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Determination of Corrosion Inhibitor–Lubricity Improver in Jet Fuels by Liquid Chromatography–Electrospray Ionization Mass Spectrometry

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By David W. Johnson [1], Milissa Flake [2], Ryan Adams [3]

Military jet fuel (JP-8) is very similar to commercial jet fuel (Jet A) except for the presence of three additives, fuel system icing inhibitor, corrosion inhibitor–lubricity improver (CI-LI), and antistatic additive, which are added to improve characteristics of JP-8. Of particular interest is the CI-LI additive; the most common active ingredient is a dimer of linoleic acid. This article focuses on quantification of the active ingredient in the CI-LI additive by liquid chromatography–mass spectrometry (LC–MS). This method will allow the determination of CI-LI content in military jet fuel samples.

Aviation fuels consist primarily of a complex mixture of linear, branched, and cyclic hydrocarbons (C8–C16) (1), aromatic carbons (2) with trace amounts of polar impurities. The polar impurities are important because their reactivity has a dramatic effect on the formation of deposits in the fuel (3). Military aviation fuels (JP-8) are supplemented by a series of additives including fuel system icing inhibitor (FSII), antistatic additive (static dissipator additive, or SDA), and corrosion inhibitor–lubricity improver (CI-LI) (4). The first two of the additives are easily analyzed by gas chromatography (GC) or other experimental methods, but the CI-LI additive is too high in molecular weight for GC. The only documented method for its determination is a complex method involving a combination of extraction and gel permeation chromatography (GPC) (5).

The typical active ingredient in several CI-LI additives is a dimer of linoleic acid. The dimer is usually prepared by the clay catalyzed dimerization of linoleic acid, which results in the formation of a mixture of acyclic, monocyclic, and bicyclic compounds (6). The reaction also results in a variable number of remaining double bonds (7,8) providing compounds with molecular weights ranging from 556 to 564 amu. The dimer of linoleic acid has found wide applicability in a range of commercial products, including cosmetics and industrial lubricants (9). It has been shown to reduce corrosion (10) and improve the lubricity (11) of crude and refined oils. In military aviation fuels, it is added to reduce the wear in roller bearings in the fuel pumps and also reduce corrosion in the fuel system tubing. Given its important function in the fuel system, analysis of fuels for their CI-LI content has become more important.

High performance liquid chromatography (HPLC) has been an important tool for the analysis and characterization of fuel samples (12). The method has been shown to group components conveniently into nonpolar and polar components. However, it does not provide an analysis of the specific contaminants in the sample. Liquid chromatography–electrospray ionization mass spectrometry (LC–ESI-MS) has been used in the analysis of specific polar components in fuels (13). Electrospray ionization is especially convenient as a soft ionization method that does not ionize the nonpolar components of the fuel sample (14). The negative ion mode is particularly useful, because of the common polar impurities only the phenols appear as negative ions under normal conditions. The dimer acid ionizes efficiently in negative ion mode. In addition, the high molecular weight of the dimer acid also separates it from the common phenols found in fuels.

In this study, we describe a simple method for the determination of CI-LI in aviation fuels using HPLC with ESI-MS detection. The method requires no sample preparation beyond dilution in methanol, provides a reproducible linear calibration curve, and suffers from few interferences. The method is demonstrated for the analysis of CI-LI in a series of fuel samples.

Samples of eight different CI-LI additives approved for use in JP-8 fuels and several fuel samples containing CI-LI additives were supplied by the Fuels branch at Wright Patterson Air Force Base in Dayton, Ohio. The HPLC–ESI-MS system used for the current study was an Agilent 1200 series liquid chromatography–mass spectrometry system.
Results and Discussion

HPLC chromatograms of fuel samples containing the CI-LI additive show a single major peak at a retention time of 0.9 min with a very weak broad feature at 1.2–2.3 min (Figure 1). The majority of the polar components are contained in the sharp peak at 0.9 min; however, the CI-LI additive appears in the broad later peak. The principal components observed in negative ion mode are phenols and carboxylic acids that form negative ions by losing a hydrogen ion in electrospray ionization (15). To identify the main component in the CI-LI additive, the LC–MS chromatogram of all of the commercial additives was examined. The total ion chromatogram (TIC) shows a sharp peak at 0.9 min with a broad peak at 1.2–2.3 min. The peak at 0.9 min is because of polar components in the additive carrier. The broad feature between 1.2 and 2.3 min is because of the dilinoleic acid components in the additive. The TIC and extracted ion chromatograms (EIC) for various components are shown in Figure 2.

Figure 2: Total ion chromatogram and the selected ion chromatograms for several components of the CI-LI additive.

Figure 3: Compounds formed from the dimerization of linoleic acid with clay catalysis: (a) acyclic, (b) monocyclic, and (c) bicyclic dilinoleic acid structures. The structures may contain additional double bonds.

Figure 4: The mass spectrum of a CI-LI additive (top) and an expansion of the region around 560 amu (bottom).
Figure 5: Calibration curves for the determination of CI-LI additive in a fuel sample.

Table I: Molecular weights, structures (Figure 3) for the components of dilinoleic acid in CI-LI additives

<table>
<thead>
<tr>
<th>Formula</th>
<th>Molecular Weight (Calculated)</th>
<th>Molecular Weight Based on M+ peak (Measured, Average of Eight Chromatograms)</th>
<th>Structure</th>
<th>Additional Double Bonds</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_{38}H_{60}O_{14}</td>
<td>564.5118</td>
<td>564.5108</td>
<td>Acyclic</td>
<td>0</td>
</tr>
<tr>
<td>C_{38}H_{60}O_{14}</td>
<td>562.4961</td>
<td>562.4944</td>
<td>Acyclic Monocyclic</td>
<td>1 0</td>
</tr>
<tr>
<td>C_{38}H_{60}O_{14}</td>
<td>560.4805</td>
<td>560.4795</td>
<td>Acyclic Monocyclic</td>
<td>2 1</td>
</tr>
<tr>
<td>C_{38}H_{60}O_{14}</td>
<td>558.4648</td>
<td>558.4635</td>
<td>Acyclic Monocyclic Bicyclic</td>
<td>3 2 0</td>
</tr>
<tr>
<td>C_{38}H_{60}O_{14}</td>
<td>556.4492</td>
<td>556.4484</td>
<td>Monocyclic Bicyclic</td>
<td>3 2</td>
</tr>
<tr>
<td>C_{38}H_{60}O_{14}</td>
<td>554.4335</td>
<td>554.4328</td>
<td>Monocyclic</td>
<td>4 3</td>
</tr>
<tr>
<td>C_{38}H_{60}O_{14}</td>
<td>552.4179</td>
<td>552.4162</td>
<td>Bicyclic</td>
<td>4</td>
</tr>
</tbody>
</table>

Table II: CI-LI determination for several jet fuel samples (sample A is not formulated to include CI-LI and is included for reference)

<table>
<thead>
<tr>
<th>Fuel Sample Identifier</th>
<th>Fuel Type</th>
<th>CI-LI Content (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>JP-8</td>
<td>&lt;0.2</td>
</tr>
<tr>
<td>B</td>
<td>JP-8</td>
<td>10.2</td>
</tr>
<tr>
<td>C</td>
<td>JP-8</td>
<td>12.6</td>
</tr>
<tr>
<td>D</td>
<td>JP-8</td>
<td>14.3</td>
</tr>
<tr>
<td>E</td>
<td>JP-8</td>
<td>11.4</td>
</tr>
<tr>
<td>F</td>
<td>JP-8</td>
<td>14.9</td>
</tr>
<tr>
<td>G</td>
<td>JP-8</td>
<td>15.5</td>
</tr>
</tbody>
</table>

Conclusions

The use of high performance liquid chromatography with time-of-flight mass spectrometry detection for the determination of dilinoleic acid as a corrosion inhibitor and lubricity increasing additive shows good linearity and day-to-day reproducibility. The high resolution of time-of-flight mass spectrometry ensures that other possible components of the fuel do not interfere significantly with the determination of the active component of the additive. The analysis is complicated by the complex nature of petroleum-based fuels and the distribution of molecular weights and structures associated with the available dilinoleic acid-based additives. For aircraft fuels without sample preparation beyond dilution with methanol, the detection limit is 0.3 mg/L. Solid-phase extraction techniques are used in sample preparation, a significantly lower detection limit is achievable.

Acknowledgments

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