Application the FT-IR spectroscopy to study the accumulations of Permian mixed petroleum systems in the central Junggar Basin, NW China

Ni Zhou\textsuperscript{1,2}, Dilidaer Rouzi\textsuperscript{1,2}, Baoli Xiang\textsuperscript{1,2}, Xiwei Gao\textsuperscript{1,2} and Haijing Wang\textsuperscript{1,2}
\textsuperscript{1} Xinjiang Laboratory of Petroleum Reserve in Conglomerate, Xinjiang Karamay, 834000, China
\textsuperscript{2} Research Institute of Experiment and Testing, Xinjiang Oilfield Company, PetroChina, Xinjiang Karamay 834000, China

The corresponding author’s e-mail address: zhouni@petrochina.com.cn

Abstract. Oil-source and its differences in mixed petroleum systems are one of the most important scientific problems in petroleum geology and geochemistry fields. Geochemistry provides useful information for exploration including source rock quality, thermal maturity, oil-source correlation, migration and accumulation relative to trap formation, which greatly reduces the risk of petroleum exploration. Traditionally, petroleum geochemistry analysis relies heavily on gas chromatography-mass spectrometry and carbon isotopes, which have been used as proxies to connect the petroleum geochemistry with oil-gas exploration, and has achieved remarkable success. These methods, however, have met with difficulties more and more along the complexity of oil compositions in exploration. This is because oils are complex mixtures of aliphatics, aromatics and NSO (nitrogen, sulfur and oxygen) compounds. Thus, to develop new methodologies to study oil geochemistry becomes more and more urgent. In this study, we demonstrate that Fourier Transform Infrared (FT-IR) spectroscopy, as a new rapid and non-expensive alternative technique, could be used to investigate the mixed. Here we address this issue based on a case study in the Permian lacustrine petroleum systems within central Junggar Basin (NW China), of which results have been restrained by traditional molecular geochemistry. Results there are two main mixed-source areas with different mixing proportions in Sinan oil-field of the central Junggar Basin. This characteristic can be applied directly in regional exploration.

1. Laboratory mixing experiments
Three sets of laboratory mixing experiments were designed to determine oil-source corrections and quantify the contributions to mixed oils. First, the pure end-member oils representing different sources were selected, which include lower Permian Fengcheng Formation-sourced (P\textsubscript{1f}) mature crude oil sample collected from well J003, and upper Permian Wuerhe Formation-sourced (P\textsubscript{2w}) high-mature crude oil sample collected from well QS1 and mature crude oil (P\textsubscript{2w}) sample collected from well M17. These oils were mixed by volume in the following proportions: 2:8, 4:6, 6:4 and 8:2.

After mixing, all samples were separated into SARA (Saturates, Aromatics, Resins, and Asphaltenes), which were determined by following procedures. Crude oil samples were mixed with n-hexane and allowed to stand for 12 hours, yielding asphaltene. These samples were then fractionated using open silica-gel column chromatography. The sequence of solvents used was n-hexane, a mixture
of n-hexane and dichloromethane (2:1), and finally methanol. These steps produced saturated hydrocarbons, aromatic hydrocarbons, and resins, respectively [6-7].

And then, the saturated hydrocarbons of oils were analysed for biomarker analysis using gas chromatography and gas chromatography–mass spectrometry (GC–MS). The analysis used a HP6890 gas chromatograph with an HP-5 column (30 m × 0.32 mm i.d.) and a film thickness of 0.25 μm. Nitrogen was employed as a carrier gas. The GC oven temperature was initially held at 80 °C for 5 min, heated from 80 °C to 290 °C using a 4 °C/min ramp, and then held at this temperature for 30 min. The GC–MS analyses were conducted using an Agilent 5973I mass spectrometer interfaced with a HP6890 gas chromatograph and fitted with the same type of column as that used for GC analyses. Helium was employed as a carrier gas. The GC oven temperature for the GC–MS analysis was initially held at 60 °C for 5 minutes, increased to 120 °C using a ramp of 8 °C/min, increased again from 120 °C to 290 °C using a ramp of 2 °C/min, and finally held at 290 °C for 30 min [6-7].

The results indicate the concentration of amount of biomarkers (e.g. β-carotane, Gammacerane, 25-norhapane) show regular change with different mixing proportions (not shown here), reflecting that these laboratory mixing experiments are effective.

The three sets of mixed oil samples were analyzed by a Thermo Nicolet 6700 FT-IR spectroscopy. The crude oil samples were respectively added into a cylindrical sample cup with 12 mm in diameter and 3 mm depth, and then analyzed in a Thermo Nicolet 6700 FTIR with a diffuse reflectance attachment from wave numbers 4000–400 cm⁻¹ at MOE Key Laboratory of Surficial Geochemistry, Nanjing University. Each analysis take about 2 min to gather 128 scans spectra at a resolution of 4 cm⁻¹ that are so-added to reduce noise [8].

2. Reservoirs FT-IR geochemical characteristics

The three sets of mixed oil samples were analyzed by a Thermo Nicolet 6700 FT-IR spectroscopy [1]. All samples present similar FTIR spectra, and the peak and area of each functional bends are defined according to previous studies [9-11].

![Figure 1. Definition of the peaks and integration limits for calculation of peak areas of the FT-IR spectra.](image-url)
Typical FTIR spectra include aliphatic, aromatic and oxygen-containing compounds. Aliphatic compounds consist of the symmetrical and asymmetrical stretching (ν) and bending (δ) vibrations of the methyl (CH$_3$) and methylene (CH$_2$) at 2962 cm$^{-1}$, 2874 cm$^{-1}$, 1457 cm$^{-1}$ and 1372 cm$^{-1}$, respectively. The bending deformation of C-H bonds of the alkane compounds were also labeled at 960 cm$^{-1}$ and 728 cm$^{-1}$. Aromatic compounds includes C=C double bonds at 1600 cm$^{-1}$ and two bending vibrations of the aromatic C-H bonds at 880 cm$^{-1}$ and 817 cm$^{-1}$. The oxygen-containing compounds contain the stretching vibrations of the hydroxy at 3160 cm$^{-1}$, carbonyl at 1700 cm$^{-1}$, and 2727 cm$^{-1}$, and sulfoxide at 1160 cm$^{-1}$ and 1070 cm$^{-1}$, respectively (Figure 1).

Based on that, several FT-IR parameters have been established to identify the oil-source corrections and mixing proportions, e.g., stretching vibrations of methyl and methylene (C-H), aromatic C=C double bonds. Taking the C=C structural parameter as an example (Figure 1), the post-peak (at 1567 cm$^{-1}$) distribution of the C=C bond shows a result of mixing between P$_1$f-sourced mature oil and P$_2$w-sourced high-mature oils with a proportion of P$_1$f (mature): P$_2$w (high-mature) < 4:6, of which reservoirs include S110, S106 and SN31 regions (Figure 2). And, the pre-peak (at 1600 cm$^{-1}$) distribution of the C=C bond shows a result of mixing between P$_1$f-sourced mature oil and P$_2$w-sourced mature oils with a proportion of P$_1$f (mature): P$_2$w (mature) < 8:2, of which reservoirs include SN42 and J001 regions (Figure 3).

**Figure 2.** The C=C structural characteristics of mixed reservoirs crude oil samples in the central Junggar Basin

3. **Complex mixed oils accumulation characteristics**

As discussed above, there are two main mixed-source areas in Sinan oil-field of the central Junggar Basin, including mature oils mixing area in J001–SN42 well regions, and mature–high-mature mixing area in S110–S106–SN31 well regions. The mixing proportions of reservoirs are closely related to the formation in spatial. In mature oils mixing area, the Jurassic Toutunhe Formation (J$_2$t) reservoirs are dominated by P$_2$w-sourced oils, and the lower Cretaceous Tugulu Group (K$_1$tg) reservoirs are dominated by P$_1$f-sourced oils (Figure 3). In contrast, mature–high-mature mixing area, the strata above J$_2$t are dominated by P$_2$w-sourced oils, and blow J$_2$t are dominated by P$_1$f-sourced oils (Figure 3). According to results above, we put forward a wave wavy-charging model of mixed petroleum systems along the direction of SN4–SN21 in study area (Figure 3).
Generally, along the direction of hydrocarbon migration, the maturity of petroleum will gradually decrease\(^1\)-\(^3\). However, the results discussed above are contrary to this theoretical tendency, which indicate that there may be complex tectonic adjustment resulting in these abnormal characteristics. But, the mechanism is not clear yet, which still needs further study in future.

![Figure 3](image.png)

**Figure 3.** The migration and accumulation model of the Permian mixed petroleum systems in the central Junggar Basin.

4. **Conclusions**
   (1) At least fifteen FT-IR functional groups have been detected from mixed oils, including aliphatic, aromatic and oxygen-containing compounds.
   (2) The FT-IR spectroscopy imply a great potential for accumulations analysis of lacustrine complex petroleum systems.
   (3) There are two main mixed-source areas with different mixing proportions in Sinan oil-field of the central Junggar Basin, of which characteristic could be applied directly in regional exploration.

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