

Analysis of saturates in vacuum residue by solid phase extraction and field desorption time-of-flight mass spectrometry



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HIGHLIGHTS

- We combined SPE and FD TOFMS to analyze saturates in vacuum residue.
- Identifications can be made based on the exact masses of the molecular ions.
- Quantification can be made based on the abundance of the molecular ions.
- Carbon number and compound type distribution of saturates can be directly measured.

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ABSTRACT

A new method for analysis of saturates in vacuum residue was developed by solid phase extraction and field desorption time-of-flight mass spectrometry. Vacuum residue was separated into saturates, aromatics, and resins by solid phase extraction. Saturates were ionized by field desorption source which produces primarily unfragmented mass spectra. This method could be applied for carbon number and compound-type distribution analysis of paraffins and 1-ring to 6-ring cycloparaffins in different vacuum residues. Molecular composition of saturates from various vacuum residue were characterized successfully by the developed method.

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Introduction

As the petroleum in world supply is shifting toward heavier and inferior, effective conversion of heavy petroleum feedstock into more valuable products becomes more pressing. The efficiency of the conversion can be significantly improved by adequate compositional information of feedstock and product components. Detailed characterization of petroleum fractions is fundamental for molecule-based petroleum refining [1]. However, the characterization of petroleum composition becomes increasingly difficult as boiling point increases. Much research effort was made to develop new analytical technologies for detailed characterization of heavy oils and petroleum residue. Mass spectrometry plays an important role in the molecular characterization of petroleum products and the development of various soft ionization methods and high-resolution mass spectrometry has promoted petroleum analysis obviously [2–7]. Soft ionization produces mainly molecular ions for petroleum samples and the high-resolution mass

spectrometry allows identification of elemental compositions of molecular ions. In recent years, ultrahigh-resolution Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry brought significant developments in petroleum analysis [8–12], and various soft ionization methods were used to ionize saturated hydrocarbons. Chemical ionization (CI) by proton transfer and charge exchange has been used for ionization of saturated hydrocarbons [3,2], but there were noticeable fragmentation. The desorption electrospray ionization (DESI) in the presence of an electric discharge and the atmospheric pressure chemical ionization using small hydrocarbons as reagents have also been used for the analysis of saturated hydrocarbons with minimal fragmentation [13,14]. However these methods result in complex spectra. Several gas-phase transition-metal ions or organometallic ions have been chosen as the CI or LDI reagent cations for ionization of saturated hydrocarbons [15–18]. Unfortunately, CI methods yield complex mass spectra and LDI methods often discriminate against higher-mass species. Nyadong et al. presented atmospheric pressure laser-induced acoustic desorption chemical ionization (AP/LIAD-CI) with O₂ carrier/reagent gas as a powerful new approach for the analysis of saturated hydrocarbon mixtures [19]. Ruthenium ion

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catalyzed oxidation (RICO) is an effective reaction for transforming saturated hydrocarbons into alcohols and ketones [20]. Zhou et al. developed a novel technique for characterization of saturated hydrocarbons [21]. Linear alkanes were selectively oxidized to ketones by RICO. Branched and cyclic alkanes were oxidized to alcohols and ketones. The ketones were then reduced to alcohols by lithium aluminum hydride (LiAlH_4). The monohydric alcohols (O_1) in the products obtained from the RICO and RICO- LiAlH_4 reduction reactions were characterized using negative-ion electrospray ionization (ESI) Fourier transform ion cyclotron resonance mass spectrometry (FTICR MS) for identification of iso-paraffins, acyclic paraffins and cyclic paraffins.

Nevertheless, FI/FD are preferred techniques that can “soft” ionize a wide range of petroleum components, including paraffins, cycloparaffins, aromatics, sulfides, thiophenes, etc. Particularly, FD can desorb the nonvolatile petroleum “bottoms” into the gas phase for mass analysis [22]. Soft ionization is critical to carbon number distribution for petroleum homologues because soft ionization produces mainly molecular ions for petroleum products and the high-resolution mass spectrometry allows identification of elemental compositions of molecular ions. However, ion yield of FI/FD is considerably lower than that of EI or CI and has typically been coupled with low-resolution mass analyzers to generate a molecular weight distribution [23–25]. Schaub et al. have interfaced a field ionization/field desorption source to a home-built 9.4-T FT-ICR mass spectrometer and shown the utility of this configuration by generating high-resolution positive-ion mass spectra of C_{60} and a middle distillate. The results demonstrated the potential of FD combined with high-resolution FT-ICR mass analysis of nonpolar molecules [26]. But no further research development has been reported until now. On the other hand, FI has been coupled with GC high-resolution time-of-flight MS for detailed speciation of hydrocarbons with a carbon number range of C_6 – C_{44} [27]. However, vacuum residue cannot be volatilized thermally and their composition is also too complex to be characterized by conventional high-resolution MS. In order to gain access to nonpolar species in vacuum residue, we combined solid phase extraction and field desorption time-of-flight mass spectrometry to analyze saturates in vacuum residue. Saturates were separated from vacuum residue by solid phase extraction and analyzed by field desorption time-of-flight (TOF) mass spectrometry. Compared to high performance liquid chromatography [28] and open column chromatography [29], solid phase extraction is more effective for high-boiling petroleum because of shorter separation time and higher mass recovery. Nonvolatile, and high molecular weight saturates can be ionized by FD directly, yielding clean mass spectra of intact molecular ions. The compound types and carbon number distributions of saturates in vacuum residue can be obtained by this unique combination.

Experimental

Chemicals

ULTRAMARK 1960A standard was purchased from Aldrich. Silica gel (particle size 75–150 μm) was purchased from Qingdao Haiyang Chemical Co., Ltd., Neutral alumina (particle size 75–150 μm) was purchased from Sinopharm Chemical Reagent Co., Ltd., vacuum residues (VR) were from Sinopec.

Residue deasphalting procedure

Deasphalting was performed according to the following procedure: about 2 g of VR was mixed with 60 mL of n-heptane. The solution was refluxed for 0.5 h and equilibrated overnight, then fil-

tered through a glass fiber and the precipitate was washed three times by hot n-heptanes and the filtrate was collected in a conical flask. The filter paper with precipitate was put into the extractor, then the conical flask containing filtrate was connected to the extractor and condenser, the system was heated and refluxed for 1 h in order to extract the component which was mixing with the asphaltene. In the end, the solution in the conical flask becomes deasphalted vacuum residue solution which was to be concentrated for the following solid phase extraction.

Solid phase extraction procedure

Deasphalted vacuum residue was separated as follows: two 6 mL solid phase extraction columns are packed with silica gel and neutral alumina respectively and connected together. About 0.05 g of deasphalted VR was dissolved in hot n-hexane. The solution was dripped into the column and eluted by 10 mL of n-hexane, 12 mL of methylene chloride and 9 mL of a mixture of methylene chloride and ethanol in a 1:1 ratio in turn. The sample then was separated into saturates, aromatics and resins. The whole procedure took only a few minutes. The saturate eluent was used for mass analysis. NMR was employed to determine the separation efficiency of this method. Fig. 1 shows ^1H NMR spectrum of the saturate eluent of Take VR. There are no aromatic proton signals in 6–9 ppm of the in the aromatic region which proved that the saturate eluent contains no aromatic compounds.

Field desorption mass spectrometry

FD is adopted to ionize nonpolar molecules in vacuum residue. The FD emitter consists of a 10 μm tungsten wire onto which carbon microneedles have been grown. The emitter is about 1.5 mm away from a pair of extraction rods held at high potential (12 kV), producing very high electric fields ($\sim 10^{-7}$ – 10^{-8} V/cm) around the tips of the carbon dendrites. Under the influence of these fields, an electron can be removed from the molecule via quantum tunneling effects, generating radical molecular ions with minimal fragmentation. About 0.1 μL of the sample solution was

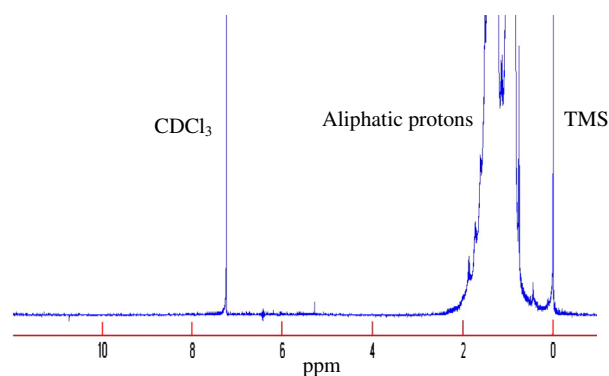


Fig. 1. ^1H NMR spectrum of the saturate eluent in CDCl_3 .

Table 1
Z value of saturates in vacuum residue.

Z value	Compound type
2	Paraffins
0	1-ring cycloparaffins
-2	2-ring cycloparaffins
-4	3-ring cycloparaffins
-6	4-ring cycloparaffins
-8	5-ring cycloparaffins
-10	6-ring cycloparaffins

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