International Journal of Mass Spectrometry xxx (2014) xxx–xxx

Contents lists available at ScienceDirect

International Journal of Mass Spectrometry

journal homepage: www.elsevier.com/locate/ijms

Application of atmospheric pressure ionization techniques and tandem mass spectrometry for the characterization of petroleum components

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ARTICLE INFO

Article history:
Received 24 April 2014
Received in revised form 7 August 2014
Accepted 8 August 2014
Available online xxx

Keywords:
Atmospheric solid analysis probe
Atmospheric pressure gas chromatography
Tandem mass spectrometry
Petroleum biomarkers

ABSTRACT

Atmospheric solid analysis probe (ASAP) and atmospheric pressure gas chromatography (APGC) are relatively new ionization techniques. In this study, we applied these two techniques to characterize complex petroleum fraction samples under atmospheric pressure. The ion formation of petroleum standards (paraffins, isoparaffins, naphthenes and aromatic hydrocarbons) in ASAP and APGC was investigated. Two primary ionization pathways were observed, nitrogen fixation (addition) and charge transfer. Paraffins and isoparaffins standards are primarily ionized by nitrogen addition. Cyclic paraffins and aromatic compounds are primarily ionized by charge transfer. ASAP was applied to analyze a saturate fraction of petroleum vacuum resid under atmospheric pressure. An expanded composition coverage was demonstrated. APGC coupled with tandem mass spectrometry was demonstrated to characterize biomarkers in complex petroleum samples with high specificity, providing similar information as compared to the traditional gas chromatography electron ionization (GC–EI) under vacuum.

1. Introduction

Petroleum crude oil is one of the most complex natural organic mixtures containing thousands of different molecules [1–3]. Saturated and aromatic hydrocarbons are the major components in non-degraded petroleum crude oils and identifying each of these molecules is challenging. Oils are frequently distilled into boiling point cuts or chromatographically separated into chemical group-type fractions that are then subjected to detailed characterization [4–6]. Petroleum biomarkers are special groups of molecules in crude oil that retain the carbon structure of their biochemical precursors. These chemical fossils are widely used to determine the biological input and depositional environment of an oil's source rocks, its geothermal history, its migration pathways, and the extent of alteration processes (e.g., biodegradation) that can occur in the reservoir [7,8]. Such information is critical for successful exploration and resource assessment. Common biomarkers include isoprenoids, steranes, and triterpanes that are conventionally analyzed by gas chromatography (GC) and tandem mass spectrometry [9,10].

High-resolution mass spectrometry (MS) has become one of the most powerful techniques for characterizing petroleum fractions in the last decade [11,12]. Previously, little was known about the composition of the fraction of oil comprised of high molecular weight hydrocarbons and heteroatomic species termed "polars" and "asphaltenes". The structural information of these species has now been investigated using collision induced dissociation (CID) coupled to fourier transform ion cyclotron resonance (FTICR) mass spectrometry [13,14]. Through such studies, the molecular complexity of petroleum can be shown to be a continuum of species in terms of boiling point, molecular weight and unsaturation [6,15,16].

Oil and oil fractions may be ionized by traditional electron ionization (EI), chemical ionization (CI) and field ionization/field desorption (FI/FD) under vacuum. However, ionization techniques such as electrospray ionization (ESI), atmospheric pressure chemical ionization (APCI), desorption electrospray ionization (DESI) [17,18], paper spray [19], laser-induced acoustic desorption (LIAD) [20–23], DART [24], LTP [25] under atmospheric pressure are desirable for their potential easy and quick analysis of hydrocarbons.

Here, we report on the characterization of petroleum components using two relatively new techniques: atmospheric solid analysis probe (ASAP) and atmospheric pressure gas chromatography (APGC). In ASAP, samples are applied on a glass capillary and heated. The vaporized sample is ionized by corona discharge under atmospheric pressure. ASAP has been applied to rapidly characterize drugs, additives, polymers pyrolysis residues, pesticides, and other commercial products [26–30]. In this study, the ion formation of paraffins, naphthenes and aromatic hydrocarbons

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http://dx.doi.org/10.1016/j.ijms.2014.08.019
1387-3806/

under ASAP and APGC conditions is discussed. One of the major advantages of using ASAP for petroleum characterization is that one can ramp up vaporization temperature gradually during ionization, allowing "on-line boiling point fractionation" of the sample. Consequently, the procedure greatly expands the dynamic range of the MS analysis and obtains a more complete composition of the petroleum sample. APGC is a relatively new technique that combines GC with APCI [31]. Similar to ASAP, the APGC ionization source is enriched with nitrogen and samples are introduced as hot vapor streams and ionized by corona discharge between the mass spectrometer inlet and the GC capillary. Here we demonstrate that APGC ionization of petroleum biomarkers generates molecule ions $M^{+\bullet}$ that can be subsequently fragmented in Q-TOF MS configurations for biomarker related applications. The traditional petroleum biomarker analysis is often based on tandem MS (e.g., multiple reaction monitoring) with standard electron ionization. APGC Q-TOF generates very similar biomarker fingerprints as compared to the traditional GC–EI tandem MS under vacuum, while providing benefits of operation and maintenance simplicity.

2. Experimental

2.1. Chemicals

Individual saturate, olefinic, aromatic and naphthenic compounds and alkylbenzene standards were purchased from Sigma–Aldrich®. The alkane standard mixture was purchased from Agilent Technologies® and it was diluted 10 times in methylene chloride for APGC analysis. The saturate fraction of petroleum resid was obtained by liquid chromatography separation of the resid at the ExxonMobil Laboratory using methods described previously [32,33]. The purity of saturate fractions was examined by both proton (^{1}H) and ^{13}C nuclear magnetic resonance (NMR) to ensure the lack of aromatic and olefinic moieties. The typical detection limits are about ~0.1 mol% for aromatic and olefinic protons and 1 mol% for aromatic/olefinic carbons. The saturate fraction used for the biomarker study was obtained from open-column separation on silica gel eluting with hexane.

2.2. ASAP on Synapt® G2S-MS

The standards were prepared at a concentration of 0.01–0.1% in CH_2Cl_2 with 0.01% coronene as the internal standard (IS). For petroleum fractions, sample solutions of 1% were prepared in methylene chloride for ASAP analysis. A glass capillary tip was dipped in the sample solution and allowed to dry before analysis. The concentration of the sample and the internal standard was controlled to keep the signal level less than 1×10^5 to avoid signal saturation for accurate mass measurements. The Synapt® G2S HDMS mass spectrometer (Waters Corp.®) instrument was operated at the high-resolution mode. A corona voltage of 3 kV, sampling cone voltage of 40 V, source offset of 21 V, source temperature of 120 °C, cone gas flow of 100 L/h, desolvation gas (N_2) of 600 L/h was used. The probe temperature was ramped from 50 to 650 °C at 150 °C/min. The spectra of the standards shown were collected at 200–350 °C probe temperature. The instrument was calibrated using 500 μM sodium formate in the positive ion mode electrospray ionization (ESI) to ensure mass accuracy. The configuration and positioning of the ASAP probe can be found in Fig. 1.

2.3. APGC and tandem MS on Synapt® G2S

An Agilent® 7890A GC was equipped with a HT ZB-5 column (30 m long, 0.25 μm film thickness, 0.25 mm ID) for the separation.

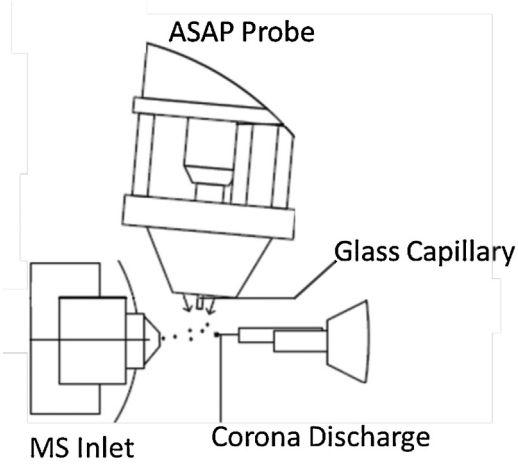

Fig. 1. Configuration of the ASAP probe relative to the corona discharge pin and the inlet of the mass spectrometer. The glass capillary was inserted into the ASAP probe and was heated during the analysis. The heated nitrogen gas helps desorption of the sample from the glass surface while heating.

The oven was ramped from 40 to 350 °C for the alkanes at 25 °C/min with a hold of 5 min. A split injection was used with a 50:1 ratio combined with a GC flow of 1.5 mL/min. 1 μL of sample solution was split between the mass spectrometer and FID detector in a 2:1 ratio. A current of 1 μA was applied to the corona discharge needle. The N_2 makeup gas was 350 mL/min, cone gas was 150 L/h. Source temperature was 150 °C, sampling cone was 20 V, and the source offset was 80 V. The instrument was calibrated by Heptacosa (perfluorotributylamine mixture) to ensure mass accuracy. The coupling of the APGC to MS is illustrated in Fig. 2.

3. Results and discussion

3.1. ASAP analysis of paraffin, naphthene, and aromatic standards

In order to understand how ASAP ionizes petroleum samples, we first tested standard chemicals including saturates, olefins, aromatic and naphthenic molecules that are the major components of oils and processed fluids. We observed that all standard chemicals could be easily ionized using ASAP at a temperature of 350 °C or less, depending on the volatility. Aromatics and olefins formed radical cations $M^{+\bullet}$ as expected according the known ionization mechanism in ASAP [30]. It was observed that protonated species were also formed for the aromatics and olefins.

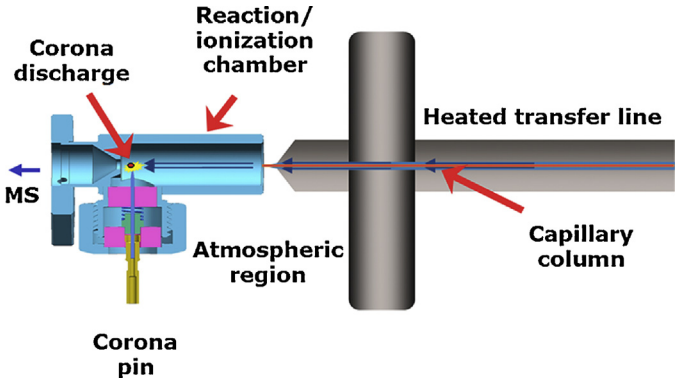

Fig. 2. GC coupled to MS. The makeup gas (N_2) is delivered to meet GC eluent at the transfer line tip and the sample is ionized at the corona discharge tip under ambient pressure before getting to the mass spectrometer. Reprinted with permission from Energy & Fuels (2013) 27, 167–171. Copyright 2013 American Chemical Society.

Please cite this article in press as: C. Wu, et al., Application of atmospheric pressure ionization techniques and tandem mass spectrometry for the characterization of petroleum components, Int. J. Mass Spectrom. (2014), http://dx.doi.org/10.1016/j.ijms.2014.08.019