A Novel Pretreatment Method of Crude Oil for the Determination of Diamondoids*

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Abstract

Diamondoids in crude oil are often used to evaluate thermal maturity and cracking degree of crude oil, due to its excellent stability in thermal degradation process and biodegradation process. The most widely used method for crude oil samples pre-treatment is column chromatography using silica gel and alumina. In this study, a novel device, termed as gas purge micro syringe extraction (GP-MSE), was developed and applied to the preparation of different kinds of oil samples. The condensates, light and normal oil samples from the Pearl River Mouth Basin were prepared by GP-MSE and analyzed with comprehensive two-dimensional gas chromatography coupled with time-of-flight mass spectrometry (GC×GC/TOFMS), and quantitative analysis of diamondoids in crude oil were carried out as an example. GP-MSE has several advantages over column chromatography, such as convenience, low-cost, sensitivity, and environmental friendly characteristics etc. The limit of detection (LOD) of adamantines and diamantanes were 25.5 ng/L, 45.4 2ng/L, respectively. The relative standard deviation (RSD %) of adamantane and diamantane were 1.57% and 2.63%, respectively. In addition, satisfactory recoveries and repeatability were obtained in GP-MSE pre-treatment, which might be a potential tool in organic geochemistry to analyze other compounds in crude oil. Diamandoids parameters indicated oil mixing in this region. And the quantitative data illuminated that the Enping Formation-derived oil contained more diamandoids than Wenchang Formation-derived oil. This result might be helpful in petroleum resource evaluation and exploration strategy determination in the Pearl River Mouth Basin.

Introduction

Diamondoids in petroleum are kinds of saturated cage-like hydrocarbons with a number of diamond subunit ranging from 1 to 11, which can be detected in crude oil and source rocks extraction. It has been speculated that adamantanes and diamantanes are formed by catalytic (i.e. Lewis acids) rearrangement of polycyclic hydrocarbons during or after oil generation (Grice et al., 2000; Lin and Wilk 1995; and Wingert 1992). Diamondoids are more thermally stable than other hydrocarbons (Dahl et al., 1999), and diamondoids become increasingly enriched in the condensate oil during thermal oil cracking process because of their thermodynamic stability. Diamondoids had little influence on the

geological chromatographic fractionation, thus, quantitative and related parameters of diamondoids can play an important role in determining the kerogen types, thermal maturity and sedimentary environments (Wei et al., 2007; Schulz et al., 2001; and Li et al., 2000), tracing oil origins (Zhang and Huang 2005; Huang et al., 2011; and Wang et al., 2006) and thermal cracking levels (Dahl et al., 1999; Wei et al., 2007; Dahl et al., 2003; and Fang et al., 2012) in subsurface of sedimentary basins.

As it is well known, some complex sample (especially crude oil) must be pre-treated before analysis and this step plays an important role for the quantitative analysis of volatile compounds. Currently, the widely used methods for crude oil pre-treatment is column chromatography (Grice et al., 2000; Wingert 1992; Li et al., 2000; Wei et al., 2006; Silva et al., 2013; and Chen et al., 1996), which is efficient for the extraction of biomarkers in crude oil. However, adamantanes, diamantanes, and their alkyl substitutions are volatile so that some steps such as rotary evaporating and volatilizing solvent would result in the loss of diamondoids during the pretreatment (Liang et al., 2012). Furthermore, the pre-treatment is time-consuming and needs a lot of glass wares and also wastes large organic solvents. Some researchers injected samples directly in order to avoid the problem mentioned above (Liang et al., 2012; Wang et al., 2013; and Li et al., 2012), which is not good for the capillary-column chromatography and ion source. In addition, the direct injection can be only used for gas condensate.

In this study, the influence of the gas purge micro syringe extraction (GP-MSE) condition was investigated systematically, and an efficient analytical method for diamondoids contained in crude oil was established. This method has been used successfully to study trace compounds in complex samples from a certain area (Qiu et al., 2012) and constantly monitor the emission of volatile compounds from plant (Yang et al., 2011). In this paper, this method was used to analyze diamondoids in crude oil from Pearl River Mouth Basin. The new method is faster, more sensitive and more environmentally friendly than the traditional method. In addition, this method exhibited a higher recovery and better repeatability, and the results showed that this new method would be a powerful technique to study diamondoids in the field of geochemistry. This method might help evaluate petroleum resource and determinate exploration strategy in the Pearl Mouth Basin.

Experimental

Chemical Reagents and Samples

Adamantane and Diamantane were purchased from Tokyo chemical industry. The purity and standards were higher than 99% and 98%, respectively. Degreasing cotton, Organic solvents (n-hexane, DCM, methanol, Chloroform were HPLC grade obtained from Fulltime (AnHui, China)), silica gel (100-200 mesh, activated at 150℃ for 8h) and Al_2O_3 (50-100 mesh, activated at 400℃ for 4h) were used for column chromatography separation.

Stock standard solutions of adamantane (396 mg/L), diamantane (568 mg/L) were prepared using n-hexane. For calibration curves, standard working solutions of different concentrations were prepared by diluting the stock solutions with n-hexane and were stored at 4℃. The mixture in the final concentrations of: 0.02, 0.06, 0.07, 0.09, 0.15, 0.18, 0.20, 0.29 and 0.58 mg/mL for adamantane and 0.03, 0.09, 0.11, 0.13, 0.22, 0.26, 0.29, 0.43 and 0.85 mg/mL for diamantane. The real oil samples were taken from Pearl River Mouth Basin.

Gas Purge Micro Syringe Extraction Pretreatment

Based on previous studies on GP-MSE, a 500 mL volume micro syringe injection syringe was used to hold the liquid phase organic solvent, and an iron wire was fitted to the bottom of the micro syringe barrel to avoid boiling to run off the organic solvent from the micro syringe barrel. A 100 mL micro syringe was used to transfer adamantane and diamantane standard stock solution, and another 100 mL micro syringe to transfer n-hexane.

The extraction was conducted as follows:

(1) the standard sample or real oil sample was put into the sample cell;
(2) the sample cell was positioned in the heater, and then it was closed with the rubber mattress tightly;
(3) the micro syringe were installed (the micro syringe was thoroughly washed with extracting solvent); and the iron wire was put into the micro syringe (the iron wire was thoroughly washed with extracting solvent);
(4) a suitable extracting solvent(100 μL) was added into extraction syringe barrel by another micro syringe, at the same time, opening the inert gas(N_2, 99.999%) valve and opening the cold valve, to start the extraction as soon as everything is set;
(5) after a defined period of time, the analytes were trapped by the solvent, the syringe was removed from the apparatus, and the extracting solvent was at constant volume before being injected into the GC×GC/TOFMS for analysis.

Instrument and Analytical Method

The GC×GC system consists of a GC (7890A model, Agilent Technologies, Wilmington, DE, USA) equipped with a flame ionization detector (FID) and a time-of-flight mass spectrometer (Pegasus 4D, Leco Corp., St. Joseph, MI, USA). The GC oven contains two capillary columns that were connected serially by means of a press-fit connector with zero dead volume along with a cold-jet modulator. The GP-MSE mainly consisted of a micro syringe, sample vial, gas flow system, evaporation and condenser instrument (Key Laboratory of Nature Resource of the Changbai Mountain and Functional Molecular, Yanbian University, China).

The results from GC×GC/TOFMS showed that the components in the crude oil were well separated under orthogonal conditions and almost spread throughout the whole region of the 2D-plane (Liang et al., 2012 and Zhu et al., 2014). Additionally, the baseline separation of compounds was achieved. Validation procedures for this GC×GC/TOFMS method for quantitative analysis of diamondoids were performed under optimum conditions, which are shown in Table 1. Moreover, and a parallel determination was carried out using GC/MS to better evaluate the GC×GC/TOFMS method.

The diamondoid compounds were identified by comparing the retention times of the standards, elution orders and mass spectra with data which have published in literatures (Grice et al., 2000 and Wingert 1992). Adamantanes and diamantines quantification were achieved by comparing peak areas of the target compounds with adamantane and diamantines calibration curves.

Results and Discussion

Condition Optimization

To optimize recovery during the extraction, the gas flow rate, extracting time, extracting solvent type, evaporation and condenser temperature were systemically investigated in this study.

In the GP-MSE technique, analytes were volatilized from sample cell, and then they were carried by N_2 into the extracting solvent. Extracting solvent was cooled by the condenser. Therefore, gas flow rate, extraction time, extracting solvent type, evaporation and condenser temperature were basic necessary parameters for this method in this study. And it was found that extraction time and evaporation temperature were crucial factors. High temperature and long extraction time were good for analytes extraction. But meanwhile, the extracting solvent would be volatilized and led to loss of the extracting solvent in this opening system, and would weaken the extracting power.

The results were compared and shown in Figure 1. The graph showed that the recovery was increased with the evaporation temperature and extracting time. Therefore, the ideal extraction time was 4 to 8 minutes, and extraction time was set as 5 minutes in the following experiments; the ideal evaporation temperature range was from 290°C to 310°C, and the evaporation temperature was set as 300C in the following experiments.

Validation of the Method

The standard mixture of adamantane and diamantane were used to investigate the linearity with the GP-MSE pre-treatment method. According to Figure 3, adamantane and diamantane were had good linearity and the square of correlation coefficient (r^2) was 0.998 and 0.995, respectively.

The reproducibility and limit of detection (LOD) were represented by the relative standard deviation (RSD) and three times the signal-to-noise ratio, respectively. To estimate the limits of detection, diluted solutions of the calibration standards were extracted under optimum conditions. The result showed that the LOD of adamantines and diamantanes were 25.5 ng/L and 45.42 ng/L, respectively, which can meet the requirement of detecting diamondoids in crude oil. And the result showed the RSD% of adamantane and diamantane were 1.57% and 2.63%, respectively. The average recoveries of adamantane and diamantane were 90.72% and 89.67%, respectively as presented in Table 2.

Application of the GP-MSE Method to Real Oil Samples

Crude oil samples were pretreated using GP-MSE and analyzed by GC×GC/TOFMS. The GC×GC/TOFMS chromatograms of adamantane and diamantane in the crude oils were shown in Figure 4 and Figure 5, respectively. Peak assignments were listed in Table 2. The chromatogram showed good peak shape and separation efficiency. It can be seen that the individual peaks of diamondoids hydrocarbons were well separated without significant interference from the background. The retention time of adamantane was between n-C_{10} and n-C_{13}, however, the retention time of diamantane were between n-C_{14} and n-C_{16}.

Evaluated the GP-MSE Pretreatment Method in Real Crude Oils

56 crude oil samples were pretreated by GP-MSE, and 3 oil samples were injected into GC×GC/TOFMS direct without pretreatment as matched group. The date in Table 3 demonstrated that deviations of adamantane and diamantane were less than 3.75% and 8.33%, respectively, which is acceptable deviations range for evaluation results. Also, deviations of geochemistry parameters of diamondoid (MAI and EAI and MDI and DMDI) were less than 8% (Table 4). The results show that all target compound scan be completely extracted after the GP-MSE pretreatment, thus this method have strong practicability.

Comparison between GC/MS and GC×GC/TOFMS

There was a big difference in separation power between GC/MS and GC×GC/TOFMS by comparing the chromatograms. All of 27 compounds could be detected in both instruments, but not all of them could be separated completely by GC/MS, such as the co-eluting peaks and high baseline. In Figure 6a, GC×GC/TOFMS chromatograms plot for m/z163, showed that 1,3,4-TMA(cis) and 1,3,4-TMA(trans), 1,2,3-TMA and 1-E-3,5- DMA(Figure 1a) were co-eluting in GC/MS but could be well separated by GC×GC/TOFMS. Furthermore, in Figure 6b and Figure 6c, GC×GC/TOFMS chromatogram plot for m/z188, showed that Diamantane and 1,4,6,7-tetramethyl-1,2,3,4-tetrahydronaphthalene (1,4,6,7-TeM-1,2,3,4-TeHN) were well separated but co-eluted in the conventional GC/MS.

Distribution of Diamondoids Compounds in Crude Oils

Absolute content of diamondoids from the Pearl River Mouth Basin were obtained by GP-MSE pretreatment and GC×GC/TOFMS test. The average content of adamantanes and diamantanes were shown in Figure 7. The average content of adamantane and diamantane in Enping and Wenchang Formation-derived oil were 17.21 μg/g, 4.47 μg/g and 0.43 μg/g, 0.28 μg/g, respectively. And the content of the mixtures formation-derived oil was between Enping and Wenchang Formation-derived oils.

Unstable molecules in petroleum hydrocarbons will be converted to more stable small molecules with the increase of maturity and the relative content. The content of adamantane would increase rapidly when crude oils reached a mature stage (R_o > 1.4-1.5%). Thus, using cross plot about 1-MA/n-C_{11} ratio and MEI can indicate the maturity of oils, and Figure 8a showed that the maturity in Enping Formation-derived oil samples were higher than that of Wenchang Formation-derived oil samples. Results using cross plot about MAI and MDI are often used to indicate the maturity and these results were shown in Figure 8b.

Conclusions

The optimal conditions for GP-MSE are as follows: extraction temperature was 300°C, extraction time was 5 minutes, carrier gas flow rate was 2 mL/min, and condensing temperature was -2°C. The LOD of adamantine and diamantane was 25.5 ng/L and 45.42 ng/L, respectively, and the RSD% of the method about adamantane and diamantane was 1.57% and 2.63%, respectively.

The experiment results indicated that the new method is faster, more sensitive and more environmentally friendly compared with traditional method. In addition, higher recovery and good repeatability were obtained with this method. Thus, this new method would be a powerful technique to study diamondoids in geochemistry and oil-source correlation.

Quantitative data indicated that the Enping Formation-derived oils contained more diamandoids than Wenchang Formation-derived oils. Diamandoids parameters indicated oil mixing in this region and the Enping Formation-derived oil were of high maturity. This method might help evaluate petroleum resource and decide exploration strategies in the Pearl River Mouth Basin.

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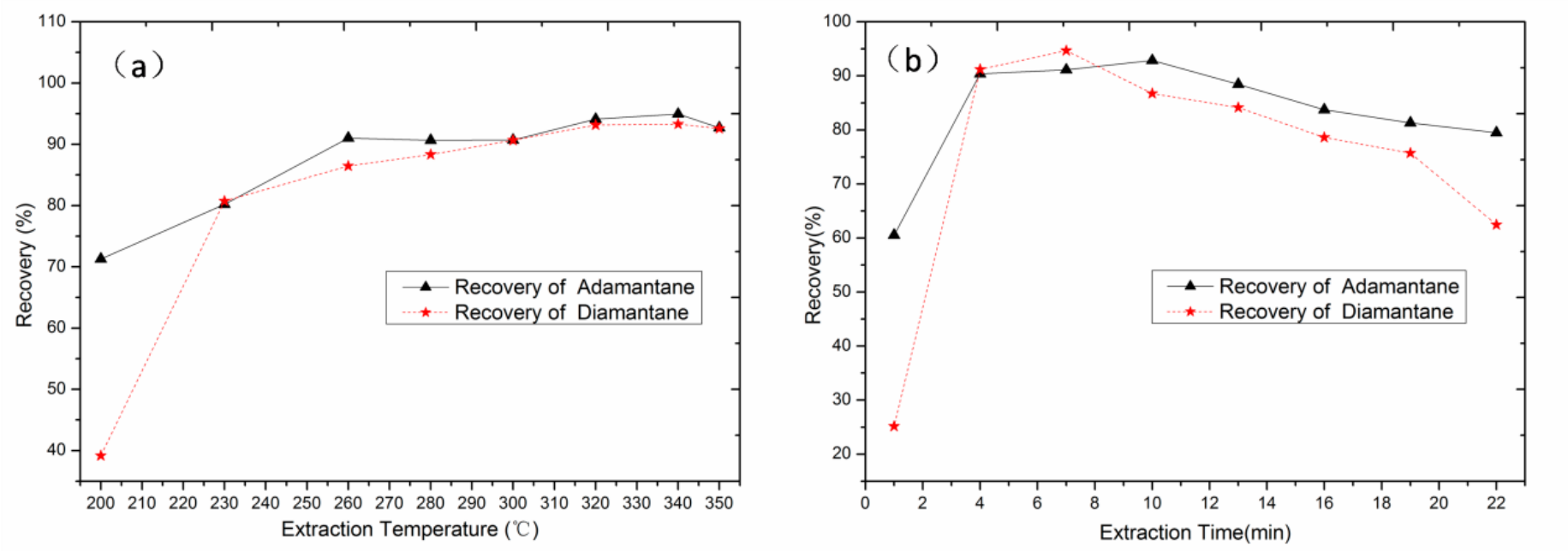

Figure 1. Effect of heating-up temperature (a) and extraction time (b) on extraction efficiency of the target compound.
(a) extracting solvent: n-hexane; extracting flow: 2.5 mL/min; condensation temperature: -2℃; extracting time: 4min.
(b) extracting solvent: n-hexane; extracting flow: 2.5 mL/min; condensation temperature: -2°C; extracting temperature: 300°C.

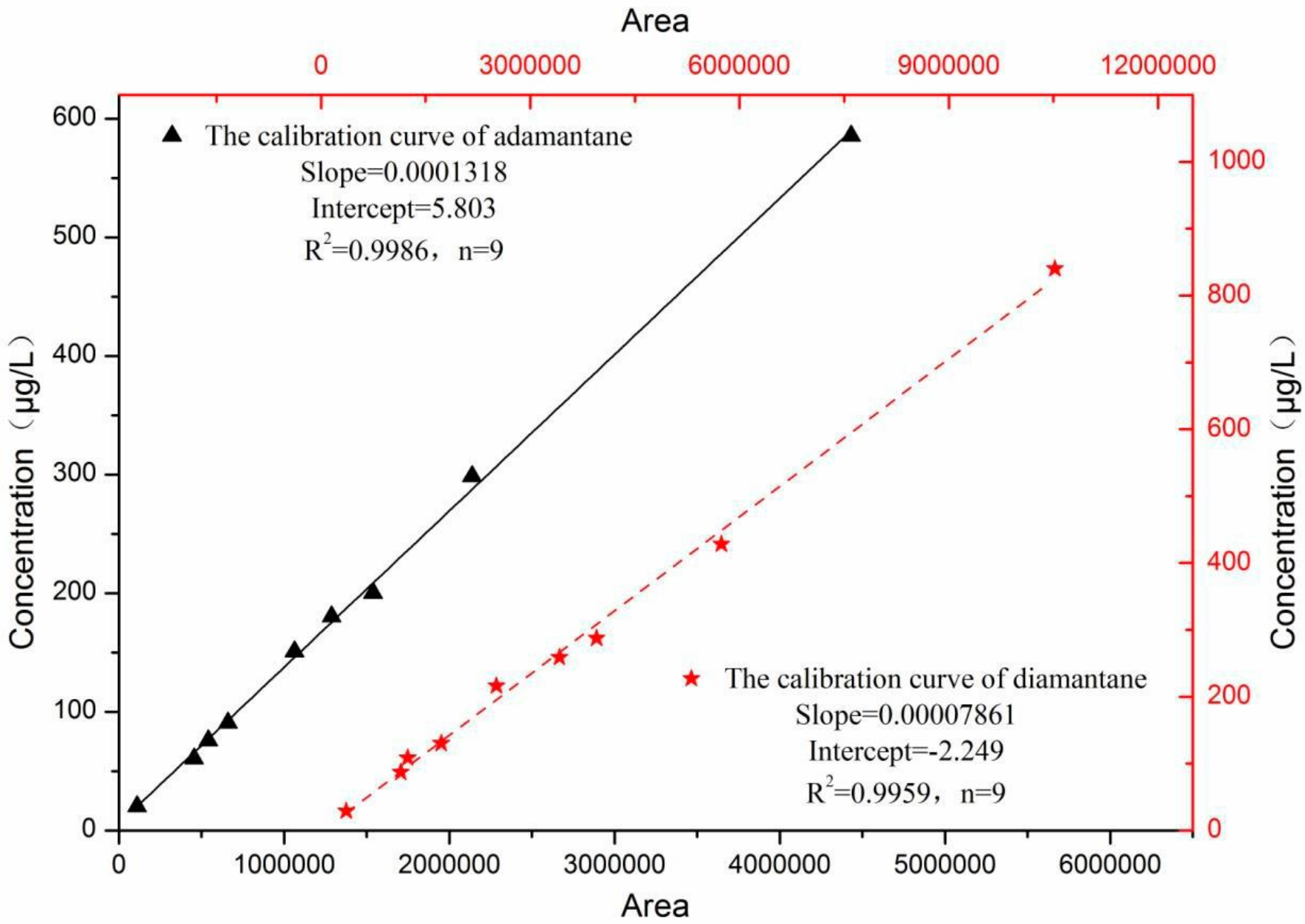

Figure 3. The linear equation about adamantines and diamantanes.

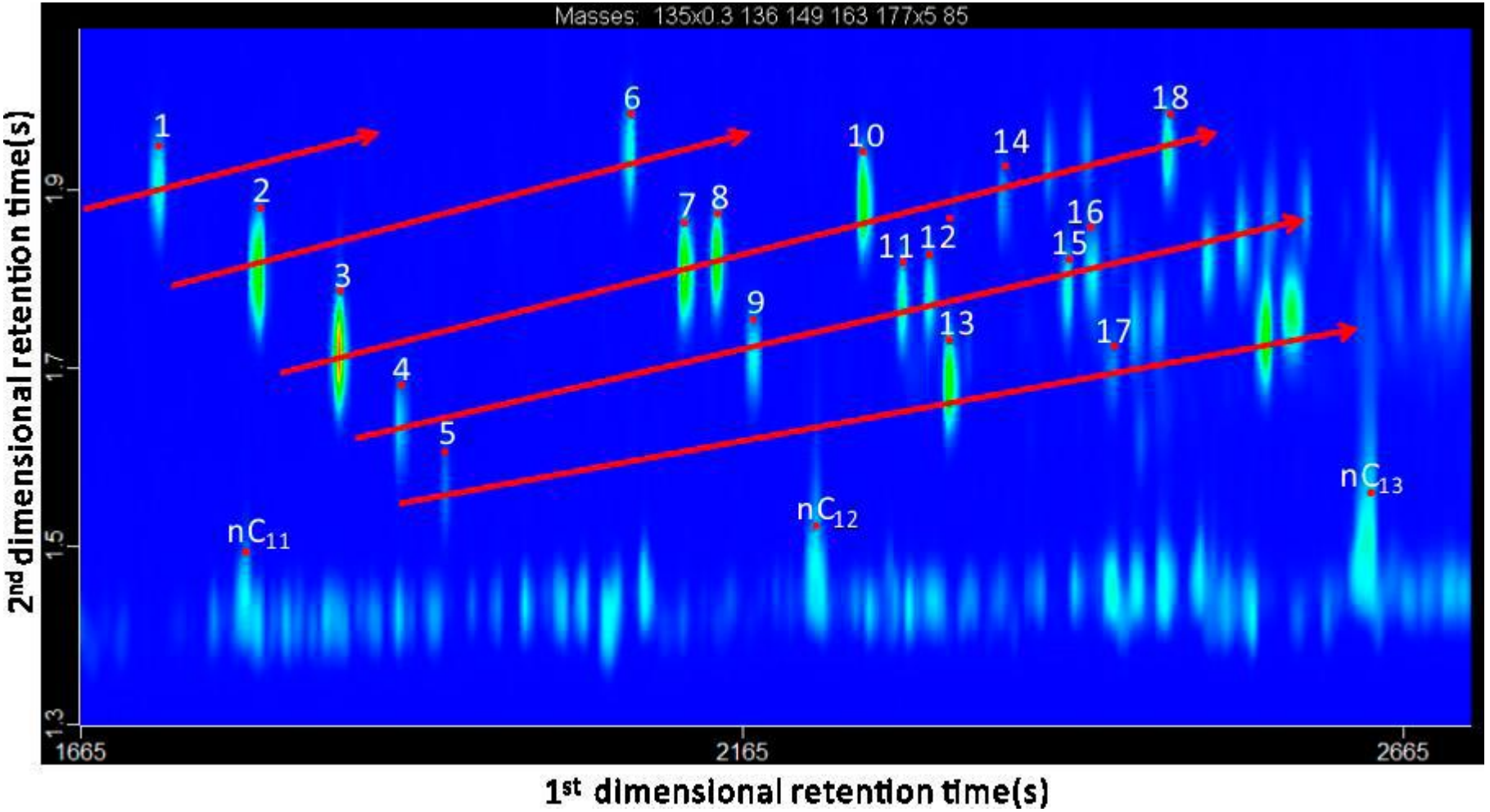

Figure 4. GC×GC/TOFMS (m/z 135×0.3 136 149 163 177×5 85) chromatogram of adamantines in Pearl River Mouth Basin oil sample (WC10-3-1).

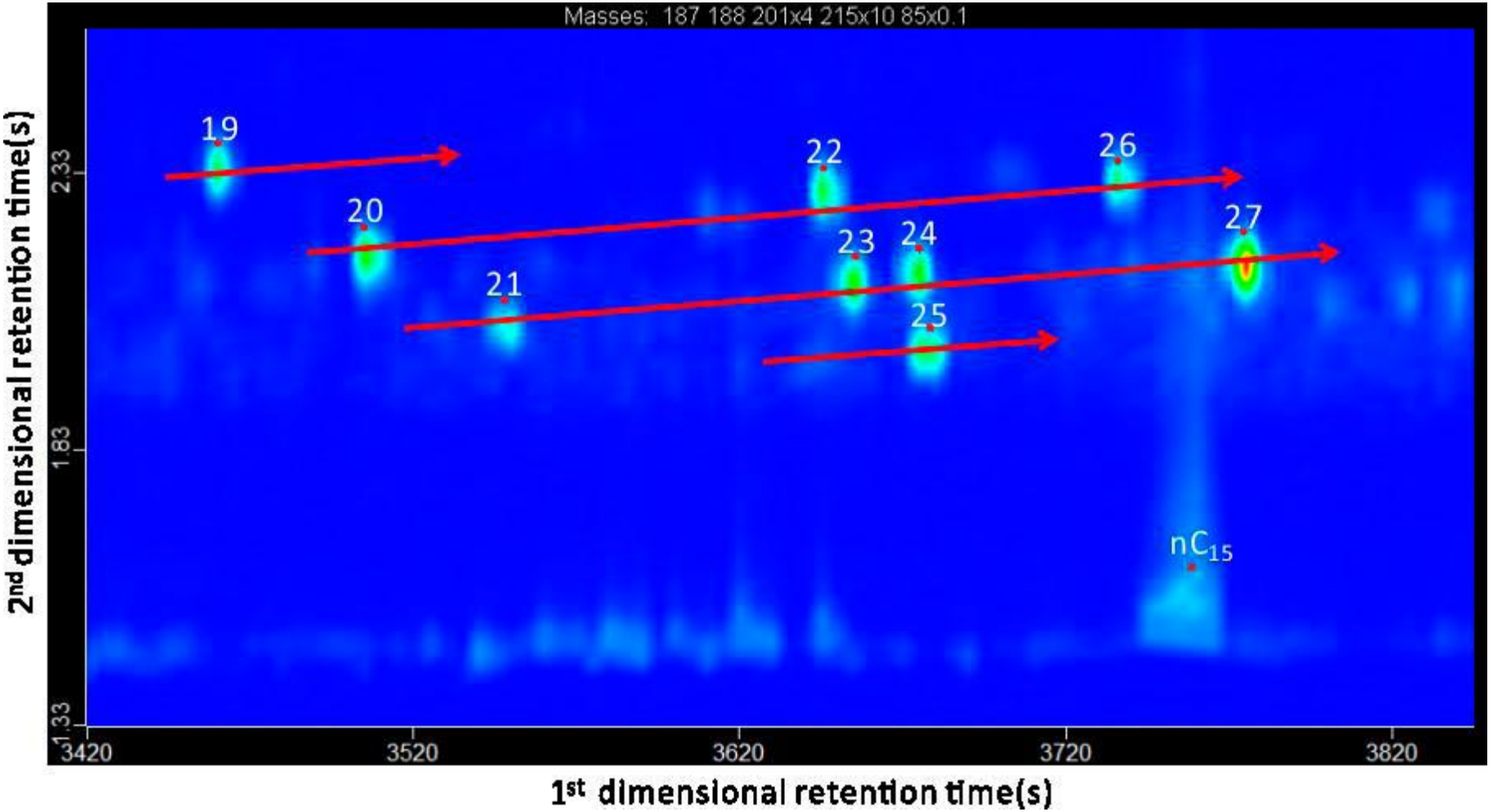

Figure 5. GC×GC/TOFMS (m/z 187 188 201x4 215x10 85x0.1) chromatogram of diamantines in Pearl River Mouth Basin oil sample (WC10-3-1).

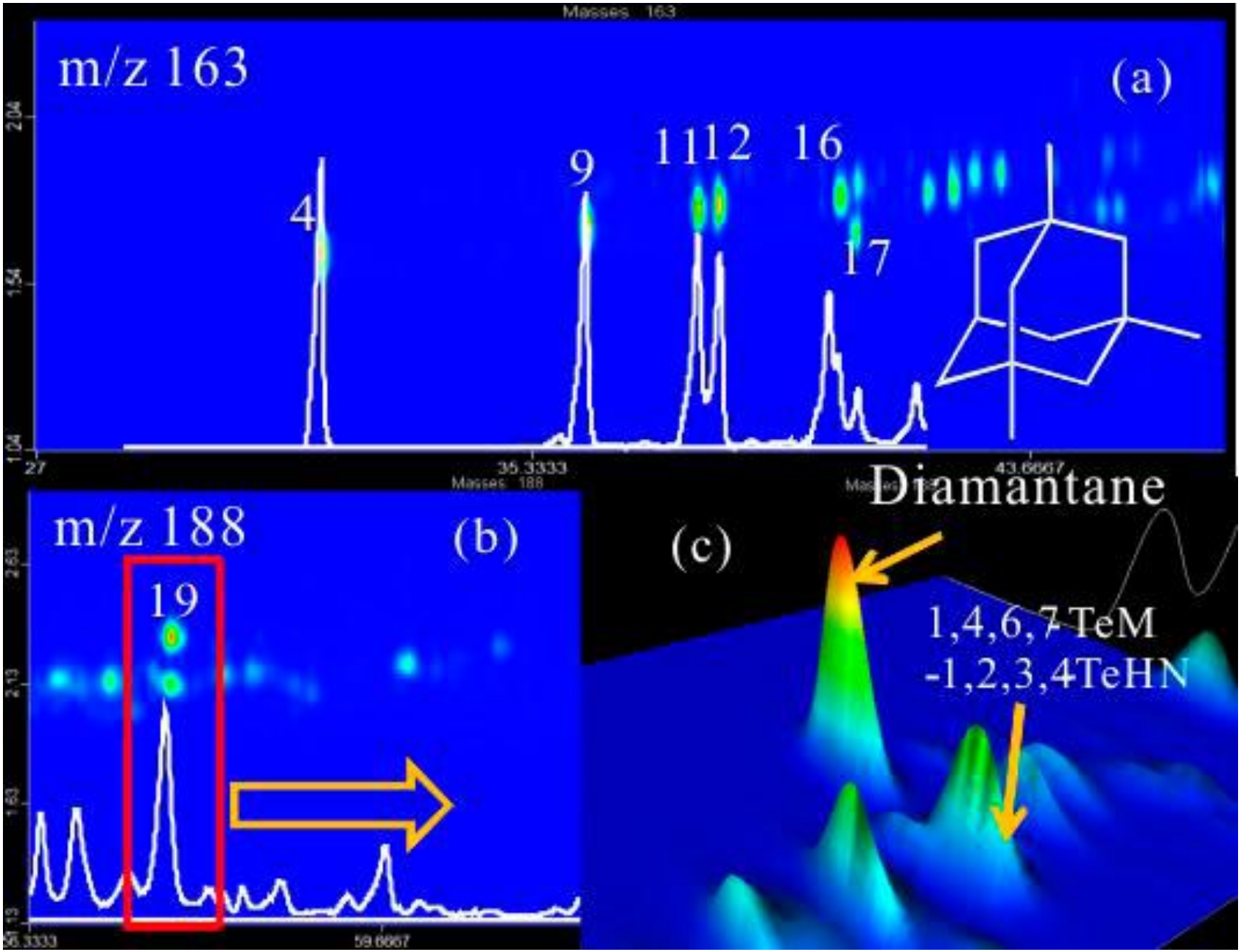

Figure 6. GC×GC/TOFMS and GC/MS (m/z163 (a) and m/z188 (b, c)) chromatograms of diamondoids fraction of Sample PY35-2-1.

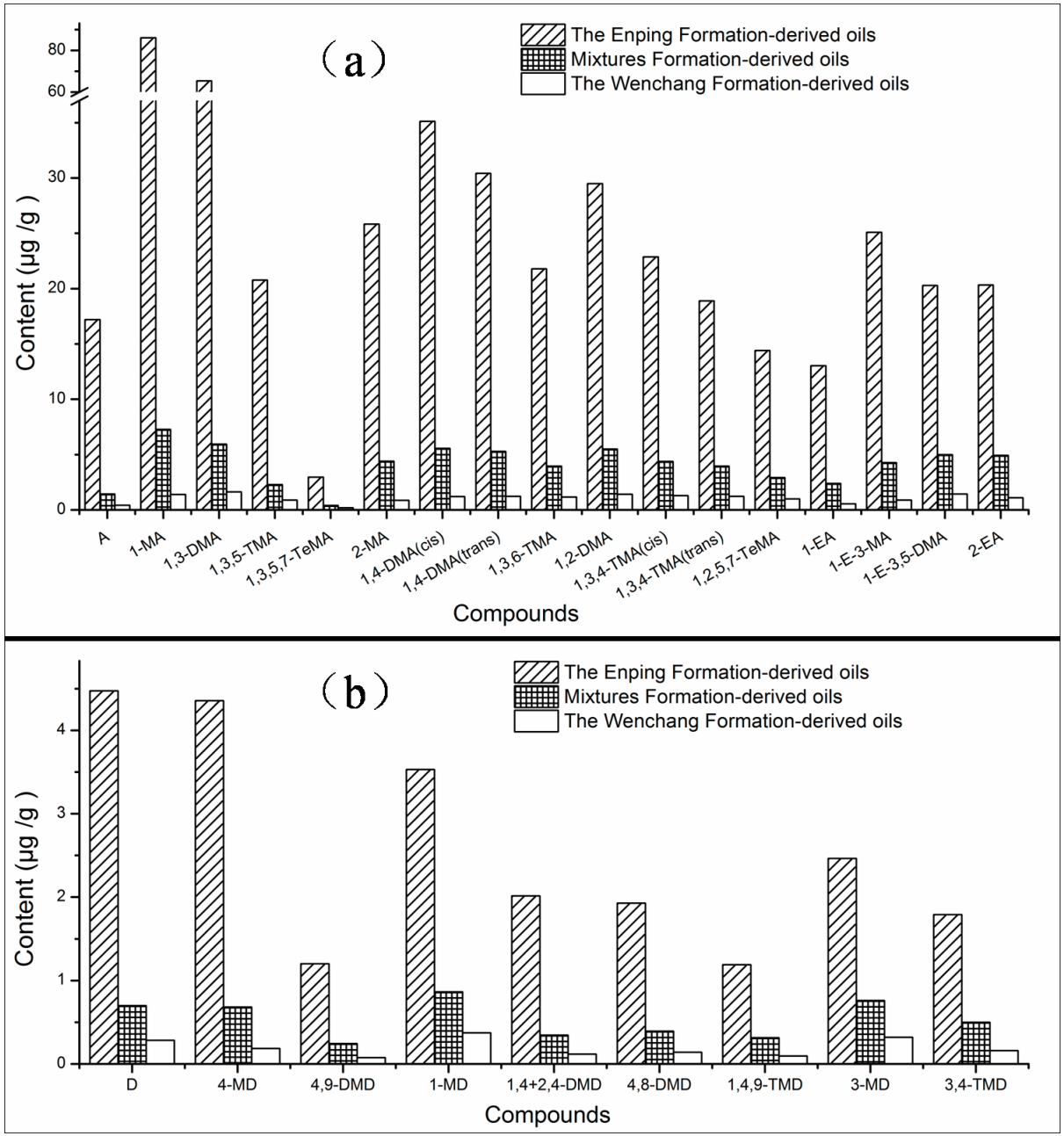

Figure 7. Distribution of diamondoids compounds in Pearl River Mouth Basin oils.

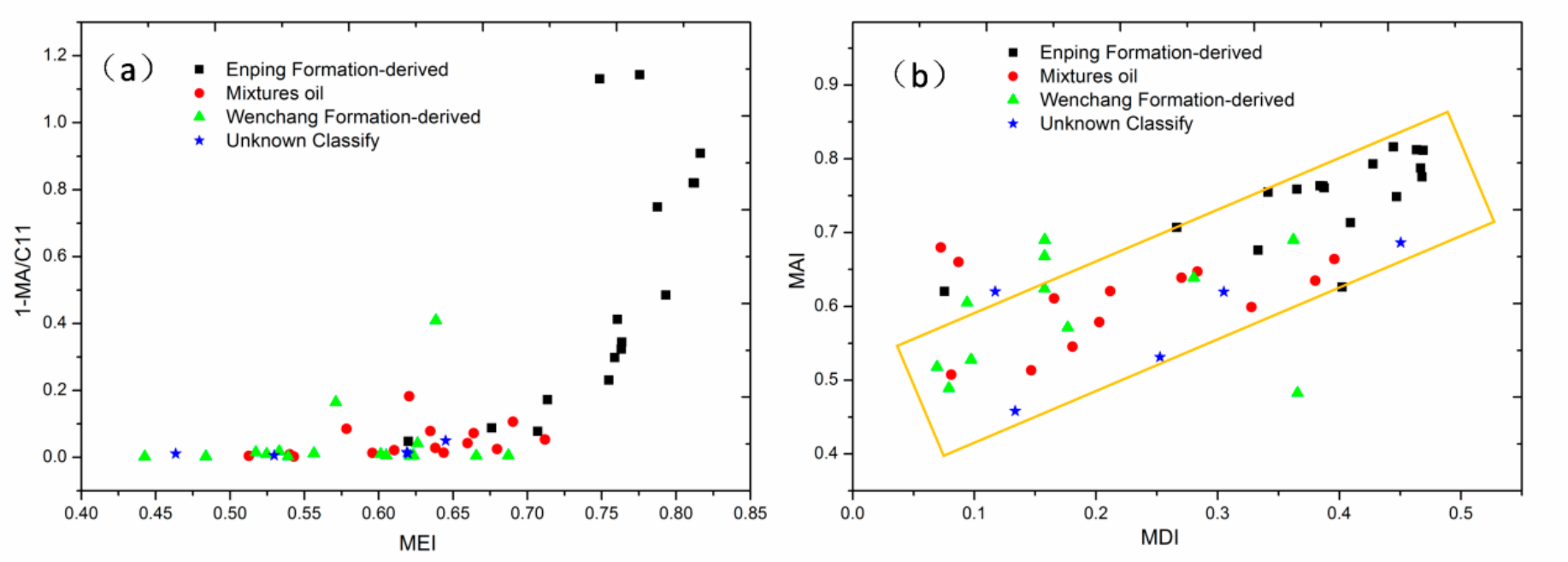

Figure 8. Cross plots of MEI vs. 1-MA/C_{11} values (a) and Cross plots of MDI vs. MAI values (b) for oil samples from Peal River Mouth Basin.

Items	Parameters	Items	Parameters
1st column	HP-5MS，60m×0.25mm×0.25μm	Autoinjection	
2st column	DB-17HT，2m×0.25mm×0.15μm	Splitless	
1st column temperature program	50℃（3min）2℃/min to 160℃ 3℃/min to 300℃（30min）	Transfer line temperature(℃)	280
2st column temperature program	60℃（3min）2℃/min to 170℃ 3℃/min to 310℃（30min）	Electron energy(Ev)	-70
Inlet temperature(℃)	300℃	Detector voltage(V)	1550V
Sample injection	0.2μL	Ion source(℃)	230
Carrier gas	He，inlet flow rate:1mL/min	Acquisition(Spectra/S)	100Spectra/S
Modulator temperature offset	15℃,relative to the GC oven temperature	Scan range(u)	50-550amu
Modulation time	5s，1.25s hot pulse time	Acquisition delay(min)	390s

Table 1. Experimental setting of GC×GC/TOFMS.

Experiment No	1	2	3	4	5	6	7	RSD(%)
Recovery of Adamantane（%）	89.09	91.60	88.60	91.29	90.28	92.16	92.03	1.57
Recovery of Ddamantane（%）	85.81	91.53	86.74	90.56	91.23	91.00	90.79	2.63

Table 2. The result of the recoveries (%) and repeatability (expressed as RSD, %) calculated from seven times experiences.

Peak Number	Assignment	Abbreviation	M/Z	^{1}D Retention time (min)	^{2}D Retention time (s)
1	Adamantane	A	136	28.75	1.90
2	1-Methyladamantane	1-MA	135	30	1.80
3	1,3-Dimethyladamantane	1,3-DMA	149	31	1.70
4	1,3,5-Trimethyladamantane	1,3,5-TMA	163	31.8333	1.63
5	1,3,5,7-Tetramethyladamantane	1,3,5,7-TeMA	177	32.3333	1.59
6	2-Methyladamantane	2-MA	135	34.6667	1.92
7	1,4-Dimethyladamantane(cis)	1,4-DMA(cis)	149	35.4167	1.79
8	1,4-Dimethyladamantane(trans)	1,4-DMA(trans)	149	35.75	1.80
9	1,3,6-Trimethyladamantane	1,3,6-TMA	163	36.25	1.69
10	1,2-Dimethyladamantane	1,2-DMA	149	37.5833	1.86
11	1,3,4-Trimethyladamantane(cis)	1,3,4-TMA(cis)	163	38.0833	1.75
12	1,3,4-Trimethyladamantane(trans)	1,3,4-TMA(trans)	163	38.4167	1.76
13	1,2,5,7-Tetramethyladamantane	1,2,5,7-TeMA	177	38.6667	1.66
14	1-Ethyladamantane	1-EA	135	39.4167	1.86
15	1-Ethyl-3-Methyladamantane	1-E-3-MA	149	40.1667	1.76
16	1,2,3-Trimethyladamantane	1,2,3-TMA	163	40.5	1.80
17	1-Ethyl-3,5- Dimethyladamantane	1-E-3,5-DMA	163	40.75	1.67
18	2-Ethyladamantane	2-EA	135	41.4167	1.91
19	Diamantane	D	188	57.6667	2.3
20	4-Methyldiamantane	4-MD	187	58.5	2.14
21	4,9-Dimethyldiamantane	4,9-DMD	201	59.25	2.02
22	1-Methyldiamantane	1-MD	187	60.75	2.26
23	1,4+2,4-Dimethyldiamantane	1,4+2,4-DMD	201	60.9167	2.10
24	4,8-Dimethyldiamantane	4,8-DMD	201	61.3333	2.10
25	1,4,9-Trimethyldiamantane	1,4,9-TMD	215	61.3333	1.97
26	3-Methyldiamantane	3-MD	187	62.25	2.28
27	3,4-Dimethyldiamantane	3,4-TMD	201	62.9167	2.13
28	3,4,9-Trimethyldiamantane	3,4,9-TMD	215	65.1667	2.11

Table 3. Peak assignments of diamondoids in GC×GC/TOFMS analysis.

Well	Pretreatment method	MAI	EAI	MDI	DMDI-1	DMDI-2	Concentration of adamantane (μg/g)	Concentration of diamantane (μg/g)
HZ33-1-1	GP-MSE	0.56	0.28	0.10	0.24	0.21	0.14	0.11
	DI	0.59	0.26	0.10	0.22	0.24	0.15	0.13
	Δ(%)	2.61	3.70	0	3.40	7.12	3.45	8.33
HZ9-2-1	GP-MSE	0.63	0.29	0.23	0.46	0.29	2.26	0.49
	DI	0.63	0.28	0.24	0.50	0.34	2.41	0.53
	Δ(%)	0	1.75	2.13	4.17	7.94	3.21	3.92
WC10-3-1	GP-MSE	0.70	0.37	0.42	0.41	0.32	7.15	1.71
	DI	0.72	0.38	0.38	0.38	0.28	7.71	1.87
	Δ(%)	0.92	0.98	5.04	3.71	6.02	3.75	4.67

Table 4. Geochemical data obtained from the direct injection and GP-MSE methods.
MAI = 1-MA/(1-MA+2-MA); EAI = 1-EA/(1-EA+2-EA); MDI = 4-MD/(1-MD+3-MD+4-MD);
DMDI-1 = 4,9-DMD/(4,9-DMD+3,4-DMD); DMDI-2 = 4,9-DMD/(4,8-DMD+4,9-DMD).
Δ means the deviation of two data obtained from the direct injection and GP-MSE methods;
$\Delta(\%) = (A_1-A_2)/(A_1+A_2)*100\%$; A_1 result from the GP-MSE method, A_2 results from GP-MSE.