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Methyldibenzothiophene isomer ratio in crude oils: Gas chromatography tandem mass spectrometry analysis

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ABSTRACT

The quantification of Methyldibenzothiophene isomers (MDBTs) is used in the geochemical characterization of crude oils. The relative ratio of these isomers can give useful information about the nature and the maturity of the source rock. This paper describes a novel analytical technique for the quantitative determination of MDBTs through triple quadrupole tandem mass spectrometry (GC–MS/MS). Through the multiple reaction monitoring (MRM) scan mode, it was possible to reach high selectivity for the MDBTs and their quantification was obtained without preliminary fractionation of the crude oil. In order to reduce the carryover of high boiling components, a recently developed backflush system in the GC program was applied. This novel protocol has been tested on sixteen samples of crude oil from different oil fields around the world. It was concluded to be more reliable than previously reported analytical methods based on selected ion monitoring (SIM) scan mode.

1. Introduction

Geochemical study of crude oils is addressed to obtain information about their composition and the description of the source rock from which the oil was generated. Petroleum geochemical knowledge, in fact, provides a wide variety of useful information for oil exploration and characterization purposes such as maturity of the sediment, hydrocarbon accumulations, and structure of the reservoir. Analytical investigations are aimed at finding and quantifying oil specific markers to provide detailed information about the oil and its source rock, such as their geological history, conditions of sedimentation (diagenesis), and age [1].

Among the markers, methyldibenzothiophene isomers (MDBTs), and, in particular, their relative ratio, has been correlated to specific properties of the reservoir, i.e. maturity [2,3], origin of the oil, and the nature of the source rock [4]. It has been shown that the isomeric ratio 1-MDBT/4-MDBT decreases as the oil is extracted at a deeper level [5,6]. This behavior is due to the lower thermal stability of the isomer 1-MDBT than that of the isomer 4-MDBT.

Moreover, it has been found that the ratio of MDBTs isomers varies in different kinds of source rocks [7]. In fact MDBTs have been successfully used to characterize different types of oil [8].

MDBTs are also used as biodegradation indicators [9]. The isomers 2- and 3-MDBT biodegrade at a higher rate, as shown by the strong decrease in their ratio to 4-MDBT, whereas instead 1-MDBT is slightly more resistant to biodegradation than 4-MDBT, indicated by an increase in the ratio 1-MDBT/4-MDBT [9,10].

Although a number of studies have been published focusing on defining these compounds, there are several analytical difficulties that remain to be addressed to determine their correct quantities. Gas chromatographic methods with selective detectors, e.g. atomic emission detector (GC-AED) [11,12] flame photometric detector (GC-FPD) [13,14], and sulfur chemiluminescence detector (GC-SCD) [15,16] have been employed for the speciation of sulfur compounds in petroleum matrices. However, these techniques can only be applied if the gas chromatographic separation is good enough to selectively separate the sulfur compounds [17].

A direct quantification of polycyclic aromatic sulfur heterocyclic compounds (PASHs) in oil samples has been previously proposed [18] through gas chromatography -mass spectrometry (GC–MS) analysis in high resolution mode (HRMS) using a magnetic analyzer mass spectrometer. This procedure allows a good separation of MDBTs isomers and avoids the interference of other compounds with similar retention times. However, it requires the simultaneous injection in the ion source of a perfluorokerosene (PFK) mixture in order to reach the lock mass stability for the high resolution and mass accuracy.

In previous studies, MDBTs have been characterized using GC/MS with selected ion monitoring mode (SIM) on the molecular ion at m/z 198. However, the chromatogram obtained using this protocol showed a strong presence of interferences that affected the quantification analysis. This was probably due to the presence of C5-naphthalenes which have a similar GC retention time and same nominal mass (m/z 198). Therefore, without a preliminary fractionation of the oil, and through the SIM scan analysis, the risk that the presence of

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polycyclic aromatic hydrocarbons (PAH) would interfere is very high [19].

In order to increase the concentration of the MDBTs and to eliminate some interferences, different preliminary step of crude oil fractionations have been proposed [20,21]. A highly selective and convenient sample preparation involves the use of Pd(II) ions immobilized on silica gel by 2-amino-cyclopent-1-ene-dithiocarboxylic acid (ACDA) as the ligand. Thus, MDBTs isomers can be collected into a separate fractions from the polycyclic aromatic hydrocarbons (PAHs) [20].

In order to overcome the drawback of the complex synthesis of organic ligand ADCA, silver(I)-mercaptopropylsilica gel (MPSG), a commercially available product, has recently been used for the separation of MDBTs and PAHs [21]. This method is easy and fast to carry out and can be applied to the separation of a high number of polycyclic aromatic sulfur heterocycles from aromatic hydrocarbons, oxygen heterocycles, and noncondensed thiophenes.

In the present work a quantitative method, based on a direct acquisition of the diluted sample of crude oil through EI-Multiple Reaction Monitoring (MRM) scan mode, is reported. It's well proved that the MRM scan mode has a higher selectivity than the SIM scan mode. Therefore, this method allows a better signal resolution without a preliminary fractionation of the oil. Only the molecules which have the selected fragmentation patterns are taken into account. Therefore, the interferences are dramatically reduced and the signal to noise ratio increases of many orders of magnitude.

Since oils contain high boiling components that might contaminate the column, in the postrun time a backflush [22] has been applied to reverse the flow and purge the column. The backflush provides higher throughput with lower carry over.

This novel analytical approach has been tested on sixteen samples of crude oil and has proved to be more accurate in the quantification of MDBTs than previously published methods.

2. Materials & methods

2.1. GC–MS-MS analysis

Sixteen samples of crude oils from different geographical areas of the world (Italy, Africa, Asia) have been analyzed through a triple quadrupole mass spectrometer (Agilent 7000B) coupled to a Gas Chromatograph (Agilent 7890). The samples of crude oil, without a preliminary separation, have been diluted in toluene (99.5% purity Carlo Erba) to reach a concentration of 0.001% w/w prior the injection. Toluene has been used also for the preparation of the standard solutions. The four isomers of MDBT (1,2,3,4-MDBT) have been purchased from Chiron (Trondheim, Norway).

The GC column used was a fused silica capillary column Agilent 190915–433 (30 m × 250 μm i.d., film thickness 0.25 μm) the flow rate of the carrier gas (He) was 1.2 ml/min. The GC oven program was 80 °C for 2 min and then a rate of 15 °C/min to reach the final

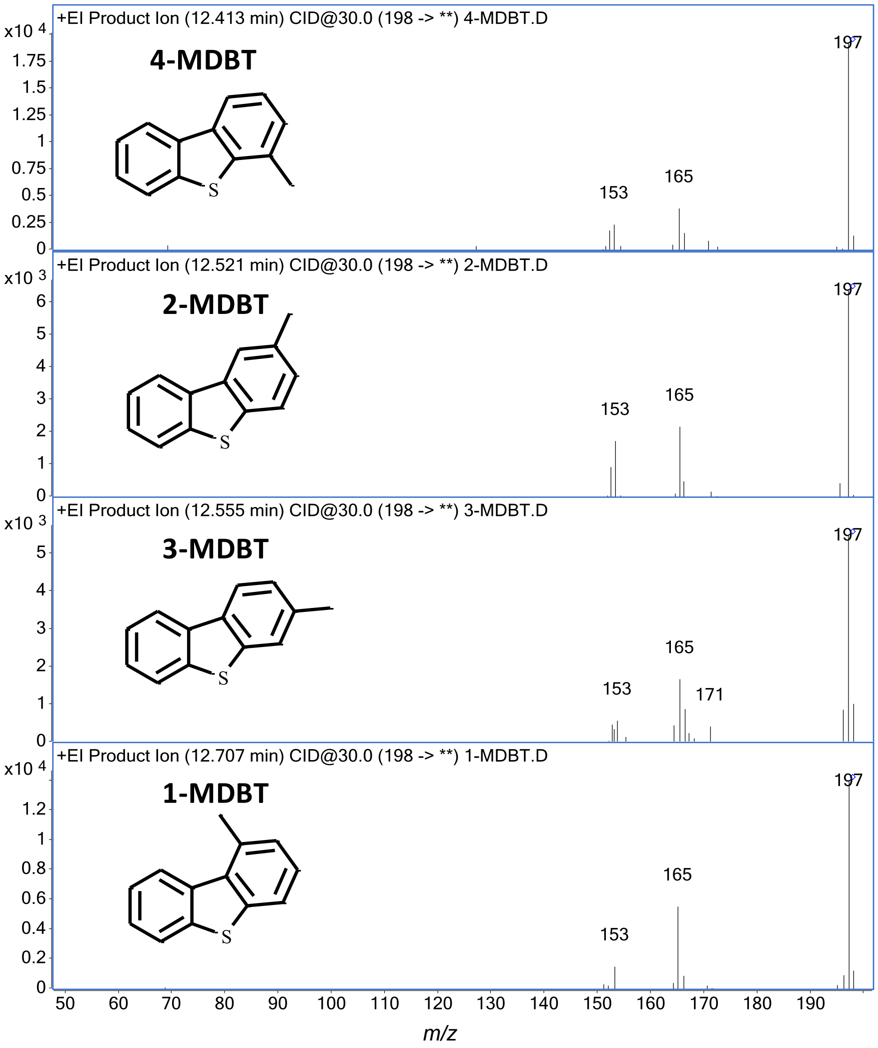

Fig. 1. Product ion mass spectra of the 4 isomers of MDBT.