As shale oil and gas are the substituted energy sources of conventional petroleum, it arouses extensive attention by many governments and oil companies in recent years. Shale oil and gas vary in many occurrence forms, e.g., free pattern, adsorption pattern and dissociation pattern. Shale is composed of different minerals, e.g., detrital minerals (quartz, feldspar, etc.), clay minerals (smectite, illite, etc.), carbonate minerals (calcite, dolomite, etc.), and each mineral varies in mineral attribute greatly (internal surface, external surface, etc.), thus leading to differences of the adsorption state of oil and gas. Therefore, it is of great significance to explore an effective method to separate and measure hydrocarbon in different occurrence patterns for understanding shale oil and gas enrichment and making exploration strategy. Shales of Paleogene in the Dongying Sag of Bohai Bay Basin were selected, and clay-sized fractions of the bulk rocks were separated. Both bulk rocks and clay-sized fractions were preformed measurements of pyrolysis, pyrolysis-GC, extraction-saponification-acidolysis treatment and GC-MS to reveal the variations of hydrocarbon in different occurrence patterns.

For bulk rocks and clay-sized fractions under heating chromatography at 300°C, 300-500°C and 500-650°C, it shows that total hydrocarbon at 300-500°C is higher than others; for the hydrocarbon components, light components (C15-) are the main components in each temperature intervals, and content of heavy components (C15+) keep in 20%. From the evolution characteristics on hydrocarbons, it is dominated by light hydrocarbon over 3100 m and dominated by heavy hydrocarbon below 3100 m at 300°C; content of light and heavy hydrocarbon component, while the depth is 3100 m up and down, is relatively stable at 300-500°C; for the hydrocarbons at 500-650°C, contents of light and heavy hydrocarbon decrease abruptly because of the appearance of methane. These characteristics indicate that the content and components of different hydrocarbons can be achieved by employing pyrolysis-GC in different temperature intervals. Comparing the characteristics of light and heavy hydrocarbon components in bulk rocks and clay-sized fractions, it can be found that variations at 300°C are not regular; and at 300-500°C, light hydrocarbon in clay-sized fractions is higher than that in bulk rocks, whilst heavy hydrocarbon in bulk rocks is higher than that in clay-sized fractions; at 500-650°C, light hydrocarbon in clay-sized fractions is higher than that in bulk rocks, and the difference of heavy hydrocarbon is not apparent. These characteristics indicate that variations of hydrocarbon components at 300°C are not correlated with clay-sized fractions, and variations of hydrocarbon components at 300-500°C are severely correlated with clay-sized fractions, which need to be concerned intimately in the study on the mineral composition and its impact on hydrocarbons occurrence.

After performing extraction-saponification-acidolysis treatment and GC-MS measurement on the clay-sized fractions, it can be obtained that the contents of soluble OM removed by extraction, saponification, acidolysis and HF treatments are 99.57 mg/g, 38.96 mg/g, 1.89 mg/g and 1.85 mg/g, respectively; and soluble OM removed by extraction, saponification, acidolysis and HF treatments enrich saturates, aromatics, nonhydrocarbon and asphaltene, respectively; these characteristics suggest that the extraction-saponification-acidolysis treatment can obtain hydrocarbons in different occurrence patterns. For the components of saturates, saturates removed by extraction is dominated by heavy component and light component only accounts 16%; while light component in saturates removed by saponification, acidolysis and HF treatments are 78%, 76% and 65%, respectively, which primarily reveal the difference of components in hydrocarbon of varying occurrence patterns.

Integrated above analysis, hydrocarbon in different occurrence states can be obtained by pyrolysis-GC and extraction-saponification-acidolysis treatment, and the hydrocarbon content of different occurrence patterns as
well as light/heavy components can be primarily presented, this is significant to study the occurrence pattern of hydrocarbon in shales.

References