International Journal of Organic Chemistry, 2017, 7, 312-318
http://www.scirp.org/journal/ijoc
ISSN Online: 2161-4695
ISSN Print: 2161-4687

Direct Mass Spectroscopy Analysis and Comparison of Middle Eastern and Texas Crude Oils

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How to cite this paper: Kaya, G., Kaya, N., Amani, M., Rahman, A.H.M.J., Kolomenskii, A.A. and Schuessler, H.A. (2017) Direct Mass Spectroscopy Analysis and Comparison of Middle Eastern and Texas Crude Oils. *International Journal of Organic Chemistry*, **7**, 312-318.
https://doi.org/10.4236/ijoc.2017.74025

Received: September 28, 2017
Accepted: November 13, 2017
Published: November 16, 2017

Abstract

We analyzed two types of crude oil samples: Middle Eastern crude oil and Texas crude oil by using a residual gas analyzer (RGA) based on the linear quadrupole principle. This portable mass analyzer is capable of measuring hydrocarbons with masses of up to 300 atomic mass units (amu) as well as low mass targets, such as methane and carbon dioxide at ppm level concentrations. The generated mass spectra revealed differences in the composition and signal intensity of hydrocarbons of Middle Eastern and Texas crude oil samples. Even if RGA 300 is manufactured to be served as a detailed gas analysis of vacuum systems, we have shown that it is sensitively capable of detection of hydrocarbons and it enables one to qualitative and quantitative analysis of the composition of the crude oils.

Keywords

Oil Composition, Mass Spectrum Analysis, Hydrocarbons Content

1. Introduction

Hydrocarbon-water phase behavior and solubility at high temperature and high pressure is very complex and varies widely. Moreover, extracting crude oil from HPHT (high pressure and high temperature) reservoir zones like the Texas Woodbine-Eagle Ford, the North Sea or the Middle Eastern fields, and preserving its original condition for analysis is costly and done only rarely [1]. The next best alternative is to have sample-testing equipment at the extraction point or at the well bore. Even when such samples are not analyzed at their down-hole condition, such remotely obtained and detailed data are a prerequisite in estimating the structure and capacity of wells, and for such analysis sensitive and selective equipment is required. At the same time this equipment must be rugged, since the wide range of hydrocarbons including heavy asphaltenes are in a mixed phase with water, crude oil and drilling mud.

The present work was performed in the laboratory since the samples came from the Middle East and from Texas. As is detailed below, the mass spectrometry profiles of the samples revealed their composition differences.

As an analytical method, mass spectrometry provides qualitative and quantitative analysis of the chemical compositions of a sample investigated, and for this purpose, several types of mass spectrometers have been produced and improved to serve for various applications. In recent years, the miniaturization of mass spectrometers, for example time-of-flight spectrometers [2], ion traps [3], sector mass filters [4], and quadrupoles [5] [6], has been given much consideration, so that such a device can be portable for field applications, while showing sufficient performance. Main advantages of these recent miniaturized mass analyzers are their lower cost and power consumption and the ability to operate at higher pressures and with smaller and less expensive vacuum systems [7].

Crude oil contains a variety of organic compounds; therefore, different techniques are required for detailed analysis of crude oil samples. While the determination of volatile and non-polar components has been achieved by gas chromatography/mass spectrometry (GC/MS), the identification of trace polar components in crude oil is performed using liquid chromatography/mass spectrometry (LC/MS) [8]. Mass spectrometric ionization techniques, namely, electron impact ionization (EI) [9], field ionization (FI) [10], and field desorption (FD) [11] are sufficient for analysis of volatile and semi volatile compounds in crude oil [8]. For the analysis of the compounds with higher boiling points, producing characteristic fragments, pyrolysis/mass spectrometry (Py/MS) or pyrolysis/gas chromatography/mass spectrometry (Py/GC/MS) needs to be considered [12]. Matrix-assisted laser desorption ionization/mass spectrometry (MALDI/MS) with the capability of detecting compounds in a wide range of mass-to-charge ratios is an effective method used for crude oil analysis in vacuum environment [13]. Electrospray ionization (ESI) [14] and atmospheric pressure photoionization (APPI) [15] are the other techniques used for crude oil analysis, but they require expensive instruments and complicated sample pretreatment.

We performed hydrocarbon analysis of crude oil with mass spectrometry, introducing the sample directly to the vacuum chamber without any prior sample preparation. A vacuum environment decreases the boiling temperature of the compounds drastically, and room temperature is enough for vaporization of most components from crude oil samples, therefore the signal is observed immediately.

2. Experimental Procedure

To analyze Middle Eastern crude oil and Texas crude oil samples, which were obtained from the Middle Eastern fields and Texas Eagle Ford reservoir, respectively, we used the portable quadrupole mass analyzer (RGA300, Stanford Research Systems), which has RF frequencies in the several MHz range and quadrupole electrodes to separate different molecules. This portable mass analyzer has small dimensions, a mass range 1 - 300 amu and the resolution better than 1 amu. The samples were injected into the vacuum chamber through a leak valve, and ions are produced by electron impact ionization. Thereby the electrons are produced by thermionic emission from a hot filament. Then by applying the radiofrequency field, the ions are separated according to their mass-to-charge ratios. The mass spectrometer is connected directly to a vacuum chamber, which contains vapor from the sample, as is shown in **Figure 1**. The spectrometer employs zero order (DC current for balancing the potential relative to the kinetic energy) and first order (AC current with resonance frequency corresponding to mass over charge ratio) operation modes for detecting ions. These frequency domains multiplexed measurements give a high signal to noise ratio.

Besides the quadrupole probe, the RGA system includes an electronics control unit, and a real-time RGA Windows software, which is used for probe control, data acquisition and analysis. The probe unit consists of three parts: an ionizer, a quadrupole mass filter and an ion detector. The electronic control unit allows controlling the operation of the RGA and transmits the obtained data to the

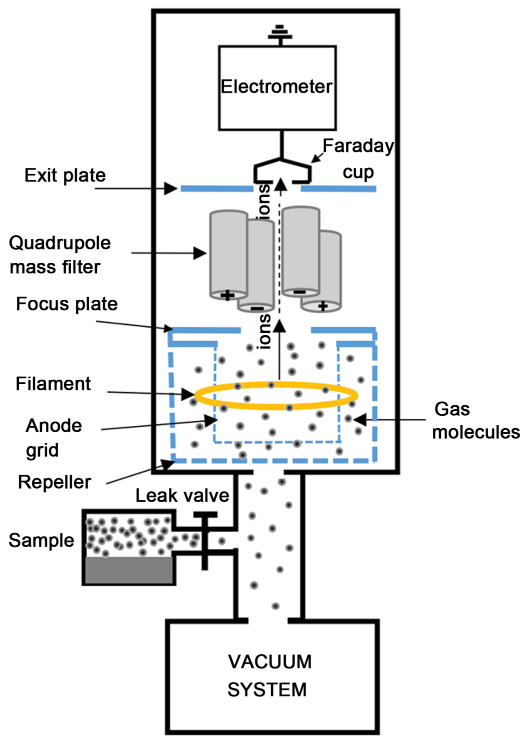

Figure 1. Schematic diagram of the mass spectrometry system used for analysis of crude oil samples.

computer, where the data are displayed and analyzed. The electron emission is supplied by a dual thoriated-iridium (ThO_2/Ir) filament, which lasts longer than single filaments. A Faraday cup detector allows partial pressure measurements in the range of 10^{-5} - 10^{-11} mbar. An electron continuous-dynode electron multiplier (CDEM), with high sensitivity and fast scan rates is capable of detecting partial pressures down to 10^{-14} mbar. Finally, a high vacuum system turbomolecular pumping station TSU 071 provided by Pfeiffer Vacuum is connected with the residual gas analyzer. It assures low background pressure (~7.8×10^{-7} mbar) and enables maintenance of operational pressure for measurements at ~5.2×10^{-6} mbar.

3. Results and Discussions

The generated mass spectra and signal intensity of hydrocarbons in Middle Eastern and Texas crude oil samples are displayed together in Figures 2-4. The total measured range of mass-to-charge ratios was divided into three regions chosen at random for interpretation of data and comparison of the mass spectra: (a) 50 - 90 amu (Figure 2); (b) 90 - 130 amu (Figure 3); and (c) 130 - 171 amu (Figure 4).

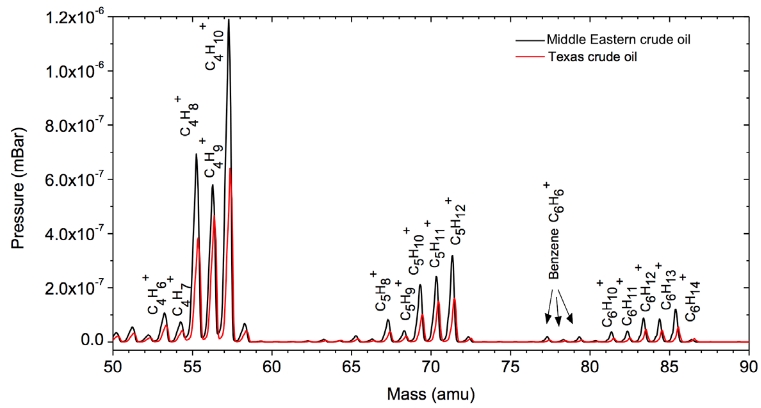

Figure 2. Crude oil hydrocarbon analysis of Middle Eastern crude oil and TX crude oil using RGA300 in the region 50 - 90 amu.

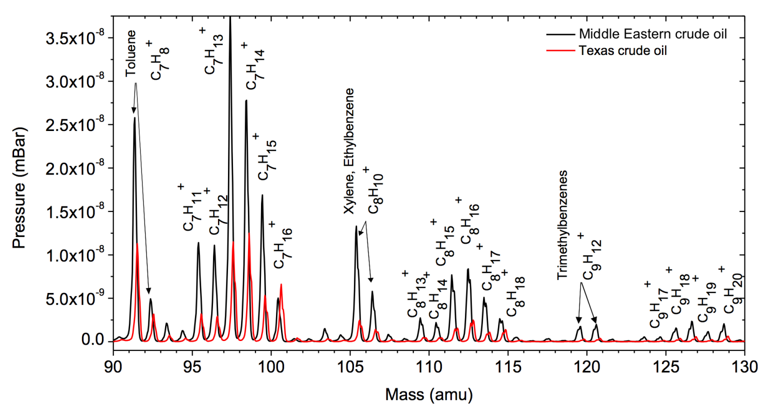

Figure 3. Crude oil hydrocarbon analysis of Middle Eastern crude oil and TX crude oil using RGA300 in the region 90 - 130 amu.

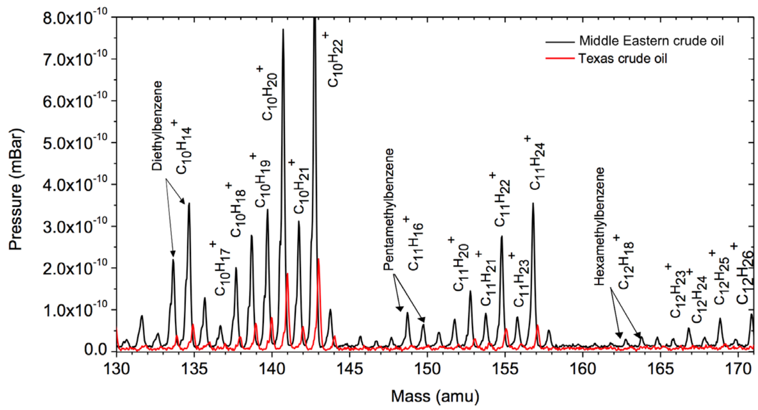

Figure 4. Crude oil hydrocarbon analysis of Middle Eastern crude oil and the TX crude oil using RGA300 in the region 130 - 171 amu.

Three major types of hydrocarbons in crude oil, *i.e.* paraffins, naphthenes, and aromatics are detected in both types of investigated samples. We observed linear and saturated hydrocarbons with mass-to-charge ratios 57, 71, 85, 99, 113, 127, 141, 155, 169 amu and naphthenes (or cycloalkanes) with mass-to-charge ratios 55, 69, 83, 97, 111, 125, 139, 153, 167 amu. The aromatics seen with mass-to-charge ratios 77 - 78, 91 - 92, 105 - 106, 119 - 120, 133 - 134 amu are characteristic of benzene derivatives. Toxic aromatic hydrocarbons, *i.e.* benzene, toluene, and xylene, with mass-to-charge ratios 77 - 78, 91 - 92, and 105 - 106 amu, respectively [16], are seen in both samples with significantly different signal intensities. The weak signals observed around mass-to-charge ratios 128 amu and 141 - 142 amu might be indicating the presence of naphtalene and methylnaphtalenes, respectively. While we have seen the peaks at 169 and 171 amu in Middle Eastern crude oil, no such peaks were detected in Texas crude oil. We measured the whole mass range of our mass analyzer 1 - 300 amu, but above 171 amu we did not detect any peaks in both samples. The abundance of hydrocarbons with higher mass-to-charge ratios in the region 91 - 171 amu in Texas crude oil is significantly lower compared to Middle Eastern crude oil, as seen in **Figure 3** and **Figure 4**. In **Figure 5**, the partial pressure ratio of different mass spectrum components of both crude oils by dividing pressure ratios of Middle Eastern crude oil to Texas crude oil is plotted, and it shows that the abundance of hydrocarbons of Middle Eastern crude oil compared to Texas crude oil is higher by a factor that ranges for different components from 4 to 21.

4. Conclusion

Analysis of two different types of crude oil samples, Middle Eastern crude oil from the Middle Eastern fields and Texas crude oil obtained from Texas Eagle Ford reservoir zones, by the portable quadrupole mass analyzer under vacuum condition without any sample pretreatment is performed. The mass spectra of these two types of oil samples show differences. The Middle Eastern crude oil samples show significant prevalence of hydrocarbons in the range of 90 - 160 amu.

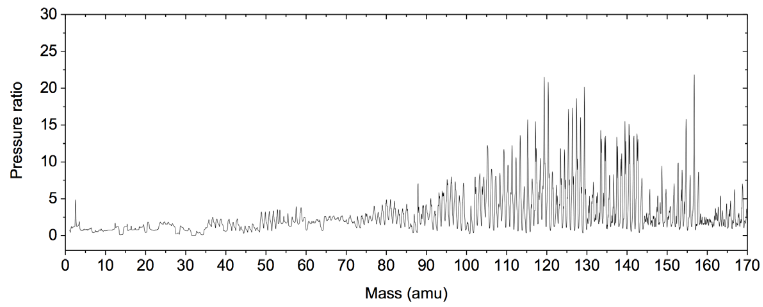

Figure 5. Partial pressure ratio of crude oil mass spectra of Middle Eastern crude oil and Texas crude oil.

Moreover, two crude oil samples reveal some differences in composition. We observed C12 paraffin, naphthene, and aromatic hydrocarbons only in Middle Eastern crude oil. Even though our measurements were done at the laboratory conditions, due to portability and rather small size of the equipment, the same approach is suitable for in-field applications if needed.

Acknowledgements

This work was supported by the Robert A. Welch Foundation (grant No. A1546).

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