

MALDI-TOF MASS SPECTROMETRY FOR THE CHARACTERIZATION OF INSOLUBLE CARBONACEOUS PITCHES

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When carbonaceous pitches are used as raw materials for advanced carbon products, the molecular composition of the pitch acquires special importance. Not only does molecular composition affect the physical properties (e.g., softening point and viscosity) of the pitch, but it also affects the final properties, such as the strength and thermal conductivity, of the resultant carbon products. Unfortunately, the problem of determining fundamental molecular information for pitches is a difficult one that has yet to be completely solved. The classic technique for molecular weight distribution (MWD) determination is gel permeation chromatography (GPC), but the technique suffers from a number of disadvantages, including poor peak resolution; lack of adequate calibration standards; and the incomplete solubility of higher MW, mesogen-containing pitches in even aggressive GPC solvents. In principle, mass spectrometry (MS) techniques would be preferred for the analysis of pitches because the calibration is absolute and excellent resolution can be obtained. Unfortunately, most of these techniques (e.g., thermospray-MS and field desorption-MS) can only be applied to that fraction of pitch that is solvent-soluble.

In the late 80s, researchers discovered that the use of a matrix could be used to greatly increase the molecular weight of those compounds that could be analyzed by laser desorption mass spectrometry (LD-MS) [1]. According to Cotter [2], the matrix efficiently absorbs most of the UV laser radiation, resulting in its rapid ionization and dissociation into the gas phase. The resultant, rapidly expanding gas phase entrains intact analyte ions. At any time during this process, charge transfer to the analyte molecules can occur, producing the protonated species that are observed in the mass spectra. Because the matrix (and not the analyte) absorbs most of the laser radiation, this technique, known as matrix-assisted, laser desorption/ionization, time-of-flight (MALDI-TOF) mass spectrometry, is preferred when low ion fragmentation and primarily singly charged ions are desired.

Most of the MALDI work performed to date on heavy fossil fuels has been by Kandiyoti and co-workers [3], who analyzed a standard coal-tar pitch and its pyridine-

soluble/insoluble fractions. Pioneering work on petroleum pitches was done by Southard et al. at DuPont and Conoco [4], who demonstrated that MALDI could be used to provide MW information on the oligomers present in both isotropic petroleum pitches and their mesophases. However, no added matrix was used in their work; instead, they relied on the pitch to act as its own matrix. Furthermore, none of their mass spectra have been reported in the open literature.

Przybilla et al. [5] evaluated MALDI for the analysis of synthesized giant polycyclic aromatic hydrocarbons (PAHs). A new matrix, 7,7,8,8-tetracyanoquinodimethane (TCNQ), was evaluated and found to be particularly suitable for these PAHs. Because of the insolubility of the PAHs, the sample and matrix were mechanically mixed together. For these single-component PAHs, highly resolved mass spectra with virtually no fragmentation or aggregate ions were obtained for MWs up to 2708 Da, and the MW obtained by MALDI was consistent with the structure expected from synthesis. We have applied this matrix to the characterization of pitches with good success (see Figure 1). For the first time, the matrix TCNQ makes possible the detection of species present in a high MW petroleum pitch fraction. Note that these species are not detectable without the use of the matrix, and the signal-to-noise level of the analysis is increased as well.

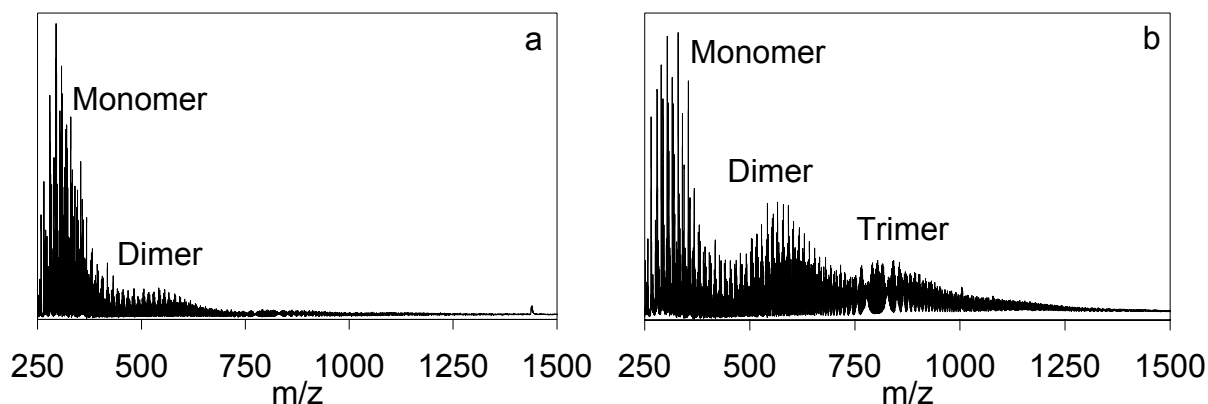


Figure 1. MALDI spectra of a high MW petroleum pitch fraction prepared with no matrix (a) and TCNQ matrix (b).

The traditional means of MALDI sample preparation involves dissolving the analyte, mixing the analyte with a solution of matrix, and applying the mixture to the target surface. The target is allowed to dry before analysis. Because the pitches analyzed here are only partially soluble in any solvent, this “solution method” of sample preparation is not a feasible option. Therefore, a solvent-free sample preparation technique was developed for our analyses. In this so-called “powder method”, the matrix and pitch sample are combined and ground together to form a fine powder. We then use the high surface tension of water to create a thin uniform coating of the matrix–pitch mixture on the target cell. To compare these preparation methods, anthracene pitch, a model pitch formed by the thermal polymerization of anthracene, was analyzed

by both the “powder method” and by “solution method”. As seen in Table 1, the powder method of sample preparation allows for analysis of insoluble high MW material that is excluded from the “solution method”.

Table 1. MWDs for anthracene pitch by MALDI using two different sample and target preparation methods

MWD Indices	Sample and Target Preparation Method	
	Solution Method	Powder Method
MW _N	442 ±17	600 ±36
MW _w	587 ±30	931 ±87
MW _z	1028 ±230	1435 ±113
PDI	1.33 ±0.11	1.55 ±0.06

Our technique has been tested on a variety of pitches, including a commercial pitch from Conoco (now ConocoPhillips), a polymerized anthracene pitch, and high MW pitch fractions obtained via dense-gas extraction (DGE). In all cases, increased detection of high MW species is made possible by using TCNQ matrix in conjunction with the “powder method” of sample preparation. A more detailed discussion of the methods described here is given elsewhere [6].

Currently, we are investigating the quantitative nature of MALDI analysis, that is, determining the response characteristics of pitches of differing MWDs. In an effort to relate response to concentration, DGE is being investigated and has already proven useful for obtaining narrow MW fractions of pitch that are suitable for calibrating the response of the MALDI [7,8]. As can be seen in Figure 2, by extracting low MW materials by DGE, higher MW materials that were not detectable become visible in the MALDI analysis. The combination of MALDI for MW information and DGE for the isolation of narrow MW pitch fractions is proving itself to be a powerful new technique for the molecular characterization of insoluble, high MW pitches.

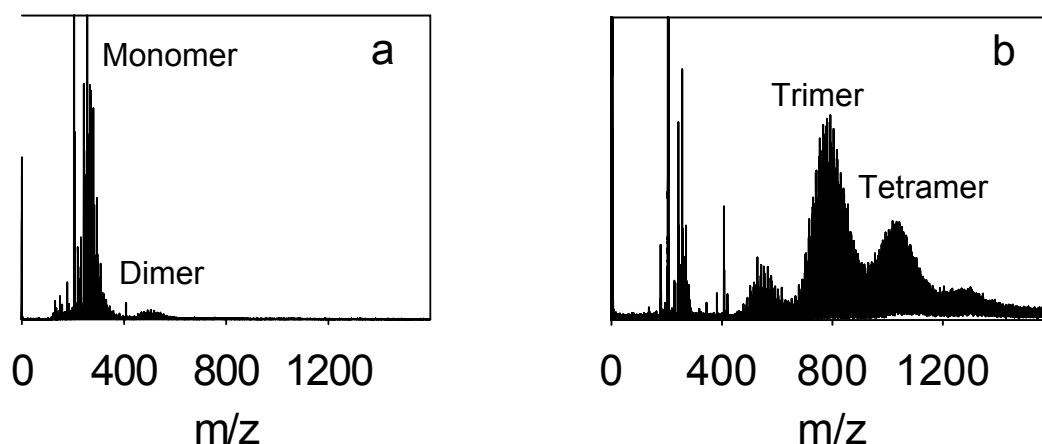


Figure 2. MALDI mass spectra showing (a) the lack of detectable high MW species in the process feed, and (b) higher oligomers in a heavy cut of the process feed by dense-gas extraction.

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