

NOVEL CHARACTERIZATION OF PETROLEUM RESIDS BY LIQUID CHROMATOGRAPHY COUPLED WITH MASS SPECTROMETRY

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The characterization of petroleum resids and asphaltenes has remained a tremendous challenge to mass spectrometry. These fractions contain thousands of heavy molecules that are difficult to separate into individual components or less complex subfractions by distillation or solvent elution due to high intermolecular van der Waals force and dipole-dipole interactions. The molecules usually lack volatility to provide a stable stream of vapor for mass spectrometric analysis. The number of isomers for a given molecular formula can be tremendous, that makes the differentiation of isomers, particularly stereoisomers, impractical and meaningless. High resolution accurate mass measurement is also very difficult because of the large number of possible elemental combinations that would require very high resolving power and mass measurement stability of the mass spectrometer. Mass spectrometric analysis of these fractions are therefore generally for the determination of molecular weight distribution. However, if high mass resolving power by mass spectrometry or molecular class separation by chromatography is achievable, then compound type and carbon number distributions would be useful information for the studies of upgrading these fractions. Due to multitude of molecules present, it would be desirable to ionize these molecule intact without fragmentation to facilitate mass spectral analysis.

Among low energy ionization techniques, field ionization (FI) and field desorption (FD) are commonly used (see Figure 1). In both FI and FD techniques, the molecules are ionized by a fine emitter with a high voltage (ca. 10-13 kilovolts) between the emitter and a counter-electrode at a short distance that creates a high electric field. The only difference between these two techniques is sample introduction. In FI, the sample is volatilized under mass spectrometric vacuum to produce vapor in the vicinity of the emitter for ionization. However, the temperature required for volatilizing resids and asphaltenes can be too high to cause thermal decomposition of the molecules. To avoid thermal decomposition, FD is used in which the sample is deposited onto a fine emitter which is inserted into mass spectrometer via a vacuum lock. When a high electric field is applied on the emitter, molecules are ionized by quantum tunneling to produce low internal energy molecular ions. To provide fluidity of the sample some emitter current is also applied during ionization. Once ions are formed, they are repelled off the emitter by Coulombic repulsion. In FD, therefore, the sample is ionized without volatilization.

The FD technique, however, suffers from two major drawbacks: weak signal and cluster formation. Since only limited surface area is available on the emitter for field ionization and field desorption, the emitter is usually activated in indene, acetonitrile or acetone vapor to grow microneedles (whiskers) to increase high-field sites or area. Nonetheless, the number of molecules accessible to the high-field sites are still limited. In addition, ionization efficiency by quantum tunneling is very low, compared to other ionization techniques, such as electron-impact ionization and chemical ionization. As a result, low ion yield and weak signal are obtained. Due to transient nature of the signal, medium and high resolution mass measurement is difficult to perform. With a somewhat larger sample load, several layers of molecules are present between the surfaces of the emitter and the sample matrix. Ions formed on the surface of the emitter will have to penetrate through these layers before they are expelled out of the source region. Some of them are neutralized, charge transferred, or undergone ion-molecule reactions. Figure 2 shows a 875-1026°F distillate from a Californian crude oil with an average molecular weight near 500. The presence of dimers with molecular weights between 700 and 1300 is also apparent.

We have resolved the difficulties encountered in FD by using thermospray (TSP) ionization, a technique used in liquid chromatography/mass spectrometry (LC/MS). In TSP,

sample is dissolved in a mobile phase that is sprayed out of a heated nebulizer. A heavy duty filament or a discharge electrode is placed near the nebulizer as an ionization means. Excess amounts of solvent (mobile phase) molecules are preferentially ionized by electron bombardment of a heavy duty filament or discharge ionization of a discharge electrode. These solvent ions then ionize sample molecules via protonation, hydride extraction, or charge exchange. Since the sample molecules are not directly heated and ionized by high energy electron beams, intact protonated, hydride-abstracted, or molecular ions are formed in TSP.

The sample molecules are well-separated by an excess amount of solvent so that ion-molecule reaction between sample ions and molecules can be avoided. Thus, cluster formation encountered in FD is eliminated. The same distillate as in the FD experiment mentioned above was dissolved in a mobile phase of 75% methylene chloride and 25% hexane. A discharge electrode is used as an external source for TSP ionization, yielding a TSP spectrum as shown in Figure 3. The most noticeable feature of the TSP spectrum is the absence of dimer cluster in the 700-1300 mass range. The distribution of the ions in TSP is quite similar to that in FD except the absence of peaks corresponding to saturated hydrocarbons. Not being able to ionize saturated hydrocarbons is a major disadvantage of TSP because all of the suitable solvents for TSP experiments have similar or higher proton affinity than saturated hydrocarbons. Hence, saturated hydrocarbons have to be separated from aromatic hydrocarbons and analyzed separately. However, there are many other advantages of using TSP for petroleum resids and asphaltenes to compensate for such limitation.

One advantage of TSP is its stable ion current. Figure 4 compares the TSP and FD spectra of a 1120-1305°F DISTACT distillate of a Middle East crude oil. Both show similar molecular distribution in the mass range of 300-1400 with an average molecular weight of about 800. A much stronger ion current was obtained in TSP, compared to a weak current in FD. With high intensity and stability of ion current, slower scans for medium/high resolution mass measurement can be performed in TSP. Another advantage of TSP is its ability of on-line coupling with liquid chromatography (1). Liquid chromatography (LC) separates aromatic hydrocarbons by increasing polarity into monoaromatic, diaromatic, triaromatic, tetraaromatic, and polar elution regions. It greatly facilitates the differentiation of overlapping aromatic and naphthenoaromatic hydrocarbons (2). Figure 5 shows monoaromatic, diaromatic, triaromatic, and tetraaromatic elution regions of the above DISTACT distillate separated by LC. It can be seen that the average molecular weight gradually decreases with increasing aromaticity. The average molecular weights are about 850 for monoaromatics, 820 for diaromatics, 790 for triaromatics, and 730 for tetraaromatics, respectively. That is, in a given distillation range LC elution regions containing compounds with higher aromaticity have lower average molecular weights.

With increasing resolving power, it is also possible to obtain accurate mass measurement for elemental composition of the compounds (3). Figure 6 shows the compound type distributions obtained from medium resolution (ca. 5000 resolving power) measurement of the monoaromatic, diaromatic, triaromatic, and tetraaromatic elution regions shown in Figure 5. The distributions are shown as relative abundance as a function of the z-number of equivalent hydrocarbon series. For this specific sample, indenenes or dinaphthenobenzenes were found to be the most abundant series in monoaromatics, benzothiophenes in diaromatics, dibenzothiophenes in triaromatics, and pyrene in tetraaromatics. The use of a mass spectrometer with higher resolving power, such as Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR), would be required for further confirmation of these compound series at high masses (4).

We have demonstrated that petroleum resids and asphaltenes can be characterized in fair details by using thermospray ionization technique. This technique can also be used in on-line liquid chromatography-mass spectrometry to further define the type of molecules present in these heavy high boiling petroleum fractions. To overcome intermolecular interaction between resid and asphaltene molecules for aggregate formation, dispersing the molecules in a solvent medium appears to be a reasonable approach for obtaining molecular information of these fractions. It would be worthwhile to study the behavior of these molecules in other type of LC/MS, such as atmospheric pressure chemical ionization (APCI) and electrospray, for the characterization of petroleum resids and asphaltenes.

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Figure 1 Simplified schematic diagram of a field ionization/field desorption ion source.

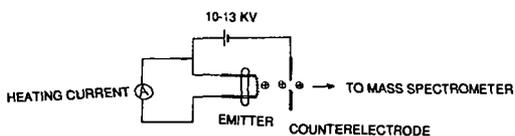


Figure 2 Field desorption mass spectrum of a 875-1026°F distillate from a Californian crude oil, showing the presence of dimers formed during ionization.

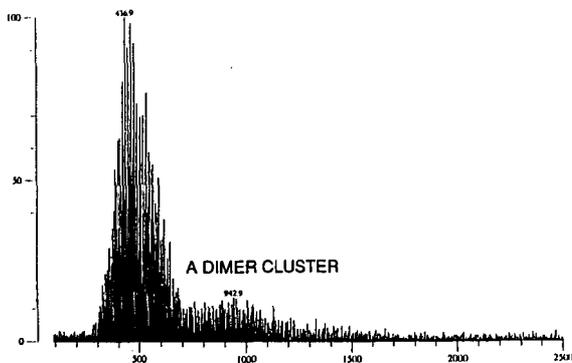


Figure 3 Thermospray ionization mass spectrum of a 875-1026°F distillate from a Californian crude oil, no dimers formed.

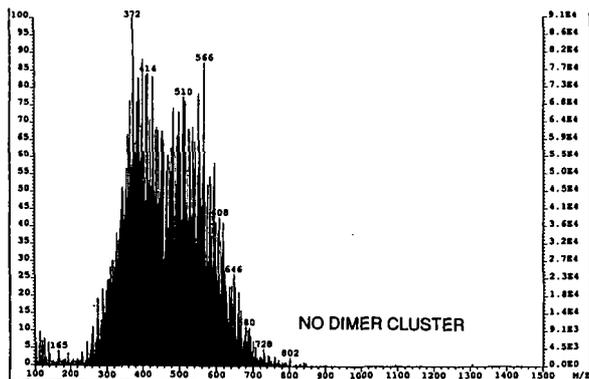


Figure 4 Similar molecular weight distributions are obtained by field desorption and thermospray of a 1120-1305°F DISTACT fraction of a Middle East crude oil.

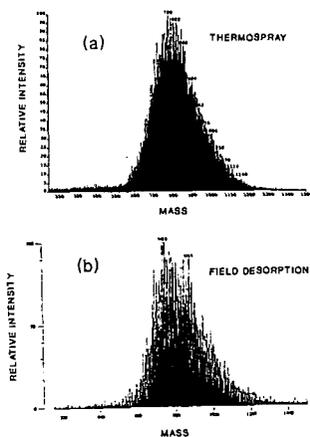


Figure 5 Molecular distributions of a 1120-1305°F DISTACT fraction of a Middle East crude oil in the monoaromatic, diaromatic, triaromatic and tetraaromatic elution regions of normal phase liquid chromatography.

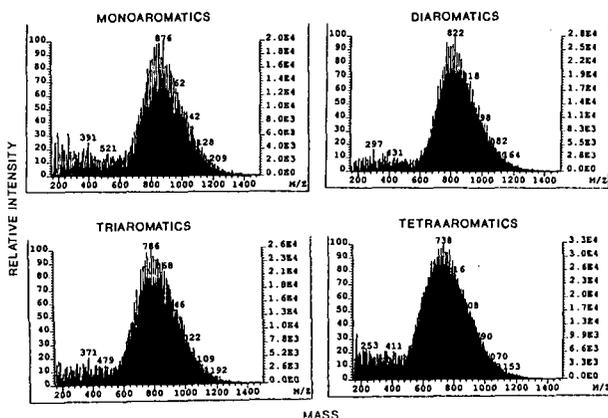


Figure 6 Compound type distributions of a 1120-1305°F DISTACT fraction of a Middle East crude oil in the monoaromatic, diaromatic and tetraaromatic elution regions of normal phase liquid chromatography.

