



Quantitative analysis of diamondoids in crude oils using gas chromatography–triple quadrupole mass spectrometry

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ABSTRACT

In this study, a simple solvent dilution followed by highly selective and sensitive gas chromatography–triple quadrupole mass spectrometry (GC–MS–MS) detection was employed to quantify diamondoids in crude oils. Runtime parameters, i.e., parent and daughter ions, collision energy (CE) and scan time, were optimized to obtain maximum selectivity and sensitivity for target analytes. Under optimum conditions, the reproducibility and accuracy of the method were tested and found to be satisfactory. Comparison of GC–MS–MS and GC–MS methods for the determination of diamondoids indicates that GC–MS–MS yields higher sensitivity (method quantitation limits of 0.08–0.37 µg/g oil) and better selectivity than GC–MS (method quantitation limits of 0.78–8.44 µg/g oil) due to the elimination of matrix ion interferences using the selected reaction monitoring (SRM) mode. In addition, quantitative data confirm that group separation has a considerable effect on the quantification of diamondoids and the effect appears to depend on multiple factors. Two crude oils (TZ261 and TD2) from the Tarim Basin, China were used to evaluate the GC–MS–MS method. The results prove that the GC–MS–MS method is a promising tool for quantitative analysis of diamondoids in crude oils, especially for oil samples with low diamondoid concentrations.

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1. Introduction

Diamondoids are cage-like alkane hydrocarbons with rigid, three dimensionally fused cyclohexyl rings (Fort and Schleyer, 1964; Wingert, 1992; Dahl et al., 1999). Since adamantane (the simplest diamondoid) was first discovered in petroleum in 1933, more diamondoids have been detected in many crude oils (Bender et al., 1986; Williams et al., 1986; Wingert, 1992; Chen et al., 1996; Dahl et al., 1999; Grice et al., 2000; Azevedo et al., 2008), petroleum products (Wang et al., 2006), coals and sedimentary rocks (Imuta and Ouchi, 1973; Aczel et al., 1979; Schulz et al., 2001; Wei et al., 2006a), and gas condensates (Lin and Wilk, 1995; Stout and Douglas, 2004; Sassen and Post, 2008). Furthermore, some higher diamondoids (more than three diamond cages) have been separated and identified from petroleum (Dahl et al., 2003). Diamondoid hydrocarbons are more stable than most other hydrocarbons and are resistant to thermal and biological destruction (Aczel et al., 1979; Williams et al., 1986; Wingert, 1992; Grice et al., 2000). Therefore, they have been widely used to determine the thermal maturity of highly mature crude oils (Chen et al., 1996; Li et al., 2000; Zhang et al., 2005), assess the extent of oil cracking (Dahl et al., 1999) and investigate the secondary alteration of crude oils, such as mixing, biodegradation and

thermochemical sulfate reduction (TSR) (Dahl et al., 1999; Grice et al., 2000; Wei et al., 2007a, 2011). Because of their stability and resistance to biodegradation, diamondoid hydrocarbons have also been utilized to identify the sources of oil spills (Stout and Douglas, 2004; Wang et al., 2006).

In addition to ratios based on their distribution (Chen et al., 1996; Grice et al., 2000; Li et al., 2000; Zhang et al., 2005), the abundance of diamondoids has proven to be very useful. For example, methyladamantane concentration (4- + 3-methyladamantane) can be used to estimate the extent of oil cracking (Dahl et al., 1999) and the relative abundance of diamondoids in light petroleum and gas condensates is an important “fingerprinting” tool to identify the sources of oil spills (Stout and Douglas, 2004). Although diamondoids occur in almost all crude oils and in most petroleum products (Wang et al., 2006), normal crude oils commonly contain very low concentrations, typically at the low ppm or even sub-ppm level (Fort and Schleyer, 1964; Wingert, 1992; Dahl et al., 1999; Wei et al., 2007a). Thus, a highly selective and sensitive detection method is required to quantify such trace components in normal crude oils and characterize their subtle variations.

Gas chromatography–mass spectrometry (GC–MS) is the most commonly used method for qualitative and quantitative diamondoid analysis. Although GC–MS has higher selectivity, interference from the matrix components can still obscure the signal of target analytes (Qu et al., 2010), especially for components having low concentrations. Therefore, before introducing oil samples into the

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gas chromatograph, a preparative group separation step is usually employed to eliminate the matrix interference. In such preparation procedures, hexane or pentane eluates are concentrated by evaporation to a small volume prior to sample injection to improve analytical sensitivity (Wingert, 1992; Chen et al., 1996; Grice et al., 2000; Li et al., 2000; Schulz et al., 2001; Zhang et al., 2005). Moreover, the sensitivity of diamondoid analysis can be enhanced by using selective ion monitoring (SIM) mode of GC–MS, such as monitoring m/z 136, 135, 149, 163, 177 and 191 for adamantanes, m/z 188, 187, 201, 215 and 229 for diamantanes, and m/z 240, 239, 253, 267 and 281 for triamantanes (Wingert, 1992; Schulz et al., 2001). However, the sample preparation procedures used in GC–MS analysis can produce errors with respect to the quantification of diamondoids. The effect has never been quantitatively discussed. For natural gas condensates and gasolines, direct injection of whole oil has been utilized to avoid evaporative loss of adamantane, which elutes just before n -C₁₁ on a non-polar capillary column (Stout and Douglas, 2004). This direct sample injection method is not applicable for crude oils due to the presence of a relatively high proportion of complex, high molecular weight, non-paraffinic components.

Gas chromatography–tandem mass spectrometry (GC–MS–MS) can offer enhanced sensitivity and selectivity by eliminating matrix ion interferences through selected reaction monitoring (SRM) without complicated sample preparation and cleanup (Frenich et al., 2005; Hernandez et al., 2005). Therefore, in the last decade GC–MS–MS has been widely used in various fields (e.g., food, medicine, agriculture and environment; Brumley et al., 1988; Ternes et al., 2002; Frenich et al., 2005, 2007; Hernandez et al., 2005; Isaacson et al., 2006; Tripp et al., 2009; Parr et al., 2011). In organic geochemistry at present, GC–MS–MS is predominantly used to investigate terpenoids and steroids (Peters et al., 2005). Other components are less commonly used and little research has been reported on diamondoid analysis. One exception is the quantitative analysis of methyladamantanes in crude oils by monitoring the m/z 202⁺ → 187⁺ transition (Dahl et al., 1999).

In selected reaction monitoring (SRM) of gas chromatography–triple quadrupole mass spectrometry, the parent ions are selected by the first quadrupole and then collide with argon molecules in the second quadrupole. The fragment ions of the collision are selected by the third quadrupole and then detected. The limits of quantification and detection for triple quadrupole mass spectrometry are as low as several ppb (Frenich et al., 2005; Gomez-Gonzalez et al., 2010). Based on the SRM mode and the optimization

of runtime parameters, the triple quadrupole technique can provide maximum selectivity and sensitivity for quantification of diamondoids in crude oils. High selectivity of triple quadrupole mass spectrometry can eliminate co-elution interference from the chemical background of crude oils or source rock extracts, while high sensitivity compensates for low concentrations that result from the lack of solvent evaporation. Consequently, a reliable quantification of diamondoids can be achieved by using GC–MS–MS even without any sample preparation.

To our knowledge, little information is available on the optimization and evaluation of GC–MS–MS to determine diamondoids in crude oils. The main purpose of this study is to: (1) optimize the run parameters of GC–MS–MS and evaluate its applicability to quantify diamondoids by a comparative study of GC–MS–MS and GC–MS methods and (2) quantitatively investigate the influence of sample preparation on diamondoid analysis.

2. Materials and methods

2.1. Reagents and chemicals

Diamondoid standards (Table 1) were purchased from Chiron AS (Stiklestadveien, Norway). Isooctane (2,2,4-trimethylpentane, ACS, 99+%), n -dodecane-d₂₆, and n -hexadecane-d₃₄ were obtained from Shanghai ANPEL Scientific Instrument Co., Ltd. n -Hexane (n -C₆, 99%) was obtained from Burdick & Jackson Co. Ltd. (ACS/HPLC, 99.99%). All other reagents in this study were of analytical grade.

A stock solution was prepared by mixing diamondoid standards in isooctane (Table 1). The stock solution was stored at 4 °C and diluted with isooctane for use in the working solutions. In each of the working solutions and the analytical samples, a mixed internal standard (IS) solution was added for quantification of target analytes. The IS solution was prepared by diluting n -dodecane-d₂₆ (IS-1) and n -hexadecane-d₃₄ (IS-2) with isooctane at concentrations of 522 µg/ml (n -C₁₂D₂₆) and 552 µg/ml (n -C₁₆D₃₄), respectively.

2.2. Sample preparation

Crude oil samples from the Tarim Basin, China were used in this study. First, 10–50 mg of each oil sample was weighed into a 4 ml glass vial. The vial was then filled with a certain volume of

Table 1
Diamondoid standards and their optimized parameters used in GC–MS–MS detection. Compounds are identified by number in Table 2.

Compound	Abbreviation	Standard purity (%)	Stock solution Concentration (µg/ml)	Segment	Scan time (s)	RT (min)	Precursor ion (m/z)	Product ion (m/z)	CE (V)
Adamantane	A	99.8	3.60	1	0.500	14.58	136	93	13
1-Methyladamantane	1-MA	98.6	4.42	2	0.500	15.43	150	135	6
1,3-Dimethyladamantane	1,3-DMA	99	4.46	3	0.500	16.14	164	149	6
1,3,5-Trimethyladamantane	1,3,5-TMA	97.4	3.63	4	0.250	16.72	178	163	6
2-Methyladamantane	2-MA	99.9	4.42	5	0.500	18.23	150	135	9
1,4-Dimethyladamantane(<i>cis</i>) ^a	1,4-DMA(<i>cis</i>)	–	–	6	0.150	18.84	164	149	8
1,4-Dimethyladamantane(<i>trans</i>) ^a	1,4-DMA(<i>trans</i>)	–	–	6	0.150	19.08	164	149	8
n -Dodecane-d ₂₆ (IS)	n -C ₁₂ D ₂₆	98% atom/D	–	6	0.150	19.35	196	82	5
1,2-Dimethyladamantane ^a	1,2-DMA	–	–	7	0.500	20.29	164	149	6
1-Ethyladamantane	1-EA	94.1	4.17	8	0.100	21.48	164	135	6
1-Ethyl-3-methyladamantane	1-E-3-MA	98.1	4.36	8	0.100	22.16	178	149	6
2-Ethyladamantane	2-EA	96.9	4.17	8	0.100	22.84	164	135	6
Diamantane	D	99.9	4.33	9	0.100	34.60	188	131	13
1-Methyldiamantane	1-MD	99.9	4.42	9	0.100	37.07	202	187	6
n -Hexadecane-d ₃₄ (IS)	n -C ₁₆ D ₃₄	98.6% atom/D	–	9	0.100	38.35	260	82	7

Concentration of all diamondoid standards was 1.0 mg/ml in isooctane. RT = retention time, CE = collision energy.

^a 1,4-DMA(*cis*), 1,4-DMA(*trans*) and 1,2-DMA standards were mixed in an ampoule (purity 92%); were used for qualitative analysis and prepared in the stock solution with the sum concentration of 4.42 µg/ml.

n-hexane or isooctane and ultrasonically treated for 10 min to improve the dissolution of analytes. After centrifugation at a rate of 3000 rpm for 10 min, the supernatant was transferred and divided into two equal parts, one of which was used to examine conventional sample preparation, i.e., column chromatography separation plus nitrogen evaporation. The other was used to determine diamondoids by direct sample injection.

The procedure of the first sample preparation was similar to that used in routine GC–MS analysis (Wingert, 1992). Briefly, the saturated hydrocarbon fraction of crude oils was separated on a silica/alumina column chromatograph with *n*-hexane and the eluate was then concentrated under a gentle stream of nitrogen to about 0.5–1.0 ml. After adding 100 μ l of the IS solution and mixing, the resulting fraction was analyzed by GC–MS in the full scan or selected ion monitoring (SIM) mode and GC–MS–MS in the SRM mode. All analyses were immediately carried out to avoid loss due to evaporation. The second protocol was that the crude oil samples were directly introduced into the GC inlet for GC–MS and GC–MS–MS analysis without further sample work-up.

2.3. Gas chromatography–mass spectrometry (GC–MS) analysis

The saturated hydrocarbon fraction was analyzed using an Agilent 7890A/5975C GC–MSD instrument. A DB-5 column (J&W Scientific, 30 m \times 0.25 mm i.d., 0.25 μ m phase thickness) was used and the GC oven was programmed from 50 $^{\circ}$ C (held for 5 min) to 80 $^{\circ}$ C at 15 $^{\circ}$ C/min, then to 250 $^{\circ}$ C at 2.5 $^{\circ}$ C/min, and finally to 300 $^{\circ}$ C at 15 $^{\circ}$ C/min, and held for 10 min. Helium at a constant flow rate of 1.5 ml/min, was used as the carrier gas. The samples were analyzed in the full scan and SIM modes, respectively. For the SIM mode, the target components were detected using the following ions: m/z 135, 136, 149, 163, 178 and 192 (adamantanes), m/z 187, 188, 202, 216 and 230 (diamantanes), and m/z 82 (*n*-C₁₂D₂₆ and *n*-C₁₆D₃₄).

The diamondoid compounds were identified by comparing the retention times of the standards, elution orders and mass spectra with those published in the literature (Wingert, 1992; Grice et al., 2000; Wei et al., 2006b). Their quantification was achieved by comparing peak areas of the target compounds with those of the corresponding internal standards, specifically, *n*-C₁₂D₂₆ for adamantanes and *n*-C₁₆D₃₄ for diamantanes.

2.4. Gas chromatography–triple quadrupole mass spectrometry (GC–MS–MS)

GC–MS–MS analyses were performed on a TSQ Quantum XLS system (Thermo Fisher Scientific, USA). Aliquots of 1 μ l of each sample were injected into the GC system using the AS 3000 auto-sampler. The GC was equipped with a PTV injector, and a DB-1 fused silica capillary column (50 m \times 0.32 mm i.d. \times 0.52 μ m film thickness). PTV splitless mode was used with the inlet temperature set at 300 $^{\circ}$ C, and the split flow at 15 ml/min following splitless time for 1.00 min. Helium (99.999%) was used as the carrier gas under constant flow mode at a rate of 1.5 ml/min. The GC oven temperature was initially set at 50 $^{\circ}$ C for 2 min, then programmed at 15 $^{\circ}$ C/min to 80 $^{\circ}$ C, then at 2.5 $^{\circ}$ C/min to 250 $^{\circ}$ C, then at 15 $^{\circ}$ C/min to 300 $^{\circ}$ C and held for 10 min.

The triple quadrupole mass spectrometer was operated in EI mode at 70 eV. The temperatures of the MS transfer line and ion source were set at 300 $^{\circ}$ C and 250 $^{\circ}$ C, respectively. The filament emission current was 25 μ A, and the filament-multiplier delay was set at 12 min. The quantification of diamondoid compounds was achieved by comparing peak areas in the SRM mode of target analytes to those of the corresponding internal standards: *n*-dodecane-d₂₆ for adamantanes and *n*-hexadecane-d₃₄ for diamantanes.

3. Results and discussion

3.1. Optimization of the GC–MS–MS method

For GC–MS–MS analysis, the critical factors that affect performance include parent ion and daughter ion, collision energy (CE) and scan time. Optimization of these GC–MS–MS parameters was performed by using working solutions described earlier.

First, a full scan mode (m/z 50–500) of the working solution containing 13 diamondoid standards was run to optimize the GC conditions and record the retention times of each compound. The full scan spectrum of each diamondoid standard was then carefully studied and the dominant fragment ions and characteristic molecular ions M^+ for particular diamondoid standards were identified. Selection of the parent ion was based on high selectivity (the highest m/z ion intensity) and high sensitivity (the most abundant ion) for each target analyte (Frenich et al., 2007). Higher m/z ion response insures less interference by impurities (Qu et al., 2010). The molecular ion M^+ was chosen as the parent ion and the corresponding base peak (m/z) was used as the daughter ion in this study, except adamantane and diamantane for which the base peak (m/z) is the same as the molecular ion peak (M^+). The most abundant fragments, m/z 93 for adamantane and m/z 131 for diamantane, were selected as the daughter ions, respectively. Similar to adamantane and diamantane, the monitoring reactions of internal standards (*n*-C₁₂D₂₆ and *n*-C₁₆D₃₄) were obtained by the same procedure, i.e., m/z 196 \rightarrow 82 (*n*-C₁₂D₂₆) and m/z 260 \rightarrow 82 (*n*-C₁₆D₃₄).

Once the parent ion and daughter ion were selected, two or three runs were made with multiple scan events and increasing collision energy (CE) from 5 V to 50 V to determine the optimum CE voltage. The voltage was selected to produce the highest yield of daughter ion intensities.

The optimum GC–MS–MS parameters, such as parent ions, daughter ions, collision energy and scan time for each diamondoid analyte are summarized in Table 1. Fig. 1 shows typical chromatograms of a working solution under optimum conditions of GC–MS–MS analysis, with peak assignments in Table 2. The figure shows good peak shape and separation efficiency.

3.2. Evaluation of GC–MS–MS methods

Validation procedures for this GC–MS–MS method for quantitative analysis of diamondoids were performed under optimum conditions. Additionally, a parallel determination was carried out using GC–MS to better evaluate the GC–MS–MS method. The linearity, sensitivity, reproducibility and recovery of the two methods were determined by analyzing the mixed diamondoid standard solution (Tables 3 and 4).

3.2.1. Calibration curves

During previous quantification of diamondoids, cyclopentadecane, deuterated *n*-alkanes or diamondoids were usually used as internal standards (Wingert, 1992; Dahl et al., 1999; Schulz et al., 2001; Wei et al., 2006a; Springer et al., 2010). To simplify, however, relative response factors (RRF) of each diamondoid to the corresponding internal standards were generally assumed to be one. In addition, the relative response factors of a diamondoid kit (including A, 1-MA, 2-MA, 1-EA, 2-EA, 1,3-DMA, 1-E-3-MA and 1,3,5-TMA) relative to deuterated *n*-alkanes (*n*-dodecane-d₂₆ and *n*-hexadecane-d₃₄) and five adamantanes (A, 1-MA, 2-MA, 2-EA, and 1,3-DMA) relative to the d₁₆-adamantane have been used for quantification of diamondoids by GC–MS (Wang et al., 2006; Azevedo et al., 2008; Springer et al., 2010). In this study, calibration curves of response factors for ten diamondoid standards

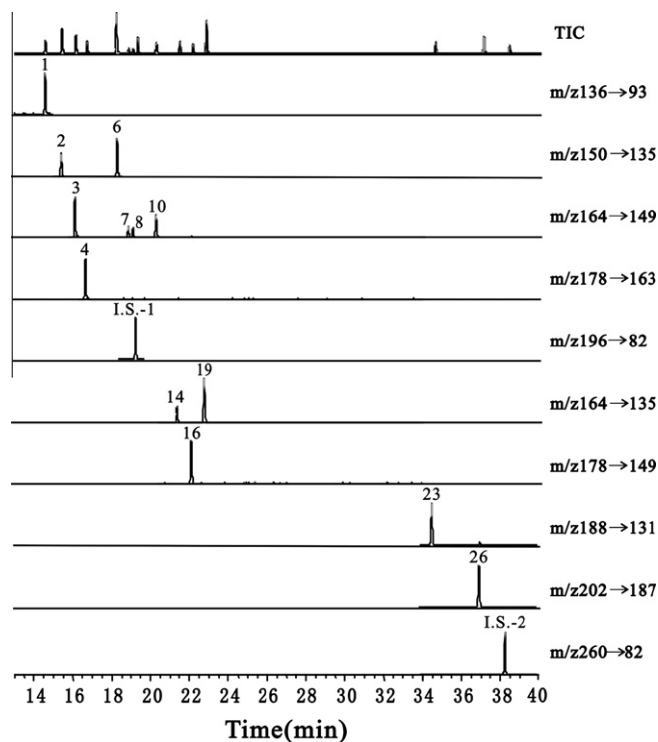


Fig. 1. GC-MS-MS chromatograms of a working solution under optimum conditions. The concentrations were 103 $\mu\text{g/l}$ (A), 127 $\mu\text{g/l}$ (1-MA), 128 $\mu\text{g/l}$ (1,3-DMA), 104 $\mu\text{g/l}$ (1,3,5-TMA), 127 $\mu\text{g/l}$ (2-MA), 127 $\mu\text{g/l}$ (1,2-/1,4-DMA), 120 $\mu\text{g/l}$ (1-EA), 125 $\mu\text{g/l}$ (1-E-3-MA), 120 $\mu\text{g/l}$ (2-EA), 124 $\mu\text{g/l}$ (D), 127 $\mu\text{g/l}$ (1-MD), 9.06 $\mu\text{g/ml}$ (IS-1) and 9.58 $\mu\text{g/ml}$ (IS-2), respectively.

(i.e., A, 1-MA, 1,3-DMA, 1,3,5-TMA, 2-MA, 1-EA, 1-E-3-MA, 2-EA, D and 1-MD) were obtained by the GC-MS-MS and GC-MS analyses.

A series of the working solutions for the calibration study were prepared by diluting the stock solution with isoctane and adding the IS solution, respectively. The calibration curves were calculated using ratios of the peak area for each target analyte to that of the corresponding internal standard (A_{C_n}/A_{IS}) versus the corresponding concentration ratios (C_{C_n}/C_{IS}). Linearity was evaluated based on correlation coefficients of the regression equations for the calibration curves. As shown in Table 3, the calculated calibration curves exhibit good linearity in the concentration range of approximate 0.007–2.6 $\mu\text{g/ml}$ for all of the diamondoid standards determined by the two detection methods.

3.2.2. Reproducibility

The reproducibility of the two methods was evaluated by replicate analyses of the working solution at concentrations of 103 $\mu\text{g/l}$ (A), 127 $\mu\text{g/l}$ (1-MA), 128 $\mu\text{g/l}$ (1,3-DMA), 104 $\mu\text{g/l}$ (1,3,5-TMA), 127 $\mu\text{g/l}$ (2-MA), 120 $\mu\text{g/l}$ (1-EA), 125 $\mu\text{g/l}$ (1-E-3-MA), 120 $\mu\text{g/l}$ (2-EA), 124 $\mu\text{g/l}$ (D), and 127 $\mu\text{g/l}$ (1-MD). The relative standard deviations (%) are given in Table 3. Both methods show good reproducibility with relative standard deviations (RSD) lower than 5% for most target compounds.

3.2.3. Method detection and quantification limits

The method detection limit in this work was expressed as the concentration with a signal/background of 3 in the mass spectra based on the calibration curve and method quantification limit as the concentration with a signal/background of 10. Thus, method detection limit (MDL) and quantification limit (MQL) were estimated from the instrumental limits of detection and quantification by considering the corresponding sample weight, dilution factor

Table 2
Peak assignments of diamondoids in GC-MS-MS analysis.

Peak number	Molecular formula	Assignment
1	$C_{10}H_{16}$	Adamantane
2	$C_{11}H_{18}$	1-Methyladamantane
3	$C_{12}H_{20}$	1,3-Dimethyladamantane
4	$C_{13}H_{22}$	1,3,5-Trimethyladamantane
5	$C_{14}H_{24}$	1,3,5,7-Tetramethyladamantane
6	$C_{11}H_{18}$	2-Methyladamantane
7	$C_{12}H_{20}$	1,4-Dimethyladamantane(<i>cis</i>)
8	$C_{12}H_{20}$	1,4-Dimethyladamantane(<i>trans</i>)
9	$C_{13}H_{22}$	1,3,6-Trimethyladamantane
10	$C_{12}H_{20}$	1,2-Dimethyladamantane
11	$C_{13}H_{22}$	1,3,4-Trimethyladamantane(<i>cis</i>)
12	$C_{13}H_{22}$	1,3,4-Trimethyladamantane(<i>trans</i>)
13	$C_{14}H_{24}$	1,2,5,7-Tetramethyladamantane
14	$C_{12}H_{20}$	1-Ethyladamantane
15	$C_{12}H_{20}$	2,6- + 2,4-Dimethyladamantane
16	$C_{13}H_{22}$	1-Ethyl-3-methyladamantane
17	$C_{13}H_{22}$	1,2,3-Trimethyladamantane
18	$C_{14}H_{24}$	1-Ethyl-3,5-dimethyladamantane
19	$C_{12}H_{20}$	2-Ethyladamantane
20	$C_{14}H_{24}$	1,3,5,6-Tetramethyladamantane
21	$C_{14}H_{24}$	1,2,3,5-Tetramethyladamantane
22	$C_{15}H_{26}$	1-Ethyl-3,5,7-trimethyladamantane
IS-1	$C_{12}D_{26}$	<i>n</i> -Dodecane- d_{26}
23	$C_{14}H_{20}$	Diamantane
24	$C_{15}H_{22}$	4-Methyldiamantane
25	$C_{16}H_{24}$	4,9-Dimethyldiamantane
26	$C_{15}H_{22}$	1-Methyldiamantane
27	$C_{16}H_{24}$	1,4- + 2,4-Dimethyldiamantane
28	$C_{16}H_{24}$	4,8-Dimethyldiamantane
29	$C_{17}H_{26}$	1,4,9-Trimethyldiamantane
30	$C_{15}H_{22}$	3-Methyldiamantane
31	$C_{16}H_{24}$	3,4-Dimethyldiamantane
32	$C_{17}H_{26}$	3,4,9-Trimethyldiamantane
IS-2	$C_{16}D_{34}$	<i>n</i> -Hexadecane- d_{34}

and injection volume. To consider the matrix effects of crude oil during analysis, a crude oil collected from the Tarim Basin, China that contains low concentrations of diamondoids was used for the MDL and MQL study. The MDLs and MQLs of diamondoids obtained by the SIM-GC-MS, which fall in the range of 0.23–2.53 and 0.78–8.44 $\mu\text{g/g}$ oil, respectively, are 4–66 times higher than those of GC-MS-MS (Table 3). The MQLs of target analytes obtained by the GC-MS-MS method, ranging from 0.08–0.37 $\mu\text{g/g}$ oil, are lower than the diamondoid baseline concentrations previously reported (Dahl et al., 1999; Springer et al., 2010). Therefore, these results demonstrate that GC-MS-MS has sufficient sensitivity for the determination of diamondoids even after sample dilution, whereas with the GC-MS method, samples with low concentrations of diamondoids (at ppm and sub-ppm levels) need to be concentrated prior to analysis to reach MQLs.

3.2.4. Recovery

Recovery can be used to evaluate the accuracy of analytical methods. Spike recovery experiments were performed using a real oil sample with a low concentration of diamondoids to compare the reliability of the two methods. First, the prepared oil sample (HD23) was divided into three aliquots. One was used to obtain the original concentration of each target compound in the initial oil using GC-MS and GC-MS-MS. The others were spiked with a mixed standard solution containing 10 diamondoid compounds at a high concentration of 600–740 $\mu\text{g/l}$ and a low concentration of 80–100 $\mu\text{g/l}$ (Table 4). Recovery (%) was calculated by using the following formula:

$$\text{Recovery (\%)} = (C_m - C_0)/C_a \times 100$$

where C_m is the measured concentration of diamondoids in a spiked sample, C_0 is the measured concentration of diamondoids in the

Table 3
Comparison of the quantitative results obtained by GC–MS and GC–MS–MS methods.

Compound	GC–MS						GC–MS–MS					
	Calibration equation ^a	R ²	Linear Range (µg/ml)	RSD (%), n = 3)	MDL (µg/g)	MQL (µg/g)	Calibration equation	R ²	Linear Range (µg/ml)	RSD (%), n = 5)	MDL (µg/g)	MQL (µg/g)
A	y = 2.742x – 0.0002	0.9953	0.0071–1.50	2.7	0.53	1.75	y = 65.56x + 0.0604	0.9991	0.0071–2.11	2.6	0.04	0.21
1-MA	y = 5.109x – 0.0015	0.9963	0.0088–1.85	0.4	0.72	2.38	y = 106.9x + 0.1040	0.9993	0.0088–2.60	2.3	0.03	0.18
1,3-DMA	y = 5.413x – 0.0007	0.9967	0.0088–1.86	1.3	0.88	2.94	y = 80.47x + 0.1318	0.9992	0.0088–2.61	1.3	0.05	0.15
1,3,5-TMA	y = 6.087x + 0.0006	0.9984	0.0072–1.52	0.3	0.23	0.78	y = 65.16x + 0.0683	0.9995	0.0072–2.13	2.4	0.05	0.20
2-MA	y = 2.559x – 0.0001	0.9962	0.0088–1.85	1.6	1.07	3.55	y = 183.5x + 0.2228	0.9993	0.0088–2.60	1.7	0.02	0.08
1-EA	y = 6.255x + 0.0032	0.9966	0.0082–2.45	0.2	0.77	2.56	y = 61.63x + 0.0670	0.9996	0.0082–2.45	2.8	0.09	0.30
1-E-3-MA	y = 6.013x – 0.0028	0.9987	0.0086–2.56	1.2	0.47	1.57	y = 41.01x + 0.0589	0.9995	0.0086–2.56	4.0	0.11	0.37
2-EA	y = 4.817x – 0.0029	0.9968	0.0082–2.45	4.5	0.83	2.77	y = 173.2x + 0.2131	0.9996	0.0082–2.45	2.0	0.03	0.15
D	y = 2.797x – 0.0046	0.9888	0.0086–2.54	4.3	2.53	8.44	y = 102.4x + 0.1127	0.9984	0.0086–2.54	2.4	0.05	0.25
1-MD	y = 3.708x – 0.0060	0.9794	0.0088–2.60	3.3	2.20	7.34	y = 190.5x + 0.2637	0.9980	0.0088–2.60	5.1	0.04	0.14

RSD – relative standard deviation; MDL – method detection limit; MQL – method quantitation limit.

^a x and y are the concentration ratio and area ratio of target compounds to internal standard, respectively. *n*-dodecane-*d*₂₆ (IS-1) is used for adamantanes and *n*-hexadecane-*d*₃₄ (IS-2) for diamantanes.

Table 4
Recoveries of diamondoids spikes in the crude oils by GC–MS and GC–MS–MS.

Compound	High level spike					Low level spike				
	Spiked (µg/l)	GC–MS		GC–MS–MS		Spiked (µg/l)	GC–MS		GC–MS–MS	
		R (%)	RSD (%), n = 3)	R (%)	RSD (%), n = 3)		R (%)	RSD (%), n = 3)	R (%)	RSD (%), n = 3)
A	600.8	104.1	0.8	99.7	2.6	80.9	65.9	3.4	107.2	1.9
1-MA	739.0	100.4	0.8	100.3	2.0	99.5	90.3	0.4	107.9	1.1
1,3-DMA	744.3	97.6	1.7	100.2	2.0	100.3	85.3	1.3	109.0	2.4
1,3,5-TMA	606.1	101.0	1.3	99.9	1.8	81.6	94.5	0.3	112.0	2.1
2-MA	739.0	101.1	0.8	98.7	1.9	99.5	97.9	1.6	107.8	0.7
1-EA	696.5	102.3	1.3	97.9	3.1	93.8	99.6	0.2	102.6	3.0
1-E-3-MA	728.4	103.0	3.2	99.8	3.8	98.1	84.2	1.2	113.9	2.5
2-EA	696.5	96.8	1.0	99.4	2.3	93.8	87.8	4.8	109.3	0.7
D	723.0	120.3	0.6	94.5	0.7	97.4	75.6	4.5	104.7	5.8
1-MD	739.0	129.7	0.6	102.0	3.3	99.5	100.1	3.3	102.6	5.1

R: recovery; RSD: relative standard deviation.

unspiked sample and C_a is the concentration of the diamondoid spike.

All the samples were analyzed three times by GC–MS and GC–MS–MS and the results are given in Table 4. For GC–MS, the recoveries of all target compounds vary between 96.8% and 129.7% with a precision (% RSD) better than 3.2% for the high level spike, and between 65.9% and 100.1% with a precision better than 4.8% for the low level spike. In contrast, the recoveries of GC–MS–MS are in the range of 94.5–102% and 102.6–113.9% for the high and low spike levels, respectively. Relative standard deviations (%) of three replicate determinations are between 0.7% and 3.8% for the high level spike and 0.7% and 5.8% for the low level spike. Recoveries of GC–MS–MS are obviously better than those of GC–MS for the low level spike, indicating that GC–MS–MS is highly suitable for determining diamondoids at low levels in normal crude oils.

3.3. Influence of sample preparation on the determination of diamondoids

Although GC–MS selectivity can be enhanced by column chromatography separation and its sensitivity improved by nitrogen evaporation, little information is available on the effect of these sample preparation processes on diamondoid analysis. It is believed that they likely cause compositional fractionation of diamondoids, especially among the adamantanes. An experiment was performed by comparing the concentrations of the diamondoids determined using direct injection and group separation to better understand the effect of sample preparation on diamondoid determination. A mixed standard solution of diamondoids and two Tarim Basin crude oil samples (HD23 and LN14) were used in the experiment. The three group separated samples obtained by

column chromatography separation plus nitrogen evaporation and their corresponding untreated samples were analyzed using both GC–MS and GC–MS–MS methods.

Due to better reliability, the results determined by the GC–MS–MS were used for quantitation. Table 5 presents the diamondoid concentrations in the mixed standard solution and the two crude oils analyzed before and after group preparation using the GC–MS–MS method. Loss (%) is defined as the mass loss rate of the individual diamondoids during sample preparation and is calculated by the following equation:

$$\text{Loss (\%)} = 100 \times (\text{concentration}(\text{direct injection}) - \text{concentration}(\text{group separation})) / \text{concentration}(\text{direct injection})$$

Loss is used to quantitatively assess the effect of group separation on the diamondoid analysis in this study. As shown in Table 5, the loss (%) of 10 target compounds varies from 7.2–13.1% for the mixed diamondoid standards, 15.8–26.1% for the well HD23 crude oil and –7.5% to 37.4% for the well LN14 crude oil. The results show that group separation can cause a considerable mass loss of diamondoids. Moreover, comparison of the loss (%) values from the three samples shows that the effect of sample preparation likely depends on multiple factors. For example, an inverse relationship is observed between the loss (%) and boiling point of diamondoid compounds in the same sample, i.e., higher boiling point corresponds to less loss (%), indicating that evaporation of compounds may be a major factor. However, considerable differences in the diamondoid loss occur among three samples, probably due to differences in the extent of evaporation or sample properties.

Table 5
Concentrations of diamondoids in the mixed standard solution and two Tarim Basin crude oil samples determined using GC–MS–MS and two sample preparation methods.

Compound	Mixed diamondoid standards				Well HD23 crude oil			Well LN14 crude oil		
	Initial concentration (μg/l)	Direct injection (μg/l)	Group separation (μg/l)	Loss (%)	Direct injection (μg/g oil)	Group separation (μg/g oil)	Loss (%)	Direct injection (μg/g oil)	Group separation (μg/g oil)	Loss (%)
A	981.9	991.0	861.1	13.1	18.2	13.5	26.1	43.9	27.5	37.4
1-MA	1207.8	1219.5	1082.8	11.2	46.9	36.0	23.2	132.8	88.6	33.3
1,3-DMA	1216.5	1226.8	1098.3	10.5	34.5	27.0	21.7	106.5	75.8	28.9
1,3,5-TMA	990.6	1005.5	905.6	9.9	10.6	8.4	20.9	33.9	25.2	25.6
2-MA	1207.8	1212.6	1112.6	8.2	32.8	26.4	19.5	70.6	51.9	26.5
1-EA	1138.3	1146.4	1050.1	8.4	10.1	8.0	20.7	24.0	18.8	21.5
1-E-3-MA	1190.4	1201.8	1103.0	8.2	11.2	9.4	15.8	35.4	29.0	18.2
2-EA	1138.3	1153.8	1053.7	8.7	16.2	13.1	19.3	26.2	21.8	16.6
D	1181.8	1158.7	1032.4	10.9	–	–	–	38.3	38.2	0.40
1-MD	1207.8	1170.6	1085.9	7.2	–	–	–	25.5	27.4	-7.5

Loss (%) = (concentration(direct injection) – concentration(group separation))/concentration(direct injection) × 100.

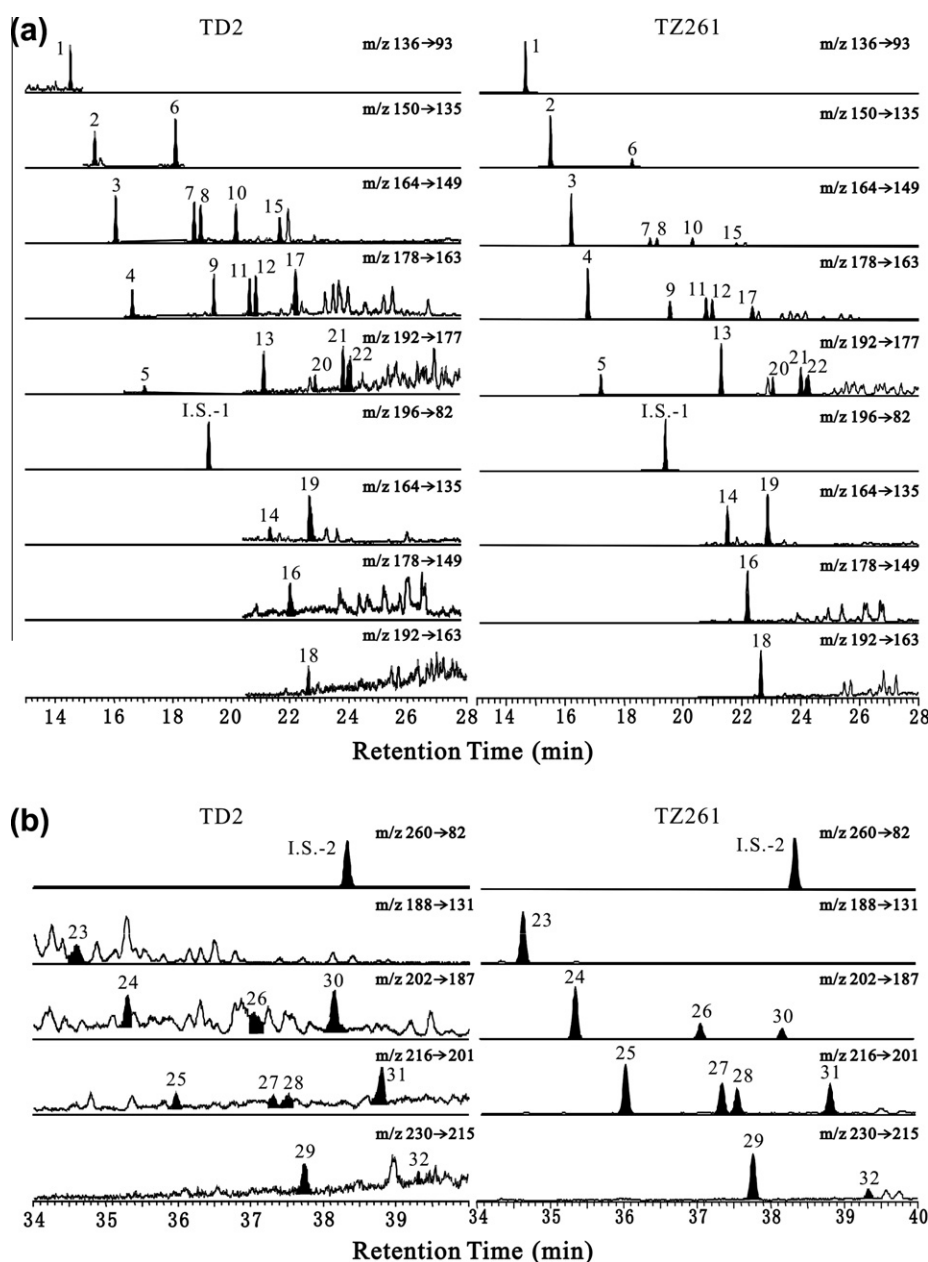


Fig. 2. GC–MS–MS chromatograms of diamondoids in the two Tarim Basin oil samples. Left is the well TD2 oil. Right is the well TZ261 oil: (a) adamantanes and (b) diamantanes.

Table 6

Diamondoid indices calculated based on the concentrations of diamondoids determined using two sample preparation methods and two detection methods.

Sample	MAI		EAI		MA/A		DMAI		MDI		MD/D		DMDI-1		DMDI-2	
	GC-MS	GC-MS-MS	GC-MS	GC-MS-MS	GC-MS	GC-MS-MS	GC-MS	GC-MS-MS	GC-MS	GC-MS-MS	GC-MS	GC-MS-MS	GC-MS	GC-MS-MS	GC-MS	GC-MS-MS
<i>STD</i>																
Calculation	0.67	0.37	0.44	0.74	3.4	5.4	–	–	–	–	–	–	–	–	–	–
Direct injection	0.67	0.37	0.46	0.74	3.5	5.4	0.70	0.65	–	–	–	–	–	–	–	–
Group separation	0.60	0.36	0.34	0.74	3.1	5.7	0.69	0.64	–	–	–	–	–	–	–	–
<i>HD23#</i>																
Direct injection	0.74	0.45	0.61	0.81	6.2	9.0	0.64	0.59	–	–	–	–	–	–	–	–
Group separation	0.71	0.44	0.67	0.81	5.9	9.6	0.62	0.58	–	–	–	–	–	–	–	–
<i>LN14#</i>																
Direct injection	0.79	0.52	0.45	0.75	7.4	9.4	0.63	0.61	0.53	0.46	2.2	6.6	–	0.62	–	0.40
Group separation	0.76	0.50	0.39	0.76	8.0	10.4	0.60	0.59	0.54	0.45	2.9	6.7	–	0.62	–	0.39

STD: mixed diamondoid standards; MAI: methyl adamantane index, $1\text{-MA}/(1\text{-MA} + 2\text{-MA})$; EAI: ethyl adamantane index, $2\text{-EA}/(1\text{-EA} + 2\text{-EA})$; MA/A: $(1\text{-MA} + 2\text{-MA})/A$; MDI: methyl diamantane index, $4\text{-MD}/(4\text{-MD} + 1\text{-MA} + 3\text{-MA})$; MD/D: $(1\text{-MD} + 3\text{-MD} + 4\text{-MD})/D$; DMAI: $1,3\text{-DMA}/(1,2\text{-DMA} + 1,3\text{-DMA})$; DMDI-1: $3,4\text{-dimethyldiamantane}/(4,9\text{-dimethyldiamantane} + 3,4\text{-dimethyldiamantane})$ and DMDI-2: $4,8\text{-dimethyldiamantane}/(4,9\text{-dimethyldiamantane} + 4,8\text{-dimethyldiamantane})$.

Therefore, complex sample preparation procedures are not recommended for the quantification of diamondoids in crude oils, especially adamantanes.

The MAI (methyl adamantane index, $1\text{-MA}/(1\text{-MA} + 2\text{-MA})$) and MDI (methyl diamantane index, $4\text{-MD}/(4\text{-MD} + 1\text{-MD} + 3\text{-MD})$) are the most commonly used maturity indices for evaluating highly mature crude oils or source rocks (Chen et al., 1996; Schulz et al., 2001; Wei et al., 2006b, 2007b). Some other indices, such as MA/A [$(1\text{-MA} + 2\text{-MA})/A$], MDI/DIA [$(1\text{-MD} + 3\text{-MD} + 4\text{-MD})/D$], EAI [$2\text{-EA}/(1\text{-EA} + 2\text{-EA})$], DMAI [$1,3\text{-DMA}/(1,2\text{-DMA} + 1,3\text{-DMA})$], DMDI-1 [$3,4\text{-dimethyldiamantane}/(4,9\text{-dimethyldiamantane} + 3,4\text{-dimethyldiamantane})$], and DMDI-2 [$4,8\text{-dimethyldiamantane}/(4,9\text{-dimethyldiamantane} + 4,8\text{-dimethyldiamantane})$], have also been used (Grice et al., 2000; Schulz et al., 2001; Wei et al., 2007b). These indices are generally calculated from the peak areas of the related compounds obtained from the mass chromatograms of the GC–MS analyses.

The above discussion demonstrates that sample preparation has a considerable effect on the quantitation of diamondoids. Table 6 shows the diamondoid indices that were calculated from relative peak areas obtained using the two sample preparation methods and two detection techniques. No obvious difference is found for most of these indices before or after group separation. This may be due to evaporation of the related compounds that constitute these indices at about the same rate in each experiment, which results in no significant change in their relative concentrations.

In summary, although sample preparation has a considerable effect on the quantification of diamondoid components, especially adamantanes, the effect does not change the diamondoid indices examined here. Therefore, the relative abundances obtained by conventional GC–MS can still be used for identification and quantification with the assumption of relative response factors equal to one.

3.4. Application of the GC–MS–MS method to real oil samples

Two crude oil samples from the Tarim Basin were used to examine the suitability of GC–MS–MS for the quantification of diamondoids in oil samples. Well TZ261 condensate contains abundant diamondoids, while the sample from well TD2 normal oil lacks

detectable diamondoids based on conventional GC–MS analysis (Li et al., 2010).

In order to eliminate the influence from complex matrix components in crude oils and avoid possible mass loss of adamantanes during sample preparation, e.g., column separation and concentration, a single solvent dilution was employed in this work (Section 2.2). The high sensitivity of GC–MS–MS can compensate for the concentration decrease of diamondoids due to dilution. Moreover, adding excessive isoctane is used to remove asphaltenes from crude oils. The MS–MS conditions for the target analytes are listed in Table 2.

The GC–MS–MS chromatograms of diamondoids in well TD2 and well TZ261 crude oils are shown in Fig. 2, where it can be seen that the individual peaks of diamondoid hydrocarbons are well separated without significant interference from the background, except for a few diamantane compounds (i.e., diamantane, 1-methyldiamantane) of the well TD2 oil. Similar to the method of Wang et al. (2006), the RRFs obtained from adamantane (A), 1-MA, 2-MA, 1-EA, 2-EA, diamantane (D) are used for quantitation of adamantane (A), 1-MA, 2-MA, 1-EA, 2-EA, diamantane (D) in crude oils; the RRFs from 1,3-DMA, 1,3,5-TMA and 1-E-3-MA for quantitation of di-, tri-, and tetra-methyladamantanes, respectively, and the RRF from 1-MD for quantitation of methyldiamantanes and other methylated diamantanes, respectively. Based on the dilution factor of samples and the determined results, the concentrations for each target analyte were calculated (Table 7).

Ten compounds were used to calculate the sum of concentrations of the diamondoids in crude oils. The result (Total 1 in Table 7) is 7132 $\mu\text{g/g}$ oil for the TZ261 oil and 162 $\mu\text{g/g}$ oil for the TD2 oil. These quantities are much more than the total concentrations of diamondoids, including $(C_0\text{--}C_5)$ -adamantanes and $(C_0\text{--}C_3)$ -diamantanes, determined by conventional GC–MS, which were 1009 $\mu\text{g/g}$ oil for the TZ261 oil and zero for the TD2 oil (Li et al., 2010). The difference between two quantification results is probably caused by two main factors, i.e., mass loss during sample preparation (i.e., column chromatography separation and solvent evaporation) and the quantitative method. Relative response factors for each target analyte to corresponding internal standards were assumed to be 1. According to our results (Table 3), this assumption is questionable for accurate quantification of individual diamondoid compounds. Based on our quantitative data,

Table 7
Concentrations of diamondoids in the two Tarim Basin oil samples.

Peak number	Assignment	Concentration in oil ($\mu\text{g/g}$)	
		Well TD2	Well TZ261
1	Adamantane	8.6	738
2	1-Methyladamantane	34.6	2319
3	1,3-Dimethyladamantane	28.8	1796
4	1,3,5-Trimethyladamantane	9.5	517
5	1,3,5,7-Tetramethyladamantane	0.04	66.5
6	2-Methyladamantane	27.8	212
7	1,4-Dimethyladamantane(cis)	26.3	259
8	1,4-Dimethyladamantane(trans)	24.1	245
9	1,3,6-Trimethyladamantane	17.9	196
10	1,2-Dimethyladamantane	27.4	274
11	1,3,4-Trimethyladamantane(cis)	17.2	227
12	1,3,4-Trimethyladamantane(trans)	18.2	218
13	1,2,5,7-Tetramethyladamantane	11.9	185
14	1-Ethyladamantane	9.7	105
15	2,6- + 2,4-Dimethyladamantane	18.8	88.3
16	1-Ethyl-3-methyladamantane	17.9	201
17	1,2,3-Trimethyladamantane	32.3	167
18	1-Ethyl-3,5-dimethyladamantane	2.3	73.4
19	2-Ethyladamantane	16.4	58.2
20	1,3,5,6-Tetramethyladamantane	3.7	61.9
21	1,2,3,5-Tetramethyladamantane	13.5	104
22	1-Ethyl-3,5,7-trimethyladamantane	8.2	73.6
23	Diamantane	8.5	919
24	4-Methyldiamantane	16.5	880
25	4,9-Dimethyldiamantane	1.8	171
26	1-Methyldiamantane	nd	267
27	1,4- + 2,4-Dimethyldiamantane	1.3	102
28	4,8-Dimethyldiamantane	4.8	84.7
29	1,4,9-Trimethyldiamantane	0.2	36.3
30	3-Methyldiamantane	22.7	173
31	3,4-Dimethyldiamantane	9.9	96.9
32	3,4,9-Trimethyldiamantane	0.5	6.1
	Total 1	162	7132
	Total 2	442	10,921

Total 1 is the sum of concentrations of ten diamondoid compounds listed in Table 3. Total 2 is the sum of concentrations of all diamondoid compounds listed in this table.

diamondoid hydrocarbons in the TZ261 oil are dominated by 1-MA, 1,3-DMA, followed by adamantane, diamantine and 4-methyldiamantane. For the TD2 oil, methyladamantanes and dimethyladamantanes are the dominant components.

4. Conclusions

In this study, a highly sensitive and selective method was developed to quantify low levels of diamondoids in crude oils. This method employed a simple solvent dilution followed by GC–MS–MS detection. The GC–MS–MS method was optimized for parent and daughter ions, collision energy and scan time. Compared with the conventional GC–MS method, GC–MS–MS shows higher sensitivity, lower detection and quantification limits and better recoveries for the detection of diamondoids in crude oils. Quantitative results proved that group separation can cause considerable mass loss of diamondoids. Thus, complex sample preparation procedures are not recommended for the quantification of diamondoids in crude oils. However, no obvious variation was found in some diamondoid indices, indicating that GC–MS combined with conventional group separation can be used to determine most diamondoid indices. Finally, the GC–MS–MS technique was successfully applied to two crude oils. The results indicated that GC–MS–MS can be more precise than GC–MS for the analysis of diamondoids, especially when they occur in low concentrations.

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