Citation: WANG Huitong, WENG Na, ZHANG Shuichang, WEI Caiyun, ZHANG Chaojun. A novel method for quantitative analysis of diamondoids in petroleum samples [J]. Petroleum Geology & Experiment, 2019 (03): 443–450.

A novel method for quantitative analysis of diamondoids in petroleum samples

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Abstract: A new method for the quantitative analysis of diamondoid hydrocarbons in petroleum geological samples was established with comprehensive two-dimensional gas chromatography–flame ionization detector (GC × GC–FID). The process included the pretreatment of the sample followed by the qualitative analysis of diamondoid hydrocarbons using two-dimensional gas chromatography with time-of-flight mass spectrometry (GC × GC–TOFMS). The diamondoid hydrocarbons could be well separated using the orthogonal separation characteristics of GC × GC. The original separation method of saturated hydrocarbon fraction in petroleum samples was improved in this study in order to reduce the loss of low-carbon diamondoid hydrocarbons in the pretreatment process. A new pretreatment method for saturated hydrocarbon by small column chromatography was established. There were many advantages such as lower sample costs, short analysis time and little consumption of reagents. The recovery of diamondoid hydrocarbons was satisfied with chromatography quantitative analysis. Compared with the traditional internal standard semi-quantitative method by gas chromatography–mass spectrometry (GC–MS), this method had high resolution and lower requirements for internal standards. The quantitative results of diamondoids could be obtained using only one certified reference material of deuterated adamantane. Moreover, the repeatability was good. The relative standard deviation (RSD, n = 7) was less than 5%, which could meet the analytical requirements of a complicated system.

Keywords: comprehensive two-dimensional gas chromatography; time-of-flight mass spectrometry; flame ionization detector; diamondoid; analysis of petroleum samples

Diamondoid is a kind of special cyclic hydrocarbon in crude oil, and its stability renders it the strong heat resistance and biodegradability in the process of geological evolution [1–3]. In the highly mature crude oil and condensate oil, steroids, hopanes and other commonly used biomarkers compounds are absent. Diamondoid can be used as the important parameter to judge the maturity [4–6] and can also be used to research the oil and gas migration direction, oil source identification and cracking degree of crude oil [7–9].

How to obtain the absolute content of diamondoid has been a challenge that geochemists have to overcome. Restricted by the interference of co-distillation peaks and the limitation of purification conditions, it is impossible to carry out an absolute quantitative analysis of diamondoid by conventional gas chromatography (GC–FID) due to the low content of diamondoid in petroleum geological samples. Currently, the commonly used quantitative method is the internal standard semi-quantitative method of gas chromatography-mass spectrometry (GC–MS). In the mass spectrometric analysis, in order to obtain more accurate quantitative results, the strict absolute quantification shall adopt the compounds having the same structure as the target compound, and the same characteristic ionic features or fragmentation mode as the internal standard compound. In overseas countries, Wei et al. [3,10] used six deuterated diamondoids with different structures as the internal standard substance to obtain the reliable quantitative results. In China, all structural diamondoids are usually quantified by using only one structural deuterated diamondoid due to the lack of samples, so the obtained results are quite different from the actual results. Ma et al. [11] used deuterated mono-diamondoid as the internal standard, determined the response factors of diamantane, deuterated methyl diamantane and deuterated dimethyl mono-diamondoid on GC–MS, and calculated the absolute contents of diamantane, methyl mono-diamondoid and dimethyl mono-diamondoid, which can be used to judge the degree of crude oil cracking in Tahe oilfield. However, there is no effective absolute quantitative method for other structural diamondoids that limit the development of geochemistry research on diamondoid.

Comprehensive two-dimensional gas chromatography (GC × GC) is a new technique for the separation of complex mixtures. Its two-dimensional orthogonal column system allows some compounds co-distilled by the same boiling

Received: 2018-09-14
Supported by: Project of Science and Technology Department of PetroChina (2017D-5006-14)
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point in conventional gas chromatography to be separated perfectly on the two-dimensional column according to their polarity. The response factor of the combined FID detector to all hydrocarbon structural compounds is approximately 1. Therefore, GC × GC–FID is currently considered to be one of the most effective methods to quantify hydrocarbon structural compounds [12–13]. On the basis of previous work [14–16], a complete chromatographic quantitative method for diamondoid in petroleum geological samples was established in this paper, which provides effective technical support for the geochemical research of diamondoid.

1 Experimental part

1.1 Instruments and equipment

Comprehensive two-dimensional gas chromatography–time-of-flight mass spectrometer (Pegasus 4D made by LECO, USA), with Chroma TOF software as the workstation, hydrogen flame ionization detector (Agilent, USA), Trace gas chromatography/DSQ Ⅱ mass spectrometer (Thermo Fisher, USA) and Organomation (imported from USA) were used.

1.2 Reagents and materials

Analytically pure n-hexane, dichloromethane and trichloromethane were purchased from Sinopharm Chemical Reagent Co., Ltd, and they were further purified before use; fine silica gel was 100 mesh–200 mesh, which was activated at 200 °C for 4 h.

1.3 Samples

Two rock extracts and seven crude oil samples were selected for analysis (Table 1).

Table 1 Background information of samples for quantitative analysis of diamondoids

Sample number	Sample name	Areas	Depth/m	Lithology
S1	AP-1	Sichuan Basin	5 055.4	Limestone
S2	JLW	Three Gorges area	Outcrop	Limestone
S3	M3	Tarim Basin	1 508.0–1 518.0	Brown crude oil
S4	LN62	Tarim Basin	5 565.0–5 578.0	Black crude oil
S5	LG38	Tarim Basin	5 619.4–5 740.0	Yellow crude oil
S6	LN57	Tarim Basin	4 341.8–4 344.0	Yellow crude oil
S7	HD4	Tarim Basin	5 069.6–5 076.3	Black crude oil
S8	JF100	Tarim Basin	4 473.0–4 475.5	Brown crude oil
S9	KL205	Tarim Basin	3 789.0–3 952.5	Condensate

1.4 Experimental conditions

1.4.1 GC × GC–TOFMS analysis conditions

The one-dimensional chromatography column was the DB1-MS column of 30 m × 0.25 mm × 0.25 μm (Agilent Company, USA); the temperature was raised to 200 °C at 2 °C/min after holding at 50 °C for 0.2 min, kept for 0.2 min and then raised to 300 °C for 10 min at the rate of 8 °C/min. The two-dimensional chromatography column was the DB-17HT column of 1.5 m × 0.1 mm × 0.1 μm (Agilent Company, USA). The temperature was 5 °C higher than that of one-dimensional chromatography at the same heating rate as that of one-dimensional chromatography. The temperature of the modulator was 45 °C higher than that of one-dimensional chromatography. He was used as the carrier gas, and its flow rate was set at 1 mL/min. The modulation period was 10 s, with 2.5 s hot blowing time. The inlet temperature was 300 °C, and the injection mode was split. For condensate samples, the split ratio was 700:1 and the injection volume was 0.5 μL. For other crude oil or rock extracts, the split ratio was 20:1 and the injection volume was 1 μL.

The transmission line and ion source temperatures of time-of-flight mass spectrometry were 300 °C and 240 °C, respectively; the detector voltage was 1 500 V; the mass scanning range was 40 amu–520 amu; and the acquisition rate was 100 spectrogram/s. For condensate samples, the delay time of the solvent was 0 min. For other crude oil or rock extracts, the delay time of the solvent was 10 min.

1.4.2 GC × GC–FID analysis conditions

The adopted chromatography conditions were identical to those of GC × GC–TOFMS. The flow rates of carrier gas, hydrogen and air in FID detector were 23 mL/min, 30 mL/min and 400 mL/min, respectively. The detector temperature was 310 °C; the sampling frequency was 200 spectrogram/s; and the delay time of the solvent was consistent with that in the TOFMS setting.

1.4.3 GC–MS analysis conditions

The chromatography column was the DB1–MS column of 30 m × 0.25 mm × 0.25 μm, with helium as the carrier gas, and the flow rate of which was 1 mL/min. The temperature rising procedure was as follows: Starting temperature of 50 °C was raised to 80 °C at 15 °C/min, then increased to 230 °C at 2 °C/min, and then enlarged to 310 °C/min at 25 °C/min for 20 min. The inlet temperature was 280 °C, and the injection mode was split, with the injection volume of 1 μL. The voltage of the mass spectrometry detector was 1 600 V; ion mode scanning was selected, and the delay time of the solvent was 10 min.

1.5 Quantitative methods

1.5.1 GC × GC–FID Quantitative methods

The samples were analyzed by GC × GC–TOFMS and GC × GC–FID, and the chromatograms of GC × GC–TOFMS

with uniform appearances under TIC and of GC × GC–FID were obtained. Based on the mass spectra of Reference [17] and the mass spectrometry information provided by the TOFMS, the standard samples and diamondoid were identified qualitatively on the GC × GC–TOFMS spectra. According to the relative retention time of the compounds on GC × GC–TOFMS, the corresponding target compounds were labeled on GC × GC–FID chromatograms and their peak areas were obtained, and the quantitative results were calculated by the internal standard method.

1.5.2 GC–MS Quantitative method

Samples were analyzed by the selective ion mode of GC–MS. The flow pattern map of chromatography–mass spectrometry TIC and the chromatography–mass spectrometry at selective ions *m/z* of 135, 136, 149, 152, 163, 177, 187, 188, 201, 215, 239, 240, 253, and 267 were obtained. The peak areas of the target compounds with different selected ions were obtained by manual integration, and the quantitative results were obtained by the internal standard method.

2 Results and discussion

2.1 Selection of analytical condition

2.1.1 Selection of pretreatment methods

The condensate samples with relatively high contents of diamondoid can be directly analyzed by GC × GC–FID without any pretreatment. Appropriate amount of condensate sample in 1.5 mL automatic injection bottle was taken. The prepared standard solution of D_{16}-mono-diamondoid (solvent was CH_2C1_2) and the appropriate amount of CH_2C1_2 solvent was added after it was weighed, and the sample was injected directly for analysis. This method avoided the loss of diamondoid with low boiling point in the pretreatment process and ensured the accuracy of the quantitative results. Figure 1a is a GC × GC–FID spectrogram of direct injection analysis of S9# condensate sample. This figure illustrates that 17 mono-diamondoid compounds could be well separated under GC × GC–FID. In this experiment, S9 sample was selected as the standard sample to determine the peak position of diamondoid in other samples on GC × GC–FID.

For normal crude oil or heavy oil samples, the relative content of diamondoid was relatively low, which was susceptible to monocyclic aromatic hydrocarbons and was not easy to be detected (Figure 1b). The samples were pretreated with chromatography columns of crude silica gel in traditional petroleum industry standard (Figure 2a), resulting in miscible alkylbenzenes and monoaromatic steroids [18] in saturated hydrocarbon fractions that affected the quantitative analysis of diamondoid by GC × GC–FID. Wang et al. [19] improved the separation method (Figure 2b) and obtained the saturated hydrocarbon fractions containing no alkylbenzene, which could be used for the quantitative analysis of diamondoid. In this paper, based on the method, the small column method was used, and a commercially available long dropper was used as a glass chromatography column with only 1 g of fine silica gel filled. About 5 mg of crude oil sample was taken and rinsed with 1.5 mL of *n*-hexane (Figure 2c). The obtained front cut fraction of saturated hydrocarbon could meet the GC × GC–FID quantitative requirements of diamondoid, save raw materials and analysis time, and reduce the volatilization loss of monoamantane, especially suitable for the analysis requirement of small samples.

The conventional methods for the analysis of diamondoid in rock samples were to extract diamondoid with $CHCl_3$, evaporate and then dissolve them in n-hexane, and obtain saturated hydrocarbon components by the method shown in Figure 2a or Figure 2b. However, in the process of evaporating $CHCl_3$, the compounds prior to C_{13} were seriously lost (Figure 3b) and mono-diamondoid could not be detected. In order to avoid drying loss, the rock samples were extracted first. When $CHCl_3$ was dried less than 1 mL, a small amount of fine silica gel was added and mixed with the solution evenly, and then it was dried. The columella of Figure 2c was filled with fine silica gel at the lower part and mixed with fine silica gel at the upper part, and then it was separated, so that the mono-diamondoid could be retained (Figure 3a)

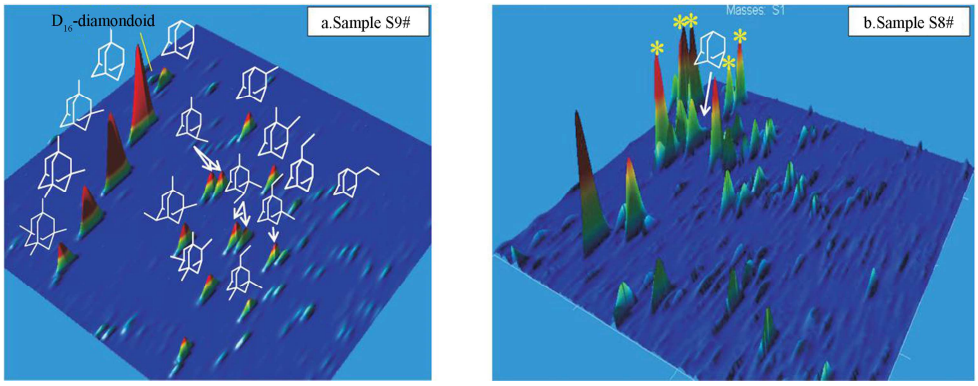
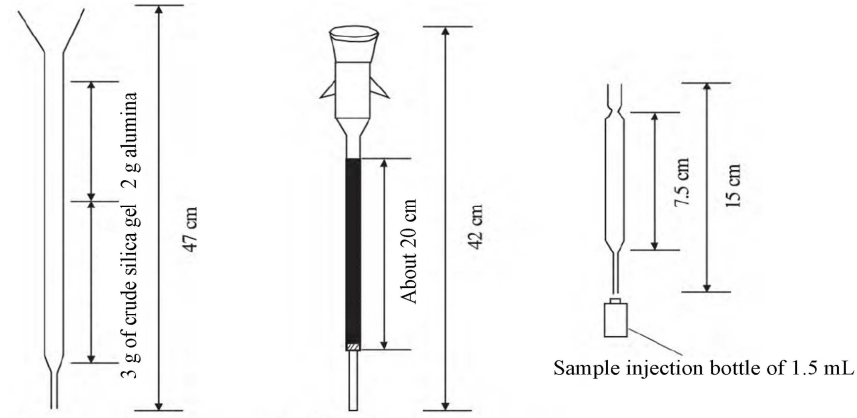


Figure 1 GC × GC–FID 3D plot from samples S9 (a) and S8 (b)

In the figure, * stands for some monocyclic aromatic hydrocarbons



a. Crude silica gel column of industry standard (80 mesh–100 mesh) , 20 mg–30 mg sample, 30 mL *n*-hexane

b. Chromatography column of fine silica gel (100 mesh–200 mesh), 20 mg sample, 2 g silica gel, and 10 mL *n*-hexane

c. Columella filled with fine silica gel, about 5 mg sample, 1 g fine silica gel, and 1.5 mL *n*-hexane

Figure 2 Separation method for preparation of saturated hydrocarbon fraction

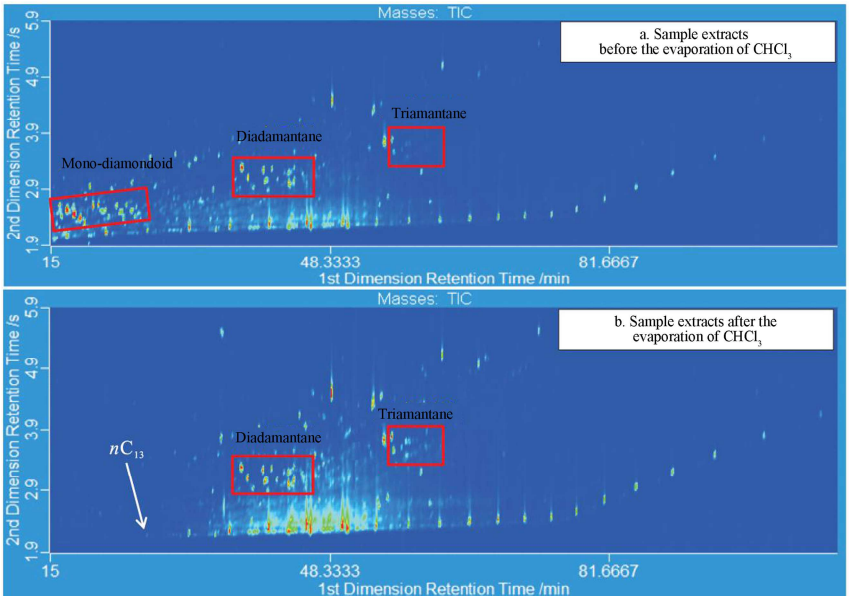


Figure 3 GC × GC–FID color contour chromatogram of sample S2

In order to verify the reliability of the pretreatment method, the mixed solutions of mono-diamondoid and diadamantane with concentration of 0.25 mg/L and 0.43 mg/L were prepared with $CHCl_3$, respectively. The recovery rates of mono-diamondoid and diadamantane were 98.2% and 99.1%, respectively.

2.1.2 Optimization of analytical methods for comprehensive two-dimensional gas chromatography

Wang et al. [14] used GC × GC–FID to quantify diamondoid in the analysis of condensate samples. However, in order to meet the requirement for the separation of nC_3–nC_8 compounds, the temperature rise rate of this method was slow and the analytical time was long. In this paper, this method was improved by selecting a shorter chromatography column to reduce the cost. Due to the small amount of heavy components collected in the pretreatment process, a slow heating rate in the early stage and a fast heating rate in the late stage were adopted to save the analysis time. In order to compare with the results of GC–MS analysis properly, the flow rate of carrier gas was 1 mL/min as well.

2.2 Analysis results of diamondoid

2.2.1 Qualitative results of GC × GC–TOFMS

When diamondoid was analyzed by GC × GC–TOFMS, there was only one chromatography peak (1# peak labeled in Figure 4a) in one-dimensional chromatography at characteristic ion of *m/z*149, and two chromatography peaks (1–1# and 1–2# peaks labeled in Figure 4a) in two-dimensional chromatography, with the characteristic ions of *m/z*149 and the molecular ion peaks of *m/z*164 and *m/z*178, respectively. In the known literatures, 1# peak was the 1-ethyl-3-methyl

mono-diamondoid [20], and thus "1–2"# peak was the target compound. The "1–1"# and "1–2"# peaks were the co-distillation peaks on one-dimensional chromatography, but could be well separated on GC × GC. Similarly, this was also the case with the characteristic ion of *m/z*163 (Figure 4b). Thus, the analysis of diamondoid by GC × GC could eliminate the influence of co-distillation peaks and achieve good separation under GC × GC–FID without resorting to mass spectrometry (Figure 5).

2.2.2 Quantitative results of GC × GC–FID

According to the qualitative information of GC × GC–TOFMS, the peak positions of 17 mono-diamondoids, nine diadamantanes and internal standard substances were marked on the GC × GC–FID spectrogram based on the relative retention time (Figure 5), and the integration results of the peak area of these compounds were obtained by Chroma TOF software. For the samples requiring pretreatment, the quantitative results of diamondoid differed from the true values and mainly manifested by the volatilization loss of compounds during pretreatment. In this experiment, the columella separation method avoided the volatilization loss of diamondoid compounds in the process of sample concentration, and the results were closer to the real value. Table 2 shows the quantitative results of diamondoid in eight samples, where the results of S1 and S2 were the diamondoid content in rock samples; the S9 sample was a non-pretreated standard sample, and it was only used to determine the peak position of diamondoid on GC × GC–FID, so the quantitative results of S9 are not given in the table.

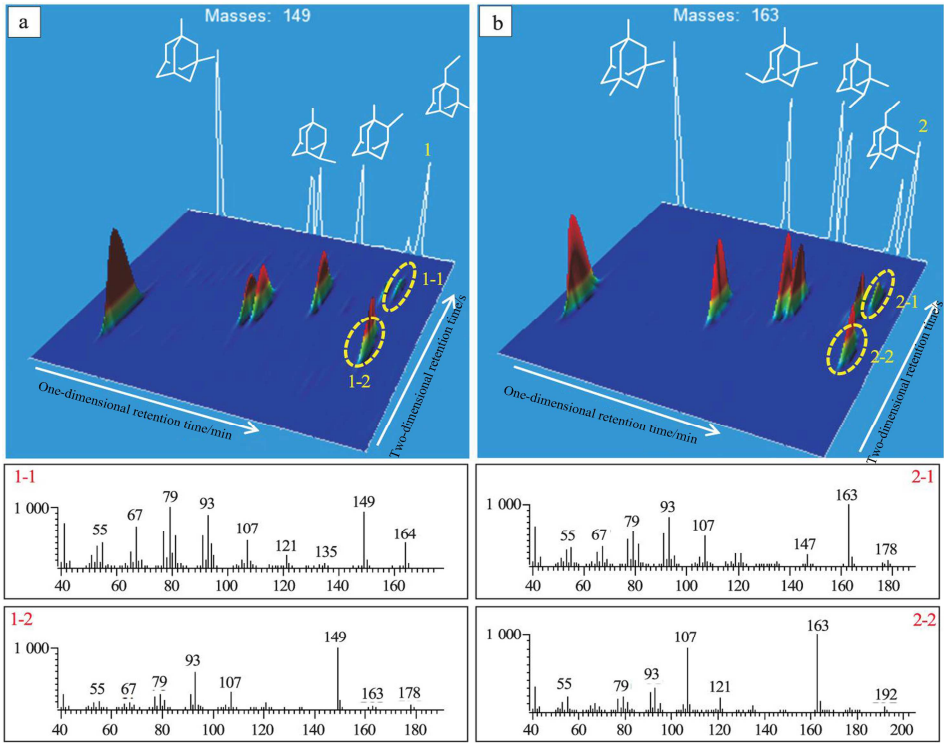
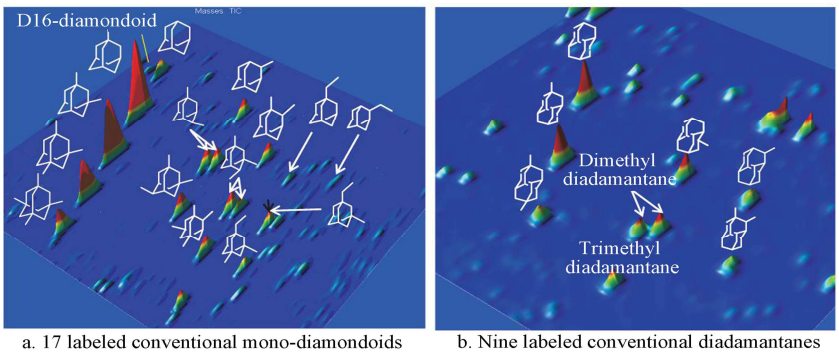


Figure 4 GC × GC–TOFMS 3D plot of sample S9

The spectrograms drawn in white line are the projections of 3D images on one-dimensional chromatography. a is the spectrogram at the selected ion of *m/z*149, and the mass spectrogram of compounds 1–1 and 1–2 are listed below. b is the spectrograms at the selected ion of *m/z*163, and the mass spectrograms of compounds 2–1 and 2–2 labeled therein are listed below.



a. 17 labeled conventional mono-diamondoids b. Nine labeled conventional diadamantanes

Figure 5 GC × GC–FID color contour chromatogram of sample S9

Table 2 Quantitative results of main diamondoid hydrocarbons by GC × GC–FID

Name of compound	Concentration of compound/(mg·kg^{-1})							
	S1	S2	S3	S4	S5	S6	S7	S8
Mono-diamondoid		0.019 4	115.5	178.0	97.4	13.1	26.5	21.2
1-Methyl mono-diamondoid	0.9	0.016 7	366.6	276.2	156.9	48.1	62.3	50.0
1,3-Dimethyl mono-diamondoid	1.1	0.005 4	459.5	428.1	219.5	64.9	89.7	58.3
1,3,5-Trimethyl mono-diamondoid		0.000 3	195.2	170.6	85.2	34.7	62.4	23.1
1,3,5,7-Tetramethyl mono-diamondoid		0.000 6	58.0	64.0				
2-Methyl mono-diamondoid	2.7	0.000 8	264.6	411.0	202.1	49.8	50.8	31.7
1,4-Dimethyl mono-diamondoid, cis form		0.000 7	376.6	386.4	190.1	83.4	85.8	43.6
1,4-Dimethyl mono-diamondoid, trans form	0.9	0.001 3	160.3	211.9	107.8	43.5	41.6	31.4
1,3,6-Trimethyl mono-diamondoid		0.001 2	211.8	276.8	98.5	45.2	19.3	17.4
1,2-Dimethyl mono-diamondoid	1.5	0.001 2	156.0	274.3	151.3	56.3	36.3	21.2
1,3,4-Trimethyl mono-diamondoid, cis form		0.001 7	102.5	173.1	102.4	53.1		
1,3,4-Trimethyl mono-diamondoid, trans form		0.003 8	134.9	196.2	112.3	63.3	65.4	
1,2,5,7-Tetramethyl mono-diamondoid		0.000 4	52.5	59.1	60.5	51.2		
1-Ethyl mono-diamondoid		0.001 0	48.2	97.6	57.4	29.4	13.7	7.7
1-Ethyl-3-methyl mono-diamondoid		0.002 6	14.1	149.3	48.1	9.9	13.7	13.2
1-Ethyl-3,5-dimethyl mono-diamondoid		0.000 8	42.9	57.2	45.1	27.3		
2-Ethyl mono-diamondoid		0.004 2	91.7	154.9	48.1	31.3	32.1	17.6
Diadamantane		0.003 9	44.2	161.7	52.1	38.2	13.3	11.9
4-Methyl diadamantane		0.000 8	45.2	172.6	63.3	37.7	13.4	10.8
4,9-Dimethyl diadamantane		0.001 8	12.1	40.5	12.4	11.8		2.6
1-Methyl diadamantane		0.001 8	15.3	67.4	36.4	20.7	8.8	6.8
1,4- + 2,4-Dimethyl diadamantane		0.000 9	13.7	64.0	23.4	14.8		3.5
4,8-Dimethyl diadamantane		0.000 2	20.1	57.7	26.4	17.2		6.3
1,4,9-Trimethyl diadamantane		0.001 0	12.3	57.4	25.4			10.2
3-Methyl diadamantane		0.000 4	19.3	87.2	37.2	27.8	10.7	7.0
3,4-Dimethyl diadamantane		0.000 6	11.3	65.1	26.9	14.2	7.2	4.2

2.3 Comparison on the analytical results between GC × GC–FID and GC–MS methods

Wang et al. [16] verified the reliability of GC × GC–FID quantification and found that it was the nearest approximation of the real quantification result, with an error of less than 5%. However, the quantitative results of GC–MS differed greatly from the real results, because a large number of standard samples with different structures were required for quantitative analysis of GC–MS, whereas, it was difficult to obtain them in practice. In this paper, six normal crude oil samples (S3–S8) were analyzed and compared by GC–MS and GC × GC–FID (Table 3, Table 4).

Table 4 shows that among the 24 compounds, only mono-diamondoid was quantitatively determined with a deviation of less than 5% between the two instruments, because the internal standard substance selected in this experiment was D_{16}-diamondoid, which owned the most similar structure to mono-diamondoid and therefore rendered the smallest deviation. Table 4 also shows the comparison between two commonly used geochemical parameters of diamantane [8,20]. The results show that the selection of standard samples affected not only the quantitative results of monomer compounds but also the geochemical parameters. Compared with mono-diamondoid, the geochemical parameters were less affected.

2.4 Repeatability

S8 sample was separated by a fine silica gel columella and repeatedly detected seven times with GC × GC–FID. The quantitative results of some compounds are shown in Table 5. The relative standard deviation (RSD) of the seven repeated tests was less than 5%, indicating that this method has good repeatability and can meet the requirements of quantitative analysis of diamondoid.

Table 3 Quantitative analysis results of main diamondoid hydrocarbons by GC–MS

Name of compound	Concentration of compound/(mg·kg^{-1})					
	S3	S4	S5	S6	S7	S8
Mono-diamondoid	127.7	182.3	93.9	13.3	27.2	21.6
1-Methyl mono-diamondoid	792.8	1120.3	505.3	99.2	130.3	110.1
1,3-Dimethyl mono-diamondoid	805.3	1040.3	479.7	135.8	122.9	99.3
1,3,5-Trimethyl mono-diamondoid	337.3	403.9	206.2	79.6	47.0	39.7
1,3,5,7-Tetramethyl mono-diamondoid	307.5	319.2	176.3	55.2	53.3	35.8
2-Methyl mono-diamondoid	407.2	448.7	246.4	105.2	69.6	47.9
1,4-Dimethyl mono-diamondoid, cis form	370.6	415.7	227.9	94.8	62.9	45.2
1,4-Dimethyl mono-diamondoid, trans form	252.9	345.2	201.8	107.2	52.4	37.7
1,3,6-Trimethyl mono-diamondoid	367.0	514.6	284.4	132.6	76.9	56.0
1,2-Dimethyl mono-diamondoid	253.7	382.7	221.2	126.9		41.6
1,3,4-Trimethyl mono-diamondoid, cis form	265.5	392.5	213.2	131.9	54.3	41.7
1,3,4-Trimethyl mono-diamondoid, trans form	167.9	281.1	159.1	114.2		29.6
1,2,5,7-Tetramethyl mono-diamondoid form	104.1	217.7	112.7	61.1	37.5	22.2
1-Ethyl mono-diamondoid	201.4	337.4	187.1	130.4	45.3	35.1
2-Ethyl mono-diamondoid	213.8	221.3	119.5	78.1	53.8	30.8
Diadamantane	84.4	272.5	91.6	70.9	21.6	19.6
4-Methyl diadamantane	110.2	346.1	133.6	98.1	28.9	25.3
4,9-Dimethyl diadamantane	32.3	103.5	41.5	32.6		7.4
1-Methyl diadamantane	52.0	211.7	73.0	56.5	19.6	15.7
1,4- + 2,4-Dimethyl diadamantane	35.5	128.9	52.6	36.8		9.1
4,8-Dimethyl diadamantane	44.0	136.1	53.5	41.6		10.9
1,4,9-Trimethyl diadamantane	32.5	91.3	37.4			7.4
3-Methyl diadamantane	26.7	125.0	49.6	35.2	13.0	9.7
3,4-Dimethyl diadamantane	28.3	145.6	55.5	43.7	15.0	11.7

Table 4 Comparisons between analytical data acquired by GC–MS and GC × GC–FID

Name of compound	Relative deviation/%					
	S3	S4	S5	S6	S7	S8
Mono-diamondoid	5.0	1.2	1.8	0.6	1.3	1.1
1-Methyl mono-diamondoid	36.8	60.4	52.6	34.7	35.3	37.5
1,3-Dimethyl mono-diamondoid	27.3	41.7	37.2	35.3	15.6	26.0
1,3,5-Trimethyl mono-diamondoid	26.7	40.6	41.5	39.2	14.1	26.4
1,3,5,7-Tetramethyl mono-diamondoid	68.3	66.6				
2-Methyl mono-diamondoid	21.2	4.4	9.9	35.8	15.6	20.4
1,4-Dimethyl mono-diamondoid, cis form	0.8	3.7	9.0	6.4	15.4	1.9
1,4-Dimethyl mono-diamondoid, trans form	22.4	23.9	30.4	42.3	11.4	9.1
1,3,6-Trimethyl mono-diamondoid	26.8	30.0	48.6	49.2	59.9	52.6
1,2-Dimethyl mono-diamondoid	23.8	16.5	18.8	38.6		32.5
1,3,4-Trimethyl mono-diamondoid, cis form	44.3	38.8	35.1	42.6		
1,3,4-Trimethyl mono-diamondoid, trans form	10.9	17.8	17.2	28.7		
1,2,5,7-Tetramethyl mono-diamondoid form	32.9	57.3	30.2	8.8		

Table 4 continued

Name of compound	Relative deviation/%					
	S3	S4	S5	S6	S7	S8
1-Ethyl mono-diamondoid	61.4	55.1	53.0	63.2	53.5	64.2
2-Ethyl mono-diamondoid	40.0	17.7	42.6	42.8	25.3	27.4
Diadamantane	31.3	25.5	27.5	30.0	23.8	24.6
4-Methyl diadamantane	41.8	33.4	35.7	44.5	36.5	40.0
4,9-Dimethyl diadamantane	45.4	43.7	54.1	46.9		48.1
1-Methyl diadamantane	54.5	51.7	33.4	46.3	38.1	39.9
1,4- + 2,4-Dimethyl diadamantane	44.3	33.7	38.4	42.6		44.0
4,8-Dimethyl diadamantane	37.2	40.5	33.9	41.5		26.7
1,4,9-Trimethyl diadamantane	45.2	22.8	19.2			16.1
3-Methyl diadamantane	16.2	17.8	14.3	11.8	9.8	16.3
3, 4-Dimethyl diadamantane	43.1	38.2	34.7	50.9	35.0	46.8
1-Methyl diamondoid/(1- + 2-Methyl diamondoid)	6.4	28.0	21.2	0.6	8.4	6.4
4-Methyl diadamantane/(1- + 3- + 4-Methyl diadamantane)	1.5	2.0	6.0	8.3	7.0	6.2

Note: The formula for calculating the relative deviation (Δ) in the table is $\Delta = |A_1 - A_2|/(A_1 + A_2)$, where A_1represents the analysis result of GC × GC–FID and A_2 represents the analysis result of GC–MS.

Table 5 Repeatability of sample S8 by GC × GC–FID

Name of compound	Concentration of compound/(mg·kg^{-1})							Relative standard deviation/%
	The first time	The second time	The third time	The fourth time	The fifth time	The sixth time	The seventh time	
Mono-diamondoid	20.64	22.18	22.34	22.82	22.76	21.49	21.03	3.9
1-Methyl mono-diamondoid	62.67	62.59	60.43	59.34	56.77	62.54	60.65	3.6
1,3-Dimethyl mono-diamondoid	81.46	86.15	81.80	80.88	78.33	77.99	75.59	4.2
1,3,5-Trimethyl mono-diamondoid	41.14	40.47	39.35	39.73	40.80	41.28	41.14	1.9
2-Methyl mono-diamondoid	38.57	39.18	39.38	39.38	36.19	35.89	37.95	3.9
1,4-Dimethyl mono-diamondoid, cis form	65.13	65.30	60.94	59.83	64.13	65.30	66.46	3.9
1,4-Dimethyl mono-diamondoid, trans form	30.35	29.96	32.01	31.41	30.46	28.16	28.43	4.7
1,2-Dimethyl mono-diamondoid	30.16	30.08	29.83	29.34	28.84	28.32	29.15	2.3
1-Ethyl mono-diamondoid	11.90	12.15	13.13	13.02	12.71	13.46	12.80	4.3
Diadamantane	15.05	14.97	14.89	14.50	15.64	15.84	15.45	3.1
4-Methyl diadamantane	15.48	14.52	16.13	15.45	15.81	16.13	15.40	3.6
1-Methyl diadamantane	9.03	8.87	9.07	8.57	9.12	9.00	8.27	3.6
3-Methyl diadamantane	11.34	11.25	11.24	10.53	10.59	10.66	10.74	3.2
3,4-Dimethyl diadamantane	6.79	6.95	7.13	7.15	7.01	7.16	7.88	4.9

3 Conclusions

(1) Due to the lack of standard substance and the influence of co-distillation peaks, the results of quantitative analysis of diamondoid by GC–MS deviated obviously from the true values.

(2) An analytical method for the absolute quantification of conventional diamondoid by GC × GC–FID was established. This method could quantify other diamondoid by using only one kind of deuterated diamondoide. It had good repeatability and was worth popularizing.

(3) The pretreatment method of columella separation was established to reduce the sample volume, solvent consumption, and the volatilization loss of diamondoid, and it was suitable for the analysis of samples with small sample volume.

(4) The method of quantitative analysis on diamondoid by GC × GC–FID was suitable for any petroleum sample. It had the characteristics of high resolution and no co-distillation

compounds and was able to obtain the objective and accurate quantitative results of diamondoid, which provided a scientific and effective new technique for the geochemical study of diamondoid.

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