

## Trapped ion mobility ultra-high resolution mass spectrometry for deciphering complex petroleomic mixtures — Insights into compositional space and isomer-Carlos Afonso<sup>1,2</sup>; Christopher Rüger<sup>3</sup>; Julien Maillard<sup>1</sup>; Johann Le Maître<sup>2, 4, 5</sup>; Mark E. Ridgeway<sup>6</sup>; Christopher Thompson<sup>6</sup>; Melvin A. Park<sup>6</sup>; Pierre Giusti<sup>5, 7</sup>

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### Overview

**Purpose:** Exploring the isobaric and isomeric continuum in petroleum fractions

Methods: Trapped ion mobility spectrometry coupled to ultra-high resolution mass spectrometry (FTICR-MS)

**Results:** Molecular formulas between fractions were discriminated by structure via the ion mobility dimension

## Introduction

The molecular description of petroleum fractions is one of the most challenging analytical tasks. Structural and compositional knowledge is a requisite for developing efficient processing strategies and, thus, for optimal ecological/economical utilization of resources. In this study, the combination of Trapped Ion Mobility Spectrometry and FTICR MS is deployed for insights into the compositional space and isomeric diversity petroleum heavy fractions.



### Method

The petroleum samples were solubilized in Toluene and diluted in a Methanol/Toluene mixture. Ion mobility-mass spectrometry analysis was performed with a prototype-grade Bruker 12 T TIMS-FTICR instrument. Briefly, a trapped ion mobility cell replaced the standard inlet funnel, and the reduced mobility was stepwise scanned.

#### -Isobaric and isomeric continuum—

**Figure 1** presents MS and IMS spectra of each petroleum fraction by the TIMS-FTICR instrument. As observed, the crude sample spread over the whole mass and mobility domain (for the mass domain, from m/z 150 to m/z 800 even if tiny ions are not observed on the figure). It can be observed that other fractions spread according to their mass. They have a narrower mobility domain which is in agreement with their restricted isomeric diversity. The ion mobility apex of gas oil species is located at a high elution time, which means that light species are predominant in this fraction. In contrast, vaccum residue which contain heavies species have a mobility domain apex located at a much lower value.



#### -Common areas between fractions-

Fractions are spreading a) along the ion mobility domain according to their \_\_\_\_\_ species shape and size. b) Figure 2 shows the IMS TIC of each fractions separated \_\_\_\_\_ in 2 areas. The first one <sup>C)</sup> allows the comparison between the crude, VGO and \_\_\_\_\_ vaccum residue. The second one allows the \_\_\_\_\_

comparison between the crude, VGO and the gas Oil.



oil, c) Vaccum gas oil and d) Vaccum residue. Common areas are surronded by a square.

Each area was extracted in order to compare them. Figure 3 shows the DBE vs carbon number maps of common species between fractions for each area. With only the mass domain, no differences can be attributed between fraction and common species can not be distinguished. In order to obtain some clues about the differences between these species and why they are located in one each fraction, the isomeric content was probed by looking at the mobility domain. One example is given in the next section.





12 14 16 18 20 22 Time [min] **Figure 4:** EIC IMS of the m/z 482.29681 for crude, VGO and VR

### Conclusion

The structural study of petroleum by ion mobility spectrometry was previously limited by isobaric interferences. TIMS in combination with ultra-high resolution mass spectrometry allowed to explore the isomeric continuum of particular molecular formulas for the different fractions composing crude oil.