# Molecular Formula Determination of Constituents in Arabian Mix Vacuum Residue by Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry

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(Received November 11, 1999; CL-990969)

Fourier transform ion cyclotron resonance mass spectrometry equipped with electrospray ionization (ESI FT ICR MS) was successfully applied to determine molecular formulas of components in Arabian mix vacuum residue (AM-VR) by measurement of highly accurate m/z values of molecular ions and analysis of spectral pattern without any pre-separation procedures.

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To develop efficient processes for conversion of heavy oil to economically more valuable products, such as gasoline, it is essential to know molecular formulas of its constituents.[1] Identification of molecules in heavy oil has been mainly carried out by GC/MS or LC/MS. Such chromatographic methods are insufficient to separate a very complex mixture such as heavy oil into its individual components.[1,2] FT ICR MS enabled us to obtain ultrahigh resolution mass spectra[3] and has been mainly applied to determine chemical structures of biomolecules, such as peptides.[4,5] Recently, it was reported that FT ICR MS was useful to analyze specific compounds in complex mixtures: organosulfur compounds in diesel fuel[6,7] as well as humic acids.[8] Molecular formulas of each constituent in a very complex mixture may be determined directly by highly accurate mass measurements when FT ICR MS is combined with a soft ionization technique, such as ESI,[8] which can give only molecular-related ions. In this letter we showed potential application of ESI FT ICR MS to determine molecular formulas of constituents in AM-VR with accurate mass without any separation procedures.

AM-VR used as a heavy oil sample has elemental composition (wt%) of C 84.3, H 9.9, S 5.2, N 0.4, and O 0.2 (diff.).[1] FT ICR MS measurements were performed on a Bruker BioAPEX 70e spectrometer equipped with a 7 T superconducting magnet. Pressure in the source chamber and the analyzer cell were maintained at $5\times10^{-6}$ and $\sim4\times10^{-10}$ mbar, respectively. Trapping voltage was 1.00 V and other instrument operational parameters were controlled by the standard XMASS software. Ions were produced with an external electrospray source. Sample solutions of AM-VR in methanol/chloroform/acetic acid (100/10/1 vol ratio) at concentration of 1.2 mg/ml were directly infused via a syringe pump running at a rate of 40 µl/h for 30 s. Nitrogen gas heated at 250 °C was used as drying gas. The spray potential was set at 4 kV. Ions were externally accumulated in the hexapole of ESI source for 6 s. Ions were excited using a broadband chirp waveform over a bandwidth of about m/z 200-1200 and detected in the same m/z range with 256 k data points (broad band). Polyethylene Glycol 600 was used as external calibrants. Accuracy of m/z value measured was at least 6 orders of magnitude.

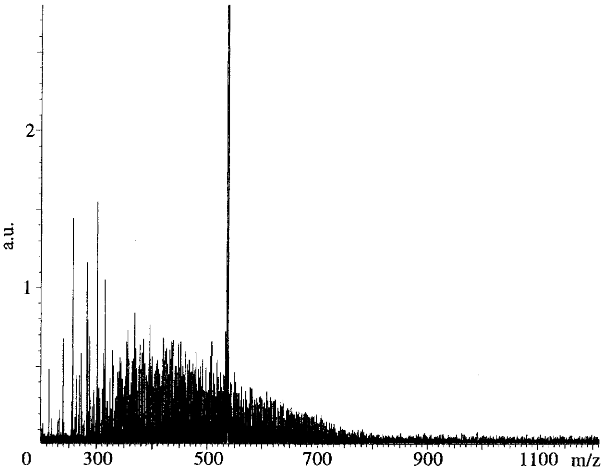


**Figure 1.** Broadband ESI FT ICR MS spectrum of Arabian mix vacuum residue.

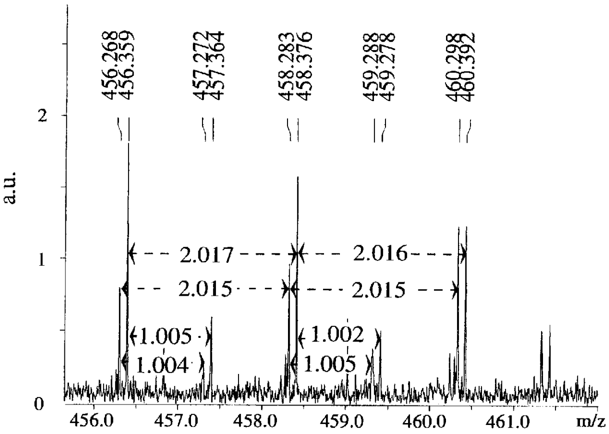


**Figure 2.** Mass scale-expanded view of signals near m/z 458.

Figure 1 shows a broad band ESI FT ICR MS spectrum of AM-VR. So many peaks were observed in the range of 250 < m/z < 750. The spectrum in the range of 450 < m/z < 465 is expanded in Figure 2 for the spectral pattern analysis. The mass differences between pair of peaks with odd and even masses are 1.005 ~ 1.002 which coincide with the atomic weight difference (1.003 u) between $^{13}C$ and $^{12}C$. The intensity ratios of peaks with odd/even masses are 30 ~ 45%. These values approximately correspond to estimated peak intensity ratio with odd/even masses according to the isotope existence ratio of $^{13}C$ (1.11% of C) and the plausible carbon number of the molecule (around 450 u) is ca. 30. Therefore the peaks with odd masses show the compounds including one $^{13}C$. A series of peaks with even masses appeared at intervals 2.017 ~

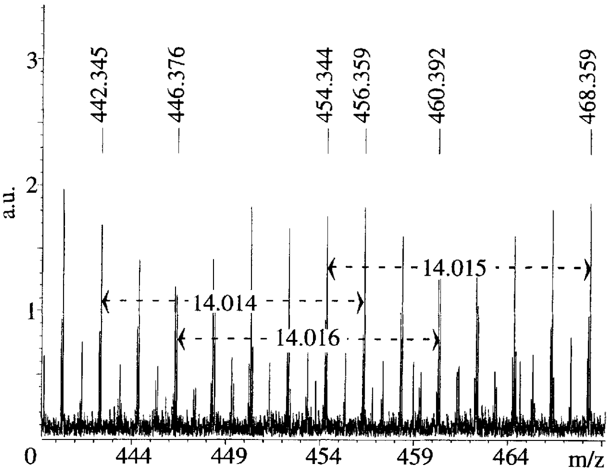


**Figure 3.** Mass scale-expanded view of signals in the range of m/z 440 ~ 470.

**Table 1.** Candidate molecular formulas having close masses to a peak with m/z=456.359

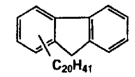
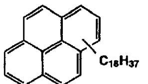
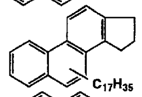
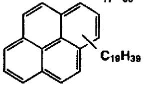
| Formula mass / u | Difference / u | Z[a] | Molecular formula $^{1}H$ | $^{12}C$ | $^{16}O$ | $^{32}S$ |
|---|---|---|---|---|---|---|
| 456.281 | 0.078 | -34 | 36 | 35 | - | - |
| 456.374 | -0.016 | -20 | 48 | 34 | - | - |
| 456.468 | -0.109 | -6 | 60 | 33 | - | - |
| 456.245 | 0.114 | -36 | 32 | 34 | 1 | - |
| 456.338 | 0.024 | -22 | 44 | 33 | 1 | - |
| 456.432 | -0.073 | -8 | 56 | 32 | 1 | - |
| 456.284 | 0.074 | -24 | 40 | 32 | - | 1 |
| 456.378 | -0.019 | -10 | 52 | 31 | - | 1 |
| 456.471 | -0.113 | -4 | 64 | 30 | - | 1 |
| 456.248 | 0.111 | -26 | 36 | 31 | 1 | 1 |
| 456.341 | 0.018 | -12 | 48 | 30 | 1 | 1 |
| 456.435 | -0.076 | 2 | 60 | 29 | 1 | 1 |

[a]Hydrogen deficiency index (see text).

2.015 u which correspond to 2.016 u of 2H. Another series of peaks were detected with a mass difference of 14.016 u ($CH_2$) (Figure 3). Essentially a similar spectral pattern was obtained for all the other peaks observed in the range of 440 < m/z < 500. Such a spectral pattern suggests that peaks with even masses are of singly charged molecular ions with no adduct such as $H^+$.

Consequently, molecular formulas for the even m/z peaks can be determined from highly accurate masses. Candidate molecular formulas for the peak with m/z 456.359 (Figure 2) are shown in Table 1 for example. The molecular formula $C_{34}H_{48}$ (formula mass 456.374 u) has the smallest mass difference (–0.015 u) for the measured m/z 456.359 and therefore, is the most probable formula. In a similar way, molecular formulas of another three even m/z peaks were estimated (Table 2). Differences in mass number between measured peaks and determined molecular formulas are within 40 ppm. Candidates of plausible chemical structure derived from molecular formula and hydrogen deficiency index Z (defined as $C_nH_{2n+Z}$)[9] are also shown in Table 2. Using the method described above, we

**Table 2.** Estimated molecular formulas and probable structures for m/z= 446.375, 454.344, 456.359 and 468.359

| Measd.mass / u | Molecular formula | Formula mass / u (Difference / u) | Z[a] | Probable structure |
|---|---|---|---|---|
| 446.375 | $C_{33}H_{50}$ | 446.391 (-0.016) | -16 |  |
| 454.344 | $C_{34}H_{46}$ | 454.359 (-0.015) | -22 |  |
| 456.359 | $C_{34}H_{48}$ | 456.374 (-0.016) | -20 |  |
| 468.359 | $C_{35}H_{48}$ | 468.376 (-0.017) | -22 |  |

[a]Hydrogen deficiency index (see text).

can determine molecular formulas for all peaks with even masses. The result suggests that major constituents consist of aromatic molecules with similar Z values (-22 ~ -26) and different length of alkyl-chains.

It is likely that only a limited number of components in AM-VR is ionized by the ESI conditions used in the present study. Further study is in progress to find the best measurement conditions. We believe that the described ESI FT ICR MS analysis, which provides highly accurate masses and spectral patterns, will become a highly effective method to determine molecular formulas of constituents in a very complex mixture, such as AM-VR, directly without any pre-separation procedures.

This work has been carried out as a research project of The Japan Petroleum Institute commissioned by the Petroleum Energy Center with the subsidy of The Ministry of International Trade and Industry.

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