

COMPARISON OF NITRO-POLYCYCLIC AROMATIC HYDROCARBON LEVELS IN CONVENTIONAL DIESEL AND ALTERNATIVE DIESEL FUELS

Crystal D. Havey¹, R. Robert Hayes², Robert L. McCormick³, and Kent J. Voorhees¹

¹Colorado School of Mines, Department of Chemistry and Geochemistry, 1500 Illinois St, Golden, CO 80401

²Renewable Fuels and Lubricants Research Laboratory, National Renewable Energy Laboratory, 1980 31st St., Denver, CO 80216

³Center for Transportation Technologies and Systems, National Renewable Energy Laboratory, 1617 Cole Blvd., Golden, CO 80401

Introduction

Use of alternative fuels for diesel engines, such as synthetic diesel and biodiesel, has the potential to reduce petroleum consumption and thus dependence on foreign imports. If the alternative fuels are produced from highly renewable sources, they lower life-cycle greenhouse gas emissions. They are also known to cause a significant reduction in certain regulated pollutant emissions: CO, NO_x, hydrocarbons, and particulate matter (PM). Ideally these emissions reductions will correspond to a decrease in the environmental risks and health hazards associated with diesel engine exhaust. Compounds, such as nitro-polycyclic aromatic hydrocarbons (NPAHs), while unregulated, are also known to pose health and environmental hazards. Measurement of the levels of NPAHs in exhaust from alternative and conventional fuels allows for evaluation of alternative fuel usage effects on emission of these unregulated toxic compounds.

Negative ion chemical ionization (NICI) has been used for the detection of NPAHs in diesel soot.¹ In NICI analysis, both solid phase extraction and LC fractionation were necessary to obtain desired results. A novel ionization source containing a trochoidal electron monochromator has been developed previously² and has been used here for analysis of diesel fuel emissions. This source allows for both electron capture and dissociative electron capture to be carried out using very controlled electron energies ($\pm 0.3\text{eV}$). NPAHs have a strong ability to undergo electron capture at near-0eV producing molecular ions, and can also be subject to dissociative electron capture at 3.5eV producing an NO₂⁻ fragment.

Incorporation of the trochoidal electron monochromator source into a mass spectrometer system creates a sensitive and selective technique for detection of NPAHs in complex matrices. The high selectivity of the electron monochromator-mass spectrometer (EM-MS) allowed for minimal sample cleanup in order to achieve desired results. Comparisons will be presented of the NPAH content, as measured by EM-MS, in the emissions produced from a modern production diesel engine running on conventional and alternative diesel fuels.

Experimental

Diesel Samples. Test fuels presented here include a conventional diesel fuel and a 50% blend of biodiesel and conventional diesel. The fuels were run in a 2002 Cummins ISB 300 engine. It is a modern engine with cooled-EGR, high-pressure common rail injection, and a variable geometry turbocharger designed to meet the EPA 2004 regulated emissions requirements. The engine was run on the federal Heavy-Duty Transient Cycle, which is used for EPA certification of engines. The PM was collected onto 47mm Teflon-coated glass fiber pads located in line.

Sample Extraction and Cleanup. Internal standards (1-nitronaphthalene-d₇, 4-nitrobiphenyl-d₉, 1,5-dinitronaphthalene-d₆, 9-

nitroanthracene-d₉, 3-nitrofluoranthene-d₉ from CDN Isotopes, Pointe-Claire, Quebec, Canada and 1-nitropyrene-d₉ from Cambridge Isotope Laboratories, Andover, MA) were spiked onto the filter pads of certain samples for quantitative purposes. The PM was extracted off of the filter pads using dichloromethane (Mallinckrodt Ultimar universal grade, Phillipsburg, NJ). The samples were placed on a shaker table for one hour. Once the filter was removed from the sample solution, hexane (HPLC grade, Mallinckrodt, Phillipsburg, NJ) was added to create a 20:80 dichloromethane:hexane mix. Solid phase extraction was carried out on aminopropyl solid phase cartridges (Alltech Assoc., Inc., Deerfield, IL), with the 20:80 mix driving polar interferences from the sample onto the phase.¹ The samples were then concentrated down to approximately 100 μL , using toluene (HPLC grade, Mallinckrodt, Phillipsburg, NJ) as a keeper.

Instrumentation. A JEOL MStation JMS-700T mass spectrometer equipped with a JEOL trochoidal electron monochromator ionization source was used for all analyses. For each sample, one microliter was injected onto a Hewlett Packard 6890 Series GC system, equipped with an on-column injection port. A 30m RTX-5Sil MS column (Restek Corp, Bellefonte, PA), i.d. 0.25mm, was used to obtain desirable separation of the NPAHs. EM-MS analysis was carried out using selected ion monitoring (SIM) of m/z 46 for the NO₂⁻ fragment at 3.5eV for identification of each compound by retention time. SIM monitoring of the molecular ions at near-0eV was used for confirmation of the individual compounds.

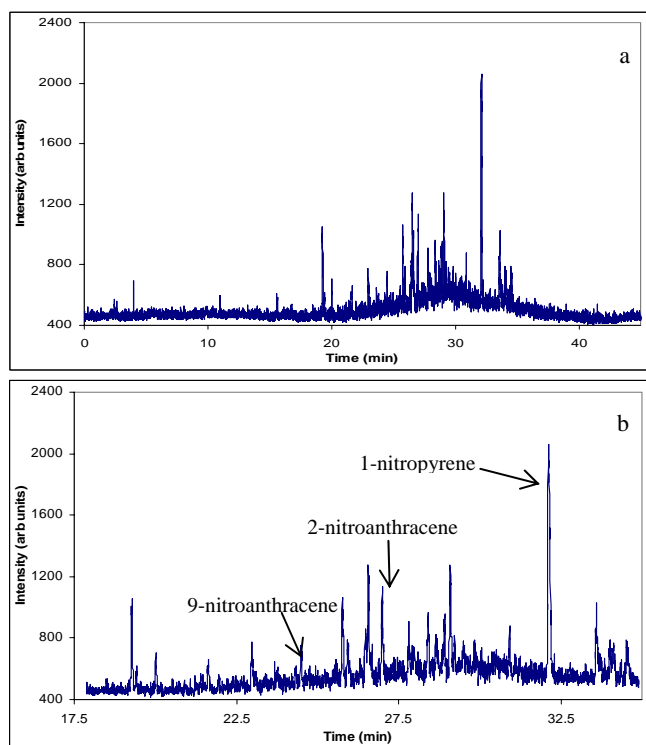


Figure 1. SIM chromatogram (m/z 46) of a conventional diesel sample a) full scale and b) expanded for detail.

Results and Discussion

Results obtained for conventional and biodiesel samples are presented here. Figure 1 shows a SIM chromatogram of m/z 46 of a conventional diesel sample (no internal standards were used). Peaks of 2-nitroanthracene, 9-nitroanthracene, and 1-nitropyrene have been identified based on retention times. Further analysis of the molecular ions (Figures 2 and 3) confirmed these assignments.

Figure 2 also contains indications of other nitroanthracene isomers and/or isomers of nitrophenanthrene.

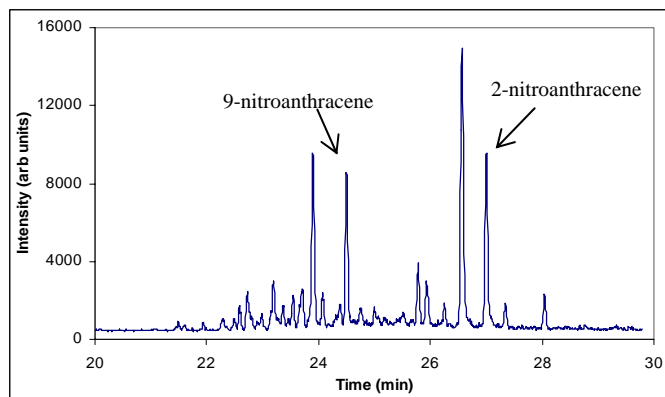


Figure 2. SIM chromatogram (m/z 223) of a conventional diesel sample.

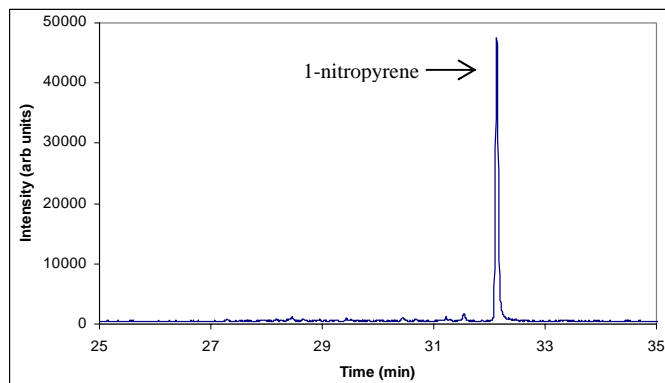


Figure 3. SIM chromatogram (m/z 247) of conventional diesel sample.

An m/z 46 SIM chromatogram of a biodiesel sample (with internal standards) is shown in Figure 4. The 6 large peaks in the chromatogram are the internal standards. No other peaks were observed at a detectable level. These results are very preliminary and additional analyses need to be conducted in order to be conclusive of these observations. It is possible that NPAHs potentially present in the sample are being masked by the internal standards. Adjustment of internal standard content as well as concentration is under review to optimize the use of the internal standards.

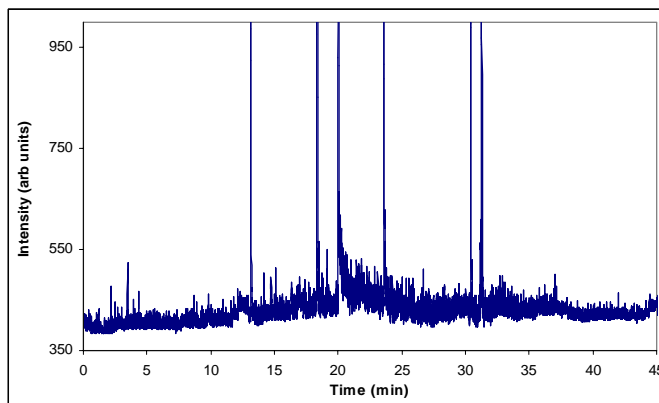


Figure 4. SIM chromatogram (m/z 46) of biodiesel sample.

Conclusions

Preliminary studies of NPAH content in conventional and biodiesel emissions have been compared. The use of an electron monochromator as the ionization source for the mass spectrometer allowed for minimal sample cleanup in order to obtain results with little interference. Further work is being conducted on a gas to liquids (GTL) synthetic diesel fuel made by the Fischer-Tropsch (FT) process and blends with various levels of FT fuel combined with more conventional refinery diesel fuel. Qualitative and quantitative comparisons will be made of all samples to provide insight on the effect of alternative fuels on production of NPAHs in diesel emissions.

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References

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