

Introduction

For solving some practical issues related to the exploration and production of petroleum hydrocarbons detailed knowledge of individual and group composition of hydrocarbons are required. The most suitable instrument for this research is high resolution mass-spectrometry with 2D gas chromatography. We have explored the crude oils from the various deposits of the field in Western Siberia, Russia. The peculiarity of this oil field is that two different source rocks were involved in the formation of the deposits. This is proved by numerous results using molecular and isotopic mass spectrometry. Oil is not affected by biodegradation. Their composition reflects only the effect of catagenesis and the mix of different hydrocarbon source rocks.

Experimental

GC×GC-QTOFMS analyses were made on Agilent Technologies 7890B 2D gas chromatograph equipped with a secondary oven (LTM module), flow modulator and tandem quadrupole time-of-flight accurate-mass detector (Agilent 7200 Accurate-Mass Q-TOF GC-MS). Tuning and operation of the instrument and data processing were performed by means of MASSHUNTER QUALITATIVE ANALYSIS B.05.00 software, pictures were done in GC image software. The GC column set consisted of HP-1MS column (30m, 0.25mm i.d., 0.25µm film thickness) as the first dimension (1D) and a DB-17 column (5m, 0.25mm i.d., 0.25µm film thickness) as the second dimension (2D).

The injector temperature was 300°C and the interface temperature was 280°C.

The temperature program used for the first column (1D) was:

60 to 110 °C at 8°C/min,

110 to 135°C at 6°C/min,

135 to 150 °C at 5°C/min,

150 to 200 °C at 4°C/min,

200 to 310 °C at 3°C/min,

The oven temperature was maintained at 310°C for 15 minutes. Total analysis time was 77 minutes.

The temperature program for the second column (2D) was:

60 to 210 °C at 10°C/min,

The oven temperature was maintained at 210°C for 5 minutes.

210 to 320°C at 2.5°C/min,

The oven temperature was maintained at 320°C until the end of analysis.

The modulation period was 6.5s, with a 0.2s injection time.

Helium was used as carrier gas; the flow rates were 1 mL/min for first dimension (1D) and 18 mL/min for second dimension (2D).

The mass detector was equipped with an EI source (70 eV).

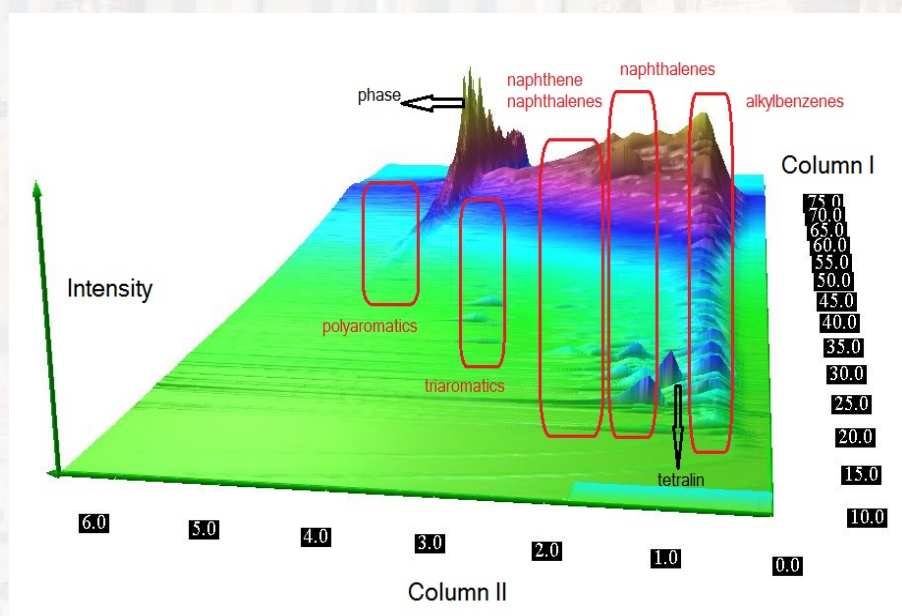


Figure 1. Crude oil sample. Depth of occurrence – 2352 m.

Results and Discussion

Figures 1-6 presents 3D chromatograms of the aromatic fractions that were extracted from the crude oils from the various deposits with different depth of occurrence. The sample at fig. 6 is the deepest deposit and the sample at fig. 1 is conversely. Submissions can be seen as the transition from oil from the upper horizons to the underlying increases the contribution of the second generation source, which is reflected in the composition of aromatic hydrocarbons. Aromatic hydrocarbons from upper layer oils (fig. 1 and 2) are presented mainly by monoaromatic hydrocarbons. The fractions of naphthalenes and phenanthrenes are significantly less. Hydrocarbons with four benzene rings are almost not visualized, although the molecular ion can be easily detected.

Aromatic fraction from mixed zone presented on 3D-chromatograms (Fig. 3 and 4) is the result of fluids accumulation from both source rocks. There is the decrease of monoaromatics and the gradual increase of hydrocarbons with two, three and even four benzene rings that contributed from underlying source rock.

The composition of aromatic compounds from the deepest horizons (fig. 5 and 6) is significantly different. The presence of monoaromatic hydrocarbons is much smaller, but sharply increases the quantity of naphthalenes and phenanthrenes. The tetracyclic compounds are clearly visualized. This information allows to draw conclusions about the source of the fluids of each deposits and to distinguish the oil deposits.

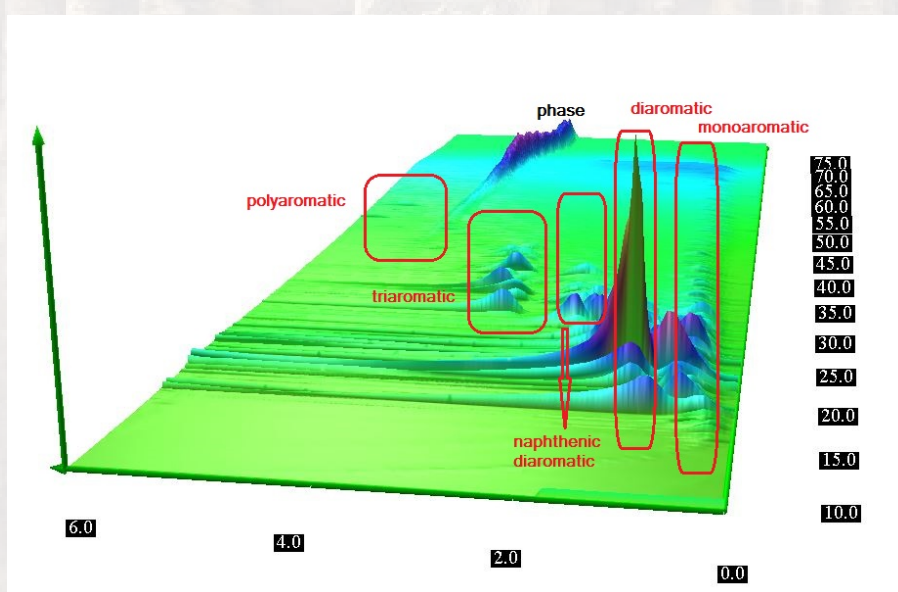


Figure 2. Crude oil sample. Depth of occurrence – 2415 m.

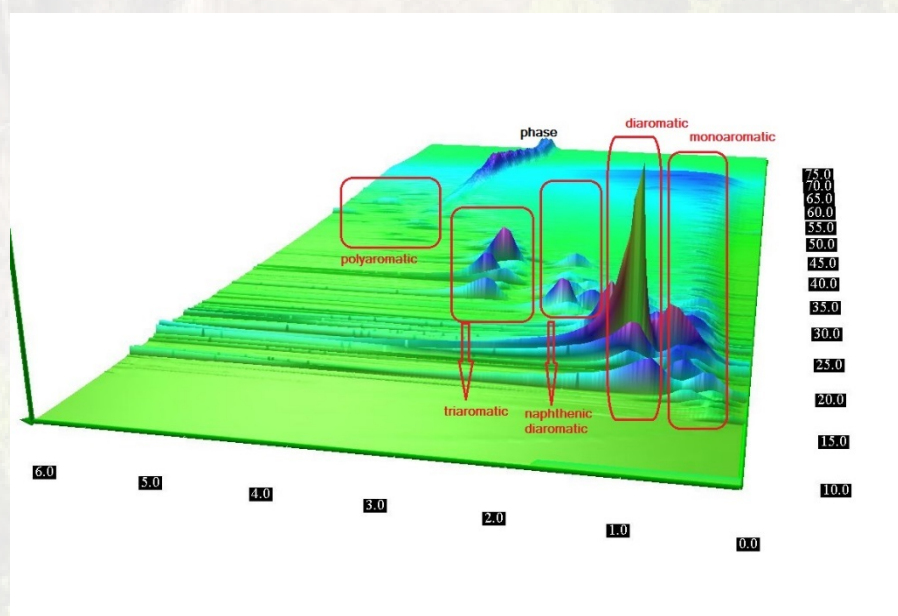


Figure 3. Crude oil sample. Depth of occurrence – 2471 m.

Results and Discussion

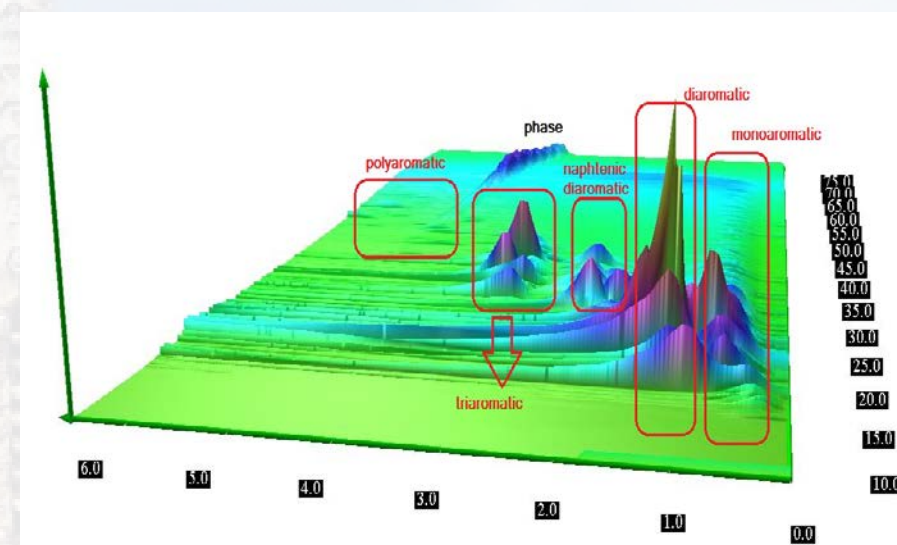


Figure 4. Crude oil sample. Depth of occurrence – 2508 m.

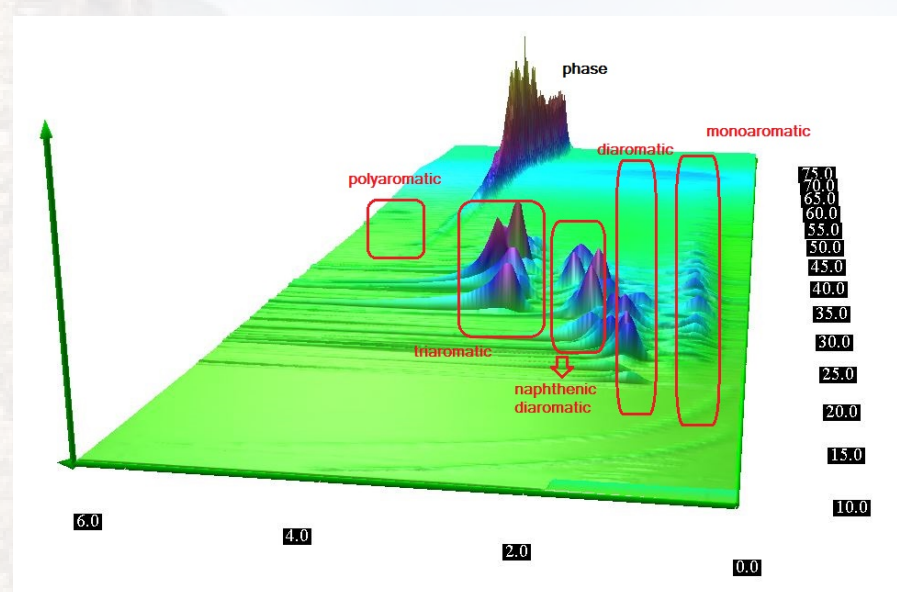


Figure 5. Crude oil sample. Depth of occurrence – 2586 m.

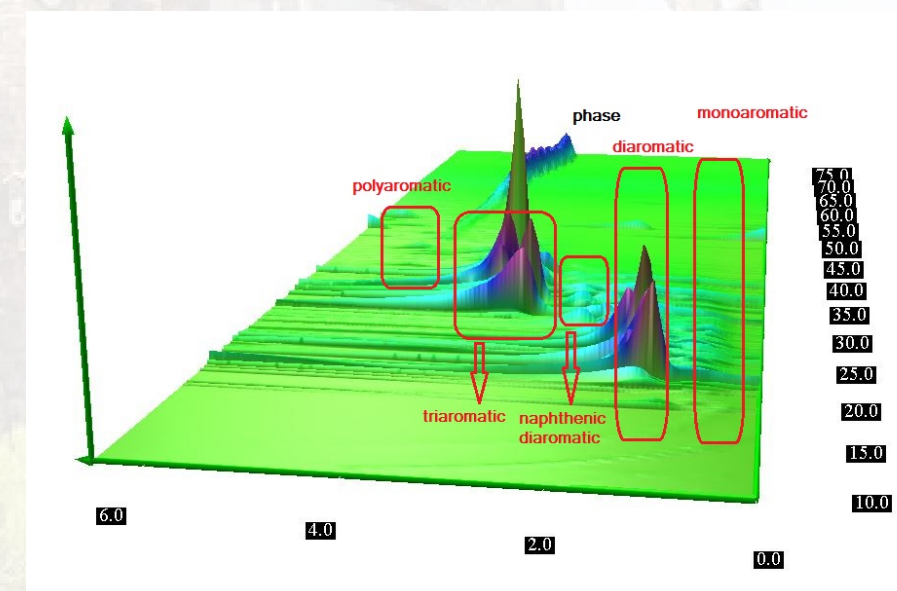


Figure 6. Crude oil sample. Depth of occurrence – 2630 m.

Conclusions

GCxGC method can reduce time and efforts for sample preparation, separate the co-eluted peaks in comparison with one-dimensional chromatography (for example, components of "naphthenic hump", polar compounds) and visualize the results in 3D format. In combination with the quadrupole time of flight high resolution mass spectrometer the part of unseparated components is reduced that allows to distinguish the fluids and realize their source rocks.