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Analyzing crude oils from the Junggar Basin (NW China) using comprehensive two-dimensional gas chromatography coupled with time-of-flight mass spectrometry (GC×GC-TOFMS)

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Abstract As a new technology of analyzing crude oils, comprehensive two-dimensional gas chromatography coupled with time-of-flight mass spectrometry (GC×GC-TOFMS) has received much research attention. Here we present a case study in the Junggar Basin of NW China. Results show that the hydrocarbons, including saturates and aromatics, were all well-separated without large co-elution, which cannot be realized by conventional one-dimensional GC–MS. The GC×GC technique is especially effective for analyzing aromatics and low-to-middle-molecular-weight hydrocarbons, such as diamondoids. The geochemical characteristics of crude oils in the study area were investigated through geochemical parameters extracted by GC×GC-TOFMS, improving upon the understanding obtained by GC–MS. Thus, the work here represents a new successful application of GC×GC-TOFMS, showing its broad usefulness in petroleum geochemistry.

Keywords Comprehensive two-dimensional gas chromatography coupled with time-of-flight mass spectrometry (GC×GC-TOFMS) · Petroleum geochemistry · Biomarkers · Diamondoid · Junggar Basin

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1 Introduction

Crude oil represents complex organic mixtures. The hydrocarbons in the oil can be divided into saturates and aromatics based on the structure, and the ranges of boiling point and polarity are very wide (Gaines et al. 1999). In petroleum geochemistry, the analysis of oil composition is usually conducted by one-dimensional gas chromatography with quadrupole mass spectrometry (GC–MS), and saturated hydrocarbons and aromatic hydrocarbons need to be analyzed separately (Peters et al. 2005b). The analytical results have important implications, e.g., determining petroleum properties, sedimentary environment, stratigraphic division, and oil source correlation (Peters et al. 2005a). However, one-dimensional chromatography has many disadvantages, such as small peak capacity, low resolution, and co-elution, which will cause inaccurate qualitative and quantitative results (Gough and Rowland 1990; Gough et al. 1992; Sutton et al. 2005). Therefore, exploring new techniques and methods for geochemical analysis of crude oil is an important task for petroleum geochemists.

Two-dimensional gas chromatography (GC×GC) is a separation technology that utilizes two orthogonal separation mechanisms, and only specific fractions from the first column through a modulator are introduced into a second dimension for further separation (Liu and Phillips 1991; Phillips and Beens 1999; Adahchour et al. 2006). This technique has multiple advantages over the conventional one-dimensional GC technique when analyzing hydrocarbon compounds in crude oils, such as enhanced resolution, higher sensitivity, larger peak capacity, and shorter analysis time (Cortes et al. 2009). Thus, it has been used widely for separating and identifying complex mixtures (Dalluge et al. 2003). In recent years, two-dimensional gas chromatography was introduced into petroleum geochemistry,

and has gained rapid development coupled with time-of-flight mass spectrometry (TOF–MS) (Wang et al. 2010; Lu et al. 2013; Zhu et al. 2013; Wang et al. 2014; Li et al. 2015). In this paper, we present a case study in the Junggar Basin of northwestern China. New analytical data were obtained and the application of the technique was discussed.

2 Samples and methods

The Junggar Basin is a typical large superimposed petroliferous basin in northwestern China (Cao et al. 2005). Four crude oil samples were collected from different regions and formations in the southern basin. The samples have variable physical properties (Table 1), providing favorable conditions for comparative analysis. In the GC×GC-TOFMS analysis, both the normal and reversed phase column systems were used for the oils from wells Ka 6 and Chang 1. In contrast, considering the low density of the crude oils from wells Xican 2 and Mana 1, only the reversed phase column system, which was believed to have good separation for the middle-to-low-molecular-weight hydrocarbons, was used (Hu et al. 2014; Li et al. 2014).

A LECO GC×GC-TOFMS instrument was used. The GC×GC system is composed of Agilent 7890 gas chromatography with hydrogen flame ionization detector (FID) and a liquid nitrogen-cooled pulse jet modulator. The time-of-flight mass spectrometry is Pegasus 4D.

The general operating conditions of the GC×GC are listed in Table 2. In the TOFMS analysis, we used electron energy of −70 eV, detector voltage of 1475 V, iron source temperature of 240 °C, acquisition rate of 100 spectra/s and scan range of 55–550 amu. The acquisition delay time of normal and reversed phase column systems is 500 and 300 s, respectively. The software of Chroma TOF version 4.43 was used for data processing with database NIST 05 and biomarkers (Wang 1993; Peters et al. 2005a). The software combines fragment peaks whose similarity is over 700 and calculates integrated peaks.

3 Results and discussion

3.1 Saturated hydrocarbons

Saturated hydrocarbons are important components of crude oils. Due to differences in molecular weight and polarity, the separation and identification of saturated hydrocarbons is easily achieved by GC×GC-TOFMS, especially for the low-to-middle-molecular-weight hydrocarbons (Li et al. 2012; Oliveira et al. 2012; Wang et al. 2012). The biomarker parameters for the crude oils in this study are listed

Table 1 Basic sample characteristics of crude oils in the GC×GC-TOFMS analysis

Well	Depth (m)	Formation	Density (g/cm³)	Viscosity (mPa.s)	Freezing point (°C)	Wax content (%)	$\delta^{13}C$ (‰)	Compound fractions (%)				Sources
								Saturates	Aromatics	NSO	Asphaltenes	
Ka 6	39,560–3980.0	J_3q	0.83	4.2	17	4.2	−26.5	65.06	13.6	2.44	1.05	J (E)
Chang 1	3375.8–3409.6	J_2x	0.82	3.9	10	2.3	−29.6	79.19	11.55	8.47	0.53	J + P
Xican 2	3644.5–3655.5	N_1s	0.79	1.2	7	1.6	−26.7	86.34	6.19	2.06	0.77	J + E
Mana 1	2414.0–2446.5	$E_{1-2}z$	0.77	0.7	−15	0.6	−27.7	41.15	2.21	0.76	0.18	K(J)

Table 2 Experimental conditions of GC×GC

Item	Normal phase column system	Reversed phase column system
1st column	HP-5MS, 60 m × 0.25 mm × 0.25 μm	DB-17HT, 30 m × 0.25 mm × 0.25 μm
2nd column	DB-17HT, 1.2 m × 0.1 mm × 0.1 μm	DB-5HT, 1.2 m × 0.1 mm × 0.1 μm
1st column temperature program	40 °C (2 min) up to 310 °C (16 min) with 2 °C/min	40 °C (2 min) up to 300 °C (7 min) with 2 °C/min
2nd column temperature program	45 °C (2 min) up to 315 °C (16 min) with 2 °C/min	45 °C (2 min) up to 305 °C (7 min) with 2 °C/min
Inlet temperature	310 °C	300 °C
Sample injection volume	0.2 μL	0.2 μL
Inlet mode	Splitless sampling	Splitless sampling
Carrier gas	He; inlet flow rate: 1.5 ml/min	He; inlet flow rate: 1.0 ml/min
Modulator temperature offset	30 °C higher than the GC oven temperature	30 °C higher than the GC oven temperature
Modulation time	6.0 s with hot pulse time of 1.5 s	7.0 s with hot pulse time of 1.7 s
Transfer line temperature	280 °C	280 °C

Table 3 Typical parameters of saturates in crude oils analyzed by GC×GC-TOFMS

Well	Depth (m)	Formation	Column combination	Pr/Ph	Range of n-alkanes	C_{19} %	C_{20} %	C_{21} %	C_{23} %	TT/C_{30}H	Ga/C_{30}H	Ts/Tm
Ka 6	3956–3980	J_3q	Normal phase	1.91	$nC_9 \sim nC_{37}$	59.20	40.80	/	/	0.11	0.03	0.45
Ka 6	3956–3980	J_3q	Reversed phase	1.54	$nC_8 \sim nC_{35}$	64.81	35.19	/	/	0.11	0.02	0.35
Chang 1	3375.8	J_2x	Normal phase	1.98	$nC_9 \sim nC_{37}$	12.96	25.65	32.10	29.28	0.12	0.03	0.92
Chang 1	3375.8	J_2x	Reversed phase	1.61	$nC_9 \sim nC_{35}$	14.41	24.07	33.94	27.58	0.15	0.03	0.94
Xican 2	3644.5–3655.5	N_1s	Reversed phase	1.01	$nC_9 \sim nC_{37}$	66.00	34.00	/	/	0.12	0.13	0.53
Mana 1	2414.0–2446.5	$E_{1-2}z$	Reversed phase	0.75	$nC_8 \sim nC_{31}$	/	/	/	/	/	/	/

C_{19}%: $C_{19} \times 100/(C_{19} + C_{20} + C_{21} + C_{23})$-tricyclic terpanes; C_{20}%: $C_{20} \times 100/(C_{19} + C_{20} + C_{21} + C_{23})$-tricyclic terpanes; C_{21}%: $C_{21} \times 100/(C_{19} + C_{20} + C_{21} + C_{23})$-tricyclic terpanes; C_{23}%: $C_{23} \times 100/(C_{19} + C_{20} + C_{21} + C_{23})$-tricyclic terpanes; TT/$C_{30}$H: the highest peak of tricyclic terpanes/C_{30} Hopane; Ga represents gammacerane; "/" represents compounds were not detected

in Table 3. Results show that the oils from wells Ka 6 and Xican 2 had high Pr/Ph values, and high contents of C_{19} tricyclic terpane, which are presumed to be resultant from the Jurassic source rocks (Wang et al. 2013). In addition, in terms of gammacerane/C_{30} hopane and Pr/Ph values, significantly higher gammacerane content and a lower Pr/Ph value were identified in the Xican 2 oil. This implies that the Paleogene source rock is detectable in the oil (Wang et al. 2013).

With respect to the Chang 1 oil, the Pr/Ph value ranges from 1.61 to 1.98, the distribution of C_{20}, C_{21}, and C_{23} tricyclic terpanes is $C_{20} < C_{21} > C_{23}$, and the gammacerane index is low (0.03). These characteristics suggest that the Chang 1 oil is a mixture of Jurassic- and Permian-sourced oils (Wang et al. 2013).

As for the Mana 1 condensate, the terpane and sterane biomarkers could not be detected. This is mainly due to the extremely low abundance of such compounds in condensates (Graas et al. 2000). However, the alkanes and isoprenoids can also be detected. Thus, according to the Pr/Ph

value of 0.75, the source of this oil is determined to be Cretaceous source rocks (Wang et al. 2013).

3.2 Aromatic hydrocarbons

The GC×GC has unique advantages for analyzing aromatic hydrocarbons in that it does not require the separation of saturates and aromatics compared with the conventional one-dimensional GC, and furthermore, qualitative and quantitative analyses for these compounds are more accurate (Li et al. 2008). In this study, abundant aromatic hydrocarbon compounds were detected.

3.2.1 Compound classes in fluorenes, dibenzofurans and dibenzothiophenes

Previous studies have shown that the series of fluorenes, dibenzofurans, and dibenzothiophenes might have shared precursors (Ding et al. 1997). The ninth carbon in the fluorenes is the alpha carbon atom and its chemical

properties are active. Thus, it may be replaced by sulfur and be converted into dibenzothiophenes under reducing environments, while under the suboxic-oxic environments, it can be oxidized to dibenzofurans. Thus, using the relative abundance of these three compounds, the source of the crude oils and their organic facies can be determined (Ding et al. 1997). As shown in Table 4, the content of dibenzofurans in this study is high in Ka 6 oil, and the contents of fluorenes, dibenzofurans, and dibenzothiophenes were 13.5 %–13.6 %, 71.4 %–72.0 %, and 14.5 %–15.0 %, respectively. A parallel result is displayed in the distribution of alkylfluorenes, alkyldibenzofurans, and alkyldibenzothiophenes; the contents of alkylfluorenes, alkyldibenzofurans, and alkyldibenzothiophenes were 21.5 %–21.9 %, 67.9 %–68.4 %, and 10.0 %–10.2 %, respectively (Fig. 1). This implies that the depositional environment of the source rock is suboxic-oxic, supporting that the crude oil is Jurassic-sourced as discussed above.

The Chang 1 oil has relatively high fluorene content (38.3 %–38.9 %), while the dibenzofuran content is not high compared with the content of dibenzothiophenes (Table 4; Fig. 1). This implies that the source of this oil should be lacustrine, i.e., Permian (Wang et al. 2013). The content of fluorenes in the oils from wells Xican 2 and Mana 1 was low, and the ratios of dibenzofurans/dibenzothiophenes and alkyldibenzofurans/alkyldibenzothiophenes were between those of wells Ka 6 and Chang 1, which displayed no characteristics of Jurassic swamp and slightly-oxic source rocks and no characteristics of Paleogene and Cretaceous salty lacustrine source rocks. As discussed in the section on saturates above, the Xican 2 oil is a mixture of Jurassic- and Paleogene-sourced oils, and the Mana 1 oil is Cretaceous-sourced with the invasion of Jurassic-sourced gas (i.e., evaporation fractionation) (Wang et al. 2013). Thus, the characteristics of fluorenes, dibenzofurans, and dibenzothiophenes of these two oils should be the result of the oil mixing between Jurassic-sourced oils and Paleogene/Cretaceous-sourced oils.

3.2.2 Phenanthrenes and alkylphenanthrenes

Phenanthrene compounds have been commonly used to evaluate the maturity of crude oils (Radke et al. 1982a, b). In immature organic matters, 9-methylphenanthrene (MP) and 1-MP are highly abundant; however, with increasing maturity, 3-MP and 2-MP become more predominant due to their enhanced thermal stability. Based on these observations, Radke et al. (1982a) proposed the MP Ratios, including $MPI_1 = [1.5 \times (3\text{-}MP + 2\text{-}MP)/(P + 9\text{-}MP + 1\text{-}MP)]$ and $MPI_2 = (3 \times 2\text{-}MP)/(P + 9\text{-}MP + 1\text{-}MP)$, to evaluate the maturity of organic matter. The relationship between MPI_1 and vitrinite reflectance was established as $R_o\% = 0.6 \times MPI_1 + 0.4$ (Radke et al. 1982b). Later, it was found that the correlation between MPI_1 and MPI_2 was not good, and there was no correlation between the abundance of phenanthrenes and maturity (Kvalheim et al. 1987). Therefore, Kvalheim et al. (1987) proposed the distribution index F_1 and F_2 ($F_1 = (3\text{-}MP + 2\text{-}MP)/MP$; $F_2 = 2\text{-}MP/MP$) to measure the maturity of organic matter.

As shown in Table 5, the MP indexes MPI_1 and MPI_2 of the crude oils in this study range from 0.47 to 0.84 and 0.51 to 0.88, respectively. The correlation between MPI_1 and MPI_2 is good (Fig. 2a), and shows that the Mana 1 oil has the lowest maturity of all oil samples. However, the correlation between F_1 and F_2 is good, implying that the Mana 1 oil has the highest maturity of all the oil samples. According to threshold lines that have been widely used in China (Bao et al. 1992), the oils in this study are mature except for the Mana 1 oil, which is highly mature (Fig. 2b). This is consistent with the physical properties of the oils (Table 1).

3.3 Diamondoids

Diamondoids are special compounds in crude oils, and have extremely stable chemical properties. Once formed, they have strong resistance to thermal degradation and

Table 4 Parameters of fluorenes, dibenzofurans, and dibenzothiophenes in crude oils analyzed by GC×GC-TOFMS

Well	Depth (m)	Formation	Column combination	1	2	3	4	5	6	7	8
Ka 6	3956–3980	J$_3$q	Normal phase	13.5	72.0	14.5	4.95	21.9	67.9	10.2	6.67
Ka 6	3956–3980	J$_3$q	Reversed phase	13.6	71.4	15.0	4.76	21.5	68.4	10.0	6.81
Chang 1	3375.8	J$_2$x	Normal phase	38.3	47.2	14.5	3.25	40.0	49.1	10.9	4.52
Chang 1	3375.8	J$_2$x	Reversed phase	38.9	47.4	13.7	3.46	34.4	54.2	11.4	4.77
Xican 2	3644.5–3655.5	N$_1$s	Reversed phase	/	79.7	20.3	3.92	2.4	80.6	17.0	4.74
Mana 1	2414.0–2446.5	E$_{1-2}$z	Reversed phase	/	80.0	20.0	3.99	/	84.7	15.3	5.55

1: fluorene%; 2: dibenzofuran%; 3: dibenzothiophene%; 4: dibenzofuran/dibenzothiophene; 5: alkylfluorenes%; 6: alkyldibenzofurans%; 7: alkyldibenzothiophenes%; 8: alkyldibenzofurans/alkyldibenzothiophenes; "/": not detected

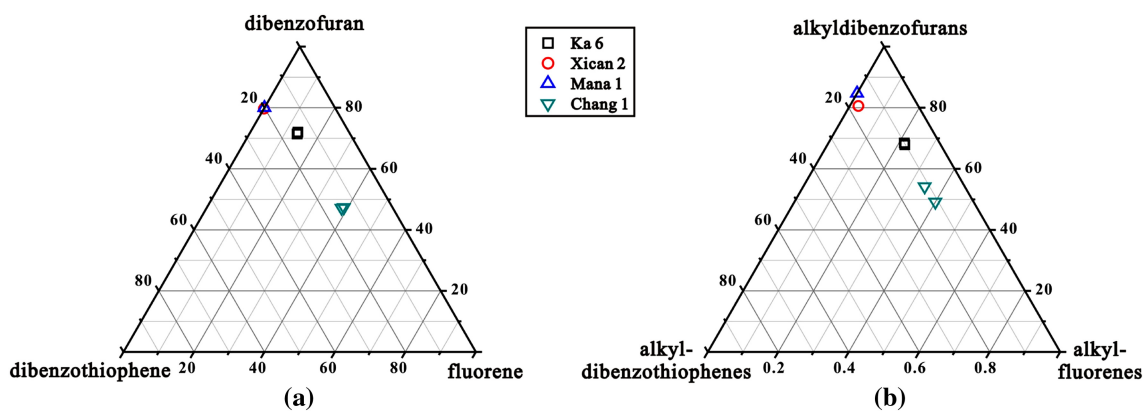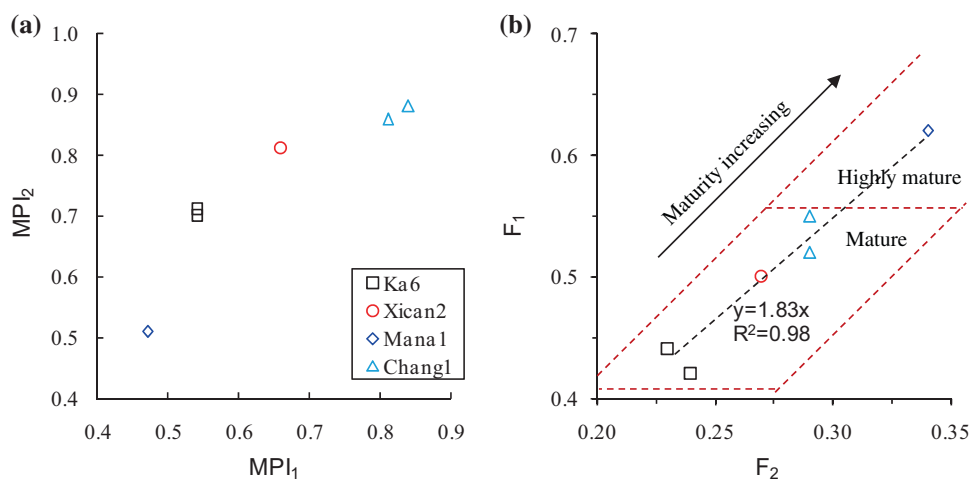**Fig. 1** Distribution of fluorene, dibenzofuran and dibenzothiophene (**a**), and alkylfluorenes, alkyldibenzofurans, and alkyldibenzothiophenes (**b**) of the crude oils analyzed by GC×GC-TOFMS

Table 5 Parameters of phenanthrenes and alkylphenanthrenes in crude oils analyzed by GC×GC-TOFMS

Well	Depth(m)	Formation	Column combination	MPI_1	MPI_2	F_1	F_2
Ka 6	3956–3980	J_3q	Normal phase	0.54	0.70	0.44	0.23
Ka 6	3956–3980	J_3q	Reversed phase	0.54	0.71	0.42	0.24
Chang 1	3375.8	J_2x	Normal phase	0.84	0.88	0.55	0.29
Chang 1	3375.8	J_2x	Reversed phase	0.81	0.86	0.52	0.29
Xican 2	3644.5–3655.5	N_1s	Reversed phase	0.66	0.81	0.50	0.27
Mana 1	2414.0–2446.5	$E_{1-2}z$	Reversed phase	0.47	0.51	0.62	0.34

$MPI_1 = (1.5 \times (3\text{-MP} + 2\text{-MP})/(P + 9\text{-MP} + 1\text{-MP}))$; $MPI_2 = (3 \times 2\text{-MP})/(P + 9\text{-MP} + 1\text{-MP})$; $F_1 = (3\text{-MP} + 2\text{-MP})/MP$; $F_2 = 2\text{-MP}/MP$

Fig. 2 Correlation between MPI_1 and MPI_2 (**a**), and between F_1 and F_2 (**b**) in crude oils analyzed by GC×GC-TOFMS

biodegradation, and thus play important roles in the evaluation of maturity (Dahl et al. 1999; Grice et al. 2000). However, the content of diamondoids in crude oils are very low and the conventional GC–MS could not detect these compounds well because of sensitivity and resolution, which made the detection and application of diamondoids very difficult (Liang et al. 2012). However, they can be effectively distinguished simultaneously with conventional hydrocarbon compounds using GC×GC-TOFMS (Li et al. 2012; Silva et al. 2013), showing the advantage of this technique. In this study, diamondoids were effectively separated and identified in the crude oils (Fig. 3).

Due to the different positions of the substituents, the thermal stability of diamondoids varies (Chen et al. 1996; Dahl et al. 1999; Li et al. 2000). Thus, the parameters related to diamondoids can be used to evaluate the thermal
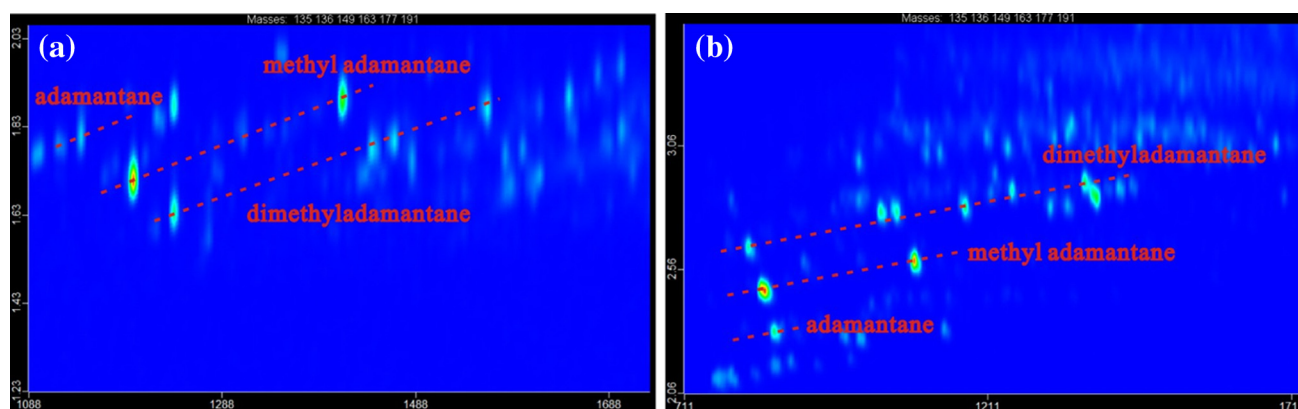
Fig. 3 Chromatographic surface of adamantanes and alkyladamantanes in crude oils analyzed by GC×GC-TOFMS. (**a**) Chang 1 oil (normal phase); (**b**) Chang 1 oil (reversed phase)

maturity of crude oils, especially in the case of a high level of evolution (Dahl et al. 1999). Generally, thermal stability of 1-methyladamantane (1-MA) is greater than 2-methyladamantane (2-MA). Moreover, 4-methyldiamantane (4-MD) is more stable than 1-methyldiamantane (1-MD) and 3-methyladamantane (3-MD). Thus, the adamantane index I [1-MA/(1-MA + 2-MA) × 100 %] and diamantane index II [4-MD/(1-MD + 3-MD + 4-MD) × 100 %] were proposed to evaluate the maturity of organic matter; they increase along with maturity and show good correlations with vitrinite reflectance Ro% (Chen et al. 1996; Dahl et al. 1999; Li et al. 2000).

The adamantane index I in the study area ranges from 47.5 to 67.8 % (Table 6). Among the samples, the adamantane index I of the Mana 1 oil is the highest at 67.8 %. According to Chen et al. (1996), the oil is highly mature, which is consistent with the understanding obtained by aromatics. For the Chang 1 oil, the adamantane index I is in the range of 50–70 %, and thus the corresponding Ro% is 1.1–1.3 (Chen et al. 1996), which means that this oil is mature. The adamantane index I and diamantane index II for the Xican 2 oil are 56.6 and 26.2 %, respectively, and the calculating Ro% is around 1.1 (Chen et al. 1996). For the Ka 6 oil, the adamantane index I is 47.5 %, and thus the calculating Ro% is less than 1.1 (Chen et al. 1996). The calculated maturities for these oils are generally consistent with the results obtained from other

parameters (Wang et al. 2013), showing the validity of this analysis.

4 Conclusions

Based on the analysis of crude oils with different physical properties in the southern Junggar Basin, it is confirmed that the GC×GC-TOFMS is an effective method for analyzing complex compounds of crude oils.

(1) Compared to conventional one-dimensional GC×GC analysis that needs to separate saturates and aromatics, separation is not necessary in the GC×GC-TOFMS analysis. This technique is well-suited for petroleum analysis owing to enhanced resolution, high sensitivity and large peak capacity.

(2) Overlapping is very common in the GC analysis; this problem can be avoided using GC×GC analysis, which is orthogonal and comprehensive, by using two distinct columns. For aromatic compounds, there are obvious differences in polarity among different compounds with similar volatility, and thus the co-elution of compounds could be well-separated. The advantages of GC×GC for aromatic analysis are prominent.

(3) Some special compounds with low molecular weights, such as diamondoids, can be effectively identified and characterized by GC×GC-TOFMS analysis with the reversed column system, which is hard by GC–MS.

(4) Through the GC×GC-TOFMS analysis, the geochemical characteristics of the crude oils in the southern Junggar Basin were further revealed, and the understanding on the oils obtained by GC were improved. The application of GC×GC-TOFMS to petroleum geochemistry has great prospects and needs more work in the future.

Table 6 Maturity diamondoid indexes of crude oils analyzed by GC×GC-TOFMS

Well	Depth(m)	Formation	Index I (%)	Index II (%)
Ka 6	3956–3980	J_3q	47.5	/
Chang 1	3375.8	J_2x	58.8	/
Xican 2	3644.5–3655.5	N_1s	56.6	26.2
Mana 1	2414–2446.5	$E_{1-2}z$	67.8	/

Analyzed by reversed phase column; "/": not analyzed

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