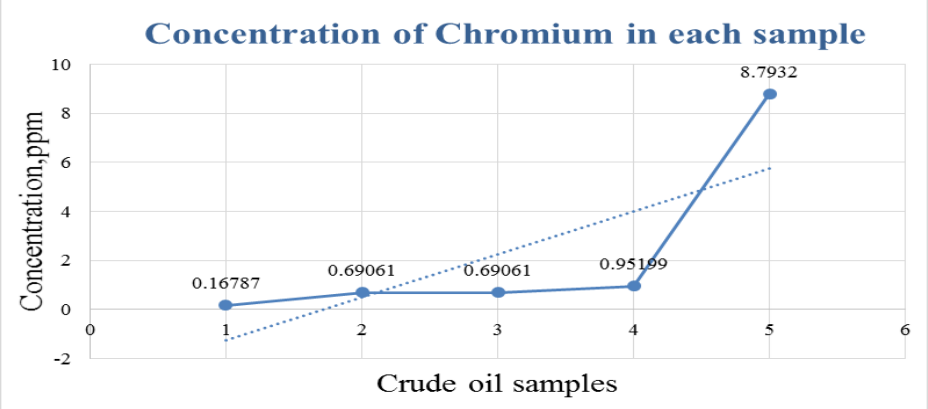

Figure 2: This graph shows the concentration of trace metals in each sample.

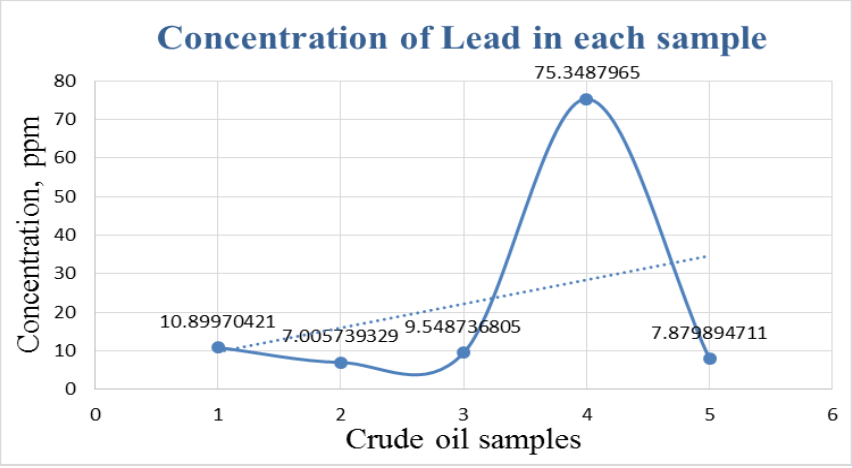

Figure 3: This graph shows the concentration of trace metals in each sample.

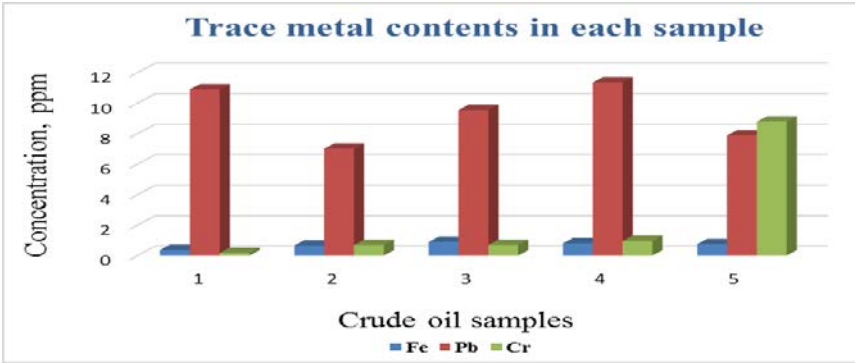

Figure 4: This graph shows the concentration of trace metals in all samples.

Table 3: Mean, Standard deviation of Iron, Chromium and Lead

#	Fe	Pb	Cr
1	0.36747	10.8997	0.16787
2	0.65815	7.00574	0.69061
3	0.8907	9.54874	0.69061
4	0.8035	11.3488	0.95199
5	0.74536	7.87989	8.7932
Mean	0.69304	9.33657	2.25886
SD	0.17957	1.67882	3.27709
VAR	0.0403	3.52303	13.4241

Table 4: Correlation table between Iron, Chromium and Lead.

	Fe	*Pb*	*Cr*
Fe	1		
Pb	-0.159	1	
Cr	0.21175	-0.4397	1

In the above correlation table of iron, chromium and lead, it shows that there is a weak relationship between these three metals.

In table 6 since $t_{stat} < t_{crtical}$, we are 95% confident that there is strong evidence and we are rejecting null hypothesis that there is no relationship between lead and iron.

In table 6 since $t_{stat} < t_{crtical}$, we are 95% confident that there is strong evidence and we are rejecting hypothesis that there is no relationship between chromium and iron.

In table 7 since $t_{stat} < t_{crtical}$, we are 95% confident that there is strong evidence and we are rejecting null hypothesis that there is no relationship between chromium and lead.

Table 5: t-Test of Iron and Lead Assuming Unequal Variances.

	Fe	*Pb*
Mean	0.693036	9.3365743
Variance	0.04030465	3.5230333
Observations	5	5
Hypothesized Mean Difference	0	
df	4	
t Stat	-10.238776	
P(T<=t) one-tail	0.00025645	
t Critical one-tail	2.13184679	
P(T<=t) two-tail	0.0005129	
t Critical two-tail	2.77644511	

Table 6: t-Test: of Iron and Chromium Assuming Unequal Variances.

	Cr	*Fe*
Mean	2.258856	0.69304
Variance	13.42414	0.0403
Observations	5	5
Hypothesized Mean Difference	0	
df	4	
t Stat	0.954185	
P(T<=t) one-tail	0.197012	
t Critical one-tail	2.131847	
P(T<=t) two-tail	0.394024	
t Critical two-tail	2.776445	

Table 7: t-Test of Lead and Chromium Assuming Unequal Variances

	Pb	*Cr*
Mean	9.3365743	2.258856
Variance	3.5230333	13.424141
Observations	5	5
Hypothesized Mean Difference	0	
df	4	
t Stat	3.8444094	
P(T<=t) one-tail	0.0042576	
t Critical one-tail	1.9431803	
P(T<=t) two-tail	0.0085151	
t Critical two-tail	2.4469119	

4. Conclusion

From this work, we conclude that the crude oil which is present in the Khurmala and Guwayar oil fields are of

good quality after measuring samples from both oil fields. The research was done by evaluating the heavy metals and proved the relationship between trace metals and API values of the samples are inversely proportional while increasing API value of crude oil samples means a decrease in the metal contents of the samples. The method of dry ashing- acid dissolution was implemented. The results concluded that crude oil samples of the Kurdistan region have low metal contents. We are 95% confident that there is strong evidence to reject null hypothesis and there is no relationship between chromium, iron and lead.

5. Recommendation

In the recent years, significant development has been achieved in Kurdistan region and this leads to the region to depend only on the oil. Dealing with oil either exporting or importing to any country is the most effective way to pollute the environment. This prosperous region has owned numerous amounts of natural gas and crude oils. The Oil industry has referred to series of operation from exploring to marketing via pipeline and tankers. These oil industries are a source of toxic gas and those which carries sulfur which is the main factor of cancer and disease. Of course, the environmental issue could be considered very well. Social awareness has enabled people to protect themselves from those areas that oil companies are busy with oil operations especially those company which refined the crude oils into its products. New technology has invented modern equipment and interested much more in determining trace metals in crude oils. However, those oil companies which are currently working in Kurdistan region should import and apply that equipment which is less harmful to environment because excessive remaining of oil industries in one place has a serious influence on the civilian. Kurdistan Regional Government should provide the oil companies an outline regarding oil operation in Kurdistan region and the way that could be acceptable for people.

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