

## Analytical-Comparative Study of Iraqi and American Light Oil Components by Gas Chromatography-Mass Spectrometry

F.A.Hassan<sup>\*</sup>, K.I. Hussain<sup>\*\*</sup> and N.A.Alassaf<sup>\*\*1</sup>

<sup>\*</sup>Ministry of Science & Technology, Chemical and Petrochemical Research Directorate.

<sup>\*\*</sup>Department of Chemistry, College of Education–Ibn Al-Haitham, University of Baghdad.

<sup>1</sup>E-mail: nahlahd@yahoo.com.

### Abstract

The analysis of Iraqi light oil (light naphtha) by capillary gas chromatography-mass spectrometry (GC-MS) was performed by the injection of whole naphtha sample without use of solvents. Qualitative analysis and the identification of the hydrocarbon constituents of light naphtha was performed and comparison had been done with American light oil (light naphtha). The obtained results showed a major difference between the two light naphthas.

Keywords: Light Naphtha, GC-MS.

### Introduction

Naphtha or full range naphtha is defined as a liquid petroleum product or the fraction of hydrocarbons in petroleum that boils from about 30°C (86°F) to approximately 200°C (392°F), (1,2). It consists of a complex mixture of hydrocarbon molecules generally having between 5 and 12 carbon atoms. It typically constitutes 15–30% of crude oil, by weight.

*Light naphtha* is the fraction boiling between 30°C and 90°C and consists of molecules with 5–6 carbon atoms. *Heavy naphtha* boils between 90°C and 200°C and consists of molecules with 6–12 carbons (3).

The physical properties of naphtha depend on the hydrocarbon types present, in general the aromatic hydrocarbons having the highest solvent power and the straight-chain aliphatic compounds the lowest (4).

Gas chromatography (GC) has become a primary technique for determining hydrocarbon impurities in individual aromatic hydrocarbons and the composition of mixed aromatic hydrocarbons (4). Chemical separations in connection with chromatography, multiple columns and reaction gas chromatography have all been used and boiling range determinations by either distillation (5) or gas chromatographic simulated distillation (6).

Capillary chromatography and the availability of data acquisition system facilitate the analysis of hydrocarbon mixtures and the successes of this approach have been

demonstrated by Varian Company with gasoline and distillate fractions. The approach is refined by the use of capillary gas chromatography-mass spectrometry (GC-MS), and this has been demonstrated for various hydrocarbon mixtures (7).

Detailed analysis of distillate fractions of Iraqi oil by capillary GC-MS has not been reported previously. This work presents the results obtained from a detailed analysis of light naphtha which contain a high concentration of low-molecular weight hydrocarbons (fraction boiling between 30°C to 90°C and consists of molecules with 5-6 carbon atoms). The selection of suitable operating conditions allows a good resolution of light naphtha components to be achieved.

### Experimental

The analysis results were obtained by using a Shimadzu gas chromatograph 9A and Shimadzu gas chromatograph 15A–Quadrupole mass spectrometer type QP-1000A, which interfaced to data processor and library search system for spectral data. The column used was fused-silica capillary column [50m (length)×0.2 mm (inner diameter) coated with SE-30 of thickness 0.25µm as a liquid stationary phase].

Helium gas was used as the carrier gas. The mass spectrometer was operated at electron-beam energy of 70 eV and scanning from 10 to 500 a.m.u. The Iraqi light naphtha was brought from Al-Dora refinery, where the distillate fraction process was carried out.

The GC-MS instrument was first calibrated and the high boiling perfluorotributylamine (PFTBA) with mass range up to 600 a.m.u. was used as a mass marker for calibration process.

Gas chromatographic conditions used for the analysis of light naphtha:

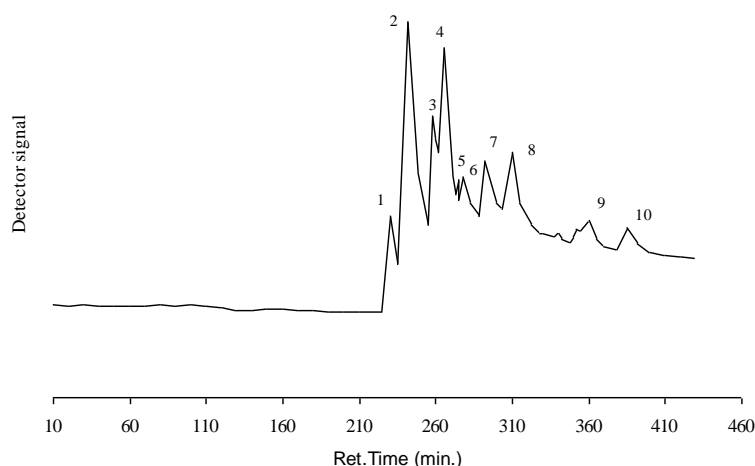
Column:  
 Dimensions: 50m×0.2mm I.D.  
 Material: Fused – silica.  
 Stationary phase: S.E.-30.  
 Film thickness: 0.25 µm  
 Column temperature:  
 Initial programmed temp: 100°C  
 Initial programmed period: 10 min.

Temp. Programmed rate: 2°C /min  
 Final programmed temp. : 250°C  
 Final programmed period: 10 min.

Carrier gas: Helium  
 Carrier gas flow-rate: 1Kg/cm  
 Injector temp. : 120 °C  
 Sample volume injected: 1µl

### Results and Discussion

The light naphtha was separated and analyzed by capillary GC with ionization detection (FID) and capillary GC-MS. Chromatogram for the studied naphtha is shown in Fig.(1), which present a total chromatogram of the sample obtained by GC-MS.



**Fig. (1) Chromatogram of IRAQI light Naphtha obtained by GC-MS.**

The hydrocarbon components identified by GC-MS through special program (library spectra) which compare the mass spectrum of the studied sample with standard mass spectra stored in the public library. This program

identified five similar mass spectra (related to the mass spectrum of the studied sample) with different similarity index. The selected hydrocarbon components are listed as peak number in Table (1).

**Table (1)**

**Analytical data from the analysis of IRAQI light-naphtha (Dora refinery) by GC-MS technique.**

Peak No	Wt %	Compound
1	7	propane
2	32	n-butane
3	0.4	iso-butane
4	24	2,2-di methyl propane
5	0.7	iso- pentane
6	0.5	n-pentane
7	12	2,2-di methyl butane
8	13	cyclopentane
9	4	2-methyl pentane
10	5	n-hexane

Fig.(1) shows that the naphtha components were partially separated, this mean that their mass spectrums were not obtained easily. Therefore, the identification of the collated components was based on the overall mass spectrum obtained. The major components of

American light Naphtha are mentioned in Table (2), according to the analysis of Poseidon crude oil (Houma station, Denver) (8).

*Table (2)  
The major components of Poseidon American light oil (light Naphtha).*

<i>Peak No</i>	<i>Wt %</i>	<i>Compound</i>
1	0.00	Propane
2	0.15	iso butane
3	1.11	n-butane
4	13.96	iso pentane
5	19.59	n-pentane
6	2.66	dimethyl butane
7	1.38	Cyclopentane
8	19.44	methyl pentane
9	19.82	n-hexane
10	6.10	methyl cyclopentane
11	1.68	Benzene
12	2.33	dimethyl pentane
13	4.70	Cyclohexane
14	4.72	methyl hexane
15	0.81	dimethyl cyclopentane

The types of the hydrocarbon group were determined from the characteristic fragmentation peaks of the mass spectra, and from the 8th peak index of mass spectra (9). Table (3) demonstrated the comparative results of Iraqi and American main constituents of light oil.

**Table (3)**  
**Comparative Results of Iraqi vs. American light Naphtha components.**

Component	Wt %	
	Iraqi	American
Propane	7.00	0.00
n-butane	32.00	1.11
isobutane	0.40	0.15
dimethyl propane	24.00	0.00
isopentane	0.70	13.96
n-pentane	0.50	19.59
dimethyl butane	12.00	2.66
cyclopentane	13.00	1.38
methyl pentane	4.00	19.44
n-hexane	5.00	19.82
methyl cyclopentane	Not detected	6.10
benzene	=	1.68
dimethyl pentane	=	2.33
cyclohexane	=	4.70
methyl hexane	=	4.72
dimethyl cyclopentane	=	0.81

The results obtained from Table (3) indicated that the Iraqi light naphtha contain a major concentration of (propane, n-butane, dimethyl propane, dimethyl butane, cyclopentane) constituents compare with American light naphtha which showed the high quantities level concentration of (isopentane, n-pentane, methyl pentane, n-hexane) with other components of branched cyclo-and aromatic of higher carbon numbers.

### Conclusion

A comparative study of Iraqi and American light Naphtha had been done using GC/MS technique. The result obtained showed a major difference of components types and their concentration percentages in addition to appear small signals of higher carbon atoms in American light oil related to their little concentration.

### References

- [1] Speight J.G, "The Chemistry and Technology of Petroleum". Marcel Dekker, New York, 3rd Edition, 1999.
- [2] Hori Y, "In: Modern Petroleum Technology". Downstream A.G. Lucas (Editor), John Wiley & Sons, New York. Volume 2 Chapter 2, 2000
- [3] Prestvic, Rune; Kjell Moljord, Knut Grande, Anders Holmen "Compositional analysis of naphtha and reformat". Catalytic naphtha reforming. USA: CRC Press. pp.2. 2004. Retrieved 2010-02-03.
- [4] James G. Speight, "Handbook of Petroleum Product Analysis", A John Wiley & Sons, Inc, Ch 4 Naphtha pp 89, 2002.
- [5] "Annual Book of ASTM Standards, D285-62". American Society for Testing and Materials, West Conshohockm, PA. 2000.
- [6] Interlaboratory study crude oil, IISOOR01, Report Summary form for Analysis (light Naphtha), R.J. Sterink, January, 2008.

- [7] Application Note, Detailed Hydrocarbon Analysis of Naphtha, Varian, Application Note SI-01285. 2008.
- [8] Poseidon oil pipeline company, LLC 620 16th street suite 308, Denver. Co 80202 (last updated on 6/8/2000).
- [9] Eight Peak Index of Mass Spectra, Vol. 1, Mass Spectrometry data centre, Aldermaston. pp 1-3; 2001.

### الخلاصة

تم استخدام عمود الفصل الشعري في فصل المكونات العضوية الأساسية للنفط العراقي الخفيف (النفثا الخفيفة) والتي تم الحصول عليها من مصفى الدورة وتشخيصها اعتمادا على تقنية الغاز كروماتوغرافي- مطياف الكتلة. تم حقن المادة الى منظومة التحليل بدون استخدام مذيب, وتم التعرف على هذه المكونات وتشخيصها, حيث اشتملت على عدة مركبات باستخدام برنامج خاص بتشخيص المركبات مخزون في ذاكرة الحاسوب المرتبط بالجهاز وتم مقارنة النتائج مع محتويات النفط الأمريكي الخفيف (النفثا) .