

# Characterization of asphaltenes obtained in the presence of minerals by MRMS



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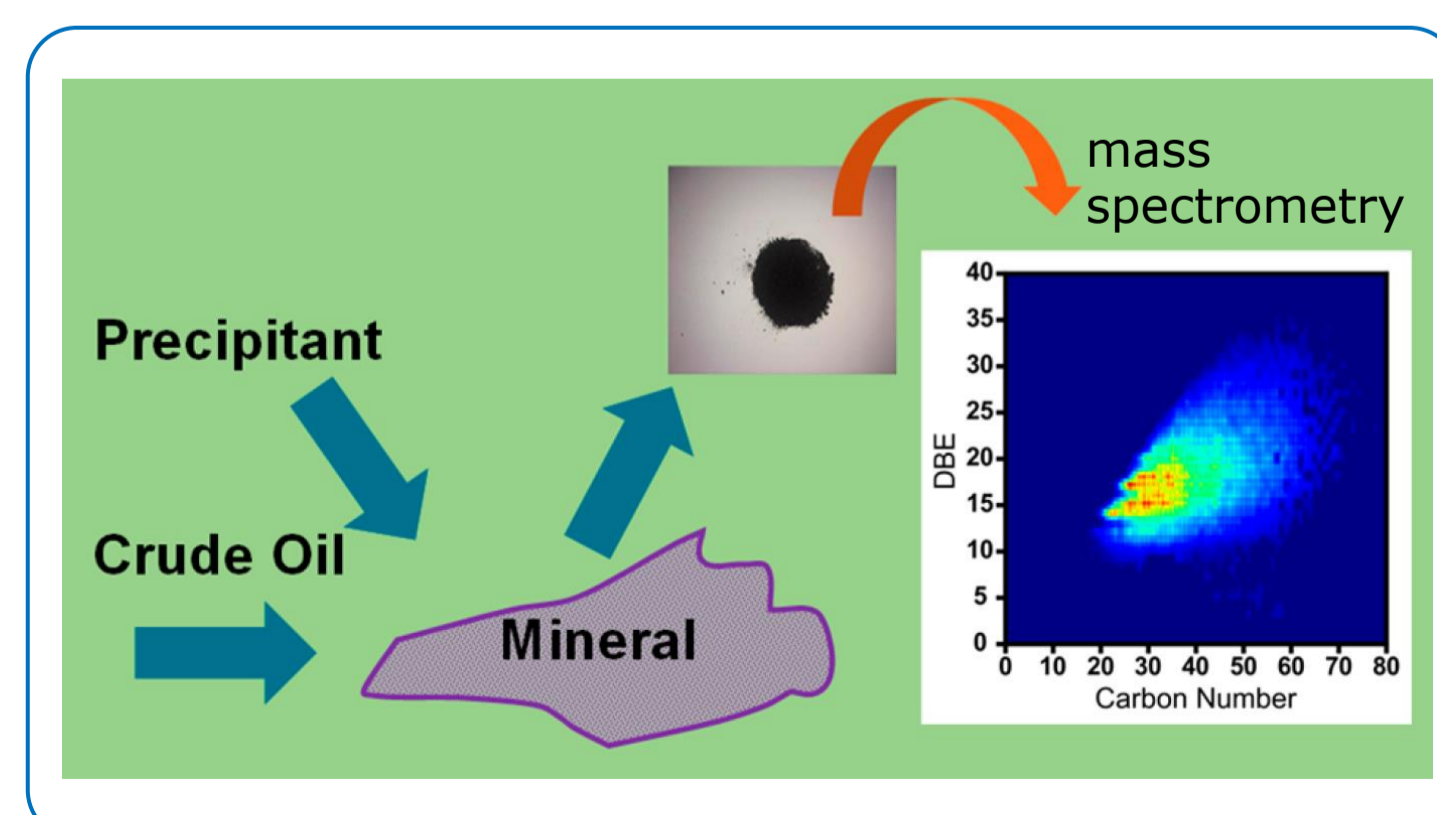
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## Introduction

Studies have shown that characteristics of precipitated asphaltenes depend upon various factors such as the type of solvent, temperature, precipitant/sample ratio etc. Additionally, asphaltene precipitation is also affected by the presence of minerals. The contact of an unstable crude oil with minerals can lead to significant differences in the nature of the precipitated asphaltenes. This study aims to examine differences in chemical composition and behavior that arise from extracting asphaltenes in the presence of different minerals by mass spectrometry (Fig.1). Asphaltenes obtained by precipitation using n-pentane in the presence of Ottawa sand and iron oxide were compared to those obtained in the absence of these minerals.

The precipitated asphaltenes were analyzed using ultra-high resolution MRMS. High-resolution mass spectrometry has shown great success in the characterization of compositional changes in crude oils and fractions as a result of chemical and physical processes. Although quantification is not possible and results are influenced by the ionization technique used, comparisons of the effect of different factors in the same sample produced significant insights in the chemical compositional space.



**Figure 1:** Concept of the experiment to examine differences in chemical composition arising from extracting asphaltenes in the presence of different minerals by mass spectrometry.

## Methods

### Sample preparation

Around 5 g of crude oil was blended with 10 g of mineral (Ottawa sand or iron oxide) and kept at 60 °C for 1 week. Then n-pentane was added (ratio 20:1). After 3 weeks at 25 °C in a shaker, the blend was filtered using a 0.45 µm nominal pore size filter. The precipitated material was extracted from the recovered solids using methylene chloride. The methylene chloride solution was dried under a nitrogen atmosphere to recover the precipitated material. Asphaltenes from the crude oils (C5-asphaltenes) were obtained following a modified ASTM D4055, where n-pentane is added to the crude oil in a ratio of 20:1 at room temperature. Table 1 shows the precipitated amount recovered for each case. Carbon, hydrogen, and nitrogen contents were determined using a Carlo Erba model 1108 analyzer. Solubility profile was evaluated using an in-line filtration technique using a HPLC system.

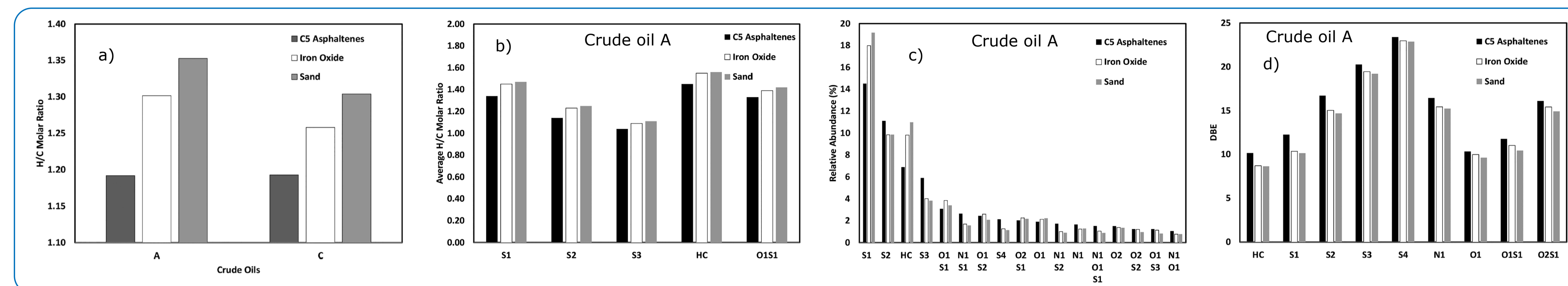
### Mass spectrometric analysis

The fractions were analyzed using a scimaX MRMS system (Bruker Daltonics GmbH & Co. KG, Bremen, Germany) equipped with a 7 T refrigerated actively shielded superconducting magnet. Spectra were acquired in quadrupole detection. Samples were analyzed by atmospheric pressure photoionization (APPI) in positive ion mode. Spectra were acquired in a mass range of m/z 129–2000 using a transient length of 2.5 s. Kilgour apodization was applied, and spectra were processed in absorption mode, resulting in a resolving power of 1,700,000 at m/z 400. Spectra were internally calibrated with the hydrocarbon, S<sub>1</sub>, and S<sub>2</sub> series.

The analysis of the data, including calculation of molecular formulas and relative abundances of compound classes, was performed using PetroOrg 18.0.3 (Florida State University). The RMS mass errors of the calculated molecular formulas were on average below 170 ppb.

**Table 1:** Precipitated Asphaltene Amounts

crude oil	asphaltene obtained using n-pentane (C5-asphaltene) (wt %)	asphaltene obtained in the presence of iron oxide (wt %)	asphaltene obtained in the presence of sand (wt %)
A	9.5	10.2	11.8
C	12.0	12.4	13.6



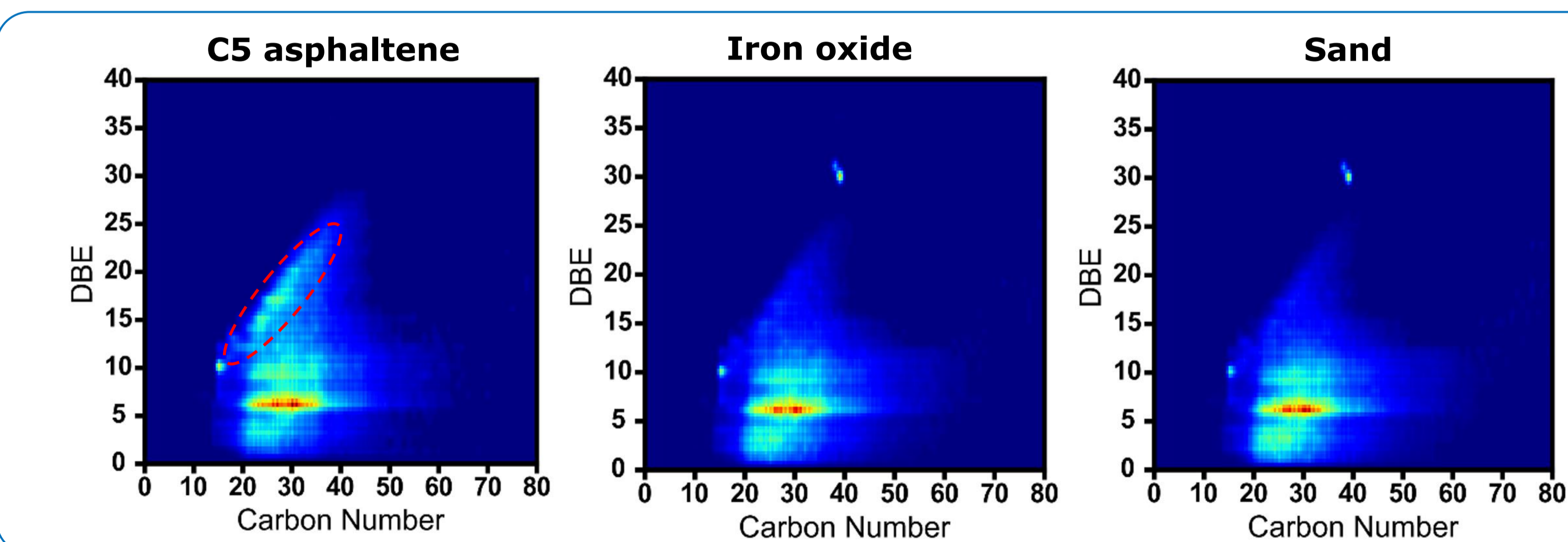
**Figure 2:** (a) H/C molar ratios of the asphaltenes of crude oil A and C by elemental analysis. (b) average H/C molar ratio for major classes by MRMS depending upon precipitating conditions of crude oil A, (c) relative abundances of classes depending upon precipitating conditions of crude oil A, (d) comparison of the average DBE for different classes depending upon precipitating conditions. Plot of average H/C of major classes, plot of relative abundance of classes and plot of average DBE of classes of crude oil C are not shown due to very similar results compared to crude oil A.

## Results

The minerals induced a slightly larger amount of precipitated material than when n-pentane was used alone (Tab. 1). The asphaltene precipitated in the presence of the substrates also had a higher hydrogen/carbon molar ratio. This trend was observed by elemental analysis (Fig. 2a) as well as by mass spectrometry (Fig. 2b). All detected compound classes showed lower average double bond equivalents independent of whether they became more or less abundant in the iron-oxide- or sand-precipitated asphaltene (Fig. 2d). An increase in some of the oxygen-containing species was observed in the

presence of Ottawa sand and iron oxide compared to the asphaltene precipitated in the absence of these minerals (Fig. 2c). The difference between the C5 asphaltene and the asphaltene precipitated in the presence of iron oxide and sand is also shown in figure 3 for class S<sub>1</sub>. Highly aromatic compounds are only observed in the C5 asphaltene and not in the asphaltene in the presence of minerals. Therefore, this study supports the idea that the characteristics of asphaltene deposits are highly dependent upon the conditions and, in this case, the effect of inorganic materials.

Inorganics seem to induce the precipitation of components that are less aromatic than those that precipitate during the standard procedures used in laboratories. Obviously, the presence of the mineral is the main factor that affects the precipitated material nature.



**Figure 3:** DBE vs. C plots of class S<sub>1</sub> of crude oil A depending upon precipitating conditions. The marked area of highly aromatic compounds is only observed in the C5 asphaltene. The high aromatic compounds are not observed in asphaltene in the presence of minerals.

## Conclusions

- Precipitation of asphaltene in the presence of inorganic substrates induce the precipitation of more “asphaltene”.
- Asphaltene in the presence of minerals have a higher H/C ratio than the asphaltene precipitated using the standard method.
- An increase in some of the oxygen-containing species was observed for asphaltene precipitated in the presence of minerals.
- Characteristics of asphaltene deposits are highly dependent upon the conditions and, in this case, the effect of inorganic material.

## Petroleomics