Weathering trend characterization of medium-molecular weight polycyclic aromatic disulfur heterocycles by Fourier transform ion cyclotron resonance mass spectrometry

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HIGHLIGHTS

- Weathering trend of medium-molecular weight disulfur aromatics.
- FT-ICR MS measurements on North Sea crude oil and its weathered samples.
- Double bond equivalents (DBE) 5–8 were less influenced by artificial weathering.
- DBE 7/DBE 8 may be used as possible source marker.
- Long alkyl groups disulfur aromatics show high degradation rate.

ARTICLE INFO

ABSTRACT

Different weathering factors act to change petroleum composition once it is spilled into the environment. n-Alkanes, biomarkers, low-molecular weight polyaromatic hydrocarbons and sulfur heterocycles compositional changing in the environment have been extensively studied by different researchers and many parameters have been used for oil source identification and monitoring of weathering and biological degradation processes. In this work, we studied the fate of medium-molecular weight polycyclic aromatic disulfur heterocycles (PAS2Hs), up to ca. 900 Da, of artificially weathered Flotta North Sea crude oil by ultra high-resolution Fourier transform ion cyclotron resonance mass spectrometry. It was found that PAS2Hs in studied crude oil having double bond equivalents (DBE) from 5 to 8 with a mass range from ca 316 to 582 Da were less influenced even after six months artificial weathering experiment. However, compounds having DBEs 12, 11 and 10 were depleted after two, four and six months weathering, respectively. In addition, DBE 9 series was more susceptible to weathering than those of DBE 7 and 8.

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1. Introduction

Crude oil or petroleum products spilled into the marine environment undergo changes in physical and chemical properties through different weathering processes such as spreading, dispersion, evaporation, emulsification, dissolution, sedimentation, biodegradation and photochemical oxidation. Due to their potential to cause considerable environmental damage, oil spills in territorial waters resulting from oil tanker accidents or from illegal discharges are of mounting concern. Monitoring the source of these oil spills is obviously essential for pollution control. It is important for government agencies to have reliable methods to determine the source of an oil spill in order to start early corrective and legal action against the polluter since in the case of a tanker discharge the source is not as clear as, for instance, in a drill hole blowout like the BP Deepwater Horizon in 2010. The compositional changes of oil through weathering factors make the unambiguous identification of the source of the release a challenge. A large number of publications deal with this subject and show how weathering parameters affect n-alkanes, biomarkers, low-molecular weight polyaromatic hydrocarbons and sulfur heterocycles (e.g. Bence et al., 1996; Wang et al., 1998; Hegazi et al., 2004; Hegazi and Andersson, 2007) in ways that can be used for oil spill source

identification. However, the extreme complexity of crude oil and the presence of many components of interest in low amounts motivate the scientist to identify novel markers and apply other parameters to face the spilled oil source identification challenge.

A series of disulfur compounds, C_{15}–C_{24} substituted 3,6-dialkyl-1,2-dithianes and two isomers of C_{20} isoprenoid 1,2-dithianes have been identified in the bitumen of a bituminous shale from the Veno del Gesso basin (Italy) and in immature sediments from the Peruvian upwelling region and the Veno del Gesso basin, respectively (Kohnen et al., 1989; Sinninghe Damsté and de Leeuw, 1990). In addition, polycyclic aromatic disulfur heterocycles have been reported to be present in coal and shale oil (Schmid, 1986; Kohnen et al., 1989; Sinninghe Damsté and de Leeuw, 1987, 1990; Sinninghe Damsté et al., 1987, 1989, 1999). C_{20} members of 5,5′-dialkyl-2,2′-bithiophenes and three C_{20} isoprenoid bithiophenes have been also tentatively identified in Rozel Point seep oil (Schmid, 1986) and in Rozel Point oils (Schmid, 1986; Sinninghe Damsté and de Leeuw, 1987; Sinninghe Damsté et al., 1987). Furthermore, the latter compounds were also found in a number of other oils (Sinninghe Damsté et al., 1989). Moreover, small amounts of C_0–C_2 substituted thienothiophenes and C_0–C_1 bithiophenes have been reported to be present in Rasa coal in addition to a series of C_0–C_6 thienobenzo[b]thiophenes, C_0–C_2 thienodibenzothiophenes and C_0–C_2 thienonaphthothiophenes (Sinninghe Damsté et al., 1999). However, the full identification of disulfur compounds is nearly impossible due to the many isomers of the parent system and the increasing number of possible isomers with the increase in the degree of alkylation (Sinninghe Damsté and de Leeuw, 1990).

Gas chromatographic techniques used in the analysis of low-molecular weight, about 300 Da, components in the light petroleum distillates cannot be utilized to obtain analytical information of complex petroleum mixtures of molecular weights much over ca. 300. The successful introduction of ultrahigh resolution Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) in the field of petroleum science provides new insights into the characterization of medium-molecular weight, ~300–1000 Da, components (Miyabayashi et al., 2002; Schaub et al., 2003; Purcell et al., 2006, 2007; Fernandez-Lima et al., 2009; Qian et al., 2001, 2010; Shi et al., 2010). A recent review of petroleum analysis including some FT-ICR MS applications is available (Rodgers and McKenna, 2011).

Although polycyclic aromatic sulfur heterocycles with one sulfur atom have been studied in great detail in recent years (e.g. Müller et al., 2005; Purcell et al., 2007; Shi et al., 2010), often by ultrahigh-resolution MS, polycyclic aromatic disulfur heterocycles have been shown to occur in crudes and petroleum products with similar distributions with respect to molecular weight and double bond equivalents (DBE) as the corresponding compounds with one sulfur atom (Al-Hajji et al., 2008; Shi et al., 2010). In a heavy crude oil, the polycyclic aromatic disulfur heterocycles were one of the major classes of 22 measured classes of aromatic heterocycles with N, O and/or S (Gaspar and Schrader, 2012).

There are no published data that show how these compounds are altered in the environment after spillage of petroleum. On the other hand, polycyclic aromatic monosulfur heterocycles are well established in environmental studies (Andersson et al., 2006). They appear to be more photostable than polycyclic aromatic hydrocarbons and thus are good candidates as markers for oil pollution (Andersson, 1993). Thiophenic components were also resistant to water washing (Manowitz and Jeon, 1992). In addition, the distribution of dibenzothiophenes has been used to distinguish *Exxon Valdez* oil and its weathered residues from background hydrocarbons in benthic sediments (Bence et al., 1996). In an oil pollution situation, it was found that the most abundant aromatic classes of the twelve recorded classes in the weathered oil of the *Hebei Spirit* tanker were polycyclic aromatic monosulfur heterocycles > polycyclic aromatic hydrocarbons > polycyclic aromatic disulfur heterocycles, showing the potential that the sulfur containing aromatic compounds have in this kind of samples (Yim et al., 2012). A recent study showed that polycyclic aromatic monosulfur heterocycles are resistant to weathering and that the ratio of dibenzothiophenes (DBE 9)/naphthenodibenzothiophenes (DBE 10) can be used as a marker for spilled oil source identification in such instances where the light components have been lost due to environmental influences (Hegazi et al., 2012). Hence, one should think about the fate of polycyclic aromatic disulfur heterocycles as a consequence of weathering and compare their stability with that of monosulfur ones.

Therefore, in this work we studied, for the first time, the effect of weathering on the distribution patterns of the medium-molecular weight polycyclic aromatic disulfur heterocycles (PAS2Hs) up to ca 900 Da, by the FT-ICR MS technique, to follow the typical changes within this group of compounds due to weathering and, simultaneously, the degree of resistance to weathering of different PAS2Hs classes.

2. Experimental

2.1. Artificial weathering of Flotta crude oil

A simulated weathering of Flotta crude oil (North Sea, 0.83 wt% sulfur) was carried out by adding 40 g sample to 2 L of distilled water contained in an opened glass basin exposed directly to sunlight placed on the roof of the Institute of Inorganic and Analytical Chemistry, University of Münster, Münster, Germany. Three samples were taken during six months (beginning in July), one sample every two months, to follow the compositional changes of PAS2Hs. To make our experiment as close as possible to the real weathering, the simulated oil spill weathering included parts of summer and winter seasons in order to expose the oil to varying climate conditions such as different temperatures, wind and sunlight.

2.2. Flotta crude and its weathered samples fractionation

A gravity-fed chromatographic column (200 mm × 28 mm) was packed with 20 g of silica gel and 35 g of alumina (both activated separately at 180 °C for 16 h) and loaded with 1 g of sample (Flotta crude or the artificially weathered sample). The saturates were collected using 120 mL of *n*-heptane as eluent, then the aromatics were eluted with 360 mL of a mixture of *n*-heptane and toluene (2:1). Chemicals were obtained from Sigma–Aldrich (Taufkirchen, Germany).

2.3. Derivatization of aromatic fractions

The PAS2Hs in the aromatic fractions were selectively derivatized by methyl iodide to yield pre-formed thiophenium salts required for the electrospray FT-ICR MS analysis (Müller et al., 2005). Briefly, about 100 mg of the aromatic fraction was dissolved in 3 mL of 1,2-dichloroethane. Then 50 µL of methyl iodide and 60 mg of silver tetrafluoroborate were added. The mixture was allowed to react in the dark for 48 h, the precipitate was removed by filtration and the methyl thiophenium salts were obtained through evaporation of the filtrate. Later research has shown that this time can be shortened to 10 min (Nolte et al., 2013).

2.4. FT-ICR MS analysis

Mass spectra were acquired using an APEX III Fourier transform ion cyclotron resonance mass spectrometer (Bruker Daltonics, Bremen, Germany) equipped with a 7 T actively shielded super