QUANTITATIVE ANALYSIS OF PETROLEUM PITCH OLIGOMERS USING 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.

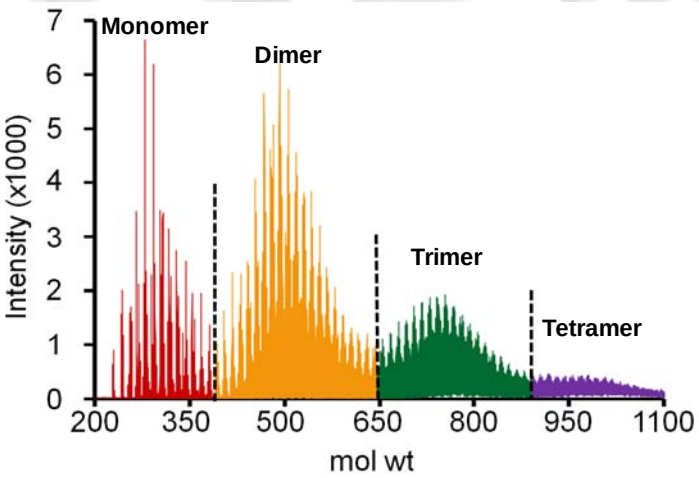

Fig. 1 MALDI spectrum for M-50 pitch.

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.

Our previous work has shown the potential of MALDI as a quantitative analysis technique [7] for petroleum pitches. In this work, the method of standard addition was applied to a pitch fraction of unknown molecular composition. A DGE-derived dimer fraction of relatively narrow MWD was used to quantify the concentration of dimer constituents present in the unknown pitch fraction. Standard addition results were then validated by an overall mass balance on the DGE process.

Experimental

Materials: An isotropic petroleum pitch, M-50 (CAS: 68187-58-6), was obtained from Marathon Petroleum Company LLC. M-50 was fractionated using our semi-batch DGE technique [2], and a pure dimer fraction was obtained. The pitch fraction of unknown oligomeric composition to which the method of standard addition was applied was obtained by fractionating of M-50 using a continuous DGE process [2]. 7,7,8,8-tetracyanoquinodimethane (TCNQ; 98% min. purity from TCI America, CAS 1518-16-7) was used as the matrix for MALDI analysis.

MALDI-TOF-MS: MALDI analysis of 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]. The solvent-free sample preparation method [8] was applied in this work.

Results and Discussion

An oligomeric fraction of M-50 of unknown composition (unknown) was isolated by DGE and analyzed by applying the method of standard addition. In particular, the dimer standard was mixed in various amounts with the same quantity of the unknown to prepare five different mixtures (Table 1). These five mixtures were then mixed with the matrix and spotted on the MALDI target plate using our solvent-free sample preparation method. All mixtures, along with the standard and unknown, were analyzed using MALDI on the same day to avoid day-to-day variation. Normalized MALDI spectra for the dimer standard, the unknown sample, and the five mixtures are shown in Fig. 2.

The dimer area fractions were then calculated for all five mixtures and for the unknown. As can be seen in fig. 3, a linear relationship was obtained when the calculated dimer area fraction was plotted vs. the mass fraction of the added dimer standard (Fig. 3). As seen in the figure, the method of standard addition predicts a concentration of 13.4 wt % dimer in the unknown sample. An independent mass balance check on these MALDI quantitative analysis calculations was obtained by performing DGE fractionation on the unknown sample. Operating parameters of the DGE process were adjusted to extract only dimer species from the starting material, and a material balance was performed. Results gave a dimer concentration of 16 wt % in the unknown sample.

Thus, we have independently confirmed by mass balance calculations the successful application of MALDI-MS as a quantitative analysis technique for mixtures of petroleum pitch oligomers with wide MWD.

Table 1. The method of standard addition was applied to five mixtures of the unknown and of the dimer standard, with quantitative analysis being performed by MALDI mass spectrometry.

Mixture	Unknown Sample (mg)	Dimer standard added (mg)	Dimer standard % mass
1	10.00	0.27	2.6
2	10.02	0.62	5.8
3	10.03	1.02	9.2
4	10.00	1.51	13.1
5	10.00	2.07	17.2

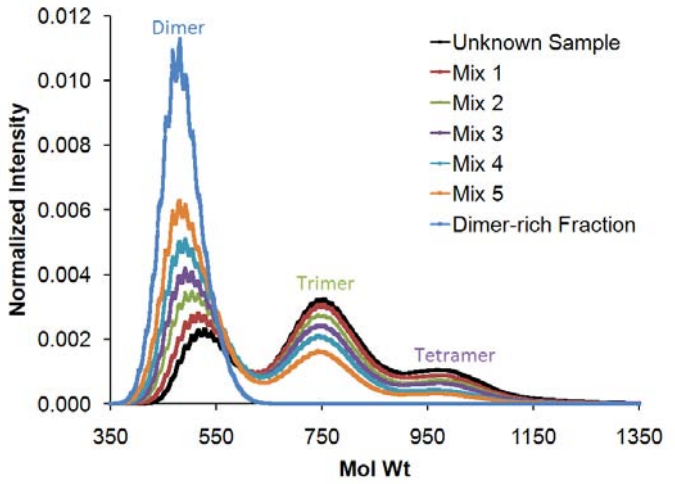

Fig 2. Normalized (Area under each curve sum to one) MALDI spectra for the unknown sample, dimer standard, and the five mixtures (see Table 1).

Conclusions

The quantitative analysis of oligomeric petroleum pitches can be accomplished by applying the method of standard addition. A petroleum pitch sample of narrow MWD was isolated by DGE and used as a standard for the quantitative analysis work. Quantitative results obtained from MALDI were comparable with the mass-balance calculations performed with the DGE process. The generation of mol wt standards by DGE and the development of solvent-free sample preparation method for sample homogeneity were breakthroughs that made this research finding possible.

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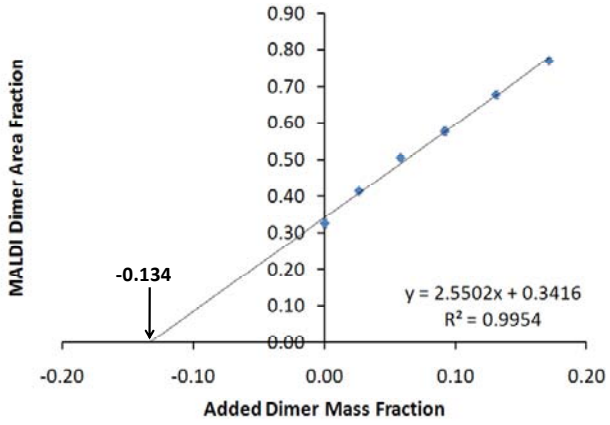

Fig 3. Application of the method of standard addition to the unknown sample gives a dimer cconcentration of 13.4 wt%.

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