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# On-Line Liquid Chromatography/Mass Spectrometry for Heavy Hydrocarbon Characterization<sup>†</sup>

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There are many advantages of using on-line liquid chromatography/mass spectrometry (LC/MS) to characterize complex mixtures. By incorporating low-voltage electron-impact ionization/high-resolution MS with moving belt LC/MS, differentiation can be made between naphthenoaromatics and alkylaromatics and between aromatic hydrocarbons and "difficult-to-resolve" thiophenes. Alternative on-line LC/MS techniques for heavy hydrocarbon characterization are also discussed.

## Introduction

Molecular level characterization of immensely complex fossil fuel fractions is essential to the understanding of the chemistry involved in processing fossil fuel streams and to make effective use of the products. However, in-depth characterization remains a challenge, especially for heavy hydrocarbon fractions. To analyze these complex mixtures, coupling of chromatography and mass spectrometry (MS) becomes highly desirable. Chromatography separates components according to their boiling points (GC) or polarity (LC) and therefore simplifies the MS analysis, while MS provides detection of compounds over a broad range of functionality with high sensitivity, specificity, and selectivity. MS also provides valuable information on the molecular weight and structure of the molecules. The development of combined gas chromatography/mass spectrometry (GC/MS) since the late 1960s has greatly facilitated the analysis of volatile fuel streams and products. Combining liquid chromatography with mass spectrometry (LC/MS) is expected to be of similar utility but will extend mixture analysis to high boiling, polar, and thermally labile compounds that are not amenable to GC/MS. In addition LC/MS adds another dimension to GC/MS by separating compounds according to their polarity or compound types rather than boiling points. As a result, LC/MS is the method of choice when the distribution of compound types, rather than individual isomers, is of interest.

In this paper, we describe work which combines the moving belt LC/MS interface and low-voltage EI/MS for the purpose of differentiating between aromatic and naphthenoaromatic compounds and between aromatic hydrocarbons and thiophenes.

## Experimental Section

A petroleum distillate with a high sulfur content (C, 85.32; H, 10.37; S, 3.72; N, 0.34; O, 0.25 by difference; H/C, 1.45; 37% aromatic carbons by <sup>13</sup>C NMR) boiling between 650 and 950 °F (340 and 510 °C) was selected for the LC/MS experiment. The sample was separated on a Varian 5560 ternary HPLC. Ring size separation was carried out with a 4.6 × 250 mm column packed with 5-μm dinitroanilinopropyl (DNAP) silica (ES Industries), using a gradient of hexane, methylene chloride, and isopropyl

alcohol modeled on that suggested by Grizzle and Thomson.<sup>1</sup> The sample was separated into saturates, 1-ring aromatic, 2-ring aromatic, 3-ring aromatic, 4-ring aromatic, and "polar" LC elution regions. The LC effluents were continuously desorbed on the moving belt by a spray depositor similar to that described by Hayes et al.<sup>2</sup> The relatively nonvolatile species were transported to the mass spectrometer through differentially pumped vacuum seals and thermally desorbed directly into the ion source. A low-voltage electron beam was used to minimize fragmentation of the components. In addition, high-resolution MS was used to measure the accurate masses of the molecular ions.<sup>3</sup> Since LC separates compounds based on molecular type, the requirement for resolving overlapping series of the same nominal mass is greatly reduced. As a result, the resolution of the VG-70 VSE double-focusing mass spectrometer used in our moving belt LC/MS experiment was set to 7000 which allowed for greater sensitivity and minimized any ambiguity that may arise due to overlapping peaks.

## Results and Discussion

LC/MS allows us to address important issues in hydrocarbon characterization such as (1) the differentiation of alkylaromatics from naphthenoaromatics, (2) the distinction between aromatic hydrocarbons and thiophenes, (3) the analysis of basic and neutral polars, and (4) the correlation of molecular polarity with elution characteristics in different chromatographic fractions.<sup>4</sup> In this paper, we will focus on the first two issues which deal with the ambiguities of structural assignment by MS. One example of such an ambiguity is the differentiation of isomers with identical molecular formulas but different number of aromatic rings. Compounds 1 and 2 have the same molecular formula, C<sub>28</sub>H<sub>44</sub>, with molecular weight 380.344. In a complex mixture they cannot be differentiated by MS alone but can be distinguished by LC/MS because they are present in the 1-ring aromatic and the 2-ring aromatic fractions, respectively. Another example is the distinction of compounds which require very high mass spectrometric resolution to differentiate. An alkyl-naphthalene and an alkylbenzothiophene such as 2 and 3 require only 4200 mass resolving power to differentiate, but the separation of 3 from 4 requires a mass resolution

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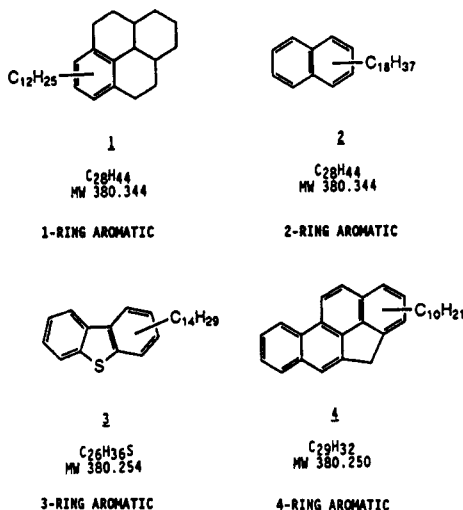
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over 110 000, thus making this differentiation nearly impossible using MS alone. The unique capability of LC/



MS is exhibited when one realizes that 3 and 4 can only be distinguished because they are present in different LC fractions. Thus, the combination of LC with MS reduces the resolution requirement for the overlapping mass series and makes structural assignment of these series possible.

Various LC/MS experiments, both on-line and off-line, have been carried out to characterize distillate fractions of petroleum and synthetic fuels.<sup>5-14</sup> The preparative LC fractions collected for off-line analysis can be subjected to various analytical MS techniques including electron-impact ionization (EI), chemical ionization (CI), field ionization/field desorption (FI/FD), and fast-atom bombardment (FAB) MS.<sup>11-15</sup> However, the off-line approach is time consuming and labor intensive and requires a relatively large sample size. On the other hand, an on-line technique offers several advantages compared to its off-line counterpart. On-line operation avoids the necessity of deciding when to begin and end the collection of each fraction and eliminates any evaporation steps. Since a smaller sample size is used with on-line analysis, the chromatographic resolution is improved. In addition, because the components eluting off the LC column are continuously monitored, quantification of compound series present within and between different chromatographic peaks can be performed by using selected ion chromatograms.

There are basic differences in the operational requirements of LC and MS. LC operates at elevated pressures

and relies on condensed-phase interactions of the solute between the liquid mobile phase and the solid stationary phase to achieve separation. MS, on the other hand, operates at reduced pressures and requires the ion to be mass analyzed in the vapor phase. As a result, an integral part of the LC/MS system is the interface between the two instruments. The interface must vaporize the LC solvent and either use the vaporized solvent as a CI reagent gas or remove the solvent so EI spectra can be obtained. Desirable characteristics of an LC/MS interface include high analyte transmission into the MS and also, in some instances, high analyte enrichment by exclusion of the LC solvents from the mass spectrometer ion source. It is also desirable to have the ability to perform a wide variety of ionization techniques and to efficiently and/or selectively ionize the analyte of interest. The moving belt interface is a relatively well-established method for LC/MS coupling. It possesses many of the desirable attributes of a LC/MS interface that were outlined above. The moving-belt interface is classified as a transport LC/MS interface because the LC is not directly coupled to the mass spectrometer but relies on a mechanical device to transfer the analyte to the MS ion source. The advantage of transport systems arises from the efficient removal of solvent from the total LC effluent. Solvent removal in the moving belt system is partially accomplished by spray deposition and more completely by passing the belt through a series of differentially pumped vacuum chambers. This allows conventional ionization techniques to be utilized which may include high (70 eV) and low (12 eV) voltage EI as well as CI using a wide variety of reagent gases. The major limitation of a moving belt system is its inability to analyze highly nonvolatile species and its mechanical complexity. The mass range limitation arises because in most instances the solute is thermally desorbed from the belt surface and the heavy nonvolatile molecules either do not vaporize or undergo thermal decomposition. This does not appear to be a significant disadvantage in the current work but could play a more critical role when higher boiling range fractions are to be analyzed.

A typical spectrum of our moving belt LC/MS experiment is shown in Figure 1 taken at the peak of the 2-ring aromatic portion of the chromatogram. Hundreds or even thousands of components are present in each scan across an LC peak. A major task of interpreting LC/MS data is therefore the reduction of mass spectral data into a simplified format without losing much of the information obtained. The major compound series in this fraction was determined by high-resolution mass measurement to have a general formula  $C_nH_{2n-10}S$  ( $Z = -10S$  series) corresponding to benzothiophenes, a 2-ring aromatic compound type. In this series, as many as 45 side-chain carbons are present, as shown in Figure 1.

Accurate mass measurement by high-resolution MS provides elemental composition of the molecules but not their structures. Figure 2 illustrates the distribution of the molecular ions with a nominal mass of 380. The  $Z = -12$  and  $-16S$  compounds are the predominant series at this nominal mass in the 1-ring and 2-ring aromatic regions. For each series, the compounds in the two LC elution regions have different ring sizes with different aromaticity. The  $Z = -12$  compounds in the 2-ring aromatic region are fully aromatic; thus, this series does not appear in the 3-ring aromatic region. By the same token, the compounds with an accurate mass of 380.25 can be either  $Z = -16S$  dibenzothiophenes or  $Z = -26$  aromatic hydrocarbons. Since the  $Z = -16S$  dibenzothiophenes in the 3-ring aromatic region are fully aromatic, the compounds in the

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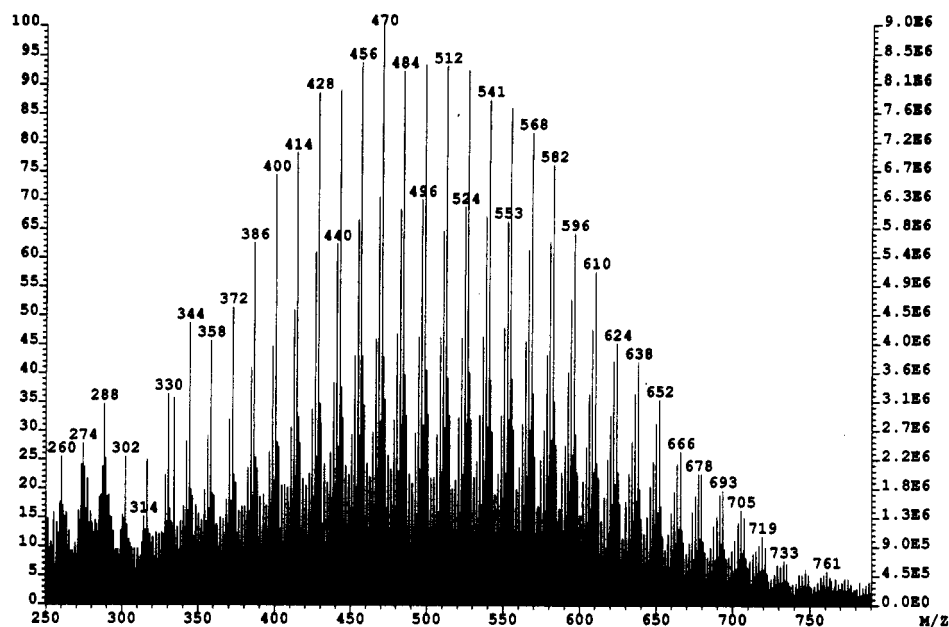


Figure 1. Low-voltage electron-impact ionization mass spectrum for 2-ring aromatic region.

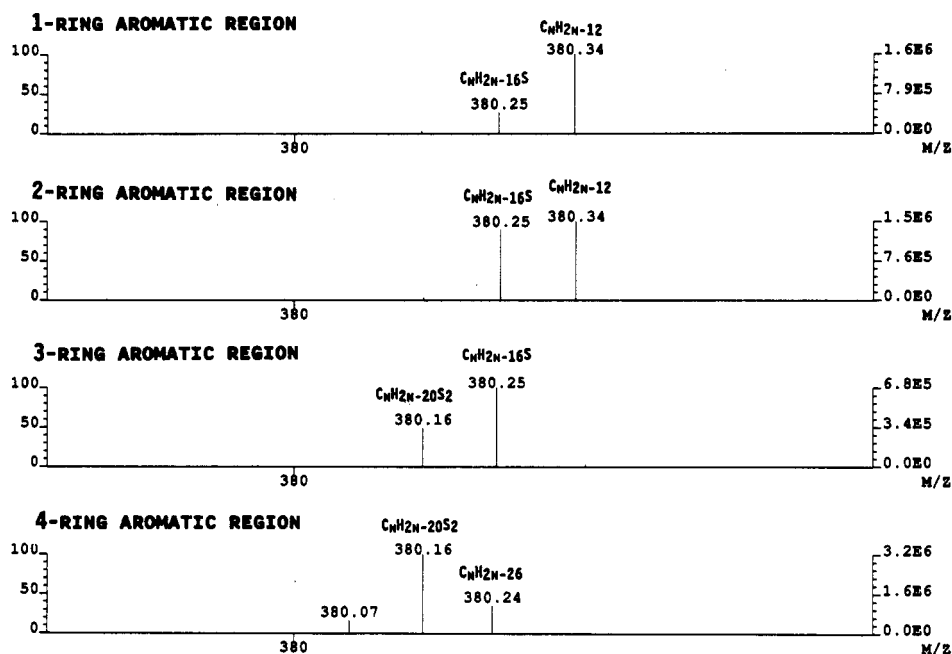


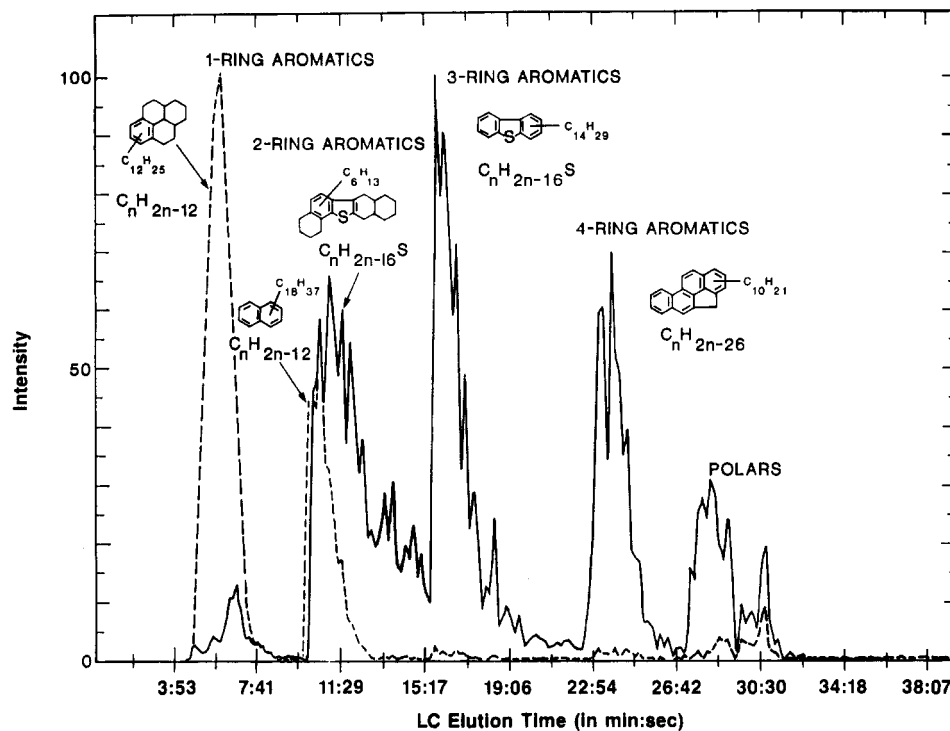
Figure 2. Distribution of molecular ions with a nominal mass 380.

4-ring aromatic region have to be in the  $Z = -26$  hydrocarbon series. This ability to identify and distinguish overlapping mass series in one single analysis illustrates the advantages of combining LC separations with high-resolution accurate mass measurements.

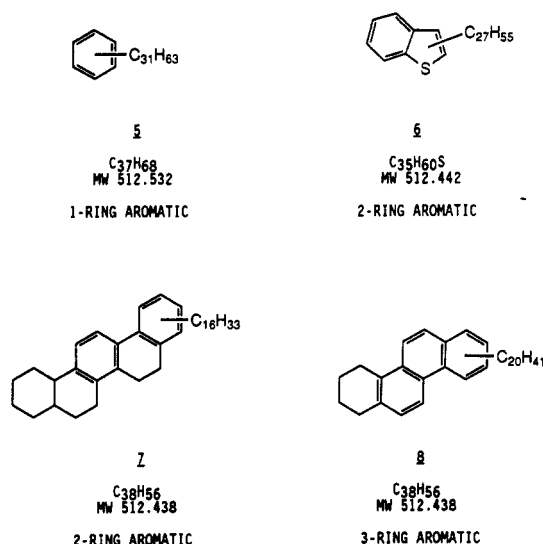
The distribution of overlapping compound series can also be determined by using selected ion chromatograms (SIC's). Figure 3 shows the SIC's of the  $m/z$  380.25 and 380.34 ions with a resolution window of 200 ppm. Two major groups of compounds are present in the  $m/z$  380.34 chromatogram; one group consists of 1-ring trinaphthenobenzenes and the other consists of the 2-ring alkyl aromatic hydrocarbons (naphthalenes). Both groups are in the  $Z = -12$  hydrocarbon series. The same situation occurs for the  $Z = -16S$  series, shown in the  $m/z$  380.25 chromatogram. Two groups of sulfur compounds in the series, trinaphthenobenzothiophenes and dibenzothiophenes, are present in the 2-ring and the 3-ring aromatic LC regions. The  $Z = -26$  compounds (such as

benzo[*g,h,i*]fluoranthenes or cholanthrenes) appearing in the 4-ring aromatic region would require a resolution at least 10 times that set by the mass spectrometer to be resolved from the  $Z = -16S$  compounds.

It should be pointed out that ambiguities still exist with some overlapping compound series. The major series in the 2-ring aromatic elution region is the benzothiophene ( $Z = -10S$ ) series. This sulfur series overlaps with the  $Z = -6$  and  $-20$  hydrocarbon series. At a nominal mass of 512, for example, there are at least four possible structures as shown in Figure 4. Benzothiophenes 6 are resolved from benzenes 5 and naphthenophenanthrenes 8 by LC ring type separations. However, trinaphthenodiaromatic hydrocarbons 7 would coelute with benzothiophenes in the 2-ring aromatics elution region. It would require a mass resolution of over 150 000 to resolve these two compound types. Further refinement of the on-line LC/MS technique to differentiate these compound types is currently in progress.



**Figure 3.** Selected ion chromatograms for masses 380.25 (solid line) and 380.34 (dotted line) with a resolution window of 200 ppm.



**Figure 4.** Possible structures of compounds with a nominal mass of 512.

As mentioned previously, the advantage of using the moving belt interface comes from the ability to use a wide variety of ionization methods including low-voltage EI. The technique is limited, however, to a specific molecular weight range due to the use of a purely thermal process to desorb the analyte from the belt's surface (this limitation may be minimized if other techniques, such as fast atom bombardment or laser desorption, are used to desorb

the analyte). Alternative LC/MS interfaces that do not employ a thermal desorption process include thermospray (TS)<sup>16-18</sup> and those employing a particle beam approach.<sup>19,20</sup>

### Conclusions

By incorporating low-voltage EI/high-resolution MS technique with on-line LC/MS, a wealth of chemical information of fuel mixtures can be obtained. On-line LC/MS reduces the resolution requirement for accurate mass measurements of aromatic and sulfur compounds present in the mixtures. Continuous monitoring of compound classes facilitates the quantification of compound series that have the same or nearly the same accurate masses but have different ring types. The abilities of on-line LC/MS to differentiate naphthenoaromatics from alkylaromatics and to distinguish aromatic hydrocarbons from "difficult-to-resolve" thiophenes can provide very useful information which can be used to understand petroleum chemistry and processes.

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