

Detection of 2-thiaadamantanes in the oil from Well TZ-83 in Tarim Basin and its geological implication

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Thermochemical sulfate reduction (TSR) causes increasing of sulfur content in the oils, reduction of oil quality, and produces a toxic and corrosive H₂S which may take great adverse effect on health and equipment. Although there are several ways to identify presence of TSR in gas field, yet in the case of oil with low H₂S content, it is still very difficult to identify TSR. 2-thiaadamantanes is one of the most effective indicators of TSR. This paper for the first time discovers 2-thiaadamantanes in the oil from Well TZ-83 in Tarim Basin. A silver nitrate silica gel chromatography was used to enrich the oil from low 2-thiaadamantanes content to the level that GC/MS and GC/MS/MS can detect. 2-thiaadamantanes were assigned by comparison of mass spectra with published data, and the fragmental ions in mass spectra were confirmed by MRM mode of GC/MS/MS. H₂S gas produced in Tazhong area is thought to be generated from TSR since 2-thiaadamantanes were present in the oil.

2-thiaadamantanes, TSR, H₂S, Tarim Basin

2-thiaadamantane is a compound which is generated after the carbon atom at C-2 in adamantane molecule replaced by sulfur atom, and methyl and dimethyl group at bridgehead location are the identified major in west Europe (Italy and France), west Canada, USA (for example, condensates and crude oils generated in Oxfordian Smackover source rocks in Gulf of Mexico), and Middle East (some oil fields located in east Saudi Arabia)^[1,2].

Most researchers believe that these compounds are present in oil and natural gas reservoir rocks with gypsum layer or gypsum layer mixed with mudstone. Under the condition of high temperature and participation of water, SO₄²⁻ from gypsum reacts with hydrocarbons and generates complex compounds including H₂S and organic sulfur compounds, which is called thermochemical sulfate reduction, abbreviated to TSR^[3-8].

Galimberti et al.^[2] and Peters^[9] regard 2-thiaadamantanes as a TSR indicator or molecular fingerprint and the compounds play an important role in recognition of TSR^[2,9]. TSR produces a toxic and corrosive H₂S which reduced oil quality and value, and also it may take great

adverse effect on health and equipment. Moreover scholars discovered that TSR may improve the porosity and permeability^[10,11], so TSR has received much concern recently in China in the exploration of carbonate rocks and organic geochemistry.

Except the salt lake deposition formation, which developed sulfate, most terrestrial gas reservoirs strata are unaffected by TSR because of their low burial depths, dilute water, and without gypsum-rock layers. While TSR happened easily in marine facies, which distinguished by great burial depths, high mineralization water, presence of gypsum-rock layers and high content of SO₄²⁻, for examples, most gas reservoirs in Sichuan Basin are affected by TSR^[12,13]. TSR has not been researched systematically in the oil and gas fields in central and north parts of the Tarim Basin from Cambrian to Ordovician and Middle-Upper Ordovician. The previous results suggested the presence of TSR from the

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geological and geochemical data, while it has not been proved by 2-thiaadamantanes^[14]. Detection of 2-thiaadamantanes in the oil of Well TZ-83 provides a credible evidence for TSR research method in this area.

1 Experiments

Aromatics, nonhydrocarbon, and asphaltene 4 fractions were separate into saturates according to CNPC standardization method of SY/T5119-1995 (extractable organic matters in rocks and oil for family groups separated by chromatographic column) for the 50 mg crude oil (it might be diluted by hexane, precipitate and remove asphaltene in the case of high content of asphaltene, but for condensate it is directly analyzed). 2-thiaadamantanes are in nonhydrocarbon fraction.

We dissolved AgNO₃ (analytical purity) in distillation water and made the water concentration at 20 mg/100 mL of solution. Then put 15 g silica gel in the solution, after 30 min remove fluid by filtering and dry the silica gel at 120°C for 6 h. A glass tube (length: 20 cm, diameter: 6 mm) equipped with a cock and a tip at the bottom and a hopper at the top were filled in the dried silica gel, making them more compacted by ramming, and then damp them by adding an appropriate amount of

hexane. Afterwards, we added the nonhydrocarbon fraction diluted with a bit of DCM at top of the column, and flushed it with 50 mL DCM and then 50 mL mixed solvent DCM/MeOH (9:1,v/v), and collected later, and then finally made it volatilize until 2 mL was left followed by GCMS and GCMS/MS analysis.

GC/MS was carried out on Agilent 6890N gas chromatograph which is connected to an Agilent 5973 mass selective detector operated at 70 eV with a mass range of 50–500 amu. The gas chromatograph was equipped with an Equity-5 capillary column (60 m, 0.25 mm, 0.25 μm), injector is 280°C, and temperature programme is 50°C(2 min), 50–200°C(3°C/min), 200–320°C(10°C/min) and 320°C(20min). He gas was used as carrier gas.

GC/MS/MS analysis was carried out on a VG Quattro II tandem mass spectrometer equipped with Agilent 6890N gas chromatograph by a db-1 capillary column (60 m, 0.25 mm, 0.25 μm). Collision voltage is 20 eV, collision gas is Ar, and the other chromatographic conditions were same as those for GC/MS analysis. The experiment in this paper adopts MRM mode, and the established channels include *m/z* 154.3→79.1 for 2-thiaadamantane, 168.3→93.1 for methyl-2-thiaadamantanes, 182.3→93.1 for dimethyl-2-thiaadamantanes,

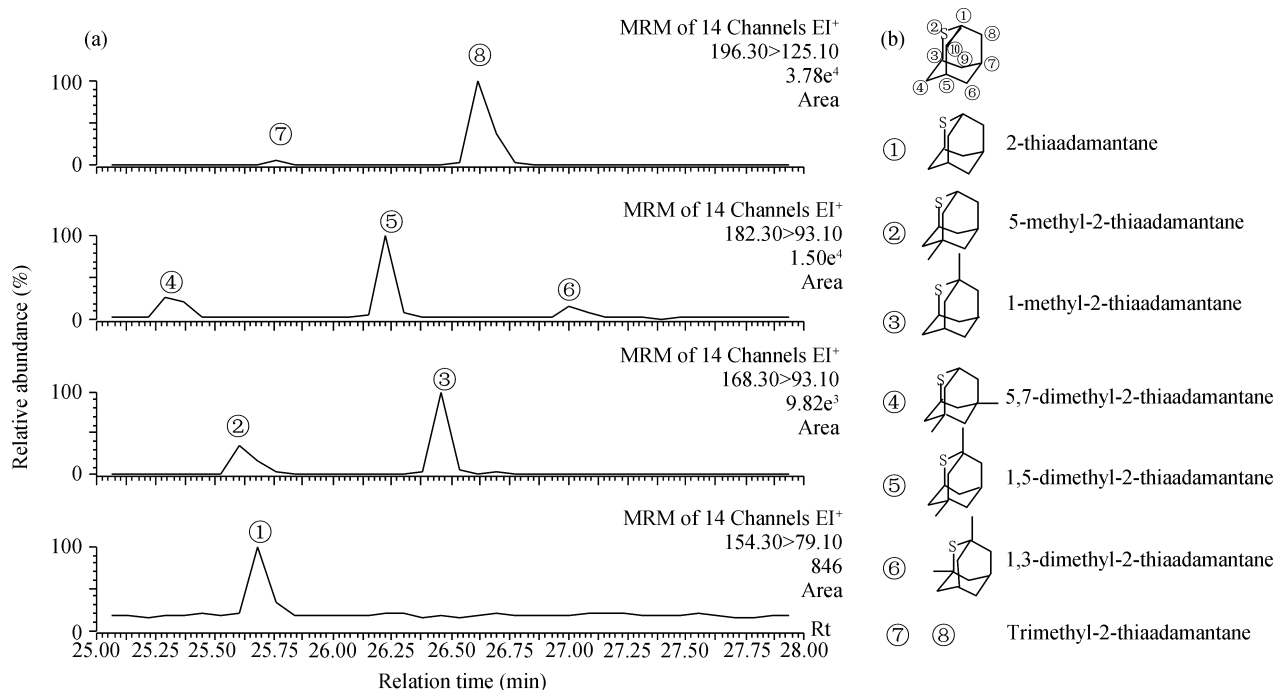


Figure 1 The MRM chromatograms of *m/z* 154.3→79.3, 168.3→93.1, 182.3→93.1, and 196.3→125.1 in the oil in Well TZ-83. ①–⑧ indicate the identified peak number (the same below). For the sake of comparison and identification, the analytical conditions are set to as similar as to those of Galimberti et al.^[2]. The figure shows that the peak order and retention time of the isomers are similar to those of Galimberti et al.^[2].

and 196.2→125.1 for trimethyl-2-thiaadamantanes. In order to confirm principal fragmental ions from parent ion, the additional channels were set up as follows: m/z 168.3→79.1, 168.3→111.1, 168.3→153.1, 182.3→107.1, 182.3→125.1, 182.3→149.1, 182.3→167.1, 196.3→107.1, 196.3→121.1, and 196.3→181.2.

2 2-thiaadamantanes identification

Hanin et al.^[1] made an important contribution to the sample preparation and identification of 2-thiaadamantanes. They separated 1,5-dimethyl-2-thiaadamantane from an oil samples, established its chemical structure by NMR, identified 2-thiaadamantanes by comparison with 1-methyl-2-thiaadamantane as a standard and then created an identification way. These compounds are characterized by strong molecular ions M^+ and minor fragmental ions at m/z 93 and m/z 107 on GC/MS data, and $M^+=154+(n\times 14)$, n =number of methyl groups, while there was not any mass spectra present in this respect. Because of the low content of the compounds in oil, as

well as coelution and interference caused by several compounds in GC analyses, better sensitive and analytical jamproof methods are needed.

A fast method to detect thiaadamantoids was suggested by Galimberti et al.^[2], which should be an effective approach and can be adopted based on our experience. GC/MS/MS MRM traces (Figure 1) of m/z 154.3→79.1 for the detection of 2-thiaadamantane, 168.3→93.1 for the detection of methyl-2-thiaadamantanes, 182.3→93.1 for the detection of dimethyl-2-thiaadamantanes, and 196.2→125.1 for the detection of trimethyl-2-thiaadamantanes respectively were applied in the work and characterized by high specificity and sensitivity.

As it is the first time to publish a 2-thiaadamantanes mass spectrogram, some intensive fragmental ions are proved to be generated from the appropriate parent ion by MRM mode in GC/MS/MS analysis in order to enhance the reliability.

2-thiaadamantane: a peak (①) is exhibited in the m/z

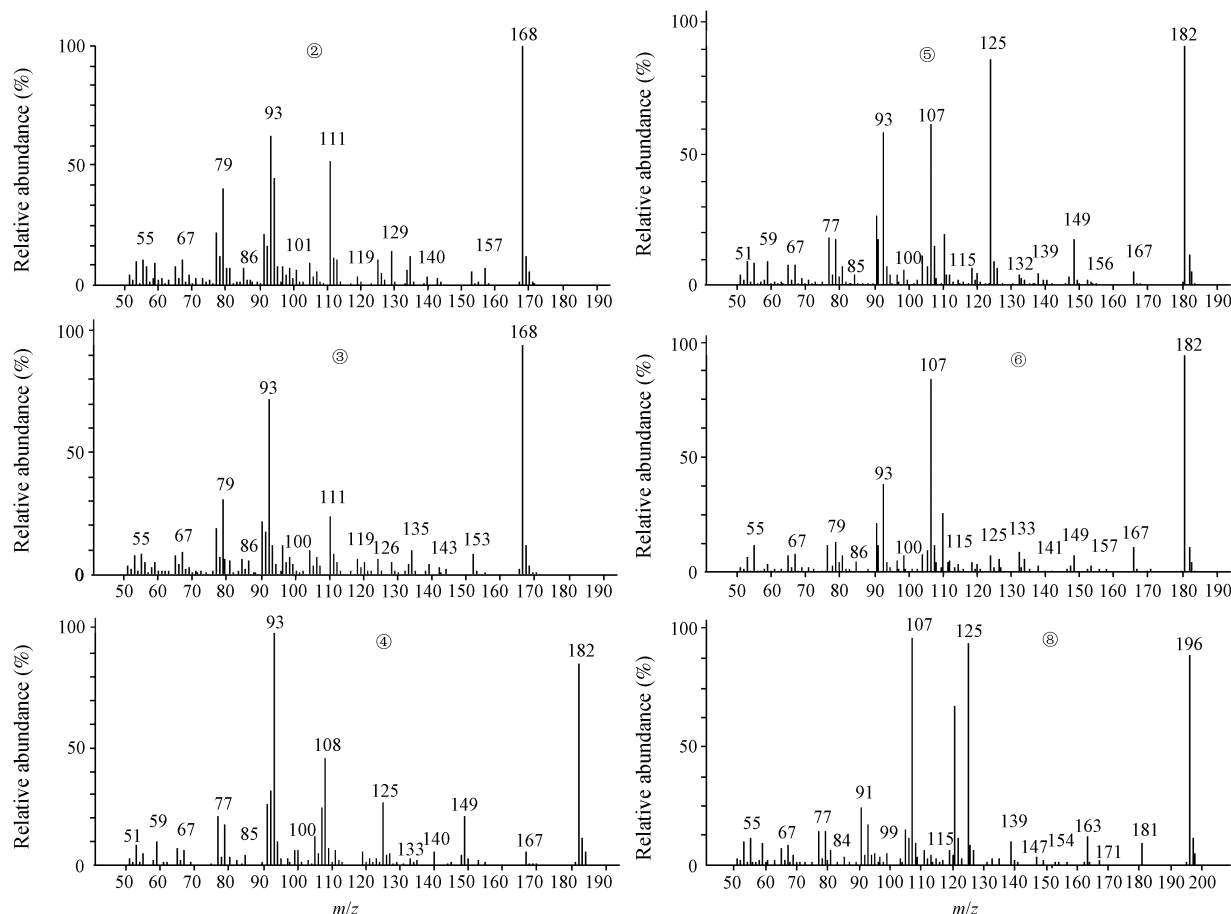


Figure 2 The mass spectra of 2-thiaadamantanes obtained from the GC/MS analysis of the oil in Well TZ-83. The most intensive fragmental ions have been proved to originate from the molecular ions by MRM mode of GC/MS/MS analysis.

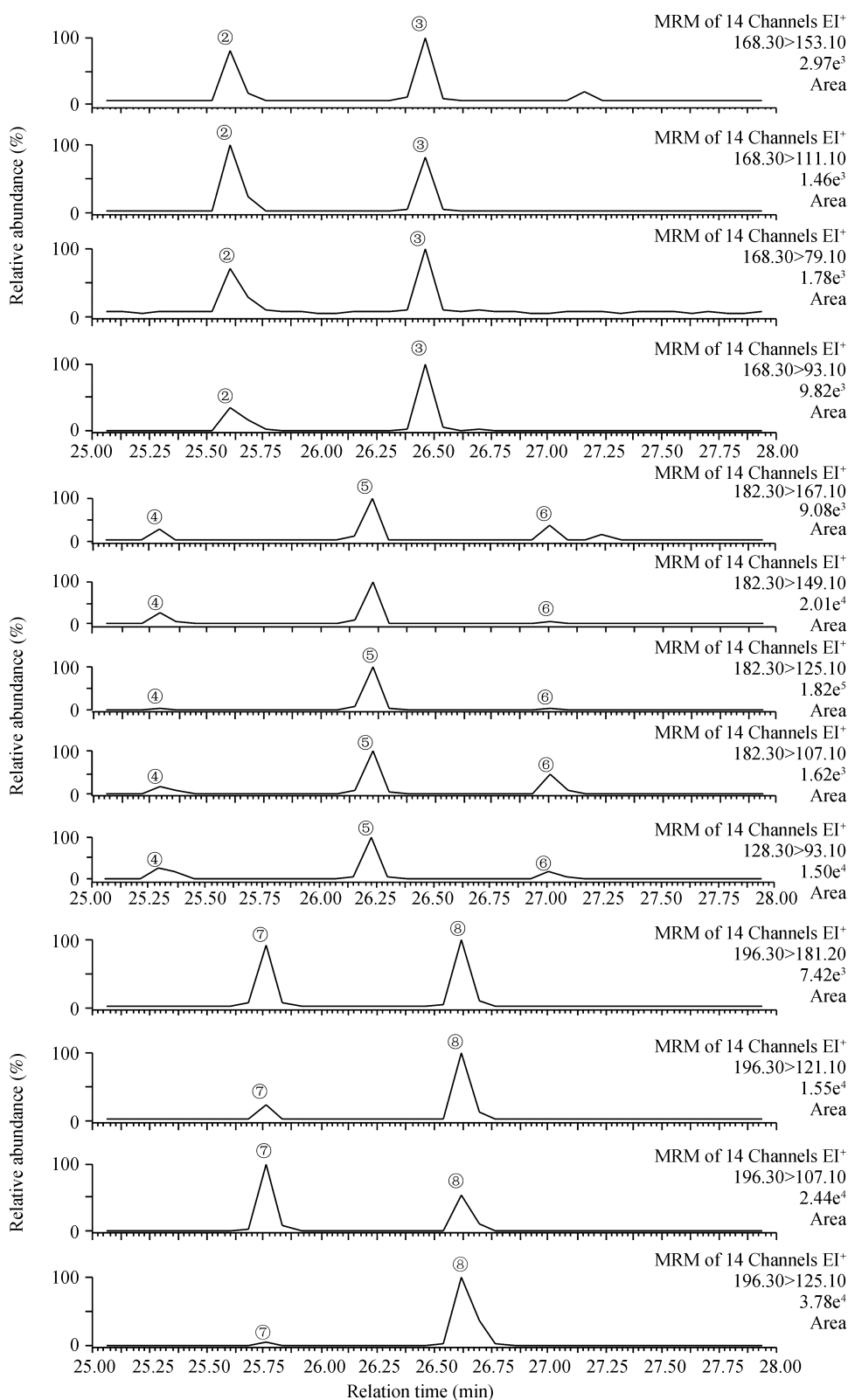


Figure 3 The principal fragments in mass spectra of 2-thiaadamantanes originating from the molecular ions from MRM monitoring channels of GC/MS/MS. The MRM monitoring channels included, m/z 168.3→79.1, 168.3→93.1, 168.3→111.1, 168.3→153.1, 182.3→93.1, 182.3→107.1, 182.3→125.1, 182.3→149.1, 182.3→167.1, 196.3→107.1, 196.3→121.1, 196.3→125.1 and 196.3→181.2.

154.3→79.1 chromatogram (Figure 1), Because of the weak intensity, the reliable mass spectrum can not be obtained, but the molecular ion is clear, and only one obvious peak (①) in m/z 154.3→79.1 trace, also the retention time coincide with what Roberto Galimberti et al.^[2] had got, so the identification should be correct.

Methyl-2-thiaadamantanes: there are two peaks in the 168.3→93.1 trace, and 5-methyl-2-thiaadamantane (②) and 1-methyl-2-thiaadamantane (③) are located on the left and right sides (Figure 1). The mass spectra were characterized by m/z 79, 93, 107, 125, 135 and 168 (Figures 2 and 3) and show the molecular ion $[M]^+$ of m/z 168 as base peak and $[M-15]^+$ of m/z 153 with minor intensity. The ion of m/z 79 has been stated as a specific ion in 2-thiaadamantanes by Galimberti et al.^[2] and m/z 93 may be m/z 79+14 (a methyl group). The more intensive ion of m/z 111 is suggested as $[SC_6H_7]^+$, and m/z 135 may be $[M-SH]^+$ ^[2].

Dimethyl-2-thiaadamantanes: the three peaks lie on the left, middle and right sides of 182.3→93.1 trace, which were identified as 5,7-dimethyl-2-thiaadamantane (④), 1,5-dimethyl-2-thiaadamantane (⑤) and 1,3-dimethyl-2-thiaadamantane (⑥) respectively (Figure 1). The mass spectra were characterized by m/z 93, 107, 125, 149, 167, and 182 (Figures 2 and 3). The ion of m/z 107 may be m/z 93+14, and m/z 182 and 167, which is thought to be M^+ and $[M-15]^+$.

Trimethyl-2-thiaadamantanes: the two peaks (⑦ and ⑧) in 196.3→125.1 trace have not exactly chemistry names and may be identified as trimethyl-2-thiaadamantanes (Figure 1). The mass spectra were characterized by m/z 107, 121, 125, 181, and 196 (Figures 2 and 3). The ion of m/z 121 may be counted as m/z 107+14, and m/z 125 as m/z 111+14, m/z 196, 181, 163 as M^+ ,

$[M-15]^+$ and $[M-SH]^+$ respectively.

3 Geological implication of the detection of 2-thiaadamantanes in the oil from Well TZ-83 in the Tarim Basin

Well TZ-83 is located in Tazhong No.1 fault belt in Tazhong uplift, in which the migration of oil and gas was effectively controlled by fracture system. The intensity of m/z 245 mass chromatogram of the oil from Well TZ-83 is too low to be diagnosed in oil-source using triaromatic dinosteroids, but the abundance ratio of steranes C_{27} , C_{28} and C_{29} in the m/z 217 mass chromatogram is 1.5:1.3:1, showing its “slant line” shape, which coincides with the point suggested by Zhang et al.^[15] that a higher content of C_{28} steranes (accounting for 20%–26% of the total C_{27} – C_{29} steranes) in the extracts from Cambrian source rocks in the Tarim Basin^[15]. So it is deduced that the oil was originated from Cambrian-Lower Ordovician source rocks.

The source rocks are composed of evaporate lagoonal facies micrite-dolomite and micrite-limestone^[16]. The original water of evaporate lagoonal facies is characterized by high salinity and high content of SO_4^{2-} , which entered into the reservoirs accompanied by the oil and gas migration under the conditions of high temperature caused by great burial depth (5666.1–5684.7m). All of the above provide good conditions for TSR occurrence. 2.6% concentration of H_2S in natural gas could be the evidence of the existence of TSR occurrence, so the identification of TSR by 2-thiaadamantanes is advisable.

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