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**“CORRELATION BETWEEN TRACE METALS OF CRUDE OILS  
WITH SULFUR AND API IN MAYSAN PROVINCE SOUTHERN  
IRAQ”**



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## Abstract

The present study aimed to estimate the trace metal constituents of crude oils in Amara city, south Iraq and correlation of it with sulfur and API . Four oil fields (Amara field, Halfaya field, Noor field, and Abogarab field ) were involved for the investigation of the API, sulfur content and metals Mn, Cu, Zn, Pb ,Ni, Fe, Co V, and Cr in crude oil. Samples analysed by using Atomic Absorption spectrophotometer (PgAA500). The results showed that the concentration of Mn ranged between ( 1384.1 to 1396.6) ppm , Cu ( 6.9 to 126.9 ) ppm, Zn ( 10.6 to 62.6) ppm , Ni ( 17.1 to 29.2 )ppm, Fe ( 14 to 31.27) ppm, Co (10.8 to 15.6)ppm , V ( 1.81 to 2.97) ppm , Pb (62 to 87.5 ) ppm. The results also showed that there are different relationship between trace metals and sulfur content and API. The current study concluded that the most abundant trace metals in crude oils samples were S, Mn, Cu , Pb, Zn, Ni, Fe, Co, and V.

## 1. Introduction

Qualitative and quantitative determination of trace element contents of crude oil is important in petroleum exploration. Trace element contents will enable prediction of the crude oil origin, maturity, migration and type or family [1]. Depending on their densities, these elements can be classified as light or heavy. Elements with densities greater than ( $5\text{g/cm}^3$ ) are heavy elements while those with densities less than ( $5\text{g/cm}^3$ ) are light elements [2]. The physical forms in which metals may exist in crude oils include true solutions of organo-metallic substances, suspended solid particles in highly divided form and colloidal or emulsified dispersions of minute bodies containing metal compounds or complexes. The form of chemical combination of a metal as it occurs in oils may be classified essentially as organic or inorganic. Inorganic forms include oxides, sulphates, carbonates, chlorides and phosphates, whereas organic forms include metal soaps and chelatetype organometallic complexes. Mostly V and Ni are found to be present in the crudes as the porphyrin complexes [3].Crude oil contains mainly hydrocarbons especially alkanes, naphthenes and aromatics. In addition to contains also some nitrogen, oxygen and sulphur containing compound along with trace amount of elements especially nickel, vanadium, iron, etc[4].However, the trace metals generally are found in concentrations 1 to over 1000 ppm[5,6]. Trace metal content in crude oil can be estimate by different techniques, atomic absorption spectrometry and related techniques have been used to analyses trace elements in crude oils [7, 8, and 9]. On the other hand the knowledge of the concentration ratio between V and Ni in crude oil provides

powerful geological information allowing oil-oil and oil-rock correlation and evaluation of the environmental conditions of sedimentation. Other metals, such as Fe, Cu and Zn, may also be present in significant amounts. [10, 11, 12, 13]. Sulfur content and the American Petroleum Institute (API) gravity are two properties which have the greatest influence on the value of the crude oil. Crude oils with higher sulfur content generally require more expensive processing than those with lower sulfur content. Many paper found that there are low concentrations presents in crude oil and the results varying from one paper to another, according to the place of study [14, 15,16,17,18, 19].In this context, the aim of this study are to investigate the trace metals crude oils in Amara city Maysan province.

## **2. Materials and Methods**

### **2.1 Crude oil Samples**

Twelve crude oil samples were collected from different wells in four producing fields, Noor field, Amara field, Halfaya field and Abogarab field in Maysan province south of Iraq.

### **2.2 API gravity Calculation**

Crude oil samples can be classified as light, (if the API is greater than 31.1), medium (Between 22.3 and 31.1) and heavy (if the API is less than 22.3). API is a specific gravity scale developed by the American Petroleum Institute for measuring the relative density of various petroleum liquids. It is defined as [20]:

$$API = \frac{141.5}{\rho} - 131.5$$

Where  $\rho$  is the density of crude oil in (g/cm<sup>3</sup>) at temperature T =15.6° C and at atmospheric pressure.

### **2.3 Sample Preparation Analysis**

The determination of the metals in crude oil requires pretreatment to the samples before presentation to the instrument [21]. The samples crude oil was digested in wet as seen in [22].

### **2.4 Trace metal and sulfur content analysis**

Nine trace metal and sulfur content in crude oil samples were measured by using Atomic Absorption Spectrometer (PgAA500) in Basra University Marine Science Centre

### 3. Results and Discussion

#### 3.1 API gravity and sulfur content

The results showed as seen in table 1 that oils have API gravity in the range (13.5–30.2). They can be classified in the range of heavy to medium oils. The heaviest sample were found in the Amara mishrif reservoirs with (13.5- 21.8) API, Abogarab mishrif reservoirs with (19.3- 21) API, Noor mishrif reservoirs with (20.8- 21.4) API, and Halfaya mishrif reservoirs with (9.0-15.2) API in (HF2-HF6), while medium sample were found in the Halfaya mishrif reservoirs with (30.2) API in (HF8) well, also Table 1 shows that all the oils are sulfur rich, ranging from (473.5 to 855.25 ) ppm or (6.42 to 11.59)% . These value of sulfur are higher than value reported by Thamer Khazal Al-Ameri [23]. API gravity as seen in figures 1- 4 have an inverse relationship with sulfur contents of crude oil. The sulfur content can be used as a source indicator, as oil of marine origin has more than 0.5% sulfur content, the high sulfur content is derived from carbonate source rocks, and oil derived from clastic source rock are typically low in sulfur [23].

**Table 1 show the characteristic of crude oil in maysan province**

field	Name of Wells	Density AT T.C g/cm <sup>3</sup>	Density AT 15 C <sup>o</sup> g/cm <sup>3</sup>	API Gravity	Sulfur concentration ppm	Sulfur concentration %
Amara	AM-4	0.911	0.9224	21.8	853.9	11.59
	AM-6	0.925	0.937	19.4	855.25	11.61
	AM-7	0.964	0.9753	13.5	854.4	11.59
Abogarab	AG-1	0.917	0.9303	20.5	622	8.44
	AG-12	0.925	0.9380	19.3	621.7	8.44
	AG-18	0.916	0.9274	21	621.3	8.43
Noor	Nr-1	0.918	0.9275	21	505.37	6.86
	Nr-2	0.912	0.9234	21.4	505.2	6.85
	Nr-4	0.917	0.9248	20.8	504.6	6.85
Halfaya	HF-2	0.988	0.9999	9.9	474.27	6.43
	HF-6	0.950	0.9638	15.2	474.1	6.43
	HF-8	0.862	0.8749	30.2	473.5	6.42

**Fig.1 relationship between API gravity and sulfur content for crude oil samples from maysan province south of Iraq**

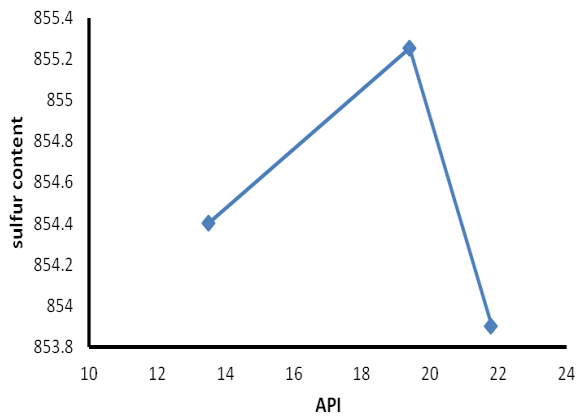


Fig 1 Correlation of sulfur content with API in Amara field

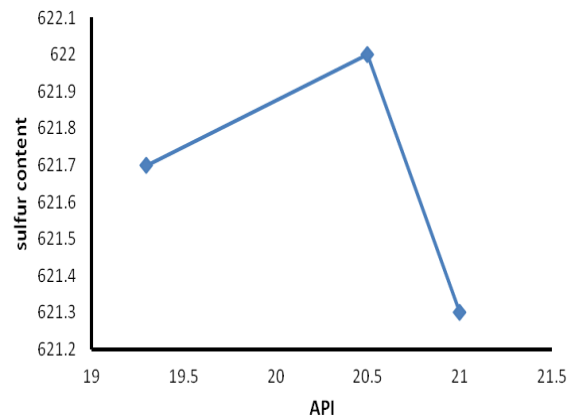


Fig 2 Correlation of sulfur content with API in Abogarab Field

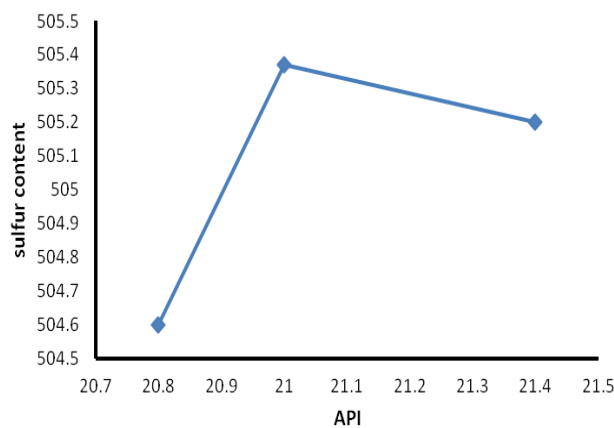


Fig 3 Correlation of sulfur content with API in Amara field

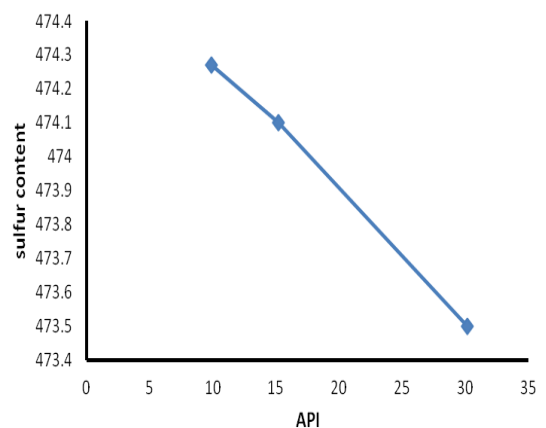


Fig 4 Correlation of sulfur content with API in Abogarab

### 3.2 Correlations of trace metal with API

There are correlations between trace metals and API content (figures 9-12) observed in the four fields involved in the current study and the results showed that Mn, Cu, Zn, Pb, Ni, Fe, Co and V decrease as the API increase except Mn content increase as the API content increase in Noor field. These correlations could be according to type of wells and position because their effects on crude oils are usually opposite these results reports that light crude oil samples usually contain relatively low trace metal contents [26].

### 3.3 Correlations of trace metal with sulfur content

Correlation between trace metal and sulfur contents were considered as shown in Figure 5-8 and we found that Cu, Pb, Ni, and V increase as the sulfur content increased while Mn, Zn, Fe and Co found to decrease as the sulfur content increase. These correlations could be explained by chemical properties of these trace metals and tendency with sulfur in crude oil. The high correlation of some trace metal with sulfur means these metals are generally associated with organic substances and sulfates in crude oil [25].

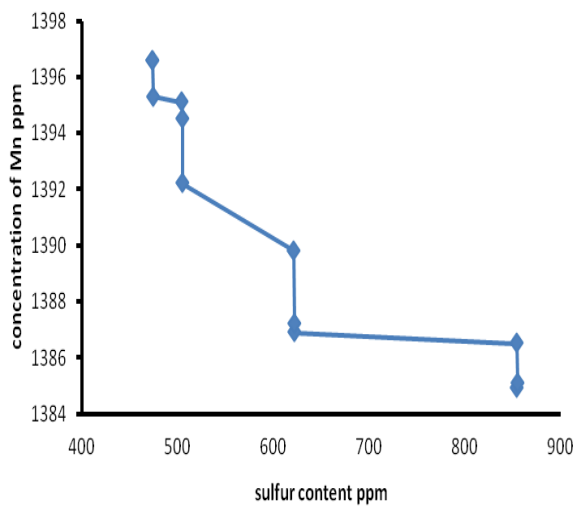


Fig 5 shown concentration of Mn metal with sulfur content

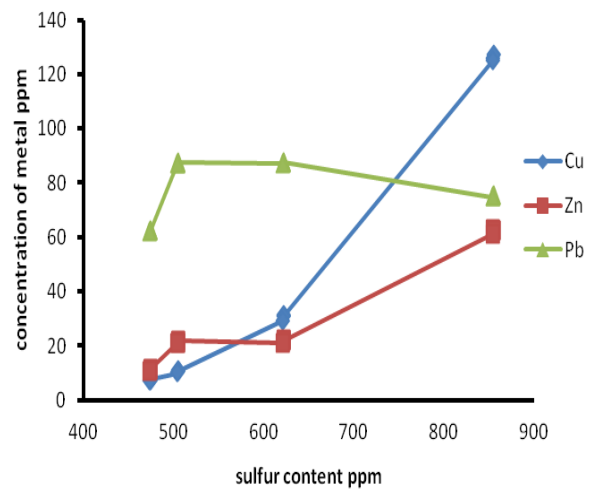


Fig 6 shown concentration of Cu, Zn, Pb metal with sulfur content

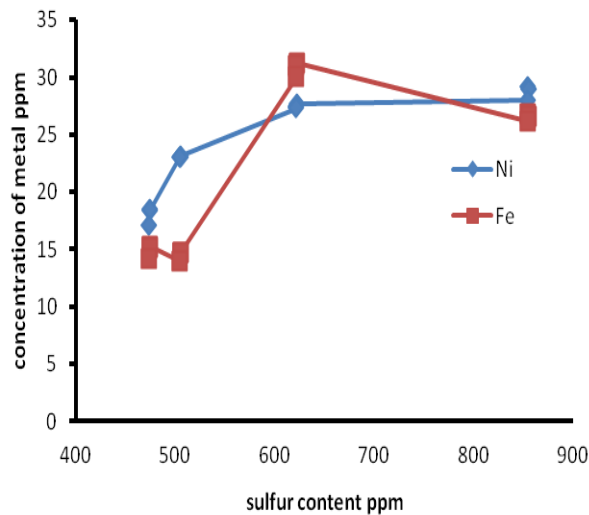


Fig 7 shown concentration of Ni, Fe metal with sulfur content

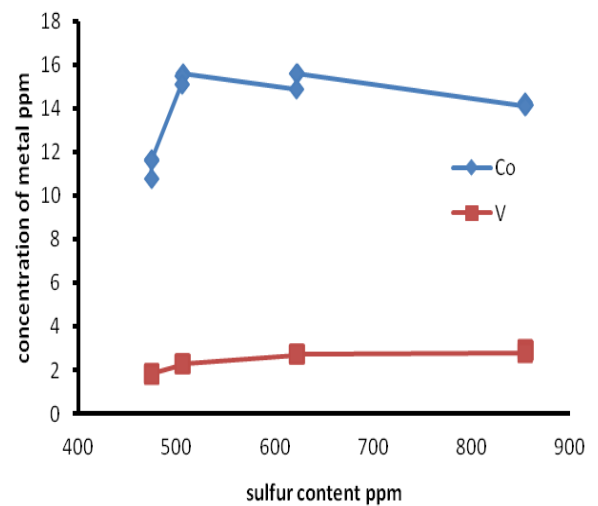


Fig 8 shown concentration of Co, V metal with sulfur

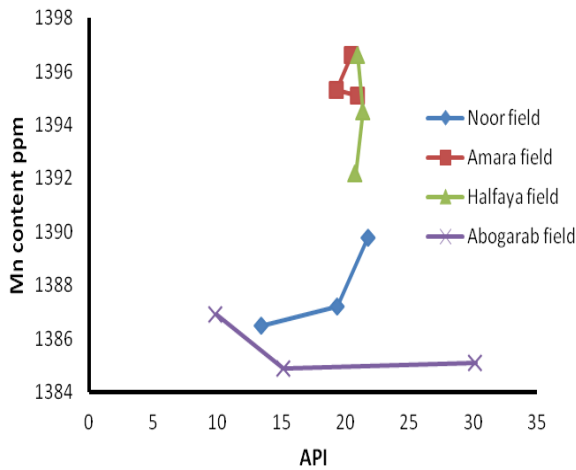


Fig 9 shown concentration of Mn metal with sulfur content

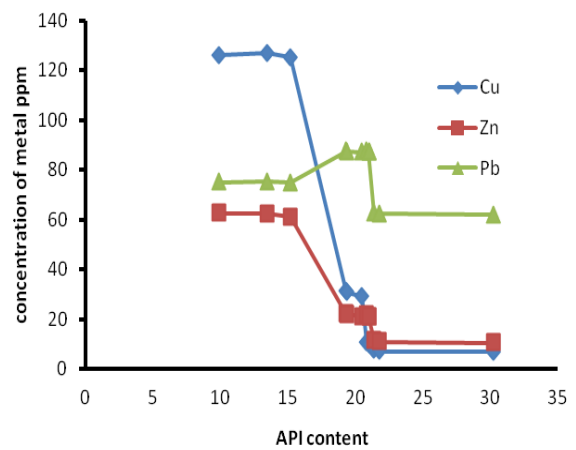


Fig 10 shown concentration of Cu, Zn, Pb metal with sulfur content

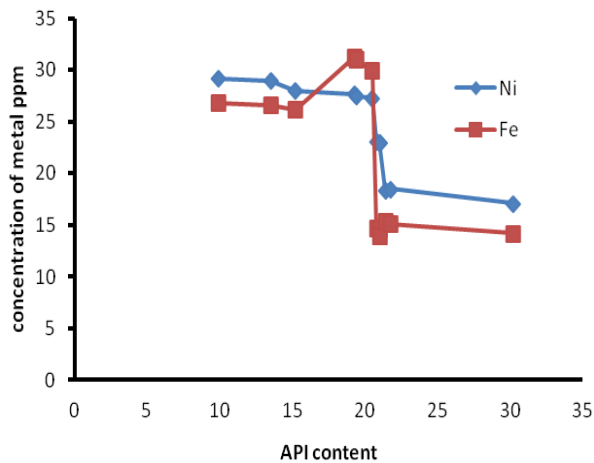


Fig 11 shown concentration of Mn metal with sulfur content

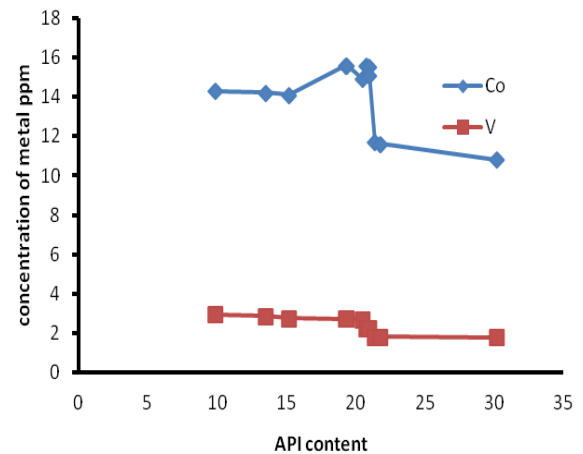


Fig 12 shown concentration of Cu, Zn, Pb metal with sulfur content

### 3.4 Trace metal content

According to the four fields involved in this study, the results showed that the most abundant metals in Amara field was Mn followed by Pb, Fe, Cu, Ni, Zn, Co, and V, While in Halfaya field was Mn followed by Pb, Ni, Zn, Co Fe, Cu, and V, moreover, in Noor field, Abogarab field the most abundant metals are Mn followed by Cu, Pb, Zn, Ni, Fe, Co, and V and Mn followed by Pb, Ni, Fe, Co, Zn, Cu, and V respectively, more details seen in table 2. These values are higher than the value which was reported by [15, 24, 25]. Generally the results of trace metal could be explained by due to the contact of crude oil with rocks contained this metal and the distribution of the metals is fairly homogenous in the samples with different well that shown in figures 1-4. This may be related to the difference in geological activity and mineral accumulation during rock deposition. The relatively higher levels of Mn, Cu, Pb, Zn,

Ni, Fe, Co, and V observed in the result except Cr should be because these are metals commonly associated with crude oil samples, and due to different proportions of the various molecular types, sizes of hydrocarbons and other elemental constituents in the crude mix [27]. Furthermore, most soils associated with the areas where crude oil is found in South of Iraq are also associated with appreciable deposits of metal ores such as iron [26].

**Table 2 concentrations of the trace metals associated with Crude Oil in Different Fields.**

Field Oil	well	Mn	Cu	Pb	Zn	Ni	Fe	Co	V	Cr
<b>Amara field</b>	AM-4	1396.6	31.1	87.5	22.1	27.7	31.27	15.6	2.75	0
	AM-6	1395.3	30.8	87.3	21.9	27.5	31	15.6	2.73	0
	AM-7	1395.1	29.1	87	21	27.3	30	14.9	2.71	0
<b>Halfaya field</b>	HF-2	1396.6	10.79	87.5	21.8	23.1	14.7	15.6	2.28	0
	HF-6	1394.5	10.6	87	20.8	23	14.7	15.5	2.27	0
	HF-8	1392.2	9.9	87	21	23	14	15.1	2.27	0
<b>Noor field</b>	Nr-1	1389.8	126	75	62.6	29.2	26.8	14.3	2.97	0
	Nr-2	1387.2	126.9	75.3	62.3	29	26.6	14.2	2.88	0
	Nr-4	1386.5	125	74.8	61	28	26.2	14.1	2.78	0
<b>Abogarab field</b>	AG-1	1386.9	7.6	62.5	11.5	18.4	15.3	11.7	1.83	0
	AG-12	1384.9	7.1	62.4	10.9	18.5	15.1	11.6	1.82	0
	AG-18	1385.1	6.9	62	10.6	17.1	14.2	10.8	1.81	0

#### 4. Conclusions

The results concluded that crude oil sample obtained from Maysan province south of Iraq have API that classified in the ranged of heavy to medium oil samples and contain high level of sulfur. There are different correlations between trace metals and sulfur content, API. The API gravity of crude oil has negative correlations with sulfur content. The study concluded that trace metals have a correlations with API and sulfur content as different also the crude oil in Amara field, have the most abundant trace metal followed by Halfaya field, Noor field and Abogarab field contain trace amount of S, Mn, Cu, Pb, Zn, Ni, Fe, Co, and V and no induction of Cr.

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