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

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Overview

- Cold weather operability is a limiting factor 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 "catch-all" matrix for ionizing 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 mixtures and neat fuels.

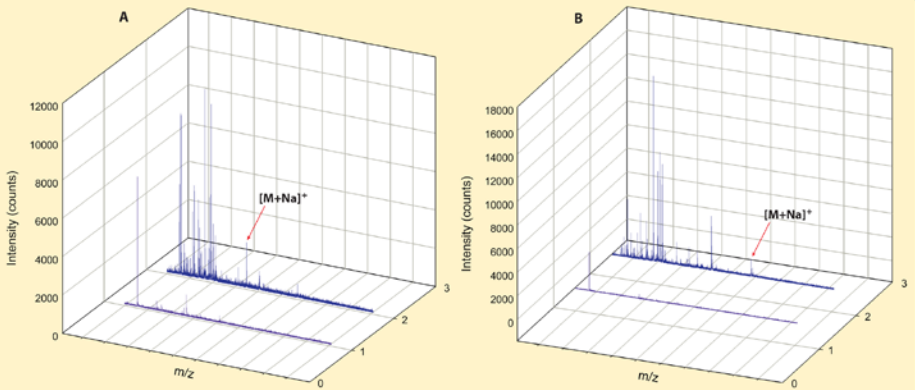


Figure 1. The spectra above are of monostearin (A) and distearin (B) analyzed with NaI-doped HCCA and NaI-doped optimized matrix mixture (front and back, respectively). The sodiated ions are absent from the spectra obtained with only HCCA and NaI.

Experimental

- Standards of mono-, di-, and triacylglycerides were obtained, as well as standards of free sterols and sterol glucosides representative of compounds present as trace components in biodiesel.
- Samples of standards were analyzed first with traditional matrix systems, then with mixtures thereof. A mixed system was explored because of its proven potential to ionize certain analytes more effectively.[1] After several mixtures were tested, an optimized system was chosen.
- The optimized mixture consisted of approximately equal parts of 2,5 dihydroxybenzoic acid (2,5 DHB), dithranol, and α-cyano-4-hydroxy-cinnamic acid (HCCA). Previous work with phospholipids indicated that sample treatment with NaI promotes the formation of sodiated ions and increases the sensitivity and S/N ratio of the measurement.[2] Sodium iodide was added to the mixed and individual matrix systems to determine its effect on ionization.
- A mixture of the aforementioned compounds was then analyzed to ensure ionization of all of the components. The data from the optimized system mixture analysis was also compared with traditional matrices.
- To confirm peak identities, TOF-TOF collision-induced dissociation experiments were performed.

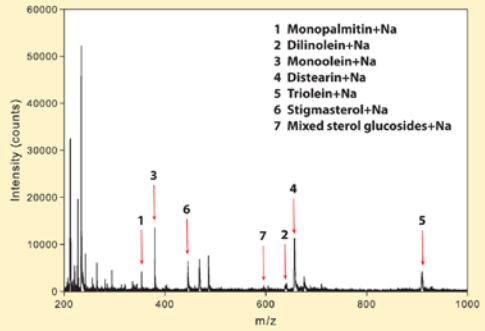
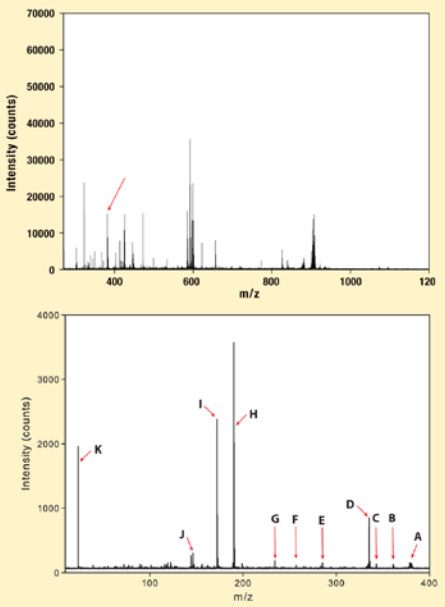


Figure 2. Shown above is the spectrum of the analysis of a seven-component mixture with the optimized NaI-doped matrix. The components (listed above) were all successfully sodiated and analyzed.



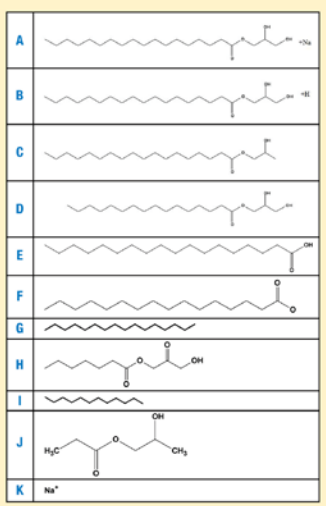


Figure 3. The spectrum (above left) monostearin selected from the monoacylglyceride "region" of the spectrum. The monostearin was then extracted for CID analysis, resulting in the observed fragmentation spectrum (bottom left). The peaks labeled A-K are identified in the table at right.

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

(1) S. Laugesen and P. Roepstorff. Combination of Two Matrices Results in Improved Performance of MALDI-MS for Peptide Mass Mapping and Protein Analysis, *Journal of the American Society for Mass Spectrometry*, 2003, 14, 992-1002.

(2) Y. Isahida, A.J. Madonna, J.C. Rees, M.A. Meetani and K.J. Voorhees, Discrimination of Enterobacteriaceae based on Spectral Patterns of Phospholipids using MALDI-TOF/MS Combined with On-Probe Sample Pretreatment, *Rapid Commun. in Mass Spectrom.*, 2002, 16, 1877.

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