

Metal Oxide Laser Ionization Mass Spectrometry for the Direct Profiling of Pyrolysis Oil Constituents

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Introduction:

• Fluids produced from the anoxic pyrolysis of biomass (py-oils) represent a promising, renewable alternative energy source.¹ These oils have a variety of chemical functionalities including: alcohols, ketones, organic acids, sugars, aldehydes and ethers.² Py-oils chemical complexity has made the development of efficient analytical methodologies problematic. Detailed information on py-oils composition is needed to efficiently direct upgrading, and processing for transportation applications.

• Metal oxide laser ionization mass spectrometry (MOLI MS) is a laser desorption method which produces molecular ions from small molecules through interactions between analytes and Lewis acid/base sites on a metal oxide.³ MOLI MS is a separation-independent method and therefore greatly reduces gas/solvent needs. Additionally, rapid analysis decreases experiment time and reduces laboratory energy usage.

• MOLI MS produces profiles of py-oil constituents that consist of molecular ions with high mass accuracy. The profile of py-oil may then be interpreted on the basis of Kendrick mass defect (KMD) which is used in petroleomic analysis to group homologues based on their chemical functionality.^{4,5}

• Structural information is then obtained using collision induced dissociation mass spectrometry (CID MS).

Experimental:

• Py-oil sample preparation is minimal and consists of dissolving 100 μL of py-oil in 0.9 mL of methanol. Samples are then applied to a droplet of nickel oxide (NiO), which has been pre-treated with methyl acetate and dried on a stainless steel sample plate. The sample plate is then loaded into the mass spectrometer for analysis.

• Mass spectra were obtained with a JEOL JMS-S3000 SpiralTOF/TOF mass spectrometer equipped with a frequency tripled solid state Nd-YLF laser (349 nm). Laser fluence and accelerating voltages were optimized at ~50% and 20 kV, respectively. Helium was used as the collision gas for CID at a pressure of 1×10^{-4} Pa.

Results:

Figure 1. MOLI MS spectrum of a typical upgraded pyrolysis oil. Peaks are observed as series of homologues spaced ~14 Da apart. Spacing of 14 Da allows for data reduction by plotting Kendrick mass defect (KMD) vs. m/z .

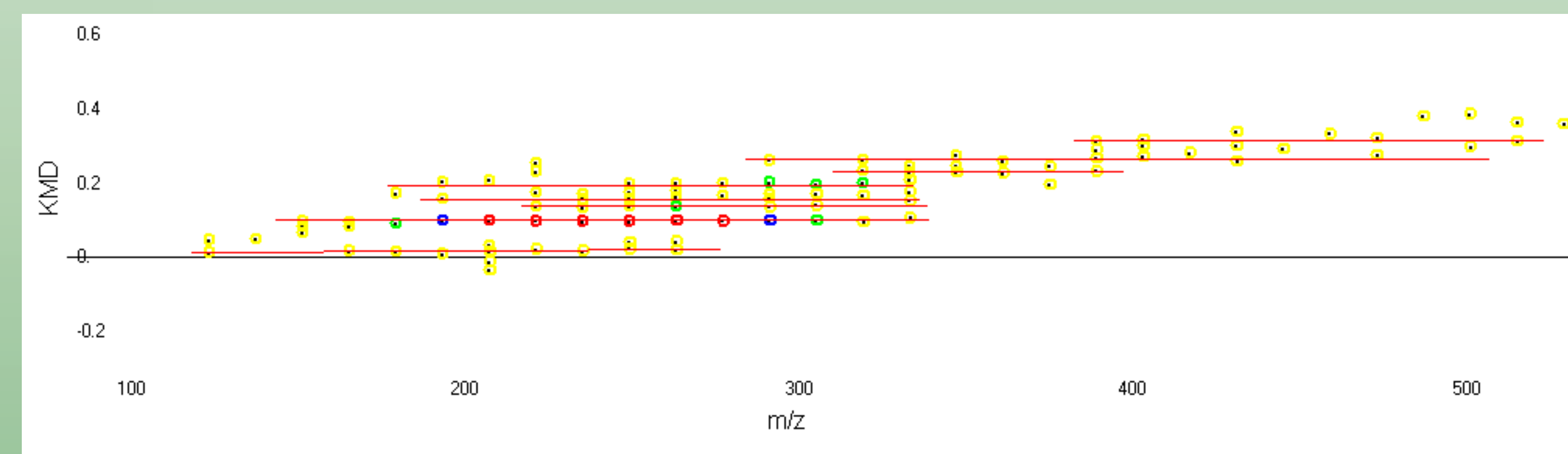
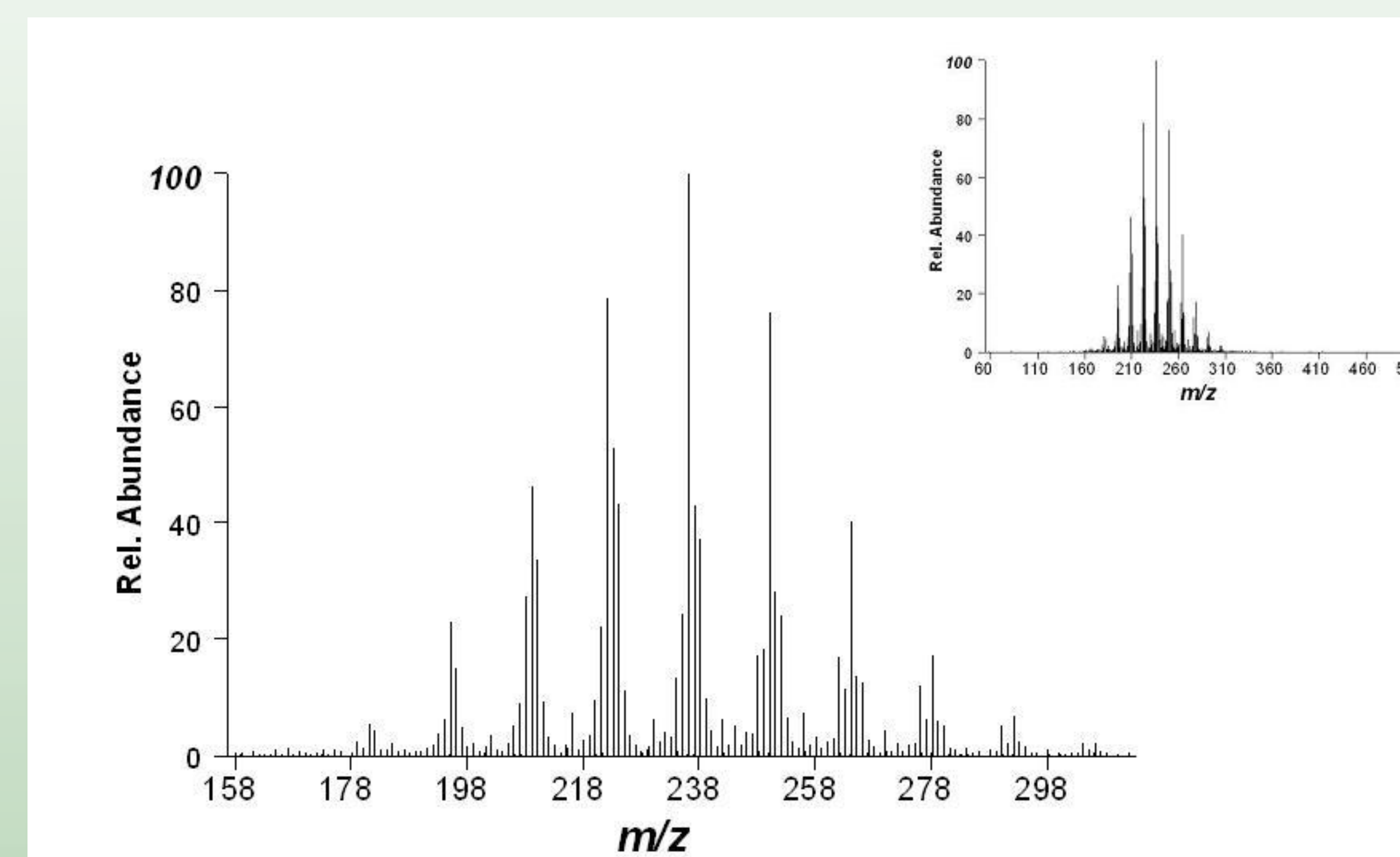


Figure 2. Plot of KMD vs. m/z for the data presented in Figure 1. Horizontal lines indicate homologous series. The addition of heteroatoms and unsaturations results in an increase in mass defect. For example, saturated alcohols would all have an identical mass defect arising from the addition of oxygen, but would be spaced 14 Da apart as the alkyl chain increases in length resulting in a horizontal line representing the series of alcohols. Abundances are represented by color. The most abundant peaks from Figure 1 are shown as the red series. The peaks in this series likely correspond to dimeric lignin-like species. The most intense peak from this series (m/z 236) was selected as the precursor for CID MS.

Figure 3. CID spectrum of precursor m/z 236. Elucidating the structure of the m/z 236 allows determination of the structure of the additional peaks from the same homologous series. Specifically, the peaks at m/z 76 and 90 both indicate bi-substituted phenyl rings. A shift in these peaks for the CID spectrum of another ion in the series would indicate an additional CH_3 attached to one of the rings.

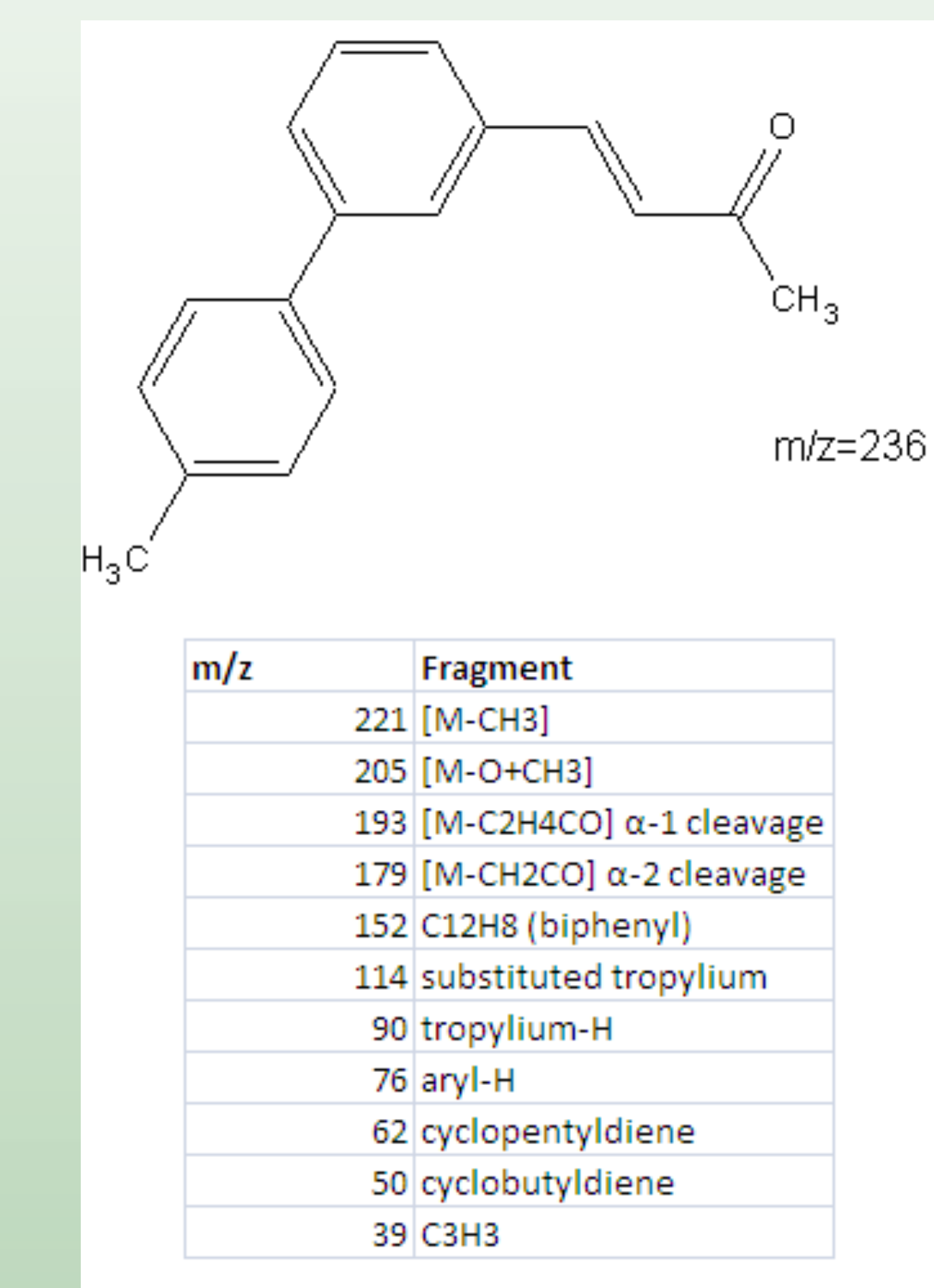
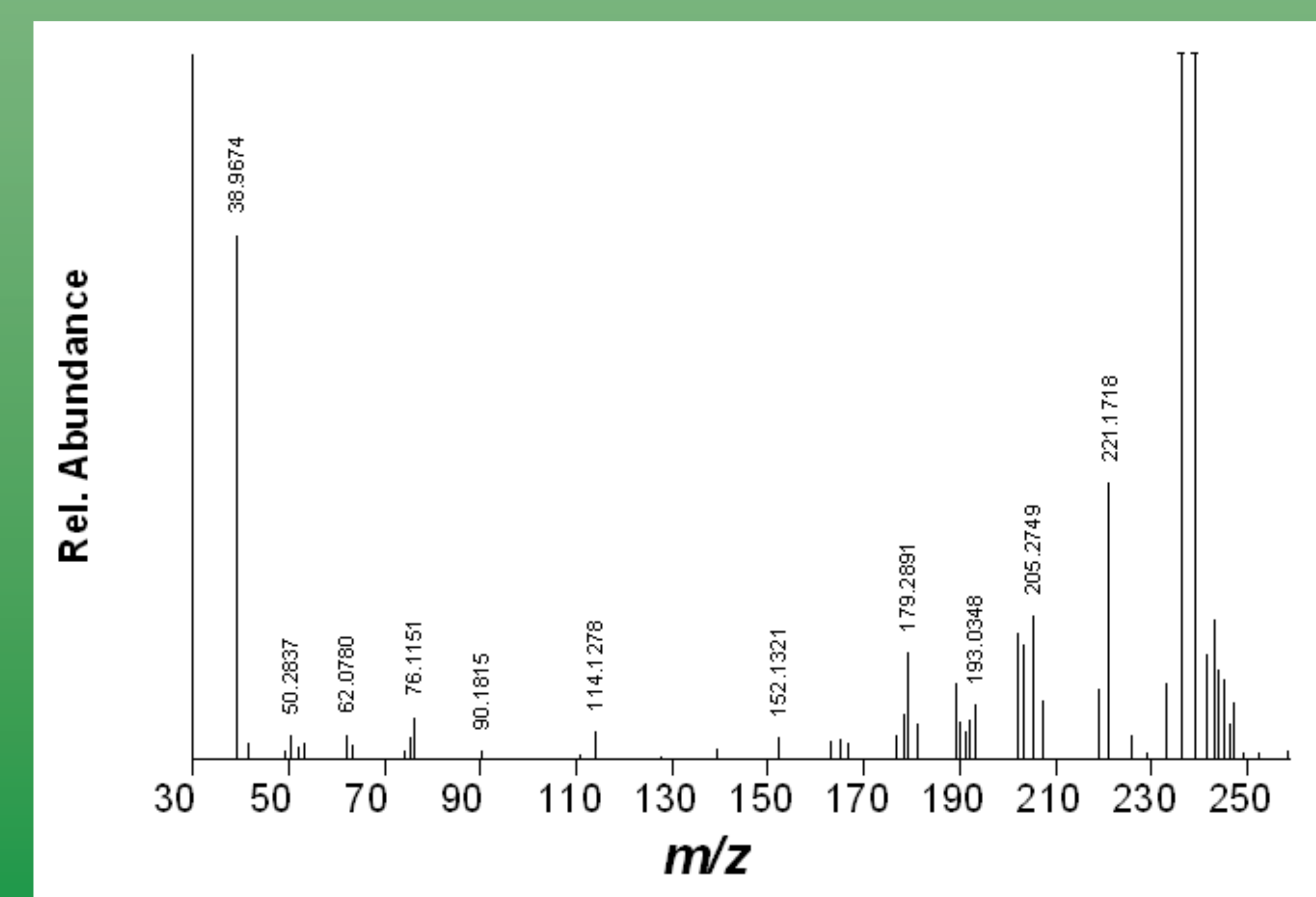


Figure 4. Proposed structure for the m/z 236 precursor based on CID fragmentation. The proposed species is in agreement with previous studies⁶ and confirms that the major series of peaks in Figure 1 correspond to lignin-like dimers.

Conclusions:

• MOLI MS produces profiles of pyrolysis oil constituents without separations. Peaks can then be grouped into homologous series by plotting KMD vs. m/z .

• Mono-isotopic precursors can be selected from each series for CID, providing structural information.

• MOLI MS is a rapid analysis free of background interferences. The method requires very little sample preparation, and minimizes laboratory power consumption. Additionally, the independence from separation methods eliminates the need for solvent/gas mobile phases, dramatically reducing resource usage.

References:

- (1) D. Mohan, C.U. Pittman, P.H. Steele, *Energy and Fuels*. **2006**, 20, 848-889.
- (2) M.K. Bahng, C. Mukarakate, D.J. Robichaud, M.R. Nimlos, *Anal. Chim. Acta*. **2009**, 651, 117-138.
- (3) C.R. McAlpin, K. J. Voorhees, A.R. Corpuz, R.M. Richards, *Anal. Chem.* (accepted)
- (4) E. Kendrick, *Anal. Chem.* **1963** 35, 2146-2154
- (5) C.A. Hughey, C.L. Hendrickson, R.P. Rodgers, A.G. Marshall, K. Qian, *Anal. Chem.* **2001**, 73 (19): 4676-81
- (6) M.A. Gofii, J.I. Hedges, *Geochimica et Cosmochimica Acta* **1992**, 56, 4025-4043