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The risks of increment of concentrations of sulfur compounds in Iraqi crude oil, gasoline and kerosene

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***Abstract*---**Estimating the concentration of sulphur compounds in crude oil and its products such as gasoline and kerosene is necessary because of environmental legislation and determinants developed by government organizations regulating sulphur levels in oil and its derivatives. Sulphur compounds found in crude oil and its products are a major problem, causing many environmental and health risks as a result of the use of gasoline as fuel for cars and kerosene as fuel for household heaters, resulting in the emission of these compounds in the form of oxides, affecting the environment and health. This study was conducted to estimate the concentration of sulphur compounds in crude oil and distillation products represented by gasoline and kerosene and to show how different the concentration of sulphur compounds in crude oil is than in gasoline and kerosene. In this study, gas chromatography technology was used. This method applies to distillation products, gasoline fuel, kerosene and other petroleum liquids. This study was conducted in basra oil company's quality control laboratories to estimate the concentration of sulphur compounds in crude oil, gasoline and kerosene.

***Keywords*---**health, sulfur compounds, fuel, environment, pollution.

1 Introduction

Crude oil is a complex compositional material consisting mainly of a combination of various hydrocarbons, and the demand for crude oil products has increased significantly in the market. The consumption of these products, especially gasoline, white oil, gas oil, aircraft fuel, and others, has been increasing significantly in the market, with total crude oil consumption exceeding 70% in

2000, so it was necessary to produce distillers as efficiently as gasoline.The presence of sulfur compounds in crude oil has a negative impact on the quality of petroleum products in addition to the damage they cause, as sulfur compounds lead to pollution of the environment through air pollution with oxides resulting from combustion made up of sulfur dioxides, which are later oxidized to trioxide sulfur, and this leads to many diseases after inhalation of air, such as asthma and shortness of breath. In addition to contaminating the soil with acid substances, as well as shortening the work of machines where it interacts with metal surfaces and leads to the eating of pipes, machinery, and equipment, in addition to bad smell. The presence of sulfur compounds in crude oil is also undesirable, reducing the extent to which gasoline responds to octane and leading to co-poisoning, resulting in ineffectiveness.. (Abdul Halim, et al., 2007)Sulfur compounds are recommended to be removed in the refining process because they cause disruption of catalysts used in crude oil processing and corrosion problems in pipelines, along with pumping and refining equipment. From an environmental point of view, the presence of sulfur in fuel causes the emission of toxic gases that interact with water and cause acid rain. Thus, these gases or acid products can damage buildings and other materials. Therefore, there is a need to determine the amount of sulfur in the oil and methods of desulfurization. It should be noted that estimating the value of refining from crude oil requires a full description of crude oil and its components, involving dozens of characteristics.. (Stumpf et al. 1998) suggest that knowledge of Sulphur compounds is important for the speed of classification and comparison of raw oils.

Sulfur compounds are found in various forms, such as hydrogen sulfide, sulfide, sulphur dioxide, mercaptan, theophin, benzothyophen, and bi-benzothyophen. Stumpf, (Bolin et al., 2016; Lababidi et al., 2013; Zeng et al., 2006; Mahe et al., 2011).These Sulphur compounds are considered harmful to the treatment units in the refinery due to catalytic toxins and cause plant erosion and atmospheric pollution (de Jong,et al,2007) .Environmental agencies reduce the maximum allowable Sulphur content in oil products around the world (EPA,2014), and Sulphur compounds in automotive fuel contribute significantly to air quality degradation leading to acid rain. (Selvavathi, et al., 2008), the presence of Sulphur compounds in transport fuel is environmentally undesirable. Corrosion, sediment formation, air pollution, and it is recommended to know their chemical structure and nature to remove these Sulphur compounds from engine fuel during an appropriate refining process (Andari,et al,1996).

2 Materials and Methods

The samples were taken from the Muthanna refinery in southern Iraq, which is part of the Central Refineries Company and includes a sample of crude oil taken from the strategic line, which runs from southern Iraq to the north and feeds all refineries of crude oil, which is supplied with crude oil from most Iraqi fields, and a sample of gasoline and kerosene for the same refinery Highly pure chemicals were used from different global origins, and the table below shows the materials used in the research.

Table 1 Materials and standards

NO	Substance (CAS Number)	Formula	Concentration(mg/kg)	Uncertainty
1-	Ethane thiol (75-08-1)	CH3 CH3 SH	104	9.3
2-	Carbon disulfide (75-15-0)	CS3	20.1	1.80
3-	2-Propanethiol(75-15-0)	(CH3) 3 CHSH	100	8.9
4-	Tert-Butyl mercaptan(75-66-1)	C4-H10-S	50.5	4.51
5-	1-Propanethiol(107-03-9)	CH3 (CH3) 3 SH	102	9.1
6-	2-Butanethiol(513-53-1)	CH3 CH3 CH(SH)CH3	50.0	4.46
7-	2-Methyl-1-propanethiol(513-44-0)	(CH3) 3 CHCH3 SH	100	8.9
8-	1- Butane thiol(109-79-5)	C4H10S	50.1	4.47
9-	Dimethyl sulfide(75-18-3)	(CH3) 3 S	99.9	8.92
10-	Ethyl methyl sulfide(624-89-5)	CH3 CH3 SCH3	50.8	4.54
11-	Thiophene (110-02-1)	C4 H4 S	100	8.9
12-	Diethyl sulfide(352-93-2)	CH3 CH3 SCH3 CH3	74.5	6.65
13-	Dimethyl disulfi de	CH3 SSCH3	20.6	1.87
14-	2-Methylthiophene(554-14-3)	C5 H6 S	74.8	6.88
15-	3-Methylthiophene(616-44-4	C5 H6 S	99.6	6.89
16-	Diethyl disulfide (110-81-6)	(C3 H5) 2 S3	20.2	1.83
17-	Benzothiophene(95-15-8)	C_8H_6S	75.0	6.70
18-	3Methylbenzothiophene(1455-18-1)	C9 H8 S	100	8.9

A two-dimensional gas chromatograph system (GCxGC) was used to analyze and identify the sulfur species in three distilled fractions. The Comprehensive GCxGC system from Agilent, model number 7890 GC, with ZX2 – Closed Cycle Refrigerated Jet Cooled Loop Thermal.

Gas Chromatograph Agilent 7890A, A gas chromatograph is a chemical analysis instrument for separating chemicals in a complex sample. A gas chromatograph uses a flow-through narrow tube known as the column, through which different chemical constituents of a sample pass in a gas stream (carrier gas) at different rates depending on their various chemical and physical properties and their interaction with a specific column filling called the stationary phase. As the chemicals exit the end of the column, they are detected and identified electronically. The function of the stationary phase in the column is to separate different components, causing each one to exit the column at a different time. Other parameters that can be used to alter the order or time of retention are the carrier gas flow rate, column length, and temperature.

Typical Operating Conditions:
Column—30 m by 0.32 mm inside diameter fused
silica wall coated open tube (WCOT) column, 4 μm thick film
of methyl silicone.
Sample size—0.1 μL to 2.0 μL
.Injector—Temperature 275 °C; Split ratio: 10:1
10 % to column.(
Column Oven—10 °C for 3 min, 10 °C ⁄min to
250° C, hold as required.
Carrier Gas—Helium, Head pressure: 70 kPa to
kPa (10 psig to 13 psig)
Detector—Sulfur chemiluminescence detector

The sample is analyzed by gas chromatography with an appropriate sulfur selective detector. Calibration is achieved by the use of an appropriate internal or external standard. All sulfur compounds are assumed to produce an equivalent response as sulfur.As sulfur compounds elute from the gas chromatographic column, they are quantified by a sulfur selective detector that produces a linear and equimolar response to sulfur compounds; for example, a sulfur chemiluminescence detector or an atomic emission detector used in the sulfur channel

3. Results

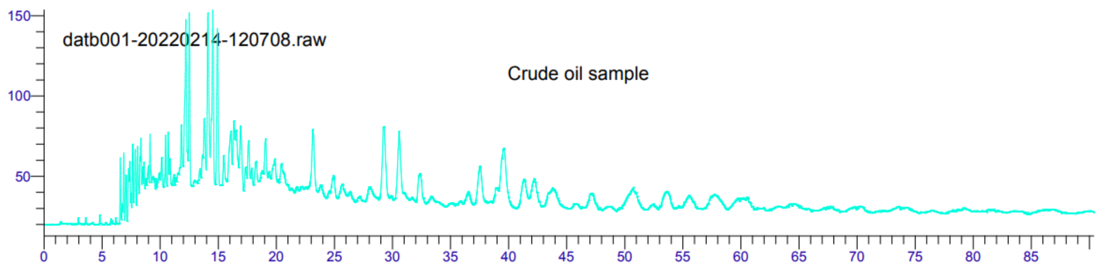
A comprehensive GC-GC system with a non-polar column followed by a polar column was used to perform the molecular analysis of distillates. The use of two columns led to a significant increase in chromatographic separation peak capacity, with the first dimension separation (non-polar column) based on hydrocarbon molecular size (i.e., melting temperature) and the second dimension separation (polar column) based on n polarity (i.e., chemical groups). The system's operating conditions were optimized using the methods outlined by(Mostafa et al., 2012).to achieve the best chromatographic separation feasible in both dimensions of the chromatogram. To make the analytical templates, standard sulfur and hydrocarbon materials were injected one at a time. The equimolar response of each detector was measured using multi-level concentration standard injections.

Table 2 Results of injection of the crude oil sample of Muthanna refinery (strategic line)

crude oil sample

Peak #	Component Name	Time [min]	Area [uV*sec]	Concentration ppmv
10	Ethanethiol	2.960	19540.44	4.0034
12	Crbon disulfide	3.414	883.39	0.0957
13	2-Propanethiol	3.591	18343.36	4.1551
15	2-Methyl-2.-propanet	4.020	4024.43	1.0712
16	Ethyl mythel sulfide	4.173	5100.49	1.0840
19	Thiophene	4.809	26073.62	5.7727
20	2-Methyl-1-propaneth	4.924	1341.20	0.3686
22	diethyl sulfide	5.142	439.90	0.1082
23	1-Butanethiol	5.278	882.10	0.2423
24	Dimethyl disulfide	5.453	629.10	0.0757
26	2-methyl thiophene+3	5.853	11542.53	2.0835
32	Diethyl disulfide	7.078	197693.71	22.6263
46	Benzo thiophene	9.319	101089.68	28.6110
52	3-methyl benzo thiop	10.481	499836.77	149.9226
			887420.73	220.2202

Figure (1) shows the chromogram model of the crude oil sample of the Muthanna refinery (strategic line tube) that stimulates the tops of Sulphur compounds to appear clearly within the sample studied .



Gasoline sample

Peak #	Component Name	Time [min]	Area [uV*sec]	Concentration ppmv
8	Ethanethiol	2.934	122091.42	25.0136
9	dimethyl sulfide	3.127	7622.82	1.4428
10	Crbon disulfide	3.424	5207.54	0.5639
11	2-Propanethiol	3.570	131978.68	29.8953
13	2-Methyl-2.-propanet	4.004	27747.07	7.3857
14	1-prppanethiol	4.155	41663.30	10.0349
17	Thiophene	4.794	264036.67	58.4582
19	diethyl sulfide	5.116	2648.58	0.6515
20	1-Butanethiol	5.323	56462.59	15.5118
22	Dimethyl disulfide	5.571	6708.81	0.8074
25	2-methyl thiophene+3	5.920	60263.33	10.8780
32	Diethyl disulfide	7.059	1028489.83	117.7117
47	Benzo thiophene	9.357	305462.15	86.4536
53	3-methyl benzo thiop	10.539	35445.00	10.6315
			2095827.78	375.4399

Figure 2 shows the chromogram model of the gasoline sample (Muthanna refinery) that induces the tops of sulphur compounds to appear clearly within the sample studied.

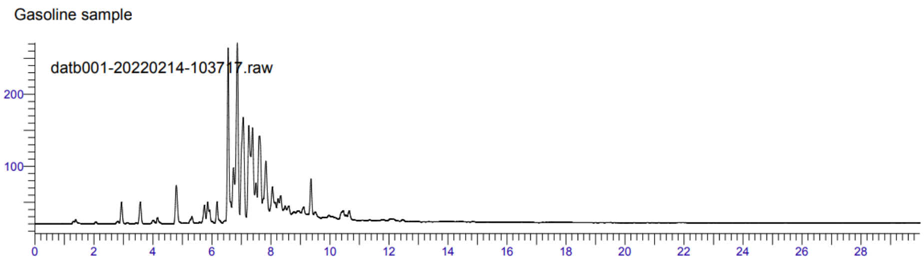
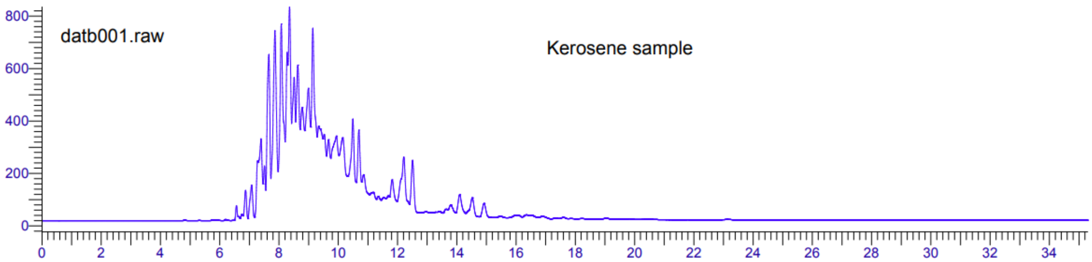


Table 4 shows the results of the injection of the kerosene sample

Kerosene sample

Peak #	Component Name	Time [min]	Area [uV*sec]	Concentration ppmv
9	Ethanethiol	2.957	766.12	0.1570
10	dimethyl sulfide	3.131	170.20	0.0322
11	2-Propanethiol	3.582	1989.29	0.4506
12	2-Methyl-2.-propanet	3.917	268.93	0.0716
13	Ethyl mythel sulfide	4.167	846.36	0.1799
15	Thiophene	4.809	13547.57	2.9995
16	1-Butanethiol	5.279	591.76	0.1626
18	Dimethyl disulfide	5.583	1004.01	0.1208
21	2-methyl thiophene+3	5.929	7797.86	1.4076
28	Diethyl disulfide	7.077	894596.04	102.3875
42	Benzo thiophene	9.339	3920910.32	1109.7179
47	3-methyl benzo thiop	10.494	3974338.21	1192.0754
			8816826.67	2409.7625

Figure 3 shows the chromogram model of the kerosene sample (Muthanna refinery) that induces the tops of Sulphur compounds to appear clearly within the sample studied.



The results of the injection of these samples into the kermatography device with vertical vacuum injection technology showed a group of sulfur compounds, and the highest concentration of sulfur compounds was recorded in (3-methyl benzo thiop) with a concentration of (ppmv149.9226), while the lowest concentration in the same sample was recorded for dimethyl disulfide) with a concentration of (0.0757 ppmv.)

Mercaptans or thoil are considered to be one of the most reactive sulfur species, and therefore the most corrosive. Its focus depends heavily on crude oil and boiling point range. Experiments have shown that mercaptan is the most interactive somewhere between 235°C and 300°C where it can accelerate sulphide. Thus, particularly medium distillation rings, are prone to mercaptan corrosion. The minimum concentration of mercaptan was found to be between

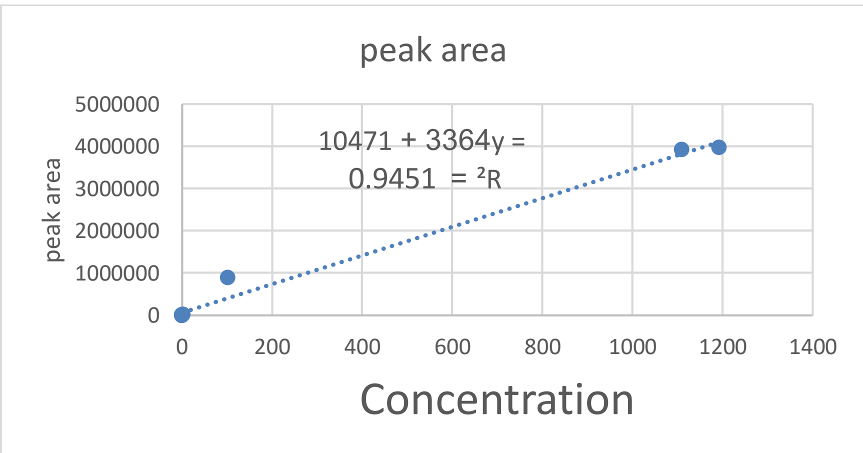
100 parts In addition, it was pointed out that corrosion rates depend on the Type of Mercaptan and that mirkaptan begins to decompose at temperatures ranging from 300°C to 400°C. (EPA, 2014) Any highly toxic, corrosive and unpleasant compounds with adverse effects on animal and human health as well as the environment (Kelly, 2010)

Table 5: Shows the average, contrast and standard deviation of the crude oil sample and the area of peaks in muthanna refinery (strategic line)

Sample No	sulfur compounds	Concentration	Area
1	Ethanethiol	4.0034	19540.44
2	Crbon disulfide	0.0957	883.39
3	2-Propanethiol	4.1551	18343.36
4	2-Methyl-2.-propanet	1.0712	4024.43
5	Ethyl mythel sulfide	1.084	5100.49
6	Thiophene	5.7727	26073.62
7	2-Methyl-1-propaneth	0.3686	1341.2
8	diethyl sulfide	0.1082	439.9
9	1-Butanethiol	0.2423	882.1
10	Dimethyl disulfide	0.0757	629.1
11	2-methyl thiophene+3	2.0835	11542.53
12	Diethyl disulfide	22.6263	197693.71
13	Benzo thiophene	28.611	101089.68
	3-methyl benzo thiop	149.9226	499836.77
	Mean	15.73002143	63387.19429
	SD	39.62978244	132143.0887

Table 6 standard deviation is greater than average.

Figure 4 shows the graph representing the relationship between the concentrations and the areas of the approved peaks and the equation of linear regression approval.



We're singing through the value of the link coefficient R2 =0.9451 There is a linear correlation between the concentrations and the areas of the peaks

4. Discussions

Sulfur is found in crude oil and petroleum derivatives in the form of heterogeneous ring compounds such as thiophen or in the form of different compounds: Mercaptan, hydrogen sulfide, sulfide, disulfide, and sulfur negatively affect the characteristics of crude oil and its derivatives. (Katasonova, Savonina, & Maryutina, 2021). Study of sulphur compounds in oil and petroleum products is a high priority task associated with increased compliance with fuel quality control standards and the negative impact of sulfur on the processing and storage of crude oil and environmental safety. (Katasonova, Savoina, & Maryutina, 2021)Seeking to remove sulphur compounds from crude oil and its derivatives for the purpose of complying with sulphur content specifications and reducing sulphur content in crude oil and its derivatives (Kitashov, Nazarov, Zorya, & Muradov, 2019), Sulfur compounds, found in large quantities in crude oil and its derivatives such as gasoline and kerosene, cause many negative effects, including pollution, reduced engine efficiency, and severe corrosion of pipelines, reactors, and equipment, as well as poisoning from catalysts. Thus, strict environmental rules and restrictions are put in place to maintain the amount of sulfur (Saleh, 2022). Sulfur affects fuel quality, and the burning of sulfur-containing fuels causes harmful effects on humans and the environment (Abdurrashid, Merican, & Musa, 2022).

The results of our study, which is the first study looking at the concentration of sulfur compounds in Iraqi crude oil, kerosene and gasoline, showed that some common compounds that were detected and measured within high-performance chromatography technology vary in concentrations depending on the product and the different locations from which samples were taken by three duplicates of your sample. Some vehicles have also shown a decrease in their concentrations in crude oil and high concentrations in kerosene and gasoline, and we are likely to cause chemical operations in some refineries from refining operations that depend mainly on the process of separating crude oil through extreme heat and pressure. The presence of these compounds in high proportions affects the quality of petroleum products due to the high sulfur content, which leads to environmental and health effects. The presence of Sulphur compounds in fuel should be reduced because of their high toxicity. The presence of Sulphur compounds in fuel causes air pollution and lung disease (Aghaei & Sobati, 2022). One of the most important problems in the oil industry is the presence of sulphur and sulphur compounds in crude oil. Sulfur compounds found in crude oil can have adverse effects on the environment, equipment, catalysts, and finished products (Mousavi-Kamazani, Siahmansouri, & Ghodrati, 2021).

5. Conclusion

This study showed that the use of the Agilent 7890A Gas Chromatograph to estimate the concentration of sulfur compounds in crude oil and petroleum derivatives is a good and reliable method within the American Association under the standard (ASTM D5623), where the results showed an urgent increase in the concentration of sulfur compounds in Iraqi crude oil. For several reasons, including the nature of Iraqi crude oil loaded with sulphur compounds, the other reason is to rely on the old method of refining crude oil, especially in the process of producing gasoline, where gasoline is produced by mixing the product of jet with high octane gasoline (95), which is supplied from outside Iraq and not adhering to the specified ratios of mixing processes, and as Iraq refineries lack gasoline grade units, all these reasons lead to harmful effects resulting from these vehicles and affecting the environment. The combustion of sulfur in gasoline used as fuel for cars, or kerosene used as fuel for heaters or furnaces, and causes acid rain, which combines with water in the atmosphere and causes acid rain, which affects buildings and plants and affects public health.Combustion caused by the use of kerosene in the heater also leads to several diseases such as asthma, shortness of breath, and other diseases as a result of high sulfur compound concentrations containing kerosene.

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