Matrix optimization for the MALDI-TOF-MS analysis of trace biodiesel components

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Overview

- Coal weathering explosively is a blessing in expanding the use of biodiesel. At low temperatures, biodiesel can form precipitates, thought to be complex mixtures of trace components.
- Previously, trace components were problematic to characterize because of the complex nature of the fuel.
- The optimized MALDI TOF method was designed to circumvent problems encountered with traditional analyses.
- The optimized matrix system was hypothesized to be a "stabilizer" matrix for isolating the range of trace compounds in biodiesel.
- Standards and mixtures of standards were analyzed to represent the range of compounds present in biodiesel.
- Optimized MALDI TOF analysis can be used as a high-throughput fuel screening tool.
- TOF/TOF mass analysis can be performed to verify peak assignment of compounds present in samples and neat fuels.

Experimental

- Standards of mono-, di-, and triacylglycerides were obtained, as well as standards of free steroids and sterol glucosides representative of compounds present in trace components in biodiesel.
- Samples of standards were analyzed first with traditional matrix systems, then with matrices themselves. A mixed system was explored because of its proven potential to isolate certain analytes more effectively. After several mixtures were tested, an optimized system was chosen.
- The optimized mixture consisted of approximately equal parts of 2.5 dicyclohexylamine oxalate (DCIOx), dithranol, and quinine-6-hydroxy-camphor (QHC). Precise work with phospholipids indicated that sample treatment with NaI promotes the formation of soluted ions and increases the sensitivity and S/N ratio of the measurement. Sodium iodide was added to the matrix and individual matrix systems to determine its effect on ionization.
- A mixture of the aforementioned compounds was then analyzed to ensure isolation of all of the components. The data from the optimized system mixture analysis was also compared with traditional matrices.
- To confirm peak identities, TOP TOF collision-induced dissociation experiments were performed.

Figure 1. The spectra above are of monoacrylate (A) and dimyristate (B) analyzed with NaI-doped HCCA and NaI-doped optimized matrix mixture (blue and black, respectively). The isolated ions are atomic from the spectra obtained with only HCCA and NaI.

Figure 2. Shown above is the spectrum of the analysis of a seven-component mixture with the optimized NaI-doped matrix. The components (listed above) were all successfully isolated and analyzed.

Conclusions

- With the use of an optimized mixed matrix system, it is possible to characterize trace biodiesel components in one rapid analysis.
- The use of MALDI-TOF-MS circumvents complications arising from complex separation techniques and has a high throughput, allowing many samples to be analyzed and compared in one experiment.
- The mixed optimized matrix when doped with NaI has a higher sensitivity than doped and undoped pure matrices.
- Tandem MS can be employed in complex mixtures to confirm peak identities.

References


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