



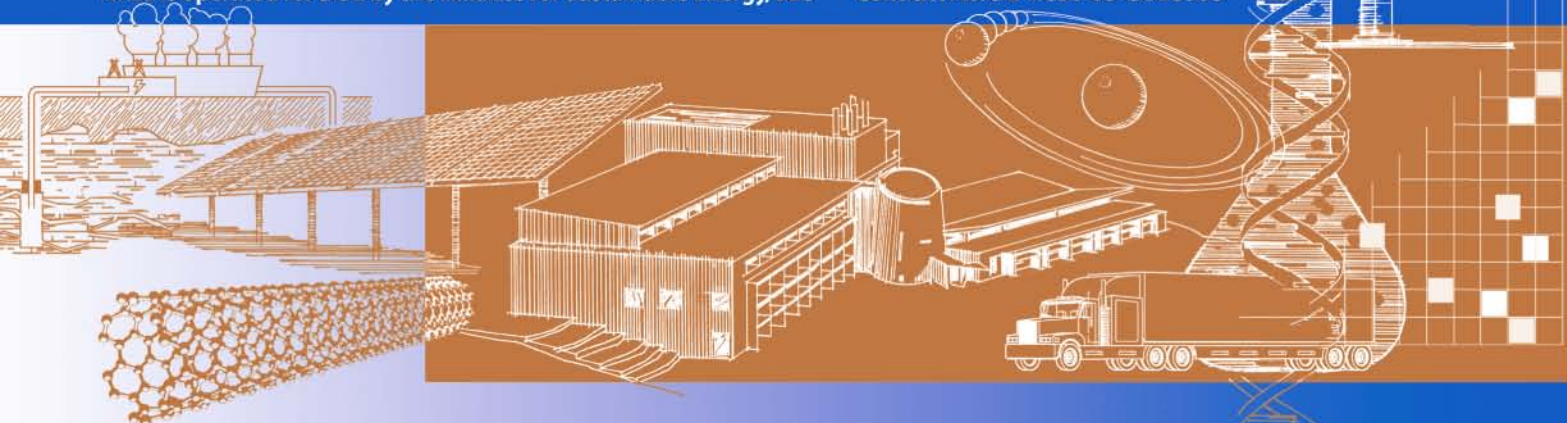
Investigation of Nitro-Organic Compounds in Diesel Engine Exhaust

Final Report
February 2007 – April 2008

John Dane and Kent J. Voorhees
Colorado School of Mines
Department of Chemistry and Geochemistry
Golden, Colorado

Subcontract Report
NREL/SR-540-45597
June 2010

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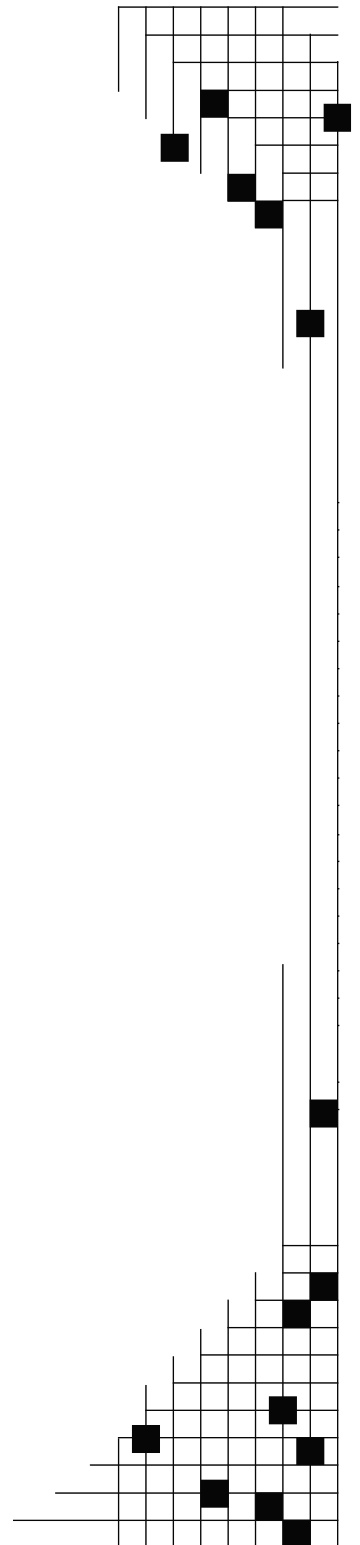
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Executive Summary

Diesel particle filters (DPF) dramatically reduce the level of particulate matter (PM) emitted by diesel engines. There has not, however, been much research to verify that unregulated organic pollutants associated with diesel PM are also reduced by the use of DPFs. The U.S. Department of Energy's National Renewable Energy Laboratory recently upgraded its ReFUEL engine and vehicle testing facility's capabilities to speciate unregulated gas-phase emissions. To complement this capability, the laboratory contracted with the Colorado School of Mines to study the effects of soy biodiesel fuel and a DPF on emissions of polycyclic aromatic hydrocarbons (PAH) and nitro-polycyclic aromatic hydrocarbons (NPAH). These are related types of harmful but unregulated emissions associated with PM from diesel engines.

In this study, the Colorado School of Mines developed procedures to sample diesel PM emissions from raw and diluted exhaust, with and without a DPF. They also developed improved procedures for extracting PAH and NPAH from the PM and quantifying those compounds with a gas chromatograph-electron monochromator mass spectrometer. While the study found the DPF generally reduced PAH emissions by 1 to 3 orders of magnitude, PAH conversion was lowest in the case of B100, suggesting that PAHs were actually being formed in the DPF. This finding warrants further investigation.

Orders of magnitude reductions were also generally found for NPAH emissions exiting the DPF. However, the conversion of 1-nitropyrene through the DPF was less than 50% for all fuels. Because 1-nitropyrene has been shown to be mutagenic and carcinogenic, and because the DPF may concentrate condensable organics on a larger number of smaller particles, this could be a very significant concern. Differences in NPAHs between raw and dilution-tunnel PM samples suggest that chemical reactions continue through the raw exhaust system or occur during dilution. The apparent net effect is to reduce the diversity of NPAH compounds and in particular increase the amount of 1-nitropyrene.

Acronyms and Abbreviations

AVL	powertrain engineering and test equipment manufacturer
B100	100% biodiesel diesel fuel
B20	20% biodiesel diesel fuel
Cert	certification diesel fuel
CSM	Colorado School of Mines
DCM	dichloromethane
DNPH	dinitrophenyl hydrazine
DOC	diesel oxidation catalyst
DPF	diesel particle filter
DPF-out	exhaust down-stream of installed DPF
ECD	electron capture detectors
EI	electron ionization
EI-	negative ion electron ionization
EI+	positive ion electron ionization
EM	electron monochromator
EM-MS	electron monochromator mass spectrometry
Engine-out	exhaust without DPF installed
EPA	Environmental Protection Agency
FAME	fatty acid methyl ester
GC	gas chromatography
GC/EM-MS	GC-MS instrument including trochoidal EM
GC-MS	gas chromatograph-mass spectrometry
HPLC	high-pressure liquid chromatography
JEOL	EM-MS instrument manufacturer
MFC	mass flow controller
NCI	negative-ion chemical ionization
NIST	National Institute of Science and Technology
NPAH	nitro-polycyclic aromatic hydrocarbons
NREL	National Renewable Energy Laboratory
PAH	polycyclic aromatic hydrocarbons
PM	particulate matter
PTFE	polytetrafluoroethylene
ReFUEL	NREL's Renewable Fuels and Lubricants Laboratory
Rel Int	relative intensity
SIM	selected ion monitoring
SPE	solid-phase extraction
TIC	total ion current
URG	Name of PM filter-holder vendor

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1. Introduction

The National Renewable Energy Laboratory (NREL) Renewable Fuels and Lubricants (ReFUEL) facility is an established leader in the field of advanced heavy-duty diesel vehicle and engine testing. The rapid development of advanced combustion cycles, exhaust aftertreatment systems, and alternative fuels has made it imperative to expand the technical capabilities of this facility for determining whether any of these new technologies have unintended consequences when it comes to the pollutants that are produced in engine exhaust.

One area of particular interest is the generation of nonregulated organic compounds by diesel combustion. These compounds may impact the environment in detrimental ways that are not accounted for by the Environmental Protection Agency (EPA) or the engine manufacturers. Diesel particle filters (DPF) have recently been integrated into all new diesel vehicle exhaust systems to significantly lower the particulate matter (PM) emitted from the engine. This reduction of PM is significant because a number of particularly harmful unregulated pollutants—including analogs of polycyclic aromatic hydrocarbons, the main focus of this study—reside in this phase of the exhaust. As a result, the assumption (without supporting research data) has been that these pollutants are also significantly reduced, particularly since the PM weight is reduced by over an order of magnitude. As for the gas-phase portion of the post-DPF exhaust, the production of unregulated volatile and semi-volatile compounds is also not well understood. Because of this lack of information for both gas and particle phases, there is concern that DPFs or other exhaust aftertreatment technologies could have negative unintended consequences that produce increased levels of nonregulated pollutants.

ReFUEL has recently expanded its capabilities to include monitoring unregulated volatile and semi-volatile pollutants in the engine exhaust gas for both a DPF configuration (termed *DPF-out*) and a non-DPF configuration (termed *Engine-out*). Additionally, the sampling scenario was expanded from diluted exhaust to also include raw exhaust immediately downstream from the engine. The sampling techniques for these configurations utilize evacuated, surface-passivated canisters for hydrocarbons and dinitrophenyl hydrazine (DNPH) cartridges for trapping aldehydes and ketones. The canister samples are then analyzed off-line by gas-chromatograph (GC) mass spectrometry (MS), and the DNPH cartridges are analyzed by high-pressure liquid chromatography (HPLC). The results for these analyses typically focus on volatile and semi-volatile organics that have molecular weights ranging from 30 to 170 amu.

These improvements to the ReFUEL testing capability do not, however, address all potential diesel pollutants. Parallel to these gas-phase efforts, NREL subcontracted the Colorado School of Mines (CSM) Mass Spectrometry Laboratory to research the nonregulated pollutants found in the particle phase produced from both non-DPF and DPF exhaust configurations. Initially, the goal for this research was to develop PM sampling and sample preparation extraction techniques that focused on nitro-polycyclic aromatic hydrocarbons (NPAH). Subsequently, the research expanded to also include identifying all non-nitrated polycyclic aromatic hydrocarbons (PAH) present in the PM. The objective was to develop a clearer understanding of the connection between these closely related classes of compounds by generating both PAH and NPAH data for each sample. Furthermore, the CSM research would demonstrate the versatility of a specialized GC-MS instrument that features a unique trochoidal electron monochromator (EM). This instrument (termed *GC/EM-MS*) enables highly selective detection of molecules with high

electron affinity, such as NPAHs, which have molecular weights ranging from 123 amu to at least 247 amu. Additionally, PAHs produce strong molecular ion signals during standard electron ionization (EI+), providing easy identifications for these compounds. The PAHs identified during this type of analysis range in mass from 128 amu to at least 202 amu.

The overall scientific goal of the CSM research, in conjunction with the ongoing research conducted at NREL, was to develop a more comprehensive characterization of the organic compounds present in heavy-duty diesel engine exhaust. Additionally, this information includes the determination of the chemical changes brought about by the use of different fuel blends (certification diesel, B20 diesel, and B100 diesel) and the use of a DPF during an advanced combustion test cycle. In particular, the DPF-out data would provide new information to a portion of the exhaust, particularly for the particle phase, that has not been well characterized in previous research.

This report covers all of the research that was conducted during the CSM subcontract period from February 2007 through April 2008. Section 2 discusses the GC/EM-MS utilized during the research and provides background information for this system. Section 3 discusses preliminary experiments that were conducted to determine the best PM collection filter, extraction techniques, and evaporation techniques. Section 4 provides a discussion of the results from both the raw and dilute exhaust PM samples. The final section discusses conclusions derived from this research project.

2. GC/Electron Monochromator-Mass Spectrometry

2.1 Background

Over the last 15 years, EM-MS has gained considerable interest for detecting electrophilic compounds because it offers the ionization stability of electron capture detectors (ECD) and the mass spectral information produced by negative-ion chemical ionization (NCI)-MS. Furthermore, EM-MS has the capability of controlling the ionization fragmentation that occurs for a given electrophilic analyte, which adds a degree of selectivity and specificity that is not realized by either ECD or NCI-MS. A schematic for the underlying design of the EM system is shown in Figure 2-1.

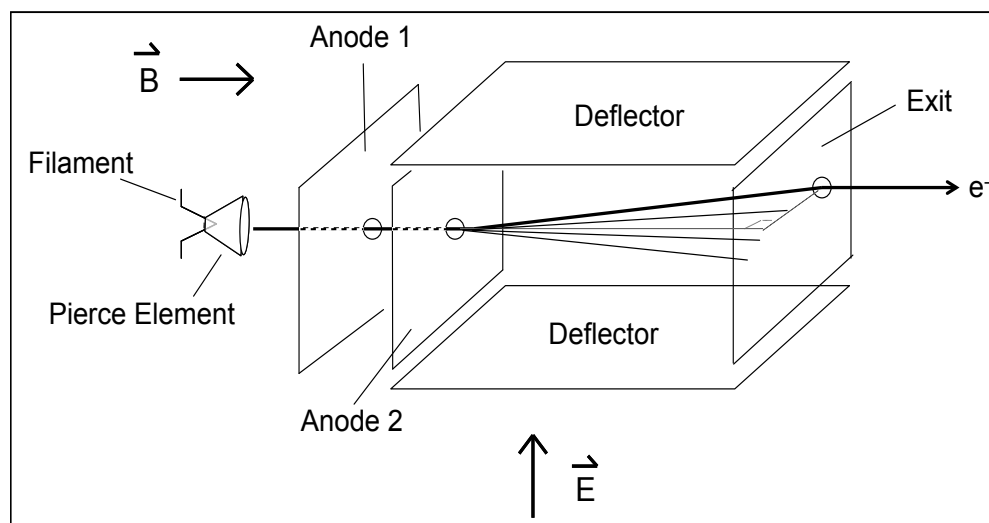
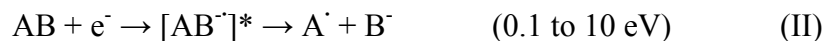


Figure 2-1. Schematic of trochoidal electron monochromator

This EM design works by using electrons emitted from a standard tungsten filament and focusing them using a Pierce element (a cone-shaped region) into an anode region that further collimates the electrons into a deflection region. The deflector region is defined by crossed magnetic (B) and electric fields (E), which cause the electrons to move with a trochoidal (spiraling) motion.¹ The magnetic field remains stationary, so the electron energy separation is made by adjusting the electric field settings. When these settings are adjusted, each electron in the beam is deflected at a right angle to both fields (magnetic and electric) according to their kinetic energy. When the magnitude of these electron deflections are controlled using the electric field parameters, only electrons with a particular kinetic energy are emitted through the offset exit aperture. This results in an electron beam energy (used for ionization) that can be precisely controlled to within 0.4 eV with beam intensities only slightly below those observed for conventional electron ionization (EI) sources.²

When the EM is set for low-energy (0–10 eV) ionization, the net effect is the capture of an electron of the proper energy, termed *resonance energy*, by electrophilic compounds. There are two types of electron capture processes utilized for the analysis of electrophilic compounds. The first ionization process is described as pure electron capture using an electron energy of ~ 0 eV (Equation I). The second ionization process is called *dissociative electron capture* and utilizes electron energies that can range from 0.1 to 10 eV (Equation II). In this scenario, the electron is

captured by the molecule but then imparts enough energy into the molecule to induce fragmentation in very specific ways, depending on the molecular constituents and the energy chosen for ionization.



By combining the EM-MS with a GC, this technique has the capability of producing data that contains molecular mass information, selected ion data for the controlled formation of fragment ions from specific functional groups, and GC retention time information.

Of particular importance to NPAH analysis is the fact that nitro-aromatic compounds produce nitro group anions (m/z 46) using the dissociative resonance energy of ~ 3.5 eV.³ This particular ion is *unique* in negative ion analysis, which allows for the differentiation of nitro-containing compounds from the background. Once the presence of these compounds is confirmed, the ionization energy is then lowered to ~ 0 eV, and the molecular radical anion is produced for further identification. Using GC/EM-MS allows a selective (EM ionization energy selection), specific (nitro group anion uniqueness), and sensitive technique to be created for NPAH analysis. Additionally, the GC/EM-MS offers the versatility of generating positive ion electron ionization (EI+) by simply increasing ionization energy to 25 eV, enabling the analysis of other nonelectrophilic compounds such as PAHs in this research.

2.2 Instrumentation

A JEOL trochoidal EM interfaced to a JEOL MStation JMS-700T high-resolution magnetic sector mass spectrometer equipped with an Agilent 6890 GC was used for all spectrometric analyses. The EM system can generate ionization energies from 0 to 25 eV with a resolution of ± 0.4 eV. Electron energy resolution and tuning for negative ion analysis were conducted using nitrobenzene as the calibration standard. Perfluorokerosene was used as the ionization energy calibration standard for all positive ion analyses. Each nitro-aromatic compound detected in the PM samples was identified through selected ion monitoring (SIM) of the m/z 46 ion and the molecular ions, while each PAH was identified through SIM of their molecular ions.

The Agilent 6890 GC had an on-column injection port installed that was programmed to remain 3°C above the GC oven temperature throughout each analysis. With the utilization of this on-column injection system, the choice was made to use an Integra-Guard RTX-5Sil MS analytical column (30 m x 0.25 mm ID x 0.25 μ m). This type of GC column has an integrated 10 m guard column that protects the analytical portion of the column from the needle and the liquid samples, which can greatly accelerate the deterioration of the column phase. For each sample analysis, the GC oven was programmed using the following temperature profile:

Isothermal at 100°C for 1 min
Programmed at 10°C/min to 190°C
Isothermal at 190°C for 2 min
Programmed at 5°C/min to 240°C
Isothermal at 240°C for 1 min
Programmed at 10°C/min to 310°C
Isothermal at 310°C for 2 min.

3. Method Development

3.1 Filter Experiments

During the early stages of the CSM project, a PM sampling filter was chosen that had two features. First, the filter had to be robust enough to handle an extraction utilizing dichloromethane. Second, based on the early direction of the research toward raw exhaust sampling, the filter had to withstand much higher temperatures than the typical 150°C–220°C dilution-tunnel temperatures. As a result, work was done to find an optimal filter to satisfy these two constraints.

As a starting point, Pall Teflo filters (Pall part R2PL047) were tested because they were the filter of choice for gravimetric PM testing at the ReFUEL laboratory. However, these filters are typically used for collecting PM during dilution tunnel experiments and consist of a polymethylpentene outer ring with a polytetrafluoroethylene (PTFE) filter through the middle (47 mm diameter, 1 μm pore size). The problems with these filters were twofold in that they cannot withstand dichloromethane extraction (see Figure 3-1) and, according to the manufacturer, PTFE filters are typically useful up to no more than 220°C. Based on this information, other types of filter membranes were investigated.



Figure 3-1. Teflo filter (a) before and (b) after dichloromethane extraction
(Credit: John Dane, Colorado School of Mines; used with permission)

The best fit for the CSM project was determined to be 47 mm Pall Tissuquartz heat-treated filters (Pall part 7202). These filters are composed of pure quartz fibers, do not contain binder, and have been heat-treated to remove all organic contaminants. Because of these attributes, they provided the best option for withstanding both the dichloromethane solvent extraction and the high raw exhaust temperatures (up to 1100°C with flow rates as high as 73 L/min/cm²) while providing a clean substrate for collecting the PM. Additionally, the Tissuquartz filters efficiently collect 99.9% of all particles with $\geq 0.3 \mu\text{m}$ diameter, which is also an improvement over the 1 μm capacity of the Teflo filters. Follow up solvent tests showed that these filters were impervious to degradation during extraction with dichloromethane. Furthermore, these

extractions showed that the filters were indeed free of contaminants detectable by GC/EM-MS. As a result, no pre-extraction was necessary prior to their use for sampling diesel exhaust.

3.2 PM Filter Conditioning and Weighing

The ReFUEL facility has a dedicated clean room/environmental chamber. It is a Class-1000 clean room with precise control over the temperature and humidity (temperature: $22^{\circ}\text{C} \pm 1^{\circ}\text{C}$ and dew point: $9.5^{\circ}\text{C} \pm 1^{\circ}\text{C}$). This room was used for all filter handling, conditioning, and weighing during this research. The Sartorius SC2 microbalance found within the lab features a readability of $0.1 \mu\text{g}$ (a federal requirement) and features static control, a barcode reader for filter identification and tracking, and a computer interface for data acquisition. This balance is installed on a specially designed table that eliminates variation in the measurement due to vibration. Additionally, the features of this clean room were designed to ensure that the room's air flow is compatible with the microbalance. Figure 3-2 contains photographs of the laboratory and the microbalance.



Figure 3-2. Photographs of the clean room exterior and the microbalance (Credit: NREL ReFUEL Laboratory photos)

All of the Tissuquartz filters were placed into separate petri dishes and allowed to equilibrate overnight to the clean room environment. The method for handling and weighing the filters was as follows:

1. Weigh a warm-up filter with similar weight to sample filters
 - Repeat until there is 0.0025 mg agreement between subsequent weighings
 - This step is used to warm up the microbalance electromagnetic coil
2. Once the microbalance is warmed up, weigh a standard calibration weight (100 mg in this case) to determine the absolute accuracy of the balance
3. Weigh a reference filter with a weight similar to that of sample filters
4. Measure two subsequent weights for each Tissuquartz filter
 - Must be 0.0025 mg agreement between these weighings or this step must be repeated
5. Repeat step 4 for next filter
6. After every four measurements (2 samples), the standard 100 mg weight must be measured to ensure balance accuracy
 - The standard deviation of these measurements cannot exceed $0.25 \mu\text{g}$ or all previous weighings must be redone

7. After every eight measurements (4 samples), the reference filter must be weighed to ensure that there are no environmental effects causing changes in filter weights
 - The average change in weight cannot exceed 10 μg or all previous weighings must be redone within that session
8. Repeat steps 4 through 7 until all filter weights have been obtained.

Several important aspects not mentioned above were also a part of the procedure. First, between every weighing, the balance was allowed to sit for 2 minutes before taring it back to zero. Second, the filters were passed through the static control device prior to placing them on the balance. If this step was not included, the microbalance drifted erratically while the filter was on the balance and never settled on a particular weight. Finally, the filter or calibration weight was left on the microbalance for 2 minutes before the value was recorded in the computer. Once each weighing was completed, the filters were placed back in the petri dishes and stored in the clean room until they were utilized for collecting the PM samples.

After testing (sample acquisition), the filters were then allowed to equilibrate in the clean room for a minimum of 1 hour. In most cases, this time period was expanded to overnight (16–20 hours). Once the allotted time had passed, the weighing procedures described above were repeated for these sample filters. The results were then compared with the clean filter weights, and gravimetric data for each PM sample were calculated. Subsequently, the samples were transferred from the ReFUEL facility to the CSM laboratory and stored in a refrigerator until extraction and analysis could be carried out.

During the course of the research, it was determined that the PM samples would require UV protection throughout the process of weighing and transferring the samples from the ReFUEL facility to the CSM laboratory. Nitro-polycyclic aromatic hydrocarbons are susceptible to photodegradation while under UV radiation, so countermeasures had to be taken to protect the integrity of the samples. As a result, several options were investigated to determine the best scenario for protecting these samples. The first course of action was to look at amber petri dishes, which like amber glass, would provide UV protection to the samples. Amber Dynalab petri dishes were the only mass-produced plastic (polystyrene) dishes available in this color. Although these dishes appeared to offer UV protection, the vendor could not guarantee this information. As a result, their UV filtering capabilities were investigated utilizing CSM's Thermo Electron Evolution 300 UV-Visible Spectrometer to scan from 190 nm–1100 nm, which covers the full region of UV and visible radiation.

A comparison of the UV-Vis spectra from the amber jar glass (a traditional UV filter) and the amber petri dish is shown in Figure 3-3. While the petri dishes had the ability to filter the UV C radiation (190–280 nm), the UV A and UV B (280–400 nm) radiation passed through with minimal filtration. Clearly these results showed that this type of petri dish was insufficient for protecting the NPAHs found within the samples. Without other amber petri dish options immediately available, it was decided that for transport purposes, enclosing the petri dishes in a cardboard container would be sufficient for transferring the samples from ReFUEL to CSM.

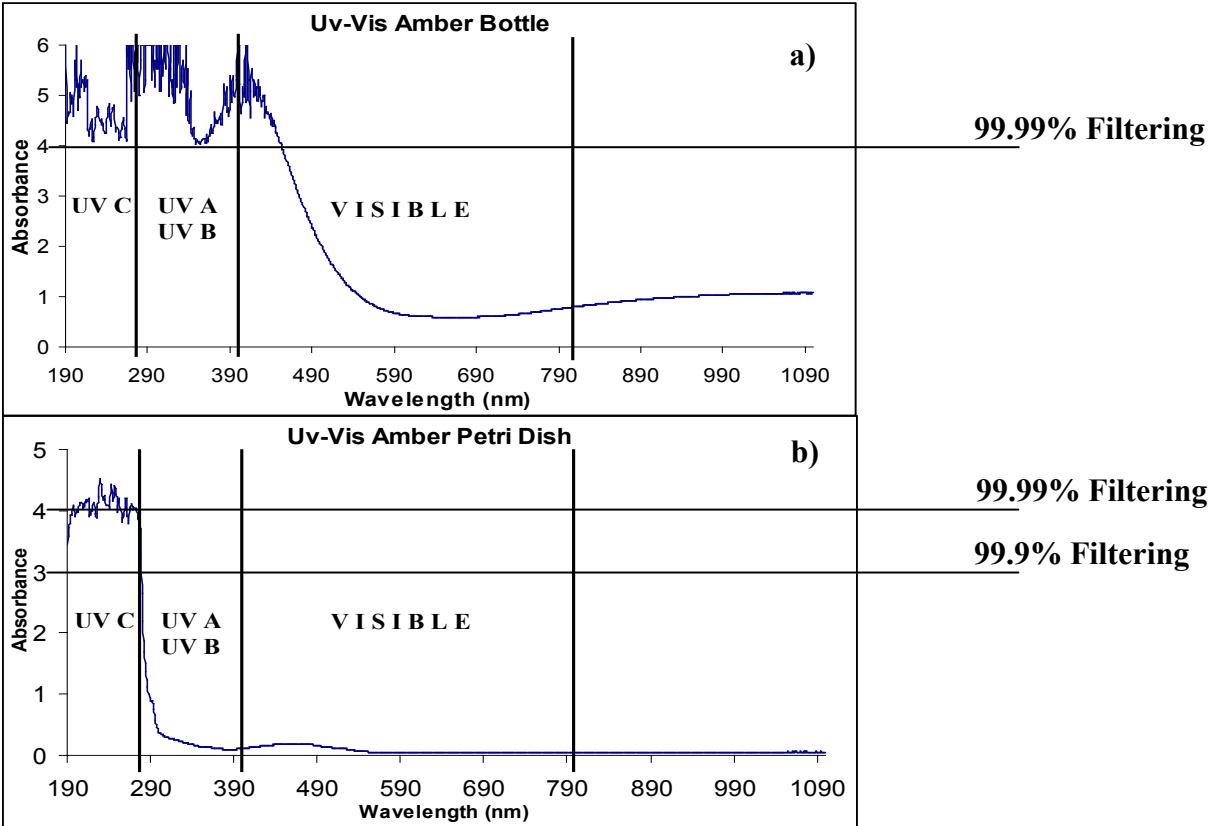


Figure 3-3. UV-visible spectrum for (a) the amber jar glass and (b) the amber petri dish

Because each sample would spend at least a few hours in the clean room prior to and during weighing, the next logical option was to find ways to eliminate the UV radiation inside this room. The best option was to find a UV-filtering acrylic plastic that could be placed over the exterior windows of the room and in front of the lights. A local plastics vendor (Plasticare, Englewood, Colo.) had an acrylic that seemed to offer the best option for accomplishing this goal. This Ultraviolet Filtering Museum Quality Material (Cyro, Rockaway, N.J.) is used by galleries to protect art from UV radiation. The UV-filtering component is fabricated into the acrylic sheets and cannot be scratched off the surface. Additionally, the manufacturer states that this material has the capability of filtering out 98% of the UV radiation. To verify these claims, a small piece of this UV-filtering acrylic was tested in the UV-Vis spectrometer. Figure 3-4 shows the resulting absorbance spectrum.

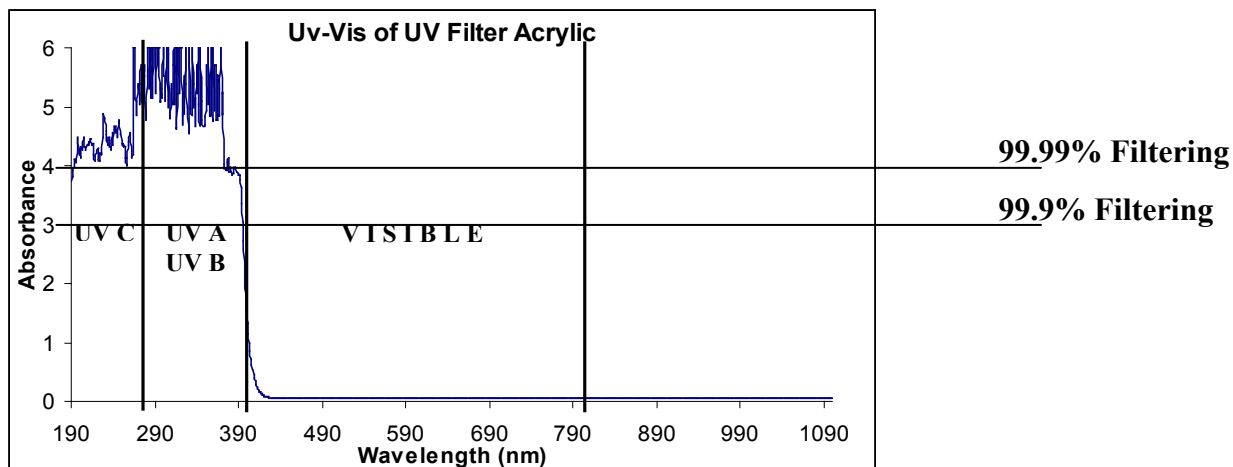


Figure 3-4. UV-Visible spectrum for the UV filtering acrylic

The results above show that this acrylic filters UV radiation to the manufacturer's specifications, if not slightly better. After this analysis, the acrylic was installed over the clean room window, door windows, and overhead lights to prevent the samples from photodegrading while they were in this room. Additionally, because the room was now 98% UV free, special handling procedures were not necessary for transferring the samples to and from the microbalance.

3.3 Solvent Purities

All solvents utilized for extraction and sample analysis were tested for impurities that could produce interfering impurity peaks in the negative ion (0 eV) pure electron capture GC/EM-MS analyses. These solvent tests were critical because every solvent utilized during this research is concentrated from a larger volume (up to 300 mL) to a lower volume (100–200 μ L) at some point during the course of the extraction/cleanup process. As a result, each solvent was tested by concentrating it under flowing nitrogen from the maximum possible volume utilized during sample preparation to 100 μ L. The solvents that showed no interfering impurities during the subsequent GC/EM-MS analyses were these:

- Malinkrodt UltimAR Dichloromethane
- Malinkrodt UltimAR Toluene
- Pharmco/Aaper HPLC/ACS Grade Toluene
- Pharmco/Aaper n-Pentane Trace Grade Pentane.

3.4 PAH and NPAH Standard Studies

A complete range of PAH and NPAH standards that represent the majority of possible compounds found in diesel exhaust PM samples was purchased for this research. Table 3-1 lists the 13 PAH standards that were acquired by CSM during this project. Table 3-2 lists all 58 NPAH standards utilized during the analyses.

Table 3-1. List of PAH Standards

naphthalene	phenanthrene
biphenyl	fluoranthene
acenaphthene	pyrene
acenaphthylene	chrysene
fluorene	benzo[c]phenanthrene
dibenzofuran	benzo[a]pyrene
anthracene	

Table 3-2. List of NPAH Standards

nitrobenzene	5-nitroquinoline	2-nitrodibenzothiophene
2-nitrotoluene	6-nitroquinoline	2,8-dinitrodibenzothiophene
3-nitrotoluene	2-nitrobiphenyl	6-nitro-3,4-benzocoumarin
4-nitrotoluene	3-nitrobiphenyl	2-nitrofluoranthene
2,4-dinitrotoluene	4-nitrobiphenyl	3-nitrofluoranthene
2,6-dinitrotoluene	2,2'-dinitrobiphenyl	1-nitropyrene
2-nitrophenol	2,4'-dinitrobiphenyl	2-nitropyrene
3-nitrophenol	4,4'-dinitrobiphenyl	4-nitropyrene
4-nitrophenol	4,4''-dinitro-p-terphenyl	1,3-dinitropyrene
2,4-dinitrophenol	5-nitroacenaphthene	1,6-dinitropyrene
2-nitro-1-naphthol	2-nitrofluorene	1,8-dinitropyrene
4,6-dinitro-o-cresol	2,7-dinitrofluorene	2,7-dinitro-9-fluorenone
2-nitro-m-xylene	3-nitrodibenzofuran	6-nitrochrysene
4-nitro-m-xylene	2-nitroanthracene	6,12-dinitrochrysene
5-nitro-m-xylene	9-nitroanthracene	7-nitrobenz[a]anthracene
1-nitronaphthalene	9,10-dinitroanthracene	5-nitrobenz[c]phenanthrene
2-nitronaphthalene	3-nitrophenanthrene	1-nitrobenzo[a]pyrene
1,3-dinitronaphthalene	4-nitrophenanthrene	3-nitrobenzo[a]pyrene
1,5-dinitronaphthalene	9-nitrophenanthrene	6-nitrobenz[a]pyrene
1,8-dinitronaphthalene		

Along with the standards shown in Tables 3-1 and 3-2, it was also necessary to obtain PAH and NPAH internal standards that were isotopically labeled. This type of standard is spiked into each sample prior to sample extraction and then used during sample analysis to determine analyte recoveries. Table 3-3 lists the deuterium-labeled PAHs and NPAHs acquired for this project.

Table 3-3. List of PAH and NPAH Internal Standards

PAH	NPAH
naphthalene- <i>d</i> ₈	nitrobenzene- <i>d</i> ₅
acenaphthene- <i>d</i> ₁₀	1-nitronaphthalene- <i>d</i> ₇
phenanthrene- <i>d</i> ₁₀	1,5-dinitronaphthalene- <i>d</i> ₆
anthracene- <i>d</i> ₁₀	4-nitrobiphenyl- <i>d</i> ₉
chrysene- <i>d</i> ₁₂	9-nitroanthracene- <i>d</i> ₉
	3-nitrofluoranthene- <i>d</i> ₉
	1-nitropyrene- <i>d</i> ₉

Next, a 13-component PAH standard test mixture was tested using electron capture (0 eV) negative ion (EI-) analysis and EI+ (25 eV) analysis. The EI- analysis did not show a strong signal for any of the PAHs (3.5 ng), while the EI+ analysis total ion current (TIC) gas chromatogram showed distinctive peaks for each of the 13 PAH compounds (see Figure 3-5) at this same concentration. Each peak is labeled with a number, and the corresponding compound is listed in Table 3-4. The peaks prior to naphthalene are toluene (sample solvent), which was mostly cut from the spectrum by delaying the detection time, and isomers of xylene, an impurity found in the toluene. Subsequently, a pure 58-component NPAH standard mixture was analyzed using the EI- dissociative electron capture (3.5 eV) to preferentially generate the NO₂⁻ (*m/z* 46). Figure 3-6 shows the *m/z* 46 SIM for this mixture. Each peak is labeled with a number, and the corresponding compound is listed in Table 3-5.

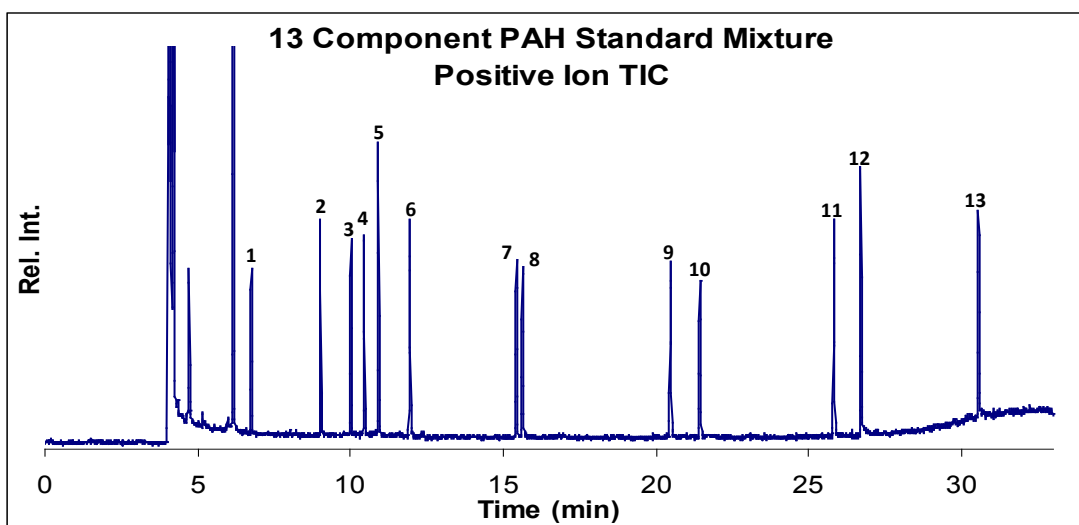


Figure 3-5. Positive ion TIC chromatogram for the PAH standard mixture (displayed as relative intensity)

Table 3-4. List of PAH Standards in Figure 3-5 and their Corresponding Peak Numbers

Peak #	PAH	Ret. Time (min)
1	naphthalene	6.76
2	biphenyl	9.02
3	acenaphthylene	10.02
4	acenaphthene	10.45
5	dibenzofuran	10.91
6	fluorene	11.94
7	phenanthrene	15.42
8	anthracene	15.62
9	fluoranthene	20.47
10	pyrene	21.43
11	benzo[c]phenanthrene	25.82
12	chrysene	26.69
13	benzo[a]pyrene	30.55

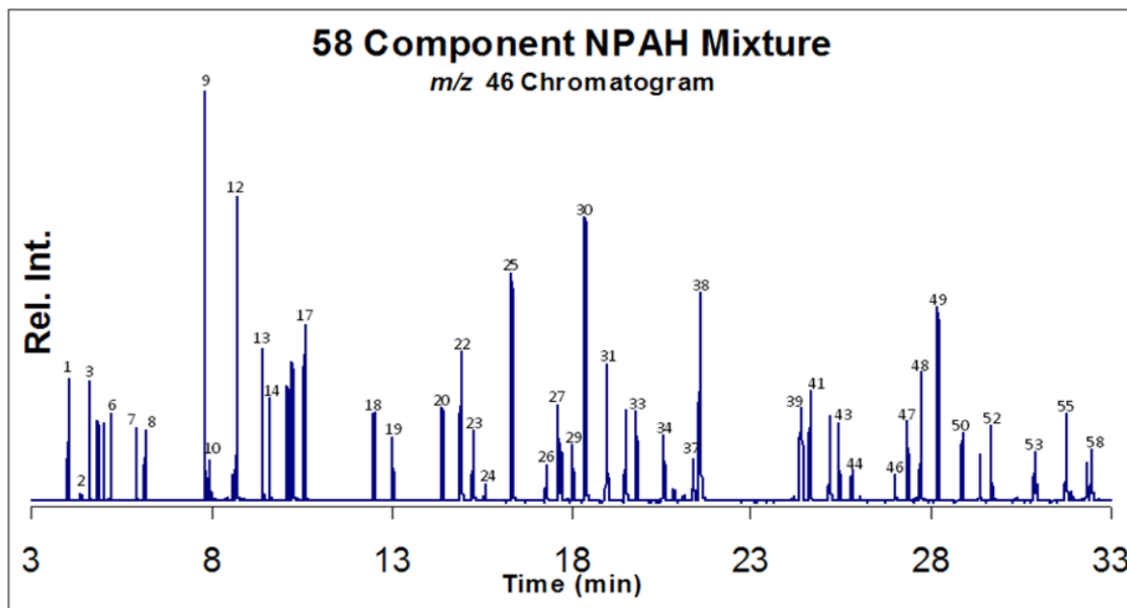


Figure 3-6. Nitro (m/z 46) chromatogram for the NPAH standard mixture

Table 3-5. List of NPAH Standards in Figure 3-6 and their Corresponding Peak Numbers

Peak #	NPAH Compound	Ret. Time (min)	Peak #	NPAH Compound	Ret. Time (min)
1	nitrobenzene	3.98	30	2,4'-dinitrobiphenyl	18.43
2	2-nitrophenol	4.36	31	9-nitrophenanthrene	19.07
3	2-nitrotoluene	4.61	32	2-nitrodibenzothiophene	19.58
4	2-nitro-m-xylene	4.83	33	3-nitrophenanthrene	19.86
5	3-nitrotoluene	4.99	34	2-nitroanthracene	20.64
6	4-nitrotoluene	5.19	35	9,10-dinitroanthracene	20.90
7	4-nitro-m-xylene	5.93	36	dinitrobiphenyl impurity	21.15
8	5-nitro-m-xylene	6.16	37	6-nitro-3,4-benzocoumarin	21.47
9	2,6-dinitrotoluene	7.84	38	4,4'-dinitrobiphenyl	21.66
10	3-nitrophenol	8.01	39	2-nitrofluoranthene	24.45
11	4-nitrophenol	8.65	40	3-nitrofluoranthene	24.49
12	2,4-dinitrotoluene	8.73	41	4-nitropyrene	24.71
13	5-nitroquinoline	9.47	42	1-nitropyrene	25.25
14	1-nitronaphthalene	9.66	43	2-nitropyrene	25.52
15	2-nitronaphthalene	10.15	44	2,7-dinitrofluorene	25.88
16	6-nitroquinoline	10.28	45	2,7-Dinitro-9-fluorenone	26.10
17	2-nitrobiphenyl	10.61	46	2,8-dinitrodibenzothiophene	27.07
18	3-nitrobiphenyl	12.58	47	7-nitrobenz[a]anthracene	27.40
19	4-nitrobiphenyl	13.08	48	5-nitrobenzo[c]phenanthrene	27.76
20	1,5-dinitronaphthalene	14.46	49	6-nitrochrysene	28.26
21	3-nitroacenaphthene	14.52	50	1,3-dinitropyrene	28.93
22	1,3-dinitronaphthalene	15.00	51	1,6-dinitropyrene	29.41
23	3-nitrodibenzofuran	15.34	52	1,8-dinitropyrene	29.74
24	5-nitroacenaphthene	15.67	53	6-nitrobenz[a]pyrene	30.96
25	2,2'-dinitrobiphenyl	16.40	54	6,12-dinitrochrysene	31.01
26	2-nitrofluorene	17.36	55	4,4'-dinitro-p-terphenyl	31.82
27	4-nitrophenanthrene	17.70	56	dinitrochrysene impurity	31.98
28	9-nitroanthracene	17.79	57	1-/3-nitrobenzo[a]pyrene	32.44
29	1,8-dinitronaphthalene	18.08	58	1-/3-nitrobenzo[a]pyrene	32.56

Next, the PAH and NPAH internal standards mixtures were analyzed by the GC/EM-MS. Representative two-ring (naphthalene- d_8), three-ring (phenanthrene- d_{10}), and four-ring (chrysene- d_{12}) PAHs were chosen for the internal standard mixture spiked into each sample. Figure 3-7 shows the labeled TIC for the PAH standards spiked into each sample. As for the NPAHs, the mixture evolved from a three-component mixture to a five-component mixture. Early in this research, it was important to imitate the work that had been previously done by Havey et al., which used only a 3-component NPAH mixture (1-nitronaphthalene- d_7 , 1,5-dinitronaphthalene- d_6 , 1-nitropyrene- d_9).^{4,5} However, despite the fact that this mixture was useful for assessing the recoveries of two-ring, four-ring, and dinitro NPAHs, it did not account for all ring types. As a result, the internal standard solution was adjusted to include a single-ring

(nitrobenzene- d_5) and three-ring (9-nitroanthracene- d_9) NPAH. Figure 3-8 shows the labeled m/z 46 chromatogram for the NPAH internal standards spiked into the samples. It is important to note that these additional standards were not added until midway through the project. Because of this, some early studies presented in this report will not include all five NPAH standards.

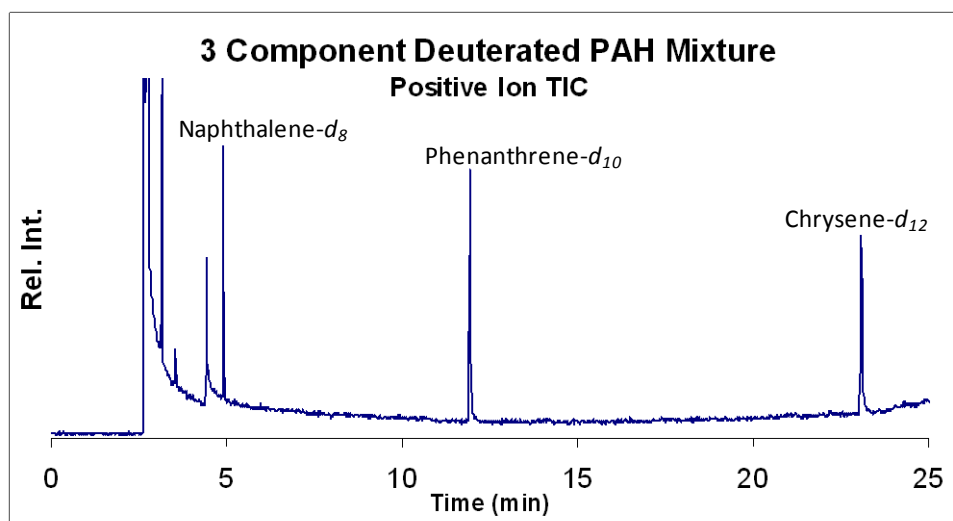


Figure 3-7. Positive-ion TIC chromatogram for the deuterated PAH standard mixture

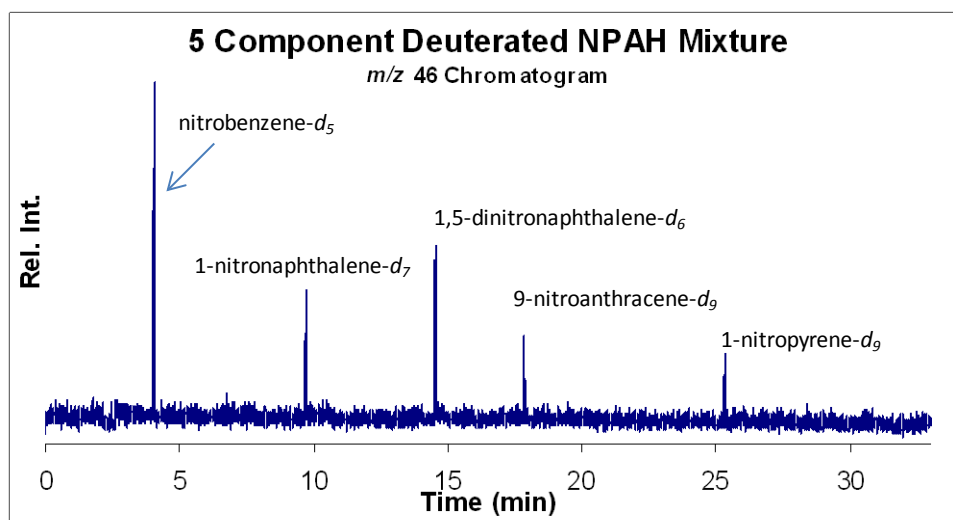


Figure 3-8. Nitro (m/z 46) chromatogram for deuterated NPAH standard mixture

3.5 Detection of Ethyl Nitrite

An early task for the CSM project was to evaluate the detection of ethyl nitrite and acetaldehyde using the GC/EM-MS. Although these compounds would be in the gas phase, it was thought that if the EM provided a better detection scenario, then a trapping/desorption scenario would be investigated for the diesel exhaust samples. The findings of these studies showed that there was a distinctive m/z 75 for the ethyl nitrite molecular ion and an m/z 44 for the acetaldehyde molecular

ion (see Figure 3-9). However, both compounds were observed to co-elute even when utilizing a starting temperature at or slightly below room temperature (15°C–25°C). As a result, the full scan data produced overlapping spectra, making it difficult to determine which ions were contributions from acetaldehyde and which were from ethyl nitrite. Despite this situation, these compounds, even when utilizing pure electron capture, produce fragment ions that can also be utilized for identification purposes. The positive result of this study was that, as predicted, compounds without aromatic systems produce EI- full-scan spectra that include both molecular radical ions and fragment ions, unlike aromatic systems such as NPAHs, which almost exclusively produce molecular ions at 0 eV ionization. If this area is to be studied further using the GC/EM-MS, it will be necessary to invest in a cryogenic GC oven cooling system and/or in a 60 m capillary GC column.

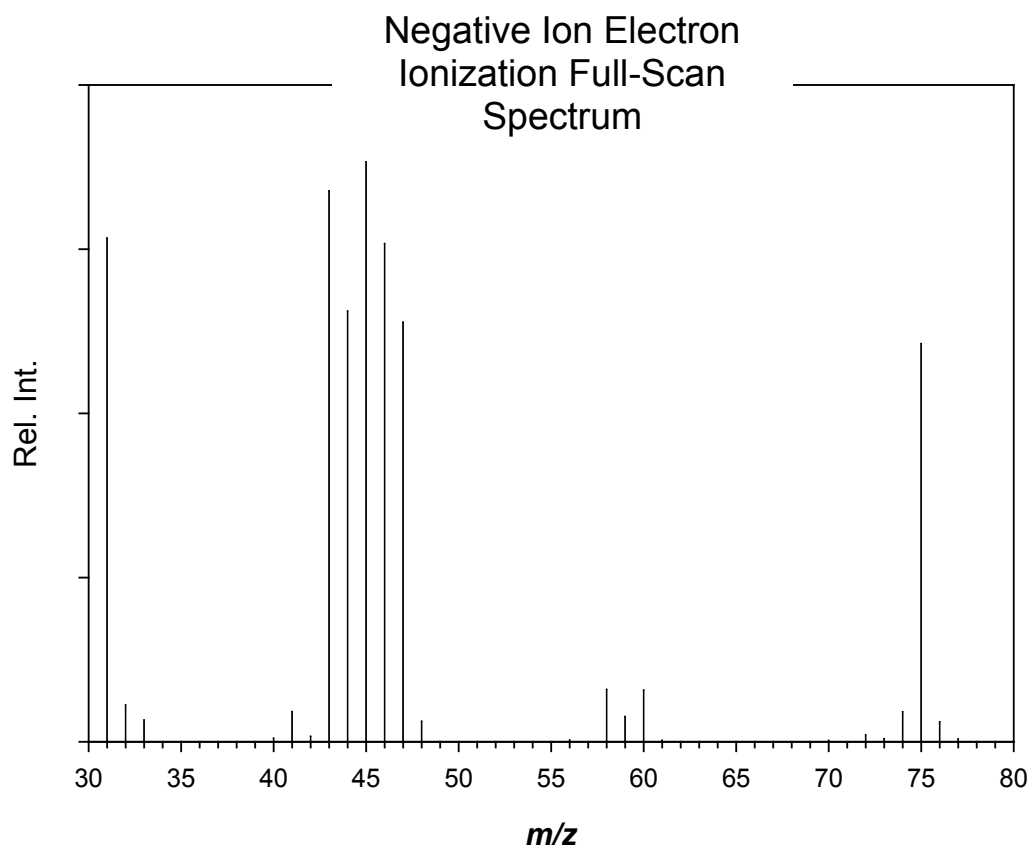


Figure 3-9. Full-scan mass spectrum of acetaldehyde and ethyl nitrite utilizing pure electron capture ionization

3.6 Solvent Extraction Studies

An area that warranted further investigation, based on the article by Havey et al., was the solvent extraction method utilized to extract the NPAHs out of the PM and into the dichloromethane solution. This earlier research had shown that using a shaker table did not provide an efficient extraction of the heavier NPAHs from the PM, as shown by the poor recoveries (5%) of 1-nitropyrene-*d*₉.⁴ As a result, two other scenarios were investigated that provided a more rigorous extraction method, sonication and Soxhlet extraction. To test these two methods, two certification (Cert) diesel PM samples were spiked with internal standards. Sample #1 was sonicated for approximately 1 hour in 25 mL of dichloromethane; Sample #2 was placed in a

Soxhlet apparatus with 200 mL of dichloromethane that was cycled 63 times. Afterward, each sample was analyzed using the GC/EM-MS to monitor the molecular ions for 3-nitrofluoranthene-*d*₉ and 1-nitropyrene-*d*₉ (see Figure 3-10).

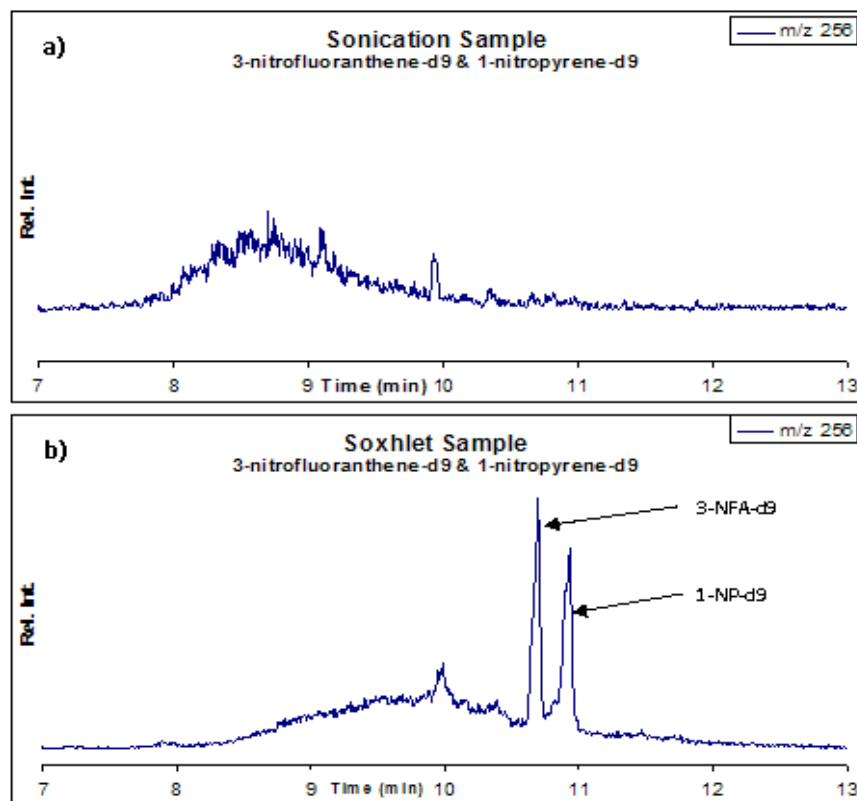


Figure 3-10. Molecular ion chromatogram for the PM sample that was (a) sonicated and (b) Soxhlet extracted

A comparison of these chromatograms clearly shows that Soxhlet extraction produces superior recovery of the two NPAH compounds. Our speculation for the poor recovery observed for the sonicated sample was that the diesel soot has a morphology that has a significant affinity toward the larger NPAHs, especially when compared with the solvent. To address this problem, it would likely require a number of sonication extractions with fresh solvent (similar to each cycle during a Soxhlet extraction) to help break up the soot and extract these compounds out of the PM. Rather than spend time devising a multiple sonication extraction method, the decision was made to use the Soxhlet extraction process for all future samples.

Further Soxhlet extraction testing revealed that the affinity of 1-nitropyrene and chrysene for the PM is much stronger than was originally anticipated, even with the choice of an improved extraction technique. Additionally, this affinity increased as more Cert diesel was incorporated into the fuel. Table 3-6 demonstrates this trend for chrysene-*d*₁₂ and 1-nitropyrene-*d*₉ by showing recoveries for a set of Cert, B20 (20% biodiesel), and B100 (100% biodiesel) Engine-out samples when utilizing only a minimum of 30 (max 60) cycles per sample.

Table 3-6. Comparison of Chrysene- D_{12} and 1-Nitropyrene- D_9 Recoveries Prior to Optimizing the Number of Soxhlet Extraction Cycles

	Cert	B20	B100
chrysene- d_{12}	32% \pm 5	41% \pm 7	73% \pm 12
1-nitropyrene- d_9	50% \pm 2	78% \pm 4	86% \pm 3

As a result, the number of extraction cycles was increased to over 200 for each sample in order to ensure that these compounds were completely extracted from the PM. Table 3-7 shows the improved recoveries for chrysene- d_{12} and 1-nitropyrene- d_9 from the PM of each fuel type. Based on these results, the 200 cycle Soxhlet extraction scenario was utilized during the PM sample preparation process.

Table 3-7. Comparison of Chrysene- D_{12} and 1-Nitropyrene- D_9 Recoveries after Optimizing the Number of Soxhlet Extraction Cycles

	Cert	B20	B100
chrysene- d_{12}	74% \pm 7	62% \pm 11	87% \pm 22
1-nitropyrene- d_9	85% \pm 14	86% \pm 14	92% \pm 11

3.7 Solid-Phase Extraction Studies

Early in the project, it was determined that it would be necessary to add an additional step to the extraction process in order to further clean the Engine-out samples. Without additional cleanup, these PM samples produced noisy, rising baselines in each molecular ion and TIC chromatogram. As a result, an amino solid phase extraction (NH_2 SPE) process was incorporated into the Engine-out sample preparation in order to remove any polar constituents extracted from the PM. These components tend to create the most problems for chromatography and signal suppression. The extraction scenario was based upon previous work conducted at CSM.⁵ To streamline the NH_2 SPE method development, we utilized steps described in *Analytical Solid-Phase Extraction* by James S. Fritz, which outlines techniques for developing SPE methods.⁶ The technique developed here is based upon prefabricated 25 mL Alltech ultra-clean cartridges containing 1.5 g of amino phase. It is worth mentioning that the DPF-out samples did not require this SPE scenario; these samples were sufficiently clean after Soxhlet extraction for analysis of PAHs and NPAHs.

Overall, several NH_2 SPE scenarios were investigated before a final method was settled upon. Each of the methods investigated was based upon NPAH research conducted previously^{7,8} but was designed to simplify the process. However, after investigating these other methods, it was determined that only a slight modification from the original technique was necessary to streamline the extraction process. First, the hexane was replaced with pentane to increase the evaporation rate achievable during sample concentration. Second, the solvent ratio was adjusted from 18:82 dichloromethane/hexane to 20:80 dichloromethane/pentane to simplify the solvent volume selections. The final SPE method utilized on each sample was as follows:

- Prepare sample solution
 - Make 10 mL dichloromethane sample solution into a 20:80 mixture by adding 40 mL of pentane
- Prepare 75 mL of 20:80 dichloromethane/pentane solution for use during SPE by combining 15 mL of dichloromethane with 60 mL of pentane
- Prepare 1.5 g ultra-clean NH₂ SPE (eliminates contaminants from phase synthesis)
 - Pass 10 mL pentane through cartridge, draining to just above NH₂ phase
 - Pass 10 mL of 20:80 dichloromethane/pentane through cartridge, draining to just above NH₂ phase
- Pass sample solution through the phase
 - Pass all 50 mL of sample solution through phase, again draining to just above NH₂ phase
- Pass 50 mL of pure 20:80 dichloromethane/pentane through phase, this time draining completely
 - Evaporate sample under flowing nitrogen to 200 µL (see exact procedure in Section 3.9).

Representative internal standard recoveries for the PM samples, which also reflect the use of the Soxhlet extraction procedure discussed in Section 3.5, are shown below in Table 3-8. All of the internal standards except naphthalene-*d*₈ (which is fairly volatile) showed recoveries of greater than 50%. These results, which include the improved Soxhlet extraction method discussed above, represent a significant improvement over the 5% recovery of 1-nitropyrene-*d*₉ reported by Havey et al.^{4,5}

Table 3-8. PAH and NPAH Internal Standard Recoveries

PAH	Recovery
naphthalene-d8	31.4%
phenanthrene-d10	72.0%
chrysene-d12	78.6%
NPAH	Recovery
1-nitronaphthalene-d7	50.0%
1,5-dinitronaphthalene-d6	86.1%
9-nitroanthracene-d9	76.1%
1-nitropyrene-d9	92.0%

3.8 Evaporation Procedure

Over the course of this research, one common effect consistently observed, no matter how much optimization was done to the extraction and cleanup procedure, was the low recovery of the smaller, most volatile components found within the samples (i.e., nitrobenzene-*d*₅, naphthalene-*d*₈, and nitronaphthalene-*d*₇). The most obvious process to account for these losses was the concentration and evaporation that occurred during the cleanup procedure. To test this hypothesis, experiments were done to determine an optimal evaporation procedure that would limit the loss of these compounds. The initial evaporation method was as follows:

- Evaporate 200–300 mL Soxhlet solution under gently flowing nitrogen to between 3 and 10 mL
- Dilute sample back up to exactly 10 mL with dichloromethane
- Conduct amino solid phase extraction
- Spike sample (~100 mL) with 3 mL of toluene for volume regulation
 - DCM/pentane evaporates too quickly under flowing nitrogen, so toluene is added to help regulate this evaporation rate
- Evaporate sample to between 1 and 3 mL
- Transfer sample to 2 mL amber vial and continue evaporation
- Once sample transfer is complete, rinse jar with two 1 mL portions of toluene and add these rinses to amber vial
- Continue evaporation under flowing nitrogen to less than 100 μ L
- Dilute solution back up to exactly 100 μ L with toluene using a pipetter to determine the final volume.

This procedure required a significant amount of focus because there were several areas where mistakes could be made that would lead to complete solvent evaporation. The most difficult aspect to control was the step in which the volume is evaporated below 100 μ L. Ideally, the goal was to go slightly below this 100 μ L volume, but at such a small volume, it was difficult to achieve this optimal situation. The problems would multiply when more than one sample was being prepared at a time.

Consequently, several steps were added to improve control of the evaporation, resulting in higher recoveries for the volatile analytes within the samples. First, all evaporation steps were done in an ice bath to slow down the solvent evaporation while retaining the volatile analytes in solution. Second, all final volumes at various stages of the evaporation process were controlled by monitoring the weight of the solution. In this way, exact volumes could be monitored and achieved. Finally, the target final volume for the sample solution was increased from 100 μ L to 200 μ L, making it less likely that the sample would be evaporated completely. Table 3-9 shows the volatile internal standard recoveries for an evaporation test conducted using these techniques.

Table 3-9. Volatile Internal Standard Recoveries for an Evaporation Test

Deuterated PAH	Recovery
naphthalene-d ₈	73%
nitrobenzene-d ₅	75%
1-nitronaphthalene-d ₇	67%

These data show that this procedure improved recoveries for these volatile components when compared with the recovery tables shown previously. Therefore, this technique was utilized during the sample preparation process.

3.9 Complete Engine-out Sample Preparation Procedure

The following is a complete description of the final sample preparation procedure for the Engine-out samples, as determined by the development work described above.

- Spike weighed PM sample with 20 μL of the 250 $\text{pg}/\mu\text{L}$ NPAH and 20 μL of the 2.5 $\text{ng}/\mu\text{L}$ PAH internal standard mixtures
- Place sample in Soxhlet apparatus with 200 mL of dichloromethane (DCM) in round bottom flask
- Cycle DCM through sample a minimum of 200 times
- Evaporate the solution in an ice bath under gently flowing nitrogen to ~ 100 mL
- Pour sample into amber jar and rinse flask twice with 20 mL of DCM
- Pour rinses into the sample amber jar
- Evaporate sample in an ice bath under flowing nitrogen to ~ 13 g
- Dilute sample back up to 10 mL (13.277 g) with DCM
- Make this sample solution into a 20:80 DCM/pentane mixture by adding 40 mL of pentane
- Prepare 75 mL of 20:80 DCM/pentane solution for use during SPE
 - 15 mL DCM to 60 mL of pentane
- Pass 10 mL pentane through cartridge, draining to just above NH_2 phase
- Pass 10 mL of 20:80 DCM/pentane through cartridge, draining to just above NH_2 phase
- Pass all 50 mL of sample solution through phase, again draining to just above the NH_2 phase
- Pass 50 mL of pure 20:80 DCM/pentane through phase, this time draining completely
- Spike sample with 3 mL of toluene for volume regulation
- Evaporate sample in an ice bath under flowing nitrogen to 2–3 g
- Transfer sample to amber vial and continue evaporation in an ice bath under flowing nitrogen

- Once sample transfer is complete, rinse jar with two 1-mL portions of toluene and add these rinses to amber vial
- Evaporate sample to just below 0.1733 g
- Dilute solution back up to 0.1733 g (200 μ L) with toluene.

3.10 Complete DPF-out Sample Preparation Procedure

For the DPF-out samples, the following is a complete description of the final preparation procedure for these samples.

- Spike weighed PM sample with 20 μ L of the 250 pg/ μ L NPAH and 20 μ L of the 2.5 ng/ μ L PAH internal standard mixtures
- Place sample in Soxhlet apparatus with 200 mL of DCM in round bottom flask
- Cycle DCM through sample a minimum of 60 times
- Evaporate the solution under gently flowing nitrogen while sitting in an ice bath to ~100 mL
- Pour sample into amber jar and rinse flask twice with 20 mL of DCM
- Pour rinses into the sample amber jar
- Spike sample with 3 mL of toluene for volume regulation
- Evaporate sample in an ice bath under flowing nitrogen to 2–3 g
- Transfer sample to amber vial and continue evaporation in an ice bath under flowing nitrogen
- Once sample transfer is complete, rinse jar with two 1-mL portions of toluene and add these rinses to amber vial
- Evaporate sample to just below 0.1733 g
- Dilute solution back up to 0.1733 g (200 μ L) with toluene.

3.11 Engine Testing Procedure

All of the PM samples collected during this project were generated from a 2002 model year Cummins ISB diesel engine with exhaust gas recirculation. Additionally, the test procedure chosen for the engine was an AVL 8-Mode test, which is a steady-state engine test procedure designed to closely correlate with the exhaust emission results obtained for the U.S. FTP heavy-duty engine transient cycle.⁹ Table 3-10 shows the parameters utilized for this test procedure. The sample time periods reflect the weightings applied to regulated emissions measurements from the AVL 8-Mode test and are based on a total of 30 minutes of sample collection.

Table 3-10. AVL 8-Mode Test

Mode	% Engine Speed *	% Load	Time (min)
1	0	0	12.5
2	11	25	2.25
3	21	63	1.03
4	32	84	1.18
5	100	18	3.00
6	95	40	3.73
7	95	69	3.65
8	89	95	2.62

* Normalized speed: 0% = low idle, 100 % = rated speed

Experiments in this report referred to as *Engine-out* were performed without a combined diesel oxidation catalyst (DOC) and diesel particle filter (DPF) installed in the exhaust system. Separate experiments were performed with the DOC/DPF installed, and are referred to as *DPF-out*. The sampling location for the raw exhaust experiments was therefore always the same. Likewise, the diluted exhaust experiments used a common (but obviously separate) sampling port. The purpose of the DOC is to catalytically oxidize the vapor phase hydrocarbons to CO₂ and H₂O. It also converts NO to NO₂ for use by the DPF to oxidize PM.

3.12 Raw Exhaust Sampling

Raw exhaust PM sampling is not commonly done within the engine testing community. As a result, a collection system for this type of sampling had to be designed for collecting Engine-out and DPF-out samples prior to the dilution tunnel. The mass flow controller (MFC) and pump associated with the regulated emissions bench at ReFUEL were used to control the sampling flow. Additionally, URG (Chapel Hill, N.C.) single-stage stainless steel filter holders at ReFUEL were incorporated into the sampling system to hold the Tissuquartz filters. Otherwise, the system was custom built and consisted of a sample probe, interconnecting stainless steel tubing, a filter holder, and the MFC bench. A PM sampling system schematic is shown in Figure 3-11.

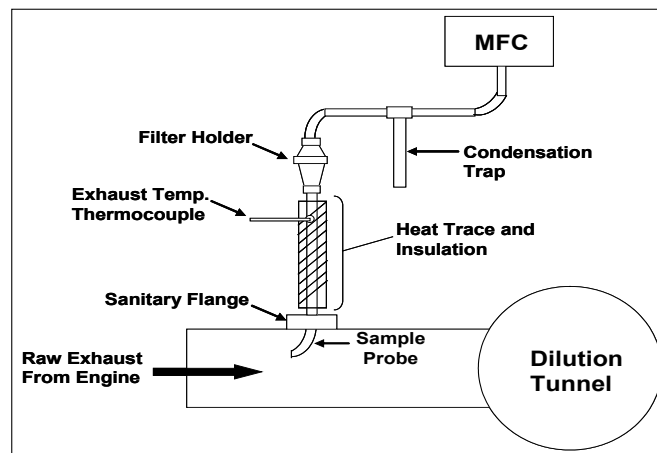


Figure 3-11. Schematic of sampling apparatus

Several heat tracing configurations were tried, and the best scenario involved keeping the exhaust temperature through the filter between 180°F and 350°F. Using a temperature any lower than 180°F would result in significant water condensation in the lines leading to the filter; using a temperature any higher than 350°F would result in the decomposition of the Delrin filter cassette used to hold the Tissuquartz filters in place within the filter holder. The exhaust flow rate through the filter was chosen to be 30 L/min for the DPF-out samples and 20 L/min for the Engine-out samples, based on the need to maximize the amount of PM while keeping the temperature in the appropriate temperature range. Also, the line into the filter was heat-traced at a setting of 212°F and insulated to help keep the temperature in the appropriate range. A photo of the sample setup is shown in Figure 3-12.



Figure 3-12. Photo of sampling apparatus (Credit: NREL ReFUEL Laboratory photos)

The sampling position in the exhaust stream was not changed for the Engine-out and DPF-out samples. Instead, the DPF was incorporated (or not) into the exhaust stream prior to the sample port. The Engine-out samples were collected from the exhaust stream when the DPF was not included in the system, while the DPF-out samples were collected with the DPF incorporated into the system. Additionally, each PM sample was collected onto a new Tissuquartz filter per the engine test.

3.13 Dilute Exhaust Sampling

The dilute exhaust samples were collected using ReFUEL's conventional PM sampling system. This system includes a sample probe installed in the dilution tunnel, the URG stainless steel filter holder, and the MFC bench. These PM samples, both Engine-out and DPF-out, were all collected using a flow rate of 60 L/min. Each Engine-out PM sample was collected onto a separate Tissuquartz filter per engine run. However, each DPF-out sample filter represented a triplicate of runs for each fuel type to maximize the amount of PM collected for analysis purposes. In this case, the final PAH and NPAH levels were then calculated by dividing the total value by 3 to determine the per-run value.

4. Results and Discussion

4.1 Raw Exhaust Gravimetric Data

The DPF-out PM samples were collected during the early stages of testing so only two fuel types (Cert and B20) were collected. The Engine-out samples, however, consisted of a complete set of PM samples representing all three fuel samples (Cert, B20, B100). All samples were collected using the apparatus and flow rates described in Section 3.12. Table 4-1 lists the DPF-out samples collected during this sampling period. Table 4-2 lists the Engine-out samples collected.

Table 4-1. Raw Exhaust DPF-out PM Samples

Run #	Filter #	Fuel	PM Mass (mg)	Run #	Filter #	Fuel	PM Mass (mg)
4	3	Cert	0.2608	11	8	B20	0.1350
6	4	Cert	0.2655	12	9	B20	0.1345
7	5	Cert	0.1840	13	10	B20	0.1070
8	6	Cert	0.0708				
9	7	Cert	0.0909				

Table 4-2. Raw Exhaust Engine-out PM Samples

Run #	Filter #	Fuel	PM Mass (mg)	Run #	Filter #	Fuel	PM Mass (mg)
14	11	B20	2.8228	21	17	Cert	4.3728
15	12	B20	2.6323	22	18	Cert	4.0315
16	13	B20	2.7166	23	19	Cert	4.3268
18	14	Cert	3.5685	25	20	B100	1.3388
19	15	Cert	3.3557	26/27	21	B100	1.1494
20	16	Cert	3.3030	28	22	B100	1.3110

After these samples were collected, they were then subjected to the cleanup processes described in Sections 3.9 and 3.10 but *without* the increased extraction period (only 60 cycles/sample) or the improved evaporation procedure. These samples were collected early during the subcontract period, prior to the integration of these procedures into the overall sample preparation process.

Note that the Engine-out gravimetric data collected during this section of the research are imperfect because the Tissuquartz filters ripped during the 8-Mode test. The cause was traced to the last three modes in the AVL test cycle in which the engine was reaching a steady state. While the engine is reaching a steady state, the pump for drawing the exhaust through the Tissuquartz filters is turned off. Because there was no valve between the filter and the engine exhaust, the filter would experience an oscillating pressure that would cause it to tear toward the exhaust stream. Then when the pump flow was turned on during sampling, the filter was pulled back into place on the stainless steel support plate at the back of the filter holder. While this would prevent soot from passing into the region beyond the filter, pieces of the filter could be seen on the inside of the exhaust inlet side of the filter holder. As a result, a significant error

could be associated with the sample weights, since the levels observed for each PM sample are in the milligram range to begin with. All three modes tested (Modes 6, 7, and 8) showed a tendency toward this filter tearing scenario. The sampling apparatus and procedure were developed during DPF-out sampling. Unfortunately, the problem of tearing Tissuquartz filters arose subsequently during Engine-out testing; that problem had not occurred while the DPF was being used. Apparently, the DPF dampens the oscillating pressures experienced by the Tissuquartz filters. Since the problem was not realized until after the DPF-out samples had been collected, an opportunity to overcome this problem was not available.

4.2 Results for Engine-out Raw Exhaust

First, the Engine-out PM samples were analyzed for nitro compounds utilizing GC/EM-MS. The m/z 46 SIM chromatograms for the Cert, B20, and B100 PM samples are shown in Figure 4-1. These chromatograms show the nitro compounds that are present in each sample and provide a starting point for the rest of the NPAH analyses. Overall, the chromatograms showed a number of similar features, which demonstrated the presence of common nitro compounds found within each sample.

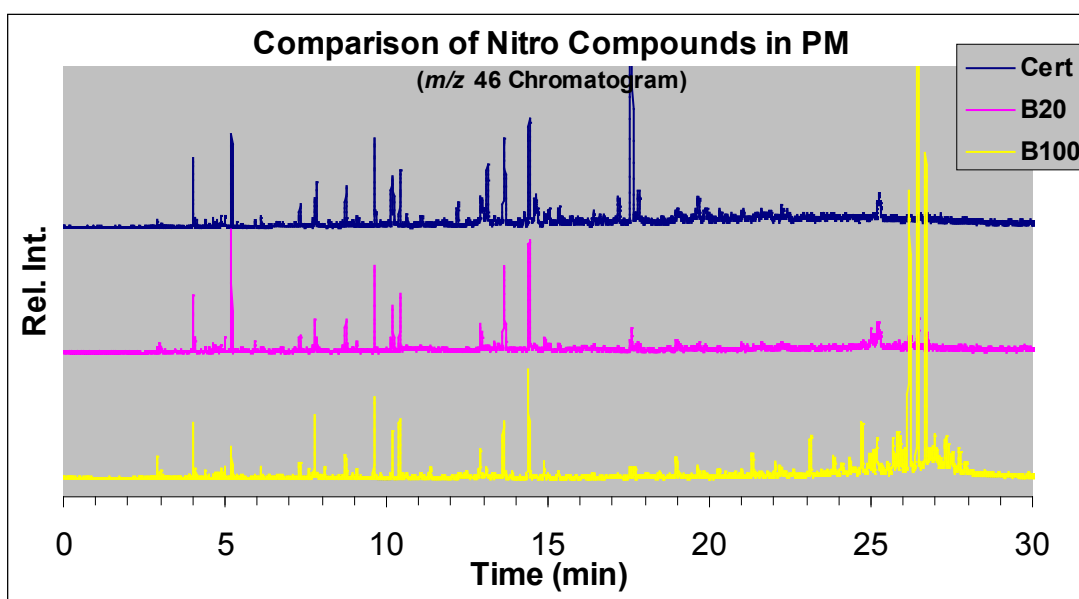


Figure 4-1. Nitro (m/z 46) chromatograms for each raw exhaust Engine-out PM sample (displayed as relative intensity)

Note that the large peak at approximately 18 minutes in the Cert chromatogram was identified as a contaminant that was introduced into the sample at the CSM laboratory. As a result, this feature can be ignored as a contribution from the PM samples. As for the peaks observed in the B100 chromatogram with retention times between 24 and 28 minutes, these peaks did not match any of the 58 NPAH standards available at the CSM laboratory. Additionally, these peaks were also observed, to a much lesser extent, in the B20 samples, which seems to suggest a connection to the biodiesel itself. Moreover, these peaks were at elution times that indicate the presence of higher molecular weight compounds. It is interesting that the detection of these heavier unknown compounds is inconsistent with the results from this study and other studies, in which an overall

decrease in all NPAH levels is observed as the amount of biodiesel is increased in the fuel. Further investigation of these peaks is discussed later in this section.

Once the nitro compounds had been preliminarily identified through their retention times in the m/z 46 chromatogram, the next step was to verify and quantify these compounds using their molecular ions. Several representative NPAHs (1- and 2-nitronaphthalene, 9-nitroanthracene, 3-nitrophenanthrene, and 1-nitropyrene) were selected for quantitation purposes. Figures 4-2 and 4-3 show the molecular ion chromatograms for 9-nitroanthracene and 1-nitropyrene, respectively. These chromatograms illustrate qualitatively that there is a trend toward lower concentrations of these species as more biodiesel is incorporated into the fuel.

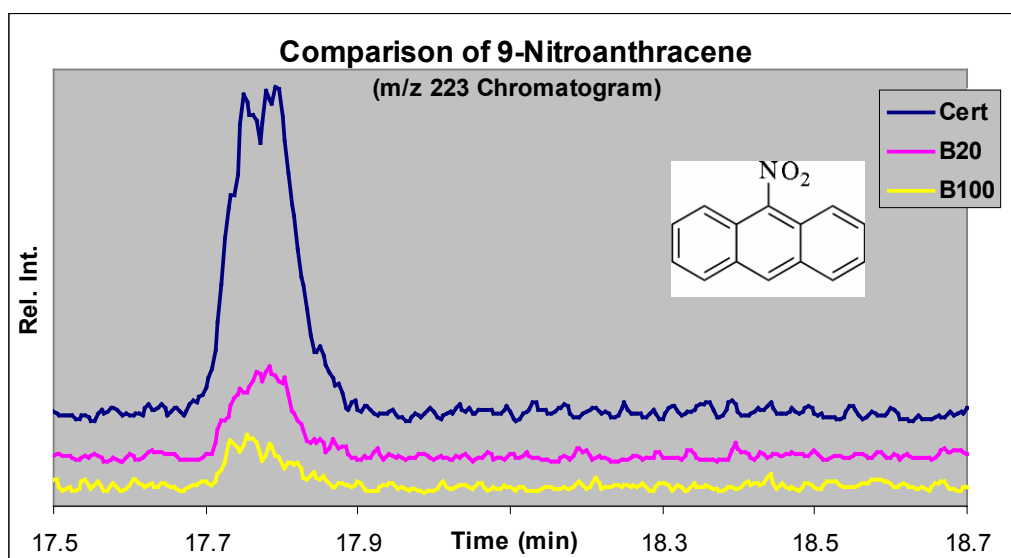


Figure 4-2. The molecular ion chromatograms (m/z 223) for 9-nitroanthracene

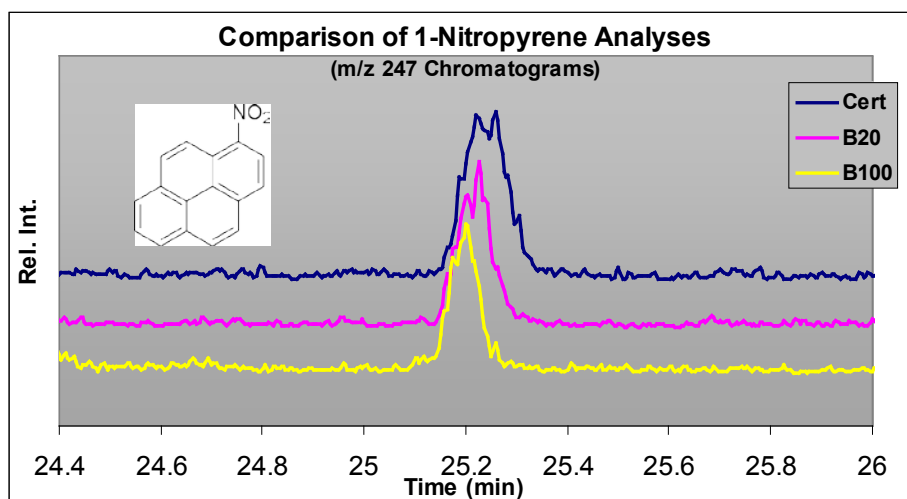


Figure 4-3. The molecular ion chromatograms (m/z 247) for 1-nitropyrene

Table 4-3 shows the total amount (average of 3 replicates) for each NPAH measured from each fuel type, with the measurement error expressed as the standard deviation. These results illustrate that as more biodiesel is incorporated into the fuel, lower levels of NPAHs are present in the exhaust. However, when these levels are related back to the total amount of PM present, this trend does not hold. Table 4-4 shows the NPAH levels as they relate to the amount of PM present for each sample.

Table 4-3. Raw Exhaust Engine-out NPAH Quantities for each Fuel (ng/sample)

	Cert (ng/sample)	B20 (ng/sample)	B100 (ng/sample)
1-nitronaphthalene	0.87 ± 0.04	0.20 ± 0.05	0.14 ± 0.02
2-nitronaphthalene	3.9 ± 0.2	1.0 ± 0.2	0.65 ± 0.19
9-nitroanthracene	9.6 ± 1.5	1.2 ± 0.2	0.45 ± 0.05
9-nitrophenanthrene	ND	ND	ND
3-nitrophenanthrene	1.3 ± 0.4	0.28 ± 0.01	0.25 ± 0.03
3-nitrofluoranthene	ND	ND	T
1-nitropyrene	2.1 ± 0.4	1.2 ± 0.3	0.54 ± 0.13
TOTAL	17.8	3.9	2.03

ND: not detected; T: trace

Table 4-4. Raw Exhaust Engine-out NPAH Quantities for each Fuel (ng/mg PM)

	Cert (ng/mg)	B20 (ng/mg)	B100 (ng/mg)
1-nitronaphthalene	0.20 ± 0.02	0.08 ± 0.02	0.11 ± 0.01
2-nitronaphthalene	0.90 ± 0.07	0.37 ± 0.07	0.51 ± 0.14
9-nitroanthracene	2.3 ± 0.4	0.46 ± 0.15	0.36 ± 0.03
9-nitrophenanthrene	ND	ND	ND
3-nitrophenanthrene	0.31 ± 0.11	0.10 ± 0.01	0.20 ± 0.01
3-nitrofluoranthene	ND	ND	T
1-nitropyrene	0.12 ± 0.03	0.39 ± 0.02	0.43 ± 0.09
TOTAL	3.8	1.40	1.61

ND: not detected; T: trace

The data in Table 4-4 do not show a clear pattern between the fuel type and NPAH levels present per PM amount. The total NPAH in the B20 samples is roughly half that from Cert samples, but the B100 samples had higher total NPAH per milligram of PM than the B20 samples. In the case of 1-nitropyrene, the B100 and B20 samples actually had higher amounts per milligram than the Cert diesel samples. While these results were unexpected, the cause is possibly related to the filter tearing situation that was discussed in Section 4.1. If the sampling system was improved to eliminate this problem, these numbers would likely change. The B100 samples had particularly bad oscillating pressure across the PM filters because the exhaust gas recirculation controls shut down for brief periods during the later modes, which would in turn cause the engine to lose power for brief periods of time during the testing period.

The samples were then analyzed for PAHs using EI+ (25 eV) in conjunction with molecular ion information obtained for each compound. These molecular ion chromatograms were then used to quantify the levels for each PAH. Figures 4-4 and 4-5 show the molecular ion chromatograms for phenanthrene, anthracene, fluoranthene, and pyrene. Each chromatogram qualitatively shows a trend toward lower concentrations as more biodiesel was incorporated into the fuel.

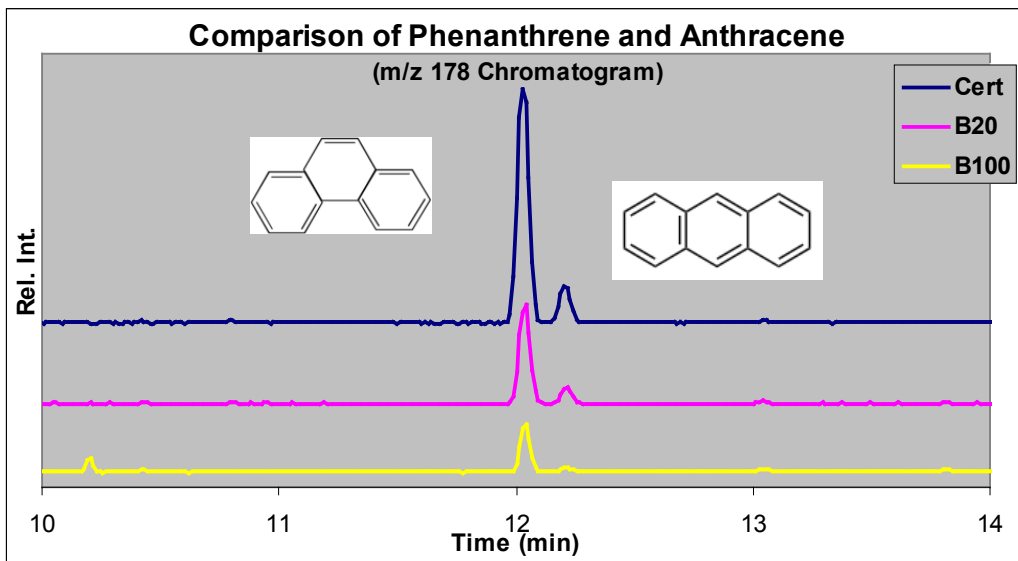


Figure 4-4. The molecular ion chromatograms (m/z 178) for phenanthrene and anthracene

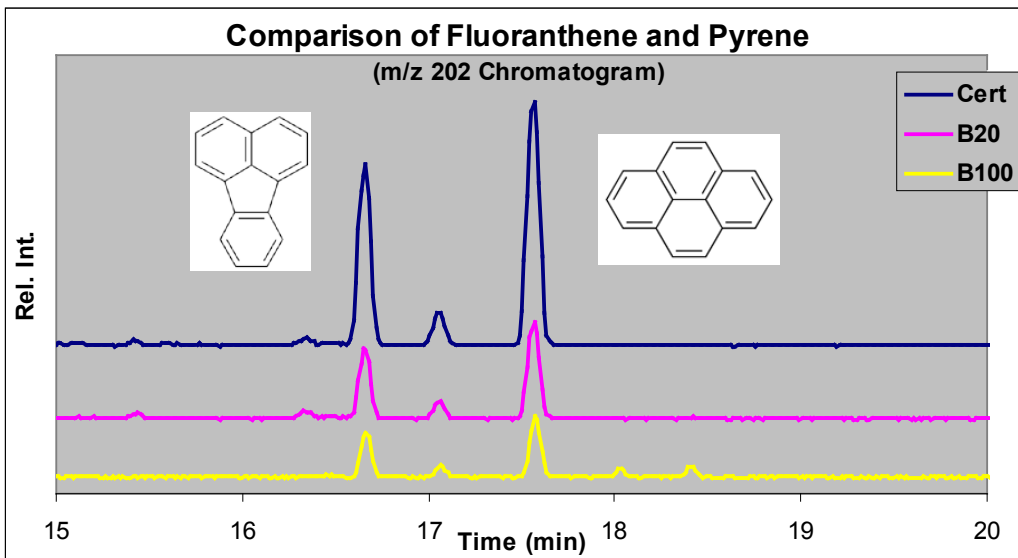


Figure 4-5. The molecular ion chromatograms (m/z 202) for fluoranthene and pyrene

Along with the four PAHs shown in the above chromatograms, naphthalene was also selected for quantitation purposes. Table 4-5 shows the total PAH quantity obtained from each PM sample (average of three replicates). The data quantitatively show that as more biodiesel is incorporated into the fuel, smaller amounts of PAHs are produced during the combustion process, just as for NPAHs. Table 4-6 shows the PAH levels as they relate to the milligram amount of PM present in each sample. Similar to the NPAHs, there is a drop of about 50% in total PAH amount from Cert to B20. However, within the error of the measurements there is no difference in total PAHs between B100 and B20 samples, and naphthalene appears to actually increase from B20 to B100.

Table 4-5. Raw Exhaust Engine-out PAH Quantities for each Fuel (ng/sample)

	Cert (ng/sample)	B20 (ng/sample)	B100 (ng/sample)
naphthalene	240 ± 70	63 ± 4	40 ± 2
phenanthrene	130 ± 10	58 ± 3	24 ± 4
anthracene	23 ± 3	12 ± 1	3.5 ± 0.3
fluoranthene	190 ± 40	62 ± 14	22 ± 5
pyrene	310 ± 30	94 ± 22	31 ± 8
TOTAL	853	289	121

Table 4-6. Raw Exhaust Engine-out PAH Quantities for each Fuel (ng/mg PM)

	Cert (ng/mg)	B20 (ng/mg)	B100 (ng/mg)
naphthalene	55.6 ± 15.3	23.1 ± 0.9	31.5 ± 1.9
phenanthrene	31.3 ± 3.5	21.4 ± 0.7	18.6 ± 1.8
anthracene	5.5 ± 0.6	4.4 ± 0.3	2.7 ± 0.1
fluoranthene	45.5 ± 11.6	22.9 ± 5.7	17.5 ± 3.4
pyrene	72.7 ± 8.9	34.5 ± 9.0	24.7 ± 4.8
TOTAL	210.6	106.3	95.0

A comparison of the NPAH levels (Table 4-3) with the PAH levels (Table 4-5) shows that all of the NPAH levels (except 9-nitroanthracene) were observed to be approximately two orders of magnitude below the observed levels for the corresponding PAH. In the case of 9-nitroanthracene, this compound was consistently at or below one order of magnitude under the relative concentration of anthracene. There seems to be a much closer relationship between these two compounds than there is for any of the other compounds.

As previously mentioned, the large late eluting nitro peaks were a surprising result observed in the B100 samples and warranted further investigation in an attempt to narrow down the identity of these compounds. Figure 4-6 shows a B100 nitro (*m/z* 46) chromatogram again, this time highlighting these unknown peaks.

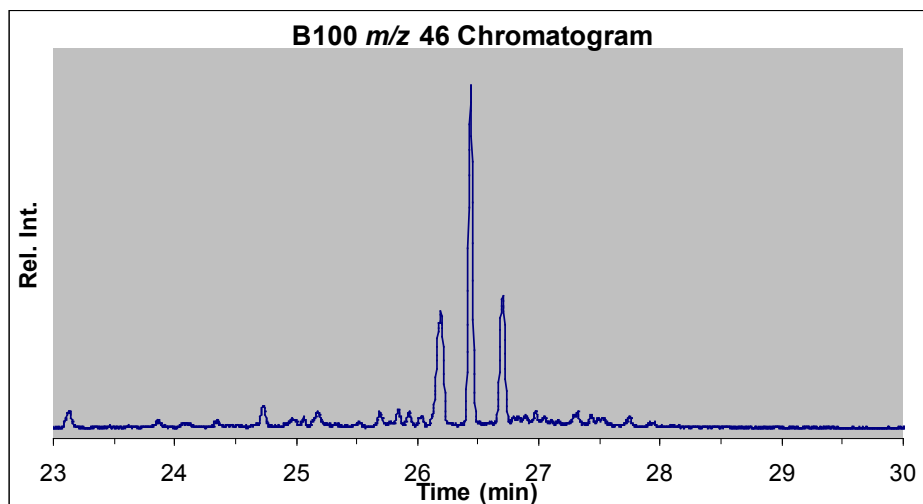


Figure 4-6. Nitro (m/z 46) chromatograms for a raw exhaust Engine-out B100 PM sample

All of the B100 raw exhaust Engine-out samples showed the presence of these unknown compounds. Additionally, the B20 Engine-out samples showed a much smaller presence of these compounds, while the Cert diesel exhaust did not show any peaks in this retention time region. All of this information indicates that these unknown compounds are most likely associated in some way with the soy biodiesel. Consequently, the biodiesel samples (which had the highest concentrations) were investigated further in an effort to identify these unknown nitro peaks. The EI+ full-scan (m/z 100-400) TICs generated in August 2007 (during the PAH analysis) were scrutinized more closely in order to see if any ions generated during this 26- to 27-minute timeframe could be associated with the nitro peak retention times. Figure 4-7 shows the TIC for a B100 Engine-out raw exhaust sample.

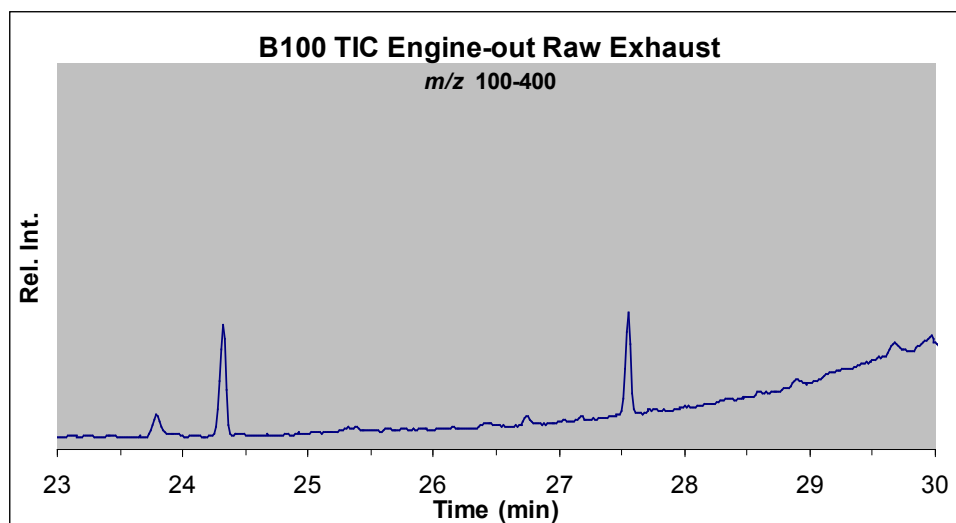


Figure 4-7. EI+ TIC (m/z 100–400) chromatogram for the Engine-out B100 raw exhaust PM samples

Based on the TIC, no obvious peaks were observed that could be related to the unknown peaks. However, by reconstructing the SIM plots from the ions in this time region, it was found that the first large peak at 26.2 minutes had only an m/z 351 associated with it. The middle, large peak at 26.4 minutes had ions of m/z 125, 143, and 365 associated with it. The third large peak at 26.7 minutes had ions of m/z 143, 339, and 382 associated with it. Using these masses as search parameters, the National Institute of Science and Technology (NIST) database did not show any possible matches for these compounds. Additionally, even with baseline subtraction to eliminate background ions, the full scan spectrum for each compound had a number of background ions present that disrupted the NIST database search.

The peaks in Figure 4-6 could possibly relate to the engine losing power during Mode 7 for the B20/B100 samples. If so, they may arise from lube oil entering the combustion chamber. However, the current evidence suggests they are likely some sort of long-chain nitro compounds produced by the incomplete combustion of the soy biodiesel. If future raw Engine-out B100 PM samples show the presence of these compounds, more effort should be focused on identifying these unknown nitro peaks.

4.3 Results for DPF-out Raw Exhaust

The DPF-out samples were analyzed using the GC/EM-MS by monitoring the samples for nitro-compounds. To do this, the instrument was set to monitor the nitro ion (NO_2^-) using an ionization energy of 3.5 eV (EI-) that selectively fragments this portion from the NPAH molecules. The m/z 46 SIM chromatograms for the Cert and B20 PM samples are shown in Figure 4-8. These chromatograms show all of the nitro compounds that are present in each sample and provide a starting point for the rest of the NPAH analyses.

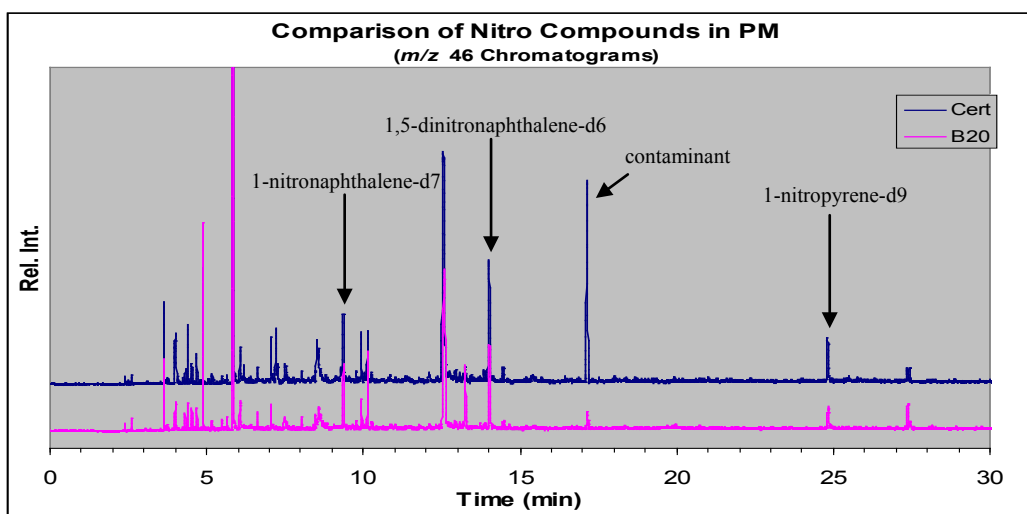


Figure 4-8. Nitro (m/z 46) chromatograms for the raw exhaust DPF-out Cert and B20 PM samples (displayed as relative intensity)

Overall, the chromatograms showed a number of similar features and demonstrate the presence of common nitro compounds found within each sample. Each of the internal standard NPAH peaks has also been indicated in Figure 4-8 to clarify its position in the chromatogram. As for the peak at approximately 17 minutes, this was identified earlier as a contaminant that was also present in the Engine-out samples.

The majority of the nitro compounds eluted between 3 and 15 minutes; when compared to the 58 component NPAH mixture, this indicates that these compounds are single- and double-ring nitro-aromatics. Figure 4-9 shows a magnified view of this time region.

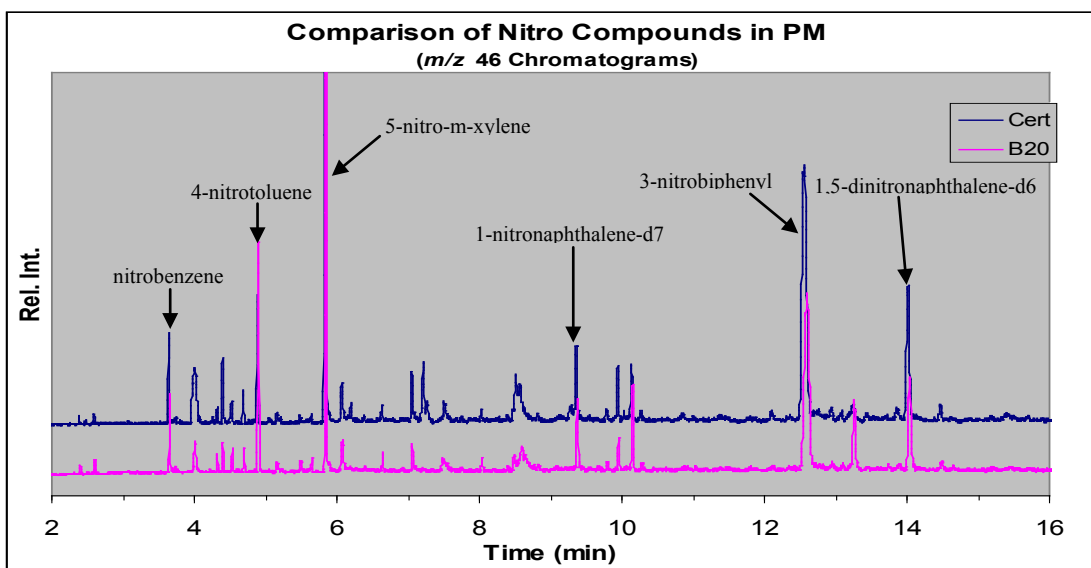


Figure 4-9. Magnified nitro (m/z 46) chromatograms from the raw exhaust DPF-out Cert and B20 PM samples

The very largest peaks observed at ~5 minutes, ~5.8 minutes, and ~12.8 minutes in these post-DPF exhaust samples are 4-nitrotoluene, 5-nitro-m-xylene, and 3-nitrobiphenyl, respectively. Table 4-7 lists all of the single and double-ring nitro-aromatics qualitatively identified from both Cert and B20. The quantities for each compound cannot be accurately reported for these samples because of large standard deviations in the peak areas. Because the PM levels were so low, even the smallest variation in engine conditions, DPF loading, or other factors could account for the changes in both PM and NPAH levels present in these samples.

Table 4-7. Nitro-aromatics Identified in the Raw Exhaust DPF-out PM Samples from Cert and B20

Compound
nitrobenzene
2-nitrotoluene
3-nitrotoluene
4-nitrotoluene
2-nitro-m-xylene
5-nitro-m-xylene
3-nitrobiphenyl
1-nitronaphthalene
2-nitronaphthalene

Along with the identified compounds, there were also a number of unidentified nitro peaks observed in Figure 4-9 that could not be associated with any of the 58 NPAH standards. Because of their early retention times, the hypothesis is that these compounds are also single-ring (and possibly double-ring) nitro-aromatics that possibly have larger side chains than the methyl groups found in nitrotoluene and nitro-m-xylene. A negative ion full-scan analysis (m/z 40–400) did not provide any additional information for these samples. Compounding this problem is the fact that the smaller single-ring nitro-aromatics do not form molecular ions very efficiently and tend to fragment more easily than the larger aromatic systems, even when using the near 0 eV ionization energy. As for the two small, late eluting peaks between 27.3 and 27.5 minutes in Figure 4-8, these nitro peaks did not correlate with any of the available NPAH standards.

A PAH analysis for the DPF-out samples was performed by setting the GC/EM-MS system for EI+ full-scan (m/z 100–400). Figure 4-10 shows the TIC for both the certification diesel and the B20 diesel samples. Qualitatively, the chromatograms show the number and type of compounds that are similar for these fuels. Generally, the B20 samples qualitatively showed lower levels of each compound. Within these chromatograms, only peaks that could be associated with PAHs were identified (although the full-scan information for each peak is available and could be analyzed for peak identities). Only three PAHs (naphthalene, acenaphthene, and phenanthrene) were observed in both the Cert and B20 diesel PM samples. To demonstrate the presence of the phenanthrene in the samples, Figure 4-11 shows the m/z 178 (molecular ion) SIM for the Cert diesel and the B20 diesel PM samples. Again, no actual quantities could be associated with these samples because of the significant fluctuations in values (>50% deviations), which are likely connected to the PM weight variations. Further work investigating samples like these will be necessary before conclusive information can be determined about PAH and NPAH levels in DPF-out samples.

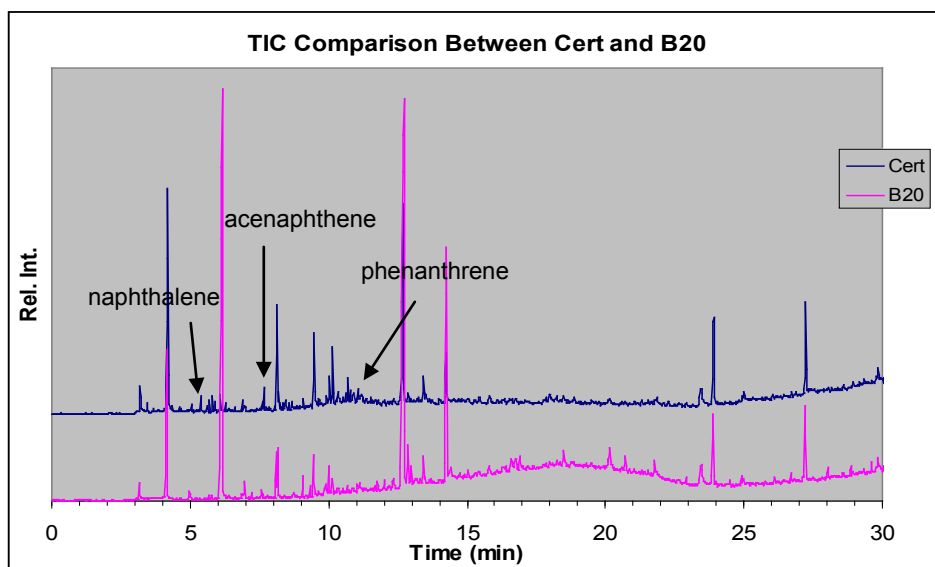


Figure 4-10. Comparison of the TIC for the raw exhaust DPF-out Cert and B20 PM samples

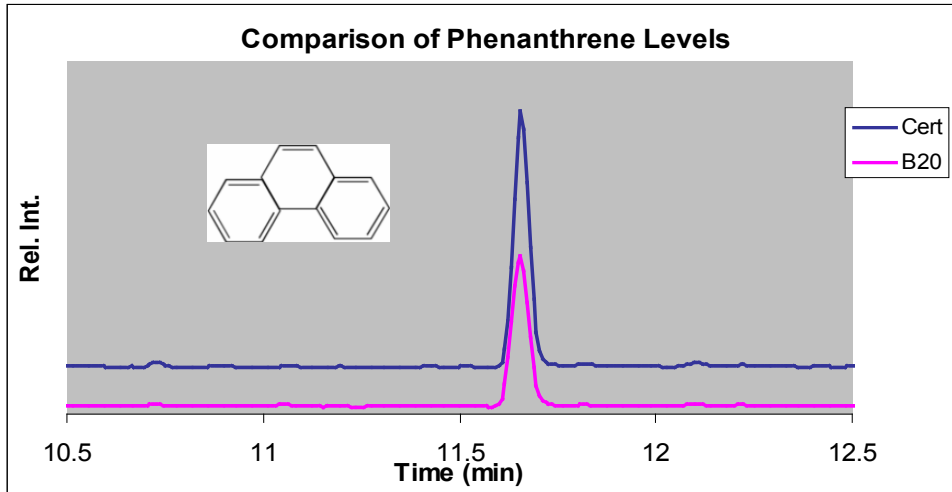


Figure 4-11. Comparison of the m/z 178 (phenanthrene molecular ion) for the raw exhaust DPF-out Cert and B20 PM samples

4.4 Dilute Exhaust Gravimetric Analysis

The Engine-out and DPF-out PM samples were collected for the Cert, B20, and B100 fuels using the sampling procedure described in Section 3.13. Table 4-8 shows a list of the Engine-out samples collected during this sampling period. Subsequently, the DPF was placed into the exhaust system and the DPF-out samples were collected. Table 4-9 shows a list of these DPF-out samples collected. Each PM sample listed in Table 4-9 represents three cumulative 30-minute runs, which was done to maximize the amount of PM collected for each analysis. After the samples were collected, they were then subjected to the complete cleanup processes described in Sections 3.9 and 3.10.

Table 4-8. Dilute Exhaust Engine-out PM Samples

Run Filename	Filter #	Fuel	PM Mass (mg)
1-29-08 Toxics Cert 01	24	Cert	3.0903
1-30-08 Toxics Cert 02	25	Cert	3.0046
1-30-08 Toxics Cert 03	26	Cert	2.9576
2-1-08 Toxics Cert 04	34	Cert	3.0212
1-30-08 Toxics B20 01	27	B20	2.4445
1-30-08 Toxics B20 02	28	B20	2.3985
1-31-08 Toxics B20 03	29	B20	2.3247
2-1-08 Toxics B20 04	35	B20	2.6768
1-31-08 Toxics B100 01	30	B100	1.3445
1-31-08 Toxics B100 02	31	B100	1.371
1-31-08 Toxics B100 03	32	B100	1.376
2-1-08 Toxics B100 04	33	B100	1.2732
3-18-08 Toxics B100 07	38	B100	1.2031
3-18-08 Toxics B100 08	39	B100	1.389
3-18-08 Toxics B100 09	40	B100	1.5256

Table 4-9. Dilute Exhaust DPF-out PM Samples

Run Filename	Filter #	Fuel	PM Wt. (mg)
4-8-08 Toxics DPF Cert 01	41	Cert	0.1503
4-8-08 Toxics DPF Cert 02			
4-8-08 Toxics DPF Cert 03			
4-9-08 Toxics DPF B20 01	43	B20	0.4932
4-9-08 Toxics DPF B20 02			
4-9-08 Toxics DPF B20 03			
4-10-08 Toxics DPF B100 01	44	B100	0.4507
4-10-08 Toxics DPF B100 02			
4-10-08 Toxics DPF B100 03			

Note that the Cert DPF-out PM sample mass was much lower than that of the B20 and B100 samples, which is just the opposite of what was anticipated for these samples. However, this sample was allowed to equilibrate in the ReFUEL Mass Lab clean room environment for only ~1.5 hours, while the other two samples (B20 and B100) were allowed to equilibrate overnight. The hypothesis is that 1.5 hours was not a sufficient time period for equilibration, and that if the sample had been left in the Mass Lab overnight prior to weighing, it would have reached equilibrium with the humidity there and shown a heavier final weight (absorption of water). Future investigation is necessary to corroborate or disprove this hypothesis.

4.5 Results for Engine-out Dilute Exhaust

The Engine-out PM samples were first analyzed for nitro compounds utilizing GC/EM-MS. The *m/z* 46 SIM chromatograms for the Cert, B20, and B100 PM samples are shown in Figure 4-12. These chromatograms show the nitro compounds that are present in each sample and provide a starting point for the rest of the NPAH analyses. Overall, the chromatograms showed a number of similar features, which demonstrated the presence of common nitro compounds found within each sample. The first thing that was quite apparent from these chromatograms was that they were very different from the raw exhaust Engine-out results shown previously. The raw exhaust Engine-out nitro chromatogram in Figure 4-1 is shown again here in Figure 4-13.

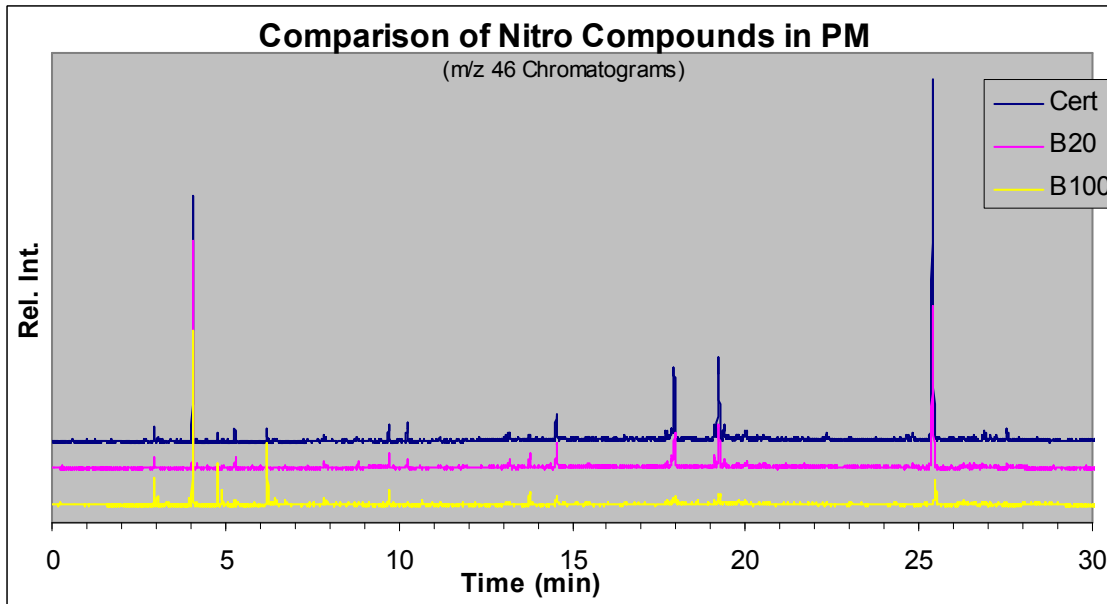


Figure 4-12. Nitro (m/z 46) chromatograms for each dilute exhaust Engine-out PM sample (displayed as relative intensity)

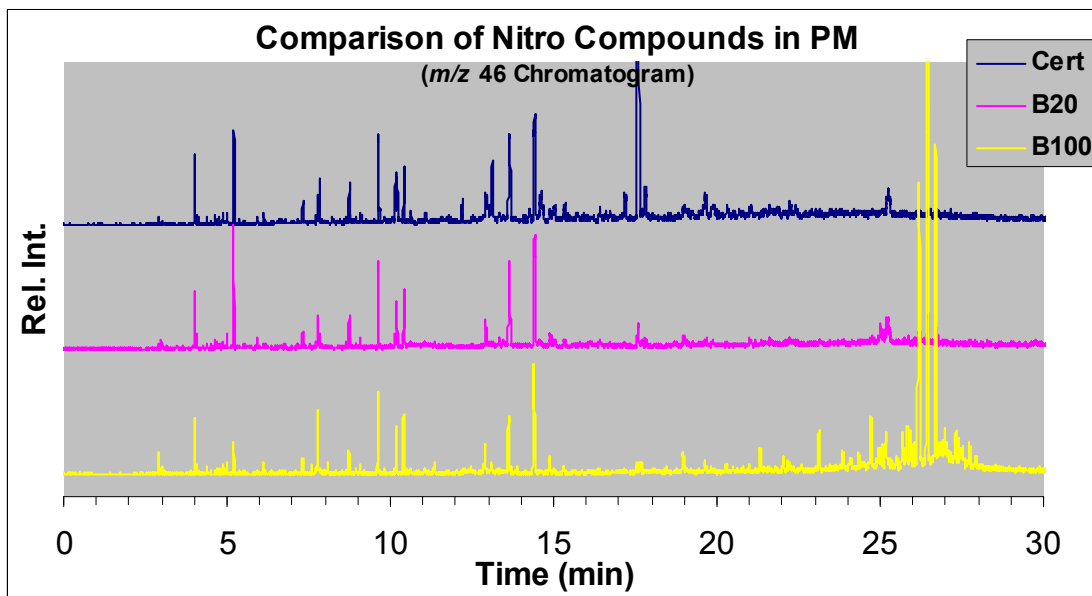


Figure 4-13. Nitro (m/z 46) chromatograms for each raw exhaust Engine-out PM sample

Evidently, collecting the PM samples from the dilution tunnel had a significant impact on the nitro-compounds present and the levels at which they are found in the PM. These results appear to indicate that the chemistry of NPAH formation is still occurring as the exhaust leaves the engine and moves into the dilution tunnel. It is interesting that the dilution tunnel samples appear cleaner in that there is less diversity among the nitro compounds present. However, the Cert and B20 dilute exhaust samples show much larger quantities of 1-nitropyrene (retention time 25.3 minutes) than those found in the raw exhaust. Apparently, there is a driving force that is focusing

the NPAHs associated with PM from a relatively large number in the raw exhaust to just a handful of compounds as the exhaust moves into the dilution tunnel and cools. To the best of our knowledge, this is new information and may warrant further investigation. It should be noted however, that the raw exhaust PM samples may be more susceptible to sampling artifacts from exposure to higher NO₂ concentrations, possibly leading to the formation of additional nitro compounds.¹⁰

Fundamentally, these dilution tunnel samples are much more representative of PM that would be emitted into the environment. Additionally, because these dilution tunnel samples were collected using conventional diesel PM collection procedures, the results shown in Figure 4-12 provide information that can be compared with that in other reports utilizing the same engine testing procedure. Once the nitro compounds had been preliminarily identified through their retention times in the *m/z* 46 chromatogram, the next step was to verify and quantify these compounds using their molecular ions. Figures 4-14 and 4-15 show the molecular ion chromatograms for 9-nitroanthracene and 1-nitropyrene, respectively. These chromatograms illustrate qualitatively that there is a trend towards lower concentrations as more biodiesel is incorporated into the fuel.

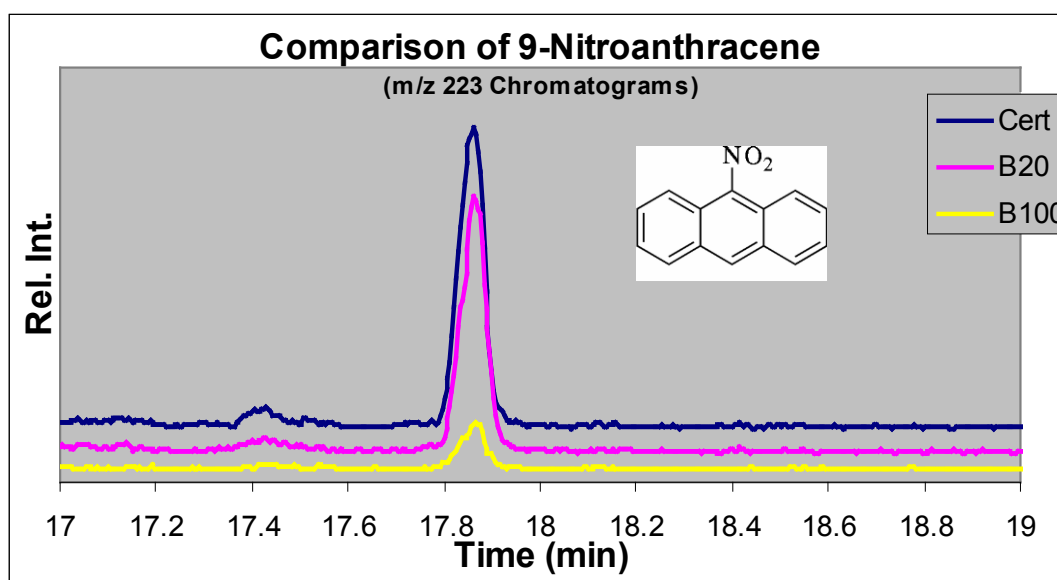


Figure 4-14. The molecular ion chromatograms (*m/z* 223) for 9-nitroanthracene

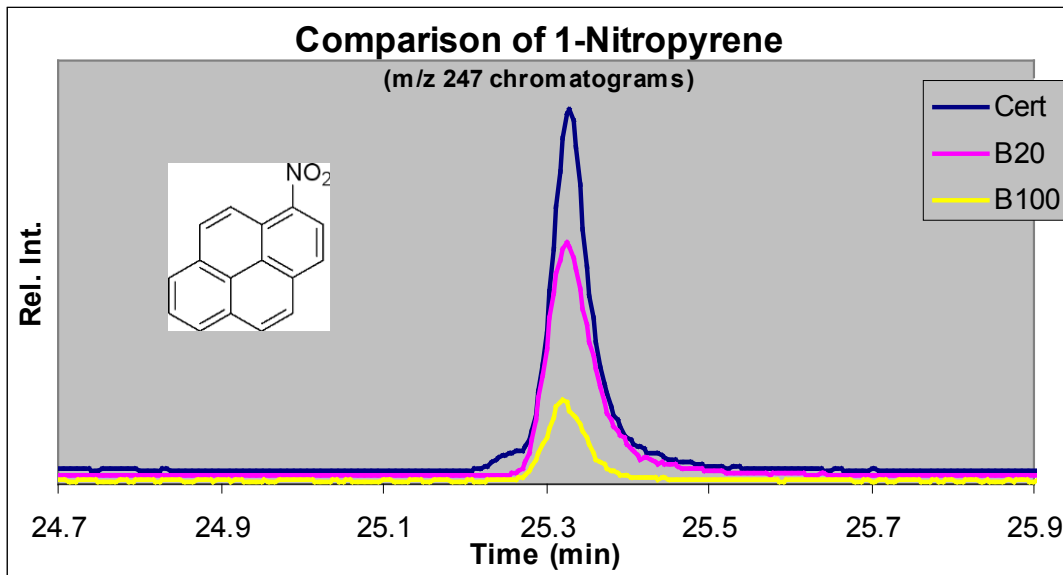


Figure 4-15. The molecular ion (m/z 247) chromatograms for 1-nitropyrene

Table 4-10 shows the total amount of each NPAH produced as it relates to a given fuel type. These results illustrate that as more biodiesel is incorporated into the fuel, smaller amounts of NPAHs are present in the PM, presumably because lower levels of NPAHs are produced during the combustion process. Table 4-11 shows the results of these NPAH levels as they relate back to the PM levels produced by each fuel. The nitrophenanthrenes and 3-nitrofluoranthene generally showed that the concentration per amount of soot is consistent for all fuel types. In other words, the average concentration for each of these compounds is generally within the standard deviation for each fuel type. The other compounds listed in Table 4-11 trend toward less NPAH per milligram as more biodiesel is incorporated into the fuel.

Table 4-10. Diluted exhaust Engine-out NPAH quantities for each fuel (ng/sample)

	Cert (ng/sample)	B20 (ng/sample)	B100 (ng/sample)
1-nitronaphthalene	0.95 ± 0.20	0.49 ± 0.18	0.23 ± 0.04
2-nitronaphthalene	4.33 ± 0.84	3.01 ± 0.0.37	0.73 ± 0.18
9-nitroanthracene	30.1 ± 5.3	18.6 ± 3.4	7.37 ± 1.89
9-nitrophenanthrene	11.8 ± 4.2	8.69 ± 1.33	5.18 ± 0.37
3-nitrophenanthrene	2.41 ± 0.48	1.51 ± 0.24	1.03 ± 0.37
3-nitrofluoranthene	2.44 ± 0.78	1.13 ± 0.22	0.66 ± 0.16
1-nitropyrene	123.4 ± 47.5	60.5 ± 11.9	26.8 ± 3.8
TOTAL	175.4	93.9	42.0

Table 4-11. Diluted exhaust Engine-out NPAH quantities for each fuel (ng/mg PM)

	Cert (ng/mg)	B20 (ng/mg)	B100 (ng/mg)
1-nitronaphthalene	0.32 ± 0.07	0.20 ± 0.07	0.18 ± 0.03
2-nitronaphthalene	1.44 ± 0.30	1.26 ± 0.14	0.57 ± 0.17
9-nitroanthracene	9.96 ± 1.51	7.76 ± 1.22	5.63 ± 1.22
9-nitrophenanthrene	3.89 ± 1.33	3.63 ± 0.47	4.00 ± 0.44
3-nitrophenanthrene	0.80 ± 0.14	0.63 ± 0.09	0.80 ± 0.34
3-nitrofluoranthene	0.80 ± 0.25	0.47 ± 0.08	0.52 ± 0.15
1-nitropyrene	40.8 ± 15.3	25.3 ± 4.4	20.6 ± 1.9
TOTAL	58.0	39.2	32.3

Analyses for PAHs were performed using EI+ (25 eV) in conjunction with molecular ion information obtained for each compound. These molecular ion chromatograms were then used to quantify the levels for each PAH. Figures 4-16 and 4-17 show the molecular ion chromatograms for phenanthrene, anthracene, fluoranthene and pyrene. Each chromatogram qualitatively shows a trend toward lower concentrations as more biodiesel was incorporated into the fuel.

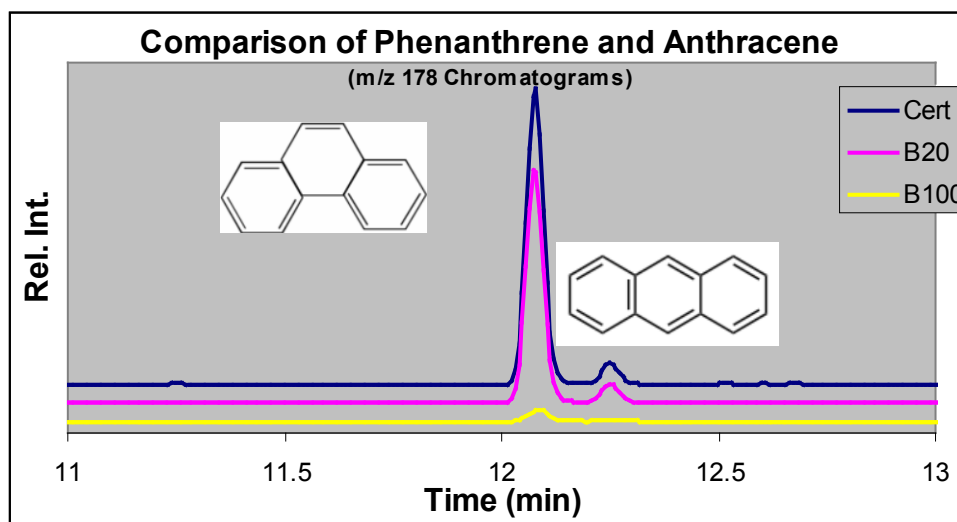


Figure 4-16. The molecular ion chromatograms (*m/z* 178) for phenanthrene and anthracene

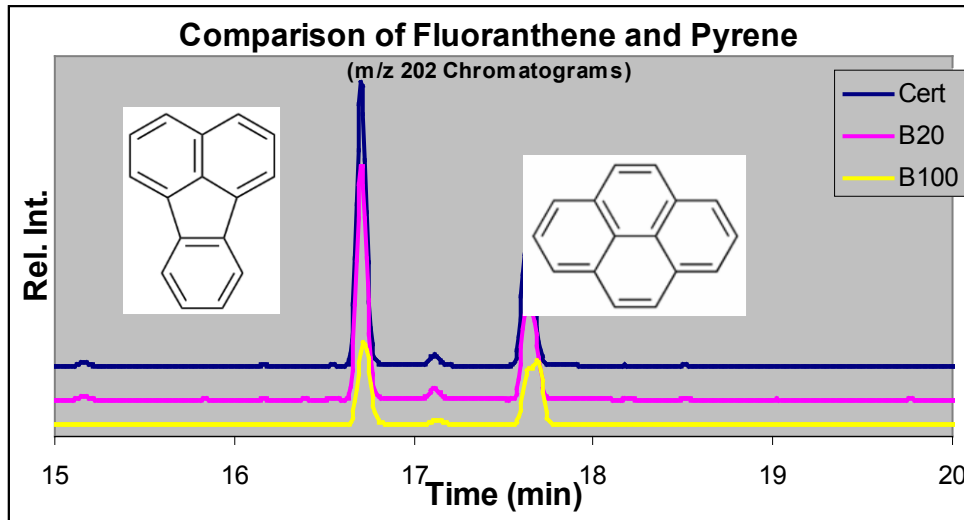


Figure 4-17. The molecular ion chromatograms (*m/z* 202) for fluoranthene and pyrene

Along with the four PAHs shown in the above chromatograms, several other PAHs were also selected for quantitation purposes. Table 4-12 shows the overall quantity of PAH produced by each fuel. Table 4-13 shows each PAH quantity as it relates to the amount of PM collected for each sample.

Table 4-12. Diluted Exhaust Engine-out PAH Quantities for each Fuel (ng/sample)

	Cert (ng/sample)	B20 (ng/sample)	B100 (ng/sample)
naphthalene	82.7 ± 15.0	62.4 ± 8.9	171.1 ± 47.5
biphenyl	16.4 ± 4.6	16.6 ± 0.4	21.9 ± 7.1
acenaphthylene	2.0 ± 0.3	1.9 ± 0.6	1.8 ± 0.3
fluorene	12.9 ± 1.2	8.4 ± 1.39	2.7 ± 0.5
phenanthrene	890.8 ± 154.6	529.9 ± 66.9	89.4 ± 16.7
anthracene	57.7 ± 6.5	35.5 ± 2.3	2.0 ± 0.4
fluoranthene	822.1 ± 177.2	594.9 ± 217.2	186.9 ± 38.2
pyrene	536.5 ± 143.7	332.0 ± 112.5	130.8 ± 23.4
benzo[c]phenanthrene	13.2 ± 5.1	9.0 ± 2.6	4.2 ± 1.2
chrysene	19.2 ± 6.9	17.7 ± 5.4	9.2 ± 3.3
TOTAL	2453.5	1608.3	620.0

Table 4-13. Diluted Exhaust Engine-out PAH Quantities for each Fuel (ng/mg PM)

	Cert (ng/mg)	B20 (ng/mg)	B100 (ng/mg)
naphthalene	29.8 ± 6.4	25.3 ± 2.2	113.3 ± 18.6
biphenyl	6.7 ± 2.8	6.8 ± 0.4	15.9 ± 5.4
acenaphthylene	0.8 ± 0.3	0.8 ± 0.2	1.3 ± 0.2
fluorene	4.7 ± 0.8	3.4 ± 0.4	2.0 ± 0.6
phenanthrene	275.9 ± 53.2	216.9 ± 38.1	67.4 ± 14.9
anthracene	18.0 ± 2.8	14.5 ± 1.6	1.4 ± 0.2
fluoranthene	306.5 ± 81.7	246.0 ± 98.5	135.7 ± 38.7
pyrene	194.3 ± 52.3	137.2 ± 52.1	95.0 ± 16.2
benzo[c]phenanthrene	5.0 ± 1.8	3.7 ± 1.2	3.0 ± 1.1
chrysene	6.8 ± 1.9	7.2 ± 2.2	6.8 ± 3.3
TOTAL	848.5	661.8	441.8

For the three-ring and higher PAHs, the data quantitatively show that as more biodiesel is incorporated into the fuel, smaller amounts of these larger PAHs are present per milligram of PM produced. However, for the double-ring PAHs, naphthalene and biphenyl, the B100 samples showed a higher concentration of these compounds. This scenario is probably related to the fuel properties themselves in that the biodiesel and Cert diesel have fundamentally different chemical properties. Soy biodiesel consists of straight-chain fatty acid methyl esters (FAMES), including significant amounts of double and triple unsaturations in the molecules that probably provide the genesis for the formation of smaller double-ring PAHs. Cert diesel is a petroleum fuel that consists of aromatic constituents that provide better precursors to the formation of the larger three- and four-ring PAHs than the FAMES. The results shown in Table 4-12 and Table 4-13 seem to corroborate this hypothesis.

4.6 Results for DPF-out Dilute Exhaust

These samples were collected in the final days of the subcontract period with the assumption that the gravimetric data would most likely be the only useful data generated for these experiments. The DPF-out exhaust produces such low levels of actual PM that it seemed unlikely that these samples would produce NPAH or PAH signals. Additionally, with the dilution tunnel factored into the sampling, this situation presented an even less likely scenario for detecting these compounds, even after focusing the three 30-minute runs for each fuel onto a single Tissuquartz filter. At most, the expectation was to observe the smaller single-ring and double-ring NPAHs and PAHs. However, upon analysis of the PM for nitro-compounds using the GC/EM-MS, some unexpected results were observed for these samples. Figure 4-18 shows the nitro chromatogram for each fuel sample.

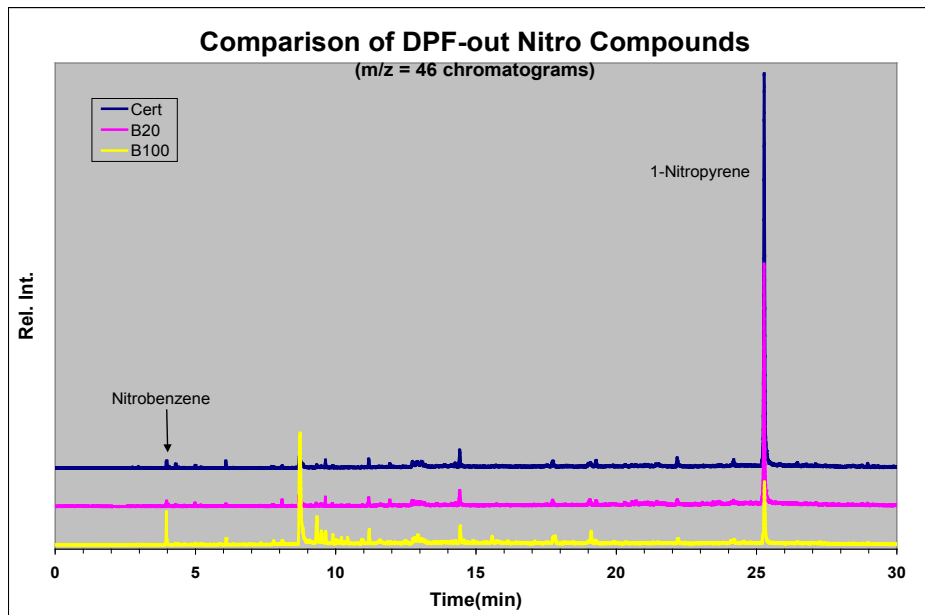


Figure 4-18. Nitro (m/z 46) chromatograms for each DPF-out PM sample (displayed as relative intensity)

The particularly interesting aspect of these chromatograms is the large peak observed at ~25.2 minutes in the Cert and B20 chromatogram (and to a much lesser extent in the B100 sample), which was identified as 1-nitropyrene. These results were very surprising in that the magnitude of these peaks indicated a significant presence of this compound in the DPF-out samples. The Cert and B20 chromatograms are largely free of other NPAHs, indicating that the DPF preferentially forms this compound over all other nitro-aromatics. This result is very surprising given the low level of PM present in the exhaust.

Despite the fact that the B100 sample showed less 1-nitropyrene and other larger NPAHs, it did show an increased number of the smaller, single- and double-ring nitro-aromatics (pre-15 minutes). Figure 4-19 shows a magnified view of the 3- to 20-minute time region for the three samples, with the internal standards labeled on the chromatogram. It is interesting that the majority of these compounds could not be correlated to the 58 NPAH standards available in the laboratory despite the fact that they were clearly nitro compounds. Additionally, the large peak at approximately 9 minutes in the B100 sample was not comparable to the NPAH standards. These unidentified peaks are most likely alkyl nitro-aromatic compounds (e.g., ethyl or propyl nitrobenzenes or nitronaphthalenes) based on their retention times. More work using full-scan analysis will be necessary to identify these unknown nitro compounds.

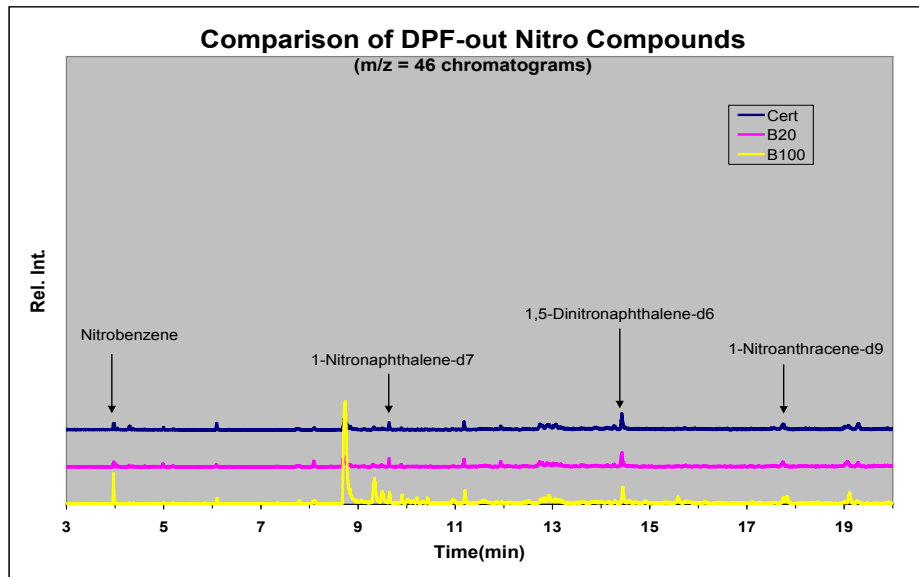


Figure 4-19. Magnified nitro (m/z 46) chromatograms for each DPF-out PM sample

Once the nitro compounds had been preliminarily identified through their retention times in the m/z 46 chromatogram, the next step was to verify and quantify these compounds using their molecular ions. Figure 4-20 shows the molecular ion chromatograms for 1-nitropyrene. These chromatograms illustrate qualitatively that there is a trend toward lower concentrations as more biodiesel is incorporated into the fuel.

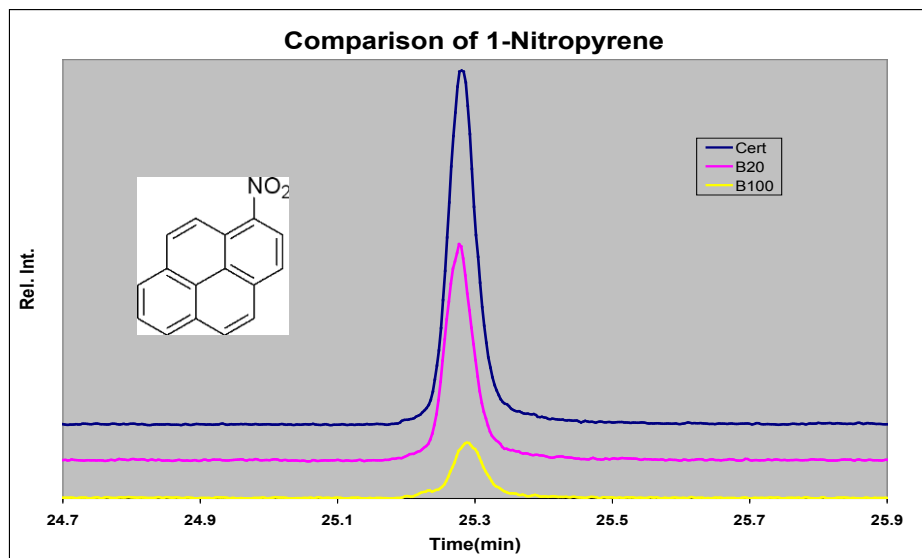


Figure 4-20. The molecular ion (m/z 247) chromatograms for 1-nitropyrene

Table 4-14 shows the total quantitative results for each fuel type for the three largest (four-ring) identifiable NPAHs. These results illustrate that as more biodiesel is incorporated into the fuel, lower levels of four-ring NPAHs are present in the PM, presumably because lower levels of four-ring NPAHs are produced during the combustion process.

Table 4-14. Diluted Exhaust DPF-out NPAH Quantities for each Fuel (ng/sample)

	Cert (ng/sample)	B20 (ng/sample)	B100 (ng/sample)
3-nitrofluoranthene	0.07	0.06	0.05
1-nitropyrene	80.3	53.5	15.0
4-nitropyrene	0.20	0.19	0.16

Normally, the next step would be to look at the relationship between these NPAH amounts and the PM masses for each sample. However, the PM mass reported for the Cert sample in Section 4.4 was far below the weights of the other samples for reasons that were explained previously. As a result, the data cannot be reliably reported at this time. The DPF-out data for the 1-nitropyrene are quite high, and in fact achieve levels comparable to the Engine-out data obtained previously. Table 4-15 shows this comparison between the two exhaust configurations.

Table 4-15. Comparison of 1-nitropyrene Levels between DPF-out and Engine-out Diluted Exhaust Samples

	DPF-out (ng/sample)	Engine-out (ng/sample)
Cert Fuel	80.3	123.4 ± 47.5
B20 Fuel	53.5	60.5 ± 11.9
B100 Fuel	15.0	26.8 ± 3.8

These data clearly show that the amount of 1-nitropyrene is largely independent of the amount of PM removed from the engine exhaust stream by the DPF. These results were completely unanticipated and have not been reported previously. Undoubtedly this finding by itself warrants further investigation to determine the reproducibility of these results, particularly since the DPF appears to be concentrating the 1-nitropyrene onto quantitatively less PM. Additionally, it is expected that DPF-out particles are smaller diameter than Engine-out particles. Thus, the DPF system may create a scenario of higher concentrations of 1-nitropyrene on smaller particles. This in turn may deliver the compound deeper into throat and lung tissues when inhaled, presenting a potential health concern because 1-Nitropyrene has been shown to be both mutagenic and carcinogenic.^{11, 12}

The samples were analyzed for PAHs using EI+ (25 eV) in conjunction with molecular ion information obtained for each compound. These molecular ion chromatograms were then used to quantify the levels for each PAH. Table 4-16 shows each PAH quantity as it relates to each sample. Again, these values were not related back to the PM levels because of the question about the Cert sample discussed in Section 4.4.

Table 4-16. PAH Quantities for Diluted Exhaust DPF-out for each Fuel (ng/sample)

	Cert (ng/sample)	B20 (ng/sample)	B100 (ng/sample)
naphthalene	28.2	58.4	7.7
biphenyl	3.4	9.6	1.9
acenaphthylene	0.08	0.09	0.10
fluorene	ND*	ND	ND
phenanthrene	1.6	1.7	11.5
anthracene	0.11	0.07	0.12
fluoranthene	2.1	1.8	25.1
pyrene	0.98	0.25	15.1
benzo[c]phenanthrene	ND	ND	ND
chrysene	ND	ND	ND
TOTAL	36.4	71.9	61.5

*ND = not detected

The data did not show any clear trends other than this one: of the three fuels studied, the B100 samples had the highest levels of phenanthrene, anthracene, fluoranthene, and pyrene. Additionally, there does not appear to be a clear numerical link between the fluoranthene and pyrene levels observed and the nitrofluoranthene and nitropyrene levels observed in these DPF-out samples other than the general trend that, as the PAH level goes higher, the NPAH level goes lower. More research in this area is necessary before any clear links can be made among the different compounds.

Next, the DPF-out PAH levels for several representative PAHs were compared to the Engine-out samples. Table 4-17 shows this comparison between the two exhaust configurations.

Table 4-17. Comparison of Phenanthrene, Fluoranthene, and Pyrene Levels of DPF-Out and Engine-out Samples

Fuel Type	Exhaust Config.	Phenanthrene (ng/sample)	Fluoranthene (ng/sample)	Pyrene (ng/sample)
Cert	Engine-out	890.8 ± 154.6	822.1 ± 177.2	536.5 ± 143.7
	DPF-out	1.6	2.1	0.98
B20	Engine-out	529.9 ± 66.9	594.9 ± 217.2	332.0 ± 112.5
	DPF-out	1.7	1.8	0.25
B100	Engine-out	89.4 ± 16.7	186.9 ± 38.3	130.8 ± 23.4
	DPF-out	11.5	25.1	15.1

In all cases, the amount of overall PAH present dropped by approximately an order of magnitude or more when the Engine-out samples were compared with the DPF-out samples. However, while the Engine-out samples showed the lowest PAH levels for the B100 samples compared among the fuels, the B100 DPF-out samples showed the highest PAH levels among the different fuels. More research for these types of fuels and exhaust configurations will be necessary to determine the reproducibility of these findings.

5. Conclusions and Future Research

This research demonstrated novel approaches in a number of areas for the analysis of PAHs and NPAHs produced during diesel combustion. The GC/EM-MS was shown to be a versatile technique that allowed for the analysis of both PAHs and NPAHs. In hindsight, because it has become clear that this system is sensitive and selective enough for the analysis of these compounds, the collected mass of Engine-out PM for all fuel types should be lowered to approximately 0.5 mg through the choice of sampling flow rate. This would simplify the sample preparation strategy by eliminating the amino solid phase extraction steps, leaving just Soxhlet extraction and evaporation. This smaller recommended gravimetric level mimics the dilute DPF-out PM samples, which did not need the additional cleanup steps. This simplified scenario would not only save time but also eliminate a number of steps that may contribute to the loss of the PAHs and NPAHs.

Comparison of the raw and diluted samples shows that the raw exhaust contains a larger variety of nitro compounds relative to the dilution tunnel samples. This indicates that chemical changes in NPAHs are still occurring in the exhaust gas as it moves from the engine into the dilution tunnel. The details of these chemical reactions remain to be determined, but we have demonstrated new tools to investigate them. Using this information, new technologies could be introduced to limit the formation of these mutagenic and carcinogenic compounds associated with the PM.

While the raw exhaust samples provided interesting new information about NPAH chemistry within the exhaust stream, the dilute samples provided a more realistic scenario for determining which compounds are actually being emitted into the environment. The DPF-out PM produced surprising results with regard to 1-nitropyrene. The fact that this compound was present in the DPF-out PM at quantities comparable to those observed in the Engine-out PM samples was unexpected, particularly since the DPF lowers the gravimetric amount of PM present in the exhaust by over an order of magnitude. This apparent independence from PM level has not been reported previously and suggests that the DPF is actually focusing the formation of NPAHs almost exclusively toward the 1-nitropyrene compound. This is a concern given the mutagenic and carcinogenic nature of this particular NPAH.

It is interesting that, in concert with the apparent insensitivity of 1-nitropyrene to the DPF, the pyrene levels found in the DPF-out samples were much lower (by 3 orders of magnitude in some cases) than the pyrene levels observed in the Engine-out samples. If pyrene is a key precursor to 1-nitropyrene, then one might reasonably expect the two compounds to trend similarly to lower concentrations via the DPF. Two possible explanations for the observed divergent trends are as follows:

1. 1-nitropyrene is formed by an alternative mechanism to pyrene nitration
2. The measured concentrations of 1-nitropyrene are at or near equilibrium limits exiting the DPF.

Further engine testing will be necessary to determine the reproducibility of these results, and, if these results are indeed reproducible, then more investigations into the mechanisms for the formation of 1-nitropyrene may be warranted.

6. References

1. Bleakney, W., and J.A. Hipple, Jr. "A New Mass Spectrometer with Improved Focusing Properties." *Phys. Rev.* **53**:521-529, 1938.
2. Laramee, J.A., R.B. Cody, and M.L. Deinzer. "Discrete Energy Electron Capture Negative Ion Mass Spectrometry." In *Encyclopedia of Analytical Chemistry*, R.A. Meyers, Ed. Chichester: John Wiley and Sons, pp. 11651-11679, 2000.
3. Voorhees, K.J., et al. In *Proceedings of 49th ASMS Conference on Mass Spectrometry and Allied Topics*. Chicago, IL, 2001.
4. Havey, C.D., et al. "Analysis of Nitro-Polycyclic Aromatic Hydrocarbons in Conventional Diesel and Fischer-Tropsch Diesel Fuel Emissions Using Electron Monochromator-Mass Spectrometry." *Anal. Chem.* **78**:4894-4900, 2006.
5. Havey, C.D., et al. "Theory and Application of Dissociative Electron Capture in Molecular Identification." *J. Phys. Chem. A.* **110**(13):4413-4418, 2006.
6. Fritz, J.S., *Analytical Solid-Phase Extraction*. New York: John Wiley & Sons, Inc., 1999.
7. Bezabeh, D.Z., et al. "Determination of Nitrated Polycyclic Aromatic Hydrocarbons in Diesel Particulate-Related Standard Reference Materials by using Gas Chromatography/Mass Spectrometry with Negative Ion Chemical Ionization." *Anal. and Bioanal. Chem.* **375**(3):381-388, 2003.
8. Dane, A.J., C. Abbas-Hawks, and K.J. Voorhees. Unpublished. Colorado School of Mines, 2005.
9. "AVL 8-Mode Heavy-Duty Cycle." Available from www.dieselnet.com/standards/cycles/avl_8mode.html, 1997 (rev. 2000); last accessed in March 2010.
10. Khalek, I.A. "Nitro-PAH Artifact Investigation." Southwest Research Institute, Project No. 10738. Final report to NREL for Subcontract No. ACI-4-44029-01, November 2004.
11. Chan, P. "National Toxicology Program Technical Report on the Toxicity Studies of 1-Nitropyrene (CAS No. 5522-43-0) Administered by Inhalation to F344/N Rats." *Toxicity Report Series* **34**:1-D2, 1996.
12. Kappers, W.A., et al. "Comparison of Three Different In Vitro Mutation Assays Used for the Investigation of Cytochrome P450-Mediated Mutagenicity of Nitro-Polycyclic Aromatic Hydrocarbons." *Mutation Research* **466**(2):143-59, 2000.

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