

CHARACTERIZATION OF CHEMICAL COMPOSITION AND SIZE OF DIESEL EXHAUST PARTICULATE MATTER BY LDITOF/MS.

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Introduction

Diesel engines see extensive use due to their high efficiency and suitable torque characteristics. In general diesel engines have lower carbon monoxide and hydrocarbon emissions than spark-ignition engines. However, they are known to create much larger amounts of particulate matter and polycyclic aromatic hydrocarbons (PAHs) and their derivatives. Contributing factors are higher temperatures and pressures in the combustion process together with larger initial concentrations of aromatics in the diesel fuel.

The presence of the aromatic compounds in the air represents a potential hazard to human health. Several PAHs and nitro-PAHs have been identified as carcinogenic and potentially carcinogenic compounds (Ref. 1). The extent of human exposure to PAHs and their derivatives depends on the partitioning between the gas and particle phases as well as the size distribution of the particle fraction containing the PAHs. There is a much greater potential carcinogenic effect if the PAHs are components of particles that penetrate and deposit into the bronchia and alveoli of the lungs. Studies show that a major fraction of particles that are 1.0 μm or less in diameter might deposit in the air ways and lungs (Ref. 2). Moreover, some recent studies have correlated health effects with the concentration of atmospheric particles, yet have failed to identify the causative agents (Ref. 3). Since the toxicity of particles from different sources varies widely, such studies would be much more valuable if the particles from a source were characterized with respect to size and composition.

Traditional methods for the determination of PAHs and nitrated PAHs are based on gas chromatography/mass spectrometry or liquid chromatography with fluorescence techniques for detection. Both approaches are time consuming, may require solvent extraction and separation, are expensive, and in most cases require multiple runs (Ref. 4). In this study performed on diesel soot, we demonstrate the applicability of Laser Desorption Ionization Time of Flight Mass Spectrometry (LDITOF/MS) as a rapid screening method in the analysis of particulate matter collected and segregated by particle size using a multiple stage portable impactor. LDITOF/MS is capable to generate parent ion dominated spectra with low fragmentation from samples containing particles in a specific size range, which makes LDITOF/MS an excellent technique for the screening for PAHs in complex mixtures without need for solvent extraction and separation.

Experimental

The source of diesel exhaust particulate matter was an experimental direct injection 1 cylinder diesel engine aspirated at normal pressure (no turbocharger was used). Samples were collected with the engine idling warm at 2,000 rpm. Reformulated California grade diesel fuel (low sulfur content) was used for the experiment.

Diesel soot samples were collected using a three stage portable impactor developed by the Delta Group at UC Davis (Ref. 5). The impactor was equipped with aluminum foil strips attached to rotary drums that, during sampling, rotated at a fixed angular speed exposing the attached aluminum strip to an inlet nozzle. The dimensions of the inlet nozzle determined the range of size of particles that hit the surface of the strip. As the drum rotates the segment of aluminum strip exposed to the inlet changed continuously, resulting in a deposition of sample with a time reference. A cyclone pump operating with a flow rate of 22.7 l min^{-1} allowed for collection of particles less than 2.5 μm in aerodynamic diameter. The 50% cut point of such an impactor has been validated both in extensive field and laboratory studies (Ref. 5 and references there in).

Samples were obtained positioning the impactor at 20 cm from the exhaust of the diesel engine. A Nucleopore® filter at the external inlet prevented coarse matter from entering the impactor. This filter permits particles of diameters smaller than 2.5 μm to penetrate into the impactor.

Particles with aerodynamic diameter between 2.5 μm to 1.15 μm were collected on the first stage of the impactor (denoted stage A). The second stage collected particles within the size range 1.15 μm to 0.24 μm (denoted stage B). The third stage accumulated particles of size 0.24 μm to 0.07 μm (denoted stage C). Particles not trapped on the aluminum strips were collected on a 0.01 μm porous teflon filter at the impactor outlet.

The laser desorption ionization time of flight mass spectrometer used has been described in previous publications (Ref. 6). Ultraviolet radiation of 266 nm produced from the fourth harmonic of a Nd:YAG laser with a 2.5 ns pulse width was used to desorb and ionize the sample. The UV laser beam was focused into the source region through a 250 mm focal length S1-UV quartz lens. The beam was directed incident to the sample surface at 45°. Neutral density optical filters were used to reduce the laser power to 10⁶ W/cm² at the focal point on the sample surface. The beam diameter at the focal point was about 90 μm . A time delay of 250 ns in the application of the extraction potential at the source allowed time for prompt decay of metastable ions and improved overall resolution.

Particulate matter from each stage and from the inlet and outflow filters of the impactor were analyzed using LDITOF/MS. Segments of the aluminum foil from the impactor were attached to the sample probe and loaded into the TOF/MS. Each spectrum recorded was the sum of 240 randomly located laser shots. Blank filters and aluminum foil were checked for contaminants. Both positive and negative mass spectra were collected and analyzed.

Results

Positive ion mass spectra for five diesel particle size ranges matter are shown in Figure 1. Spectrum in *1a*) was obtained from the particles trapped at the external inlet filter with diameters larger than 2.5 μm ; *1b*) shows the spectrum resulting from particles with aerodynamic diameter between 2.5 μm to 1.15 μm , stage A; *1c*) from the size range 1.15 μm to 0.24 μm , stage B; *1d*) was obtained from particles in the stage C whose diameters range between 0.24 μm and 0.07 μm . At the bottom *1e*) display the ion yield obtained from the outlet filter, with particles smaller than 0.07 μm .

Low mass peaks (identified as PAHs), are more abundant in large particles, > 2.5 μm diameter, than small particles, < 0.07 μm diameter. The general trend of the shift of PAH mass, with high mass PAH being associated with the fine particulate is clear in Figures *1a*) through *1e*). Only the smallest particles, 0.07 μm have significant amounts of PAH with mass greater than 400 amu. In contrast, in *1a*) ion yield of mass above 400 Da decreases rapidly.

Two series of PAH ions are observed in all the positive ion spectra in Figure 1. The two series are most apparent in Figure *1e*). The first series is comprised of *m/z*: 178, 202, 228, 252, 276/278, 302, 326/328, 350/352, 374/376, 398/400/402, and higher masses. The second series has twice the frequency as the first series, with every other peak overlapping (with some exceptions) with the first series. The second series is comprised of *m/z* 190, 202, 216, 226, 240, 252, 266, 276, 290, 302, 326, 342, 350/352, 366, and higher masses. Both series have been labeled in Figure *1b*). A surprisingly large potassium signal is observed in the smallest particles, Figure *1e*).

Negative ion spectra of the diesel particulate matter are shown in Figure 2. As in the case of the spectra of positive ions, each plot corresponds to a different fraction. From *2a*) to *2e*), spectra were taken from particles larger than 2.5 μm ; from 2.5 μm to 1.15 μm , stage A; from 1.15 μm to 0.24 μm , stage B; ranging from 0.24 μm to 0.07 μm , stage C; and smaller than 0.07 μm .

In contrast to positive ion spectra, the highest mass negative ions (*m/z*: 369, 414, and 447) are associated with the larger particles.

Inorganic ions, OH⁻, Cl⁻, NO₂⁻ and NO₃⁻ are observed for all five particle size range.

Very fine particles, < 0.07 μm , show significantly higher HSO₄⁻ than any of the spectra for larger particles.

Discussion

In a recent study by Reilly and collaborators (Ref. 7), organic composition of individual particles of diesel soot are obtained using an excimer laser for ablation ionization. Using this technique they are able to detect known compounds in diesel soot and to establish some differences in

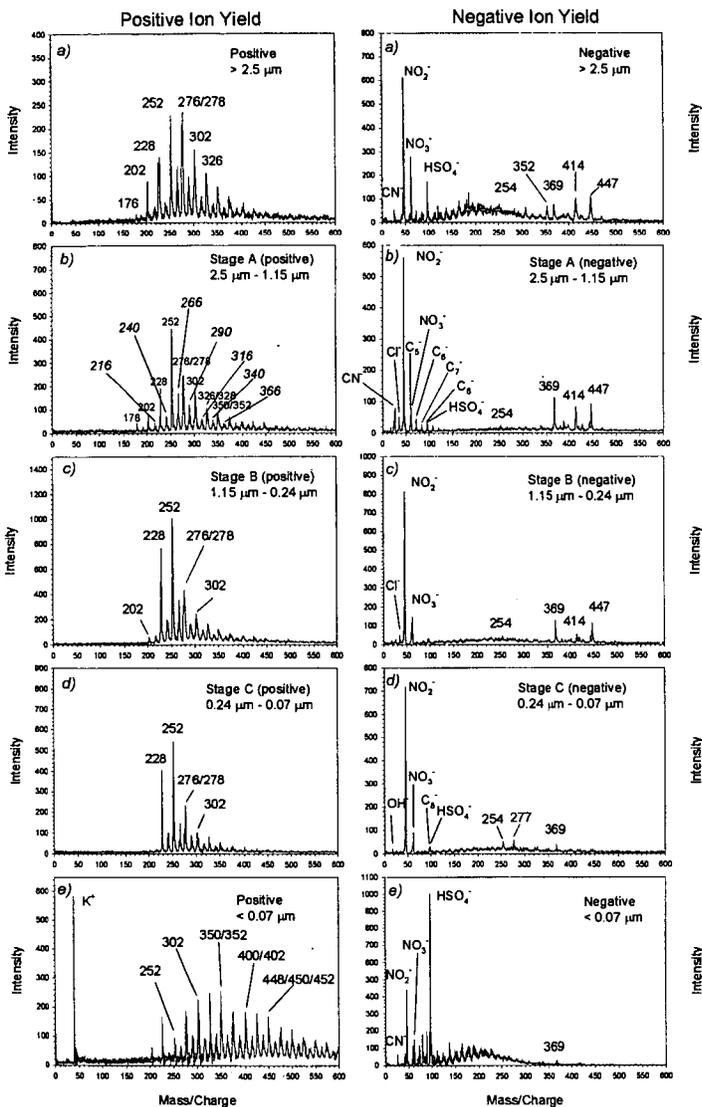


Figure 1. Positive ion mass spectra for five diesel particle size ranges.

Figure 2. Negative ion mass spectra for five diesel particle size ranges.

chemical composition according to particle size. However their method involves unavoidable fragmentation that obscures their results. On other study, Hankin and John (Ref. 8) examine the chemical composition of individual particles of diesel soot SRM 1650. In their experiment using LDITOF/MS, individual particles fixed to a sample support are subject to microlaser beam that desorbs compounds from the particle, and a second beam ionizes the compounds in the plume of desorbed material. The Hankin and John TOF/MS analysis of SRM 1650 yielded the mass of some certified compounds in their sample as well as some other compounds not certified but

known to be present in such standard such as alkylated PAHs. The Hankin and John study examined only very large particles (~ 20 µm).

In our study we report the first mass spectra of particles that were sized using an impactor. Working with a laser spot of 90 µm of diameter, the signal was derived from many particles at the same time thus obtaining reproducible results that are representative of a particular particle

Table I
PAHs commonly found in diesel soot.

PAH	mass
phenanthrene	178
fluoranthene	202
pyrene	202
benz[a]anthracene	228
chrysene	228
benzo[a]pyrene	252
benzo[e]pyrene	252
benzo[k]fluoranthene	252
perylene	252
benzo[ghi]perylene	276
indeno[123-cd]pyrene	276

size range. In positive ion mode, the most intensive peaks in Figure 1 correspond to PAHs commonly found in diesel exhaust. The spectrum from stage A shows peaks corresponding to the mass of PAHs listed in Table I. Moreover from Figure 1, it is clear that many other PAHs are present in the samples. The first series corresponds to PAHs isomers containing only 6 member rings. The second series, with every other peak overlapping with the first series (with a few exceptions), corresponds to PAHs containing five member rings.

Spectra in Figure 1 shows identifiable peaks up to mass 448; some authors have detected such

mass in environmental samples and have assigned tentatively benz[a]ovalene as the most probable identity of the isomer (Ref. 9). Table II list a few possible assignments to peaks in the second series (Ref. 10).

Soot particles emitted from a diesel engine are usually observed as chain aggregates composed of several tens to hundreds of primary spherical particles. Ishiguro and collaborators (Ref. 11), have found that the structure of such spherical particles consist on an inner core surrounded by an outer shell. The inner core of 0.010 µm are composed of nonplanar molecules. The surrounding

Table II. Few possible mass assignments for peaks in the second series (see text).

Formula	Mass (Da)	Compounds
C ₁₆ H ₁₀	202	Fluoranthene
C ₁₇ H ₁₂	216	Cyclopentaphenanthrene Cyclopentaanthracene Benzofluorene
C ₁₈ H ₁₀	226	Benzo(ghi)fluoranthene
C ₁₉ H ₁₂	240	Cyclopentapyrene Benzofluoranthene Cyclopentachrysene Benzopyrene
C ₂₀ H ₁₂	252	Benzocyclopentantracene
C ₂₁ H ₁₄	266	Benzocyclopentantracene Indenophenanthrene Dibenzofluorene Benzochrysene
C ₂₂ H ₁₂	276	Benzocyclopentapyrene
C ₂₃ H ₁₄	290	Benzocyclopentachrysene Dibenzopyrene
C ₂₄ H ₁₄	302	Cyclopentindenophenanthrene
C ₂₅ H ₁₆	316	Benzinindenophenanthrene
C ₂₆ H ₁₄	326	Indenoperylene
C ₂₇ H ₁₆	340	Tribenzopyrene
C ₂₈ H ₁₄	350	Diindenopyrene
C ₂₉ H ₁₈	366	Dibenzopentacene

outer shell is compose of micro crystallites comprising several polycyclic aromatic hydrocarbon layers oriented concentrically in a soot particle. During shell formation, molecules, radicals, or ions including two to four carbon atoms could contribute the surface reactions promoting the polycyclic growth of the graphitic crystallites. Those observations by Ishiguro and collaborators support the assignment of peaks in Figure 1 as PAHs compounds. The extreme high mass range of PAHs observed for small particles would not be observable by traditional GC/MS.

Diesel soot particles exhibit size ranging (Ref. 12) from 4 µm to 0.04 µm, with a peaking distribution about 0.1 µm. Our study reveal that there are differences in the chemical contents of particles in such range. This information may be relevant in toxicological studies that assess the health hazard imposed by the continuous use of diesel engines. Toxicological assessments, regulation and development of

cleaner running diesel engines(Ref. 13) require development of analytical methods that can examine the exhaust by particle size. Our results may provide a guide for pollutants reduction in the emissions of diesel engines based in a better understanding of the process that generate soot and pollutants.

Conclusions

The ability to use TOFMS to characterize the chemical composition of diesel soot particles captured using an impactor has been demonstrated. The analysis of size segregated particles from the impactor was performed without further preparation loading directly a sample collected on aluminum foil into the MS chamber. Results indicate a variation of the compound contents according to particle size. In general finer particles have high concentration of extremely large PAHs, potassium, and sulfate. The larger particles contain lower mass PAHs. Our data show the presence of many PAHs in diesel soot that have not been fully characterized as compounds found in diesel soot. Our method detected extremely large PAHs not amenable to GC/MS analysis.

Our technique may be useful for the characterization of emissions of different sources according to the size of the particles. Accurate assessment of human health hazards associated with particulate matter requires chemical analysis associated with particle size and source. This information would be very valuable for addressing the question of which are the most important factors on the bioactivity associated with different class of particles.

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