SOLVENT-BASED VS. SOLVENT-FREE SAMPLE PREPARATION METHODS FOR THE QUANTITATIVE ANALYSIS OF PETROLEUM PITCH OLIGOMERS BY MALDI MASS SPECTROMETRY

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Introduction

Petroleum pitches are obtained from the thermal polymerization of an aromatic decant oil, a byproduct of the catalytic cracking of the heavy gas oil fraction of crude oil. As shown in Fig. 1, these materials are oligomeric in nature, with a molecular weight (mol wt) that extends from about 200 to more than 1000 [1]. Petroleum pitches consist of polycyclic aromatic hydrocarbons (PAHs) with primarily methyl group substitutions to their backbones [2, 3] and can serve as raw materials for a wide range of carbon products, such as high thermal conductivity carbon fibers and high performance carbon–carbon composites [4]. Thies and co-workers [5] have been investigating the technique of dense-gas extraction (DGE) for separating pitches into fractions of well-defined molecular weight distribution (MWD), to which advanced characterization methods, such as Matrix Assisted Laser Desorption/Ionization (MALDI) mass spectrometry [6], can be applied.

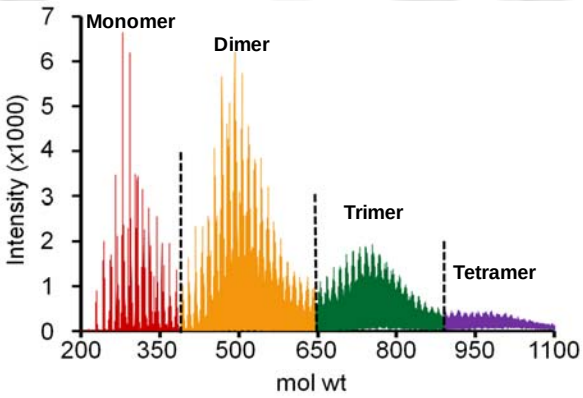

Fig. 1 MALDI spectrum for M-50 pitch.

Furthermore, with the recent development of solvent-free sample preparation methods for MALDI, researchers have developed the ability to characterize the heavier, insoluble constituents of petroleum pitches. However, even though MALDI has allowed us to monitor MWD information for DGE derived fractions, this information is essentially qualitative. Thus, a specific goal of this work is to establish a quantitative relationship between the constituents of pitches and the resultant MALDI response. Such quantitative information is consistant with our long term goal of using DGE to isolate pitch fractions of optimum molecular composition for specific, end-product applications.

One of the requirements for reliable quantitative analysis via MALDI is the preparation of a homogeneous mixture of analyte and matrix. In this work, both solvent-free and solvent-based sample preparation methods were investigated for the development of a reliable quantitative analysis technique for the oligomeric constituents of petroleum pitch.

Experimental

Materials: An isotropic petroleum pitch, M-50 (CAS: 68187-58-6), was obtained from Marathon Petroleum Company LLC. M-50 was separated using our semi-batch DGE technique [2] to obtain the dimer-rich (DR) and trimer-rich (TR) fractions that are discussed in this work. Toluene (HPLC grade, 99.8% purity, CAS 108-88-3) and carbon disulfide (CS_2, CAS 75-15-0) were obtained from Fisher Scientific. 1,2,4-Trichlorobenzene (HPLC grade, 99% purity, CAS 120-82-1) was purchased from VWR International. The above were used as solvents for the solvent-based sample preparation method. 7,7,8,8-tetracyanoquinodimethane (TCNQ; 98% min. purity from TCI America, CAS 1518-16-7) was used as the matrix for MALDI analysis. Details of both the solvent-based and solvent-free sample preparation methods are discussed elsewhere [7].

MALDI-TOF-MS: MALDI analysis of petroleum pitch samples was performed using a Bruker Daltonics Autoflex MALDI mass spectrometer equipped with a 337 nm nitrogen laser; the operating parameters for the technique are given elsewhere [2].

Results and Discussion

Quantitative analysis using MALDI mass spectrometry is one of the active areas of research in the field of polymer characterization [8]. Two important requirements for successful quantitative analysis with MALDI are the availability of samples with well-defined molecular mass distribution that can serve as calibration standards and the ability to prepare homogeneous samples for analysis.

DR and TR calibration standards were obtained by our DGE technique. These standards were mixed in various known proportions using both solvent-based and solvent-free sample preparation methods. Five binary mixtures were prepared and studied in this work. Sample homogeneity was investigated for both sample preparation methods. The MALDI target plate was spotted with three spots, using both sample preparation methods for all the five mixtures, and samples were then analyzed by MALDI (Fig. 2.). MALDI results (Fig. 2a) indicate good spot-to-spot reproducibility for the samples obtained using solvent-free methods. Solvent-based samples, on the other hand, showed poor spot-to-spot reproducibility (Fig. 2b). The solvent-free method was further investigated to determine the potential of MALDI as a quantitative analysis tool for petroleum pitches of broad MWD. In particular, five binary mixtures of varying composition were prepared from DR and TR fractions using the solvent-free sample preparation method. MALDI area fractions for the mixture constituents (i.e. the dimer and trimer) were calculated from the normalized MALDI spectra,

and then compared with the known quantities of the mixture constituents. As shown in fig. 3 and 4, a good corelation between MALDI response and the oligomer mole fraction was obtained, clearly indicating the applicability of MALDI as a quantitative analysis tool when the appropriate sample preparation method is used.

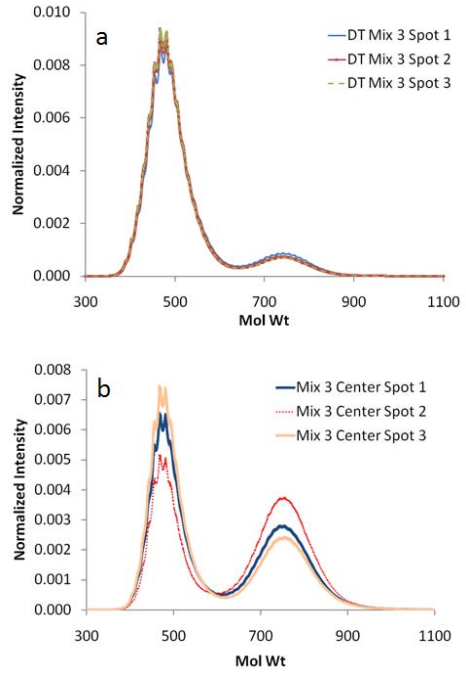

Figure 2: Comparison between normalized MALDI mass spectra for DR/TR mixtures: a) solvent-free sample preparation method. b) CS_2-based sample preparation method. (As three spectra shown in fig. 2a give virtually identical responses)

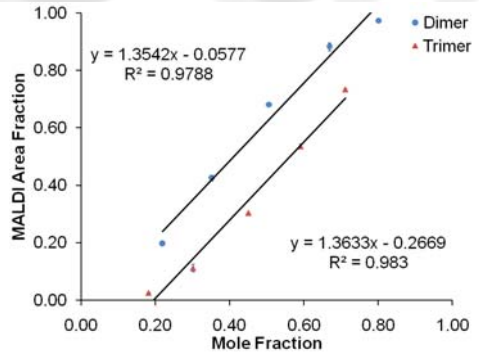

Figure 3: Quantitative analysis results for Dimer Rich – Trimer Rich binary mixtures obtained with solvent-free sample preparation method.

Conclusions

Both solvent-based and solvent-free sample preparation methods were investigated for the development of a reliable quantitative analysis technique for MALDI mass spectrometry. A representative petroleum pitch (M-50) was fractionated to produce dimer-rich and trimer-rich calibration standards. Binary mixtures were then prepared from the standards using both sample preparation methods and analyzed by MALDI. Solvent-based sample preparation resulted in samples of poor homogeneity. The solvent-free sample preparation method, on the other hand, gave samples with good homogeneity. Quantitative analysis work performed to date by the solvent-free method indicate that MALDI can indeed be developed into a quantitative analysis tool.

Acknowledgments. Acknowledgments for financial support are made to the donors of the American Chemical Society Petroleum Research Fund, the U.S. Department of Energy, (Office of Basic Energy Sciences), the Air Force Research Laboratory AFRL/RZSM, and the Center for Advanced Engineering Fibers and Films (CAEFF) at Clemson University.

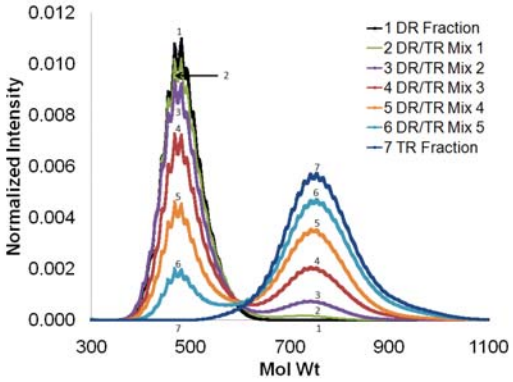

Figure 4: Normalized MALDI spectra for Dimer Rich fraction (Spectrum # 1), Trimer Rich Fraction (Spectrum # 7), and for the five binary mixtures (Spectra # 2 to 6) produced there from.

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