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Determination of diamondoids in crude oils using gas purge microsyringe extraction with comprehensive two dimensional gas chromatography-time-of-flight mass spectrometry

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ABSTRACT

Based on a homemade device, gas purge microsyringe extraction (GP-MSE) of crude oil samples was developed for the first time. As a simple, fast, low-cost, sensitive and solvent-saving technique, GP-MSE provides some outstanding advantages over the widely used sample preparation methods for crude oils such as column chromatography (ASTM D2549). Several parameters affecting extraction efficiency were optimized, including extraction temperature, extraction time, extraction solvent, condensing temperature and purge gas flow rate. With the optimized GP-MSE conditions, several real crude oil samples were extracted, and trace diamondoids were determined using comprehensive two dimensional gas chromatography-time-of-flight mass spectrometry (GC × GC-TOFMS). In total, more than 100 diamondoids were detected and 27 marker compounds were identified and quantified accurately. The limits of detection (LODs, S/N = 3) were less than 0.08 μg/L for all diamondoids. The relative standard deviation (RSD) was below 8%, ranging from 1.1 to 7.6%. The linearity of the developed method was in the range of 0.5–100.0 μg/L with correlation coefficients (R^2) more than 0.996. The recoveries obtained at spiking 50 μg/L were between 81 and 108% for diamondoids in crude oil samples. The developed method can also be extended to the analysis of other components in crude oils and other complex matrices.

1. Introduction

Diamondoids in petroleum are alkanes with diamond-like structure and a number of diamond-subunits ranging from 1 to 11, which are volatile and have been detected in both crude oil [1,2] and sedimentary rocks [3,4]. It has been speculated that diamondoids are formed by way of catalytic (i.e. Lewis acids) rearrangement of polycyclic hydrocarbons during or after oil generation [2,5,6]. Diamondoids are more thermally stable than other hydrocarbons [1], and so become increasingly enriched in condensate oils during oil cracking [7]. Since geochromatographic effect in petroleum migration has little influence on them, some geochemical parameters derived from the quantitative analysis of diamondoids can play important roles in determining maturity and sedimentary environments [3,8], tracing oil origins in the subsurface of sedimentary basins [9–11], identifying the source of oil spills [10,12] and thermal cracking level [1,8,13,14] etc. Therefore, the sensitive and accurate analysis of diamondoids is essential for petroleum exploration and development.

Gas chromatography (GC) or GC coupled to mass spectrometry (MS) is the common used method for the analysis of volatile and semi-volatile compounds in crude oils. However, direct injection is not suitable for complex samples like crude oils, due to the existence of non-volatile components such as asphaltenes and resins etc. Additionally, some compounds at low concentration levels have to be enriched before GC analysis to improve the sensitivity. Therefore, for the analysis of crude oils, the first thing to do is sample preparation such as preconcentration and matrix isolation etc. Currently, the widely used method for the crude oil preparation is column chromatography described in ASTM D2549, where the crude oil sample is usually subjected to a standard procedure of

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group separation [2,4,6,15,16]. Besides the time-consuming steps and too much consumption of solvent, some enrichment steps, such as rotary evaporation etc., can result in the loss of analytes. It has been reported that up to 34% of diamondoids were lost when using the above method [17].

Compared with traditional sample preparation methods like column chromatography and liquid-liquid extraction (LLE) etc., solid-phase microextraction (SPME) provides a solvent-free method including simultaneous extraction and preconcentration of analytes from aqueous samples or the headspace of the samples [18]. However, the SPME fiber is fragile, and has limited lifetime and low extraction capacity. In addition, sample carry-over and discrimination effect can also exist in many cases [19]. Especially in the analysis of crude oil with complex matrix, SPME showed no significant advantages over traditional methods. For example, D'Auria et al. concluded that SPME exhibited high sensitivity for compounds with volatility more than Tetradecane (n-C_{14}), but failed within the range of n-C_{14}–n-C_{25} alkanes [20]. As another microextraction technique, liquid-phase microextraction (LPME) or single drop microextraction (SDME) has been applied to different sample matrices such as environmental waters [21,22], foods [23,24], and medicines [25,26] etc. However, the disadvantages of LPME are as follows: fast stirring would tend to dislodge the microdrop suspended on the needle of microsyringe; extraction is time-consuming and equilibrium cannot be attained after a long time in most cases [27]; the efficiency of extraction and enrichment is low due to the limited surface area of organic solvent [28]. Additionally, the extraction system is closed and the highest enrichment factors can be obtained only when extraction equilibrium is established [29]. The above disadvantages of LPME greatly limit its further applications, especially to complex samples like crude oils. Therefore, some simple, rapid, clean, sensitive and efficient techniques are required.

In this study, gas purge microsyringe extraction (GP-MSE) of crude oil samples was developed for the first time based on a homemade device, and trace diamondoids were determined by using GC × GC-TOFMS. The optimal extraction conditions were investigated in detail. In contrast to the closed system of LPME, GP-MSE provided an open extraction system and larger solvent volume, which greatly shortened the extraction time, increased the extraction capacity and surface area, and improved the enrichment efficiency for analytes by purging inert gas to sample matrix. The whole process of extraction only takes 10 min, only 20 μL of organic solvent is needed, and almost complete extraction of analytes is achieved. Additionally, the proposed method can be extended to the analysis of other kinds of complex sample matrices.

2. Experimental

2.1. Samples and chemicals

The standards of diamondoids were purchased from Tokyo Chemical Industry co., Ltd. (Japan) and Shanghai Chemical Reagent Corporation (China), respectively. Dichloromethane, hexane, methylbenzene and acetone were of HPLC grade quality and purchased from Anhui Fulltime Co. (China). The crude oil samples were obtained from the Pearl River Mouth Basin, China.

2.2. Preparation of working standards

Stock standard solutions of diamondoids (50 mg/L) were prepared in hexane. For calibration curves, standard working solutions for different concentrations were prepared by diluting the stock solutions with hexane and stored at −20 °C before use. The final concentration of diamondoids working solution is 0.1, 0.2, 0.5, 1, 5, 10, 20, 50, 100, 200 and 500 μg/L.

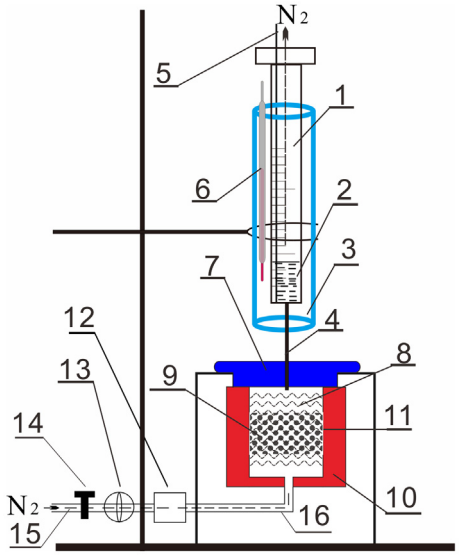

Fig. 1. The schematic diagram of the GP-MSE device. The dotted line means gas flow pathway. 1. Microsyringe; 2. extraction solvent; 3. thermoelectric cold trap system; 4. microsyringe needle; 5. stainless steel wire; 6. thermometer; 7. PTFE silicone septum pad; 8. glass wool; 9. sample; 10. thermoelectric heating system; 11. fused-silica hollow tube; 12. digital monitor; 13. gas flow controller; 14. T valve; 15. carrier gas; 16. copper tube.

2.3. Sample preparation

The developed GP-MSE method was compared with several other sample preparation methods, such as direct injection method, single drop microextraction (SDME) and column chromatography method (ASTM D2549). The comparison was performed by using standard solutions and real crude oil samples, respectively.

2.3.1. GP-MSE of crude oil and standard solution

The GP-MSE device mainly consists of a microsyringe, an open purge-and-trap system, a heating system and an automatic control system [30]. The schematic diagram are shown in Fig. 1. In the heating system unit, a platinum resistor is used as the temperature sensor. A cylindrical sample cell is fixed in the middle of the heating mantle. The samples are loaded into a fused-silica hollow tube with glass wool and put into the sample cell with PTFE silicone septum pad, followed by insertion of the microsyringe. When the power is supplied to the heating system, a metal-oxide ceramic heater (MCH) generates high temperature and rapidly heats samples to a set temperature. The volatile and semi-volatile compounds are evaporated to the headspace of the fused-silica hollow tube, and then carried through the needle to the extraction solvent in the microsyringe barrel by the inert gas (nitrogen) purge. In the purge-and-trap system unit, a stainless steel gas pipe is connected to the bottom of the sample cell to purge nitrogen. In order to increase the capacity of extraction and avoid the dislodgement of microdrop as in LPME, 20 μL of organic solvent is used as extraction solvent in the microsyringe barrel with the plunger pulled out. A stainless steel wire is inserted into the microsyringe barrel in order to avoid the boiling and spilling of extraction solvent. A thermoelectric trap system has also been developed for cooling the microsyringe barrel and trapping target compounds. It consists of a platinum resistor sensor, an insulation cover, an aluminum box, an aluminum plate, a heat sink, a cooling fan and some refrigeration pieces. Compared with the traditional LPME techniques, stability of the extraction solvent and capacity of extraction in the GP-MSE