Analysis of High Boiling Components in Petroleum Products by LC/MS

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**Goal:** To develop a robust LC/MS method for the complete analysis of petroleum products, particularly for non-volatile or semi-volatile components not amenable to separation by GC or GC/MS.

**Introduction**

The analysis of petroleum feedstock and finished products is traditionally achieved using gas chromatography (GC) coupled to a number of detectors, the most sensitive and selective being the mass spectrometer. One of the major obstacles to routine analysis for the heavier-cut petrochemical products using GC/MS methods has been the ability to volatilize the high-boiling components. LC/MS methods do not suffer the limitation of volatility or molecular weight; however traditional LC/MS instrumentation suffered contamination to the LC/MS interface as a result of the complicated and dirty sample matrices. Without rigorous sample preparation, the MS would be become contaminated and completely blocked by hydrocarbon build-up on the LC/MS interfaces.

In this communication, we demonstrate a simple but efficient LC/MS platform for the analysis of petroleum finished products. The extended mass range of the LC/MS instrument combined with the ability to inject, separate, and ionize heavy compounds, provided data not available by GC/MS. The patented cone-wash integrated into the electrospray source of the mass spectrometer allowed for the uninterrupted analysis of hydrocarbon samples. The methodology described in this publication can be used to characterize chemicals in wide range of petroleum and petrochemical analyses.

**Methods**

**Instruments**

The method was developed using an LC/MS system comprised of a Thermo Scientific Surveyor MS Pump Plus, Thermo Scientific Surveyor Autosampler Plus, and Thermo Scientific MSQ Plus single quadrupole mass spectrometer with electrospray ionization (ESI). The integrated cone wash delivered a continuous flow of 200 µL/min methanol to the skimmer cone (Figure 1), eliminating hydrocarbon deposition and entrance cone blockage. Direct infusion of samples and standards was used for instrument tuning and optimization of MS parameters. Comparative GC analysis was performed on a Thermo Scientific TRACE GC Ultra™ with Thermo Scientific DSQ™ single-quad mass spectrometer.

**Sample Preparation**

Three commercial fuel system cleaners were obtained and prepared as follows: 10 µL of original sample was diluted into 2 mL of hexane. 100 µL aliquot of the diluted sample was further diluted to 1 mL in hexane.

**LC/MS Conditions**

A 10 µL prepared sample was injected using partial-loop injection onto a Thermo Scientific Hypersil GOLD, 50 × 2.1 mm, 1.9 µm column at 50°C. A 15-minute gradient using water with 0.1% formic acid and methanol with 0.1% formic acid was created for the separation with a 2-minute equilibration following each injection (Table 1). Both APCI and ESI were evaluated with positive and negative polarity switching, with optimized sensitivity in the positive ESI mode.

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- ESI prob temp: 550 °C
- Cone voltage: 75 V
- Solvents: A: Water with 0.1% formic acid
  B: Methanol with 0.1% formic acid.
- Column oven temperature: 50°C
- Flow rate: 0.5 mL/min
- Column: 50 × 2.1 mm, 1.9 µm Hypersil GOLD

Table 1: Optimized HPLC and MS parameters used in this analysis

Figure 1: Cone wash nozzle positioned at skimmer cone entrance for oil analysis
Results

Figures 2, 3, and 4 illustrate the systematic interpretation of the complex polymer distributions by LC/MS. The total ion chromatogram (TIC) of each of the three samples analyzed is shown in the top trace of Figure 2. The averaged mass spectra in the bottom reveals the complex polymer distributions contained in each sample, which can be seen in the chromatograms. These complex traces are separated into individual polymeric distribution series in Figure 3, with individual component mass identification in Figure 4.

The detailed mass spectra of the three samples are shown in Figure 3, where the existence of multiple polymer distributions in all three products is clearly seen. However, the polymer distribution patterns are different and unique in each sample. Only one major polymer distribution is found in sample C with a mass difference of 29 amu, while three major polymer distribution patterns...
are visible in both samples A and B with a mass difference of 72 amu and two 36 amu difference patterns in each. Samples A and B contain similar distribution patterns, however the data suggest that these polymers are different due the mass differences in each of the distributions. The abundance ratios differ for each of the polymer samples as shown in Figure 3.

The expanded baseline of Sample B, with clearly defined hydrocarbon separation of the complex mixture due to the separation efficiency of the small particle column is shown in Figure 4. The extracted mass spectra for each of the chromatographic peaks shown in Figure 4 confirm complete separation of all polymer components.

Figure 4: Three sets of polymer distributions in Sample B separated by HPLC. The mass spectrum of each chromatographic peak is sequentially displayed under the chromatogram.

Figure 5: Representative GC/MS results of sample C. The TIC collected from the mass range of 50 to 1050 m/z is shown in the top trace. The averaged mass spectra from 2 to 14 minutes in the bottom screen reveals the majority of mass distributions occurred below 200 m/z.

The GC/MS results of Sample C are shown in Figure 5. The TIC collected from the mass range of 50 to 1050 m/z is shown in the top trace. The averaged mass spectra from 2 to 14 minutes in the bottom screen reveals the majority of mass distributions occurred below 200 m/z.
Confirmation studies were run by GC/MS with a temperature ramp from 40°C to 300°C, with the results of sample C shown in Figure 5. Comparison of mass distribution between GC/MS and LC/MS show common identification of lower boiling point components, while the higher m/z components shown in the LC/MS results do not appear to be volatilized for detection by GC/MS.

Conclusions
An LC/MS method was successfully established for the analysis of high boiling point components in commercial polymeric fuel additives using a simple sample preparation process. The patented cone-wash feature of the MSQ Plus enabled the mass spectrometer to operate with no sample deposition on the skimmer cone over an extended series of experiments. The high m/z components in each of the samples were easily separated and identified using this method, providing supplemental information to conventional GC methods which are limited by sample volatility.