

Characterization of Chemical Composition and Size of Diesel Exhaust Particulate Matter by LDITOF/MS

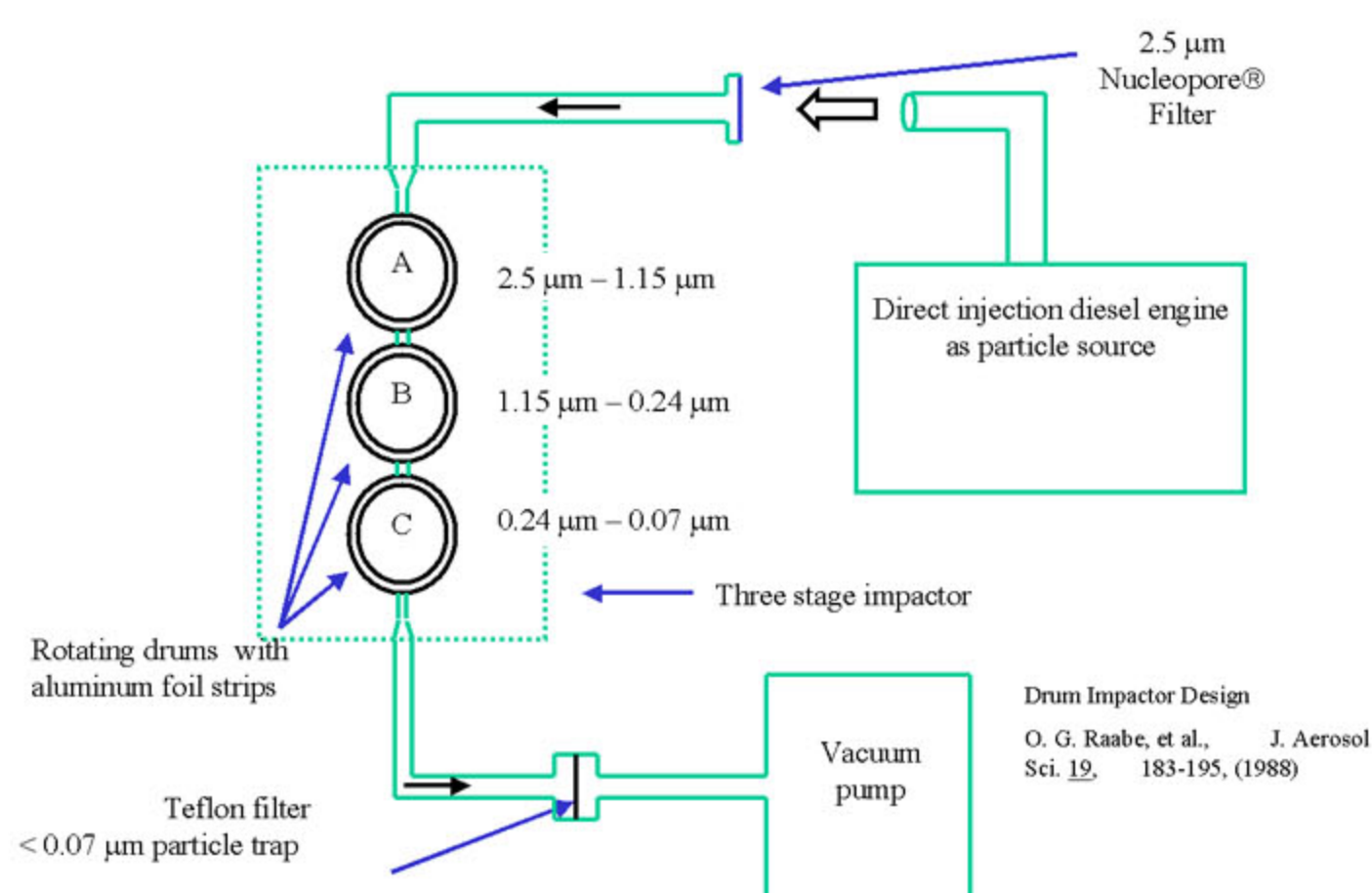
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Abstract

Combustion in a diesel engine occurs at higher temperatures and pressures than gasoline engines. The combustion characteristics and the aromatic content in the fuel yields larger amounts of particulate matter as well as many polycyclic aromatic hydrocarbons (PAHs) in the exhaust. Health effects related to diesel exhaust depend on the particle size and chemical composition. Particles that are 1.0 μm or less in diameter can be inhaled into the lungs. Toxicology assessments, regulation and development of cleaner diesel engines require analytical methods that can examine the exhaust by particle size. In this study, diesel exhaust particulate is separated by size using a portable impactor and analyzed by LDI TOF-MS.

UC Davis Three Stage Drum Impactor



Diesel Soot: Chemical Fingerprint and Particle Size

Positive Ion Spectra

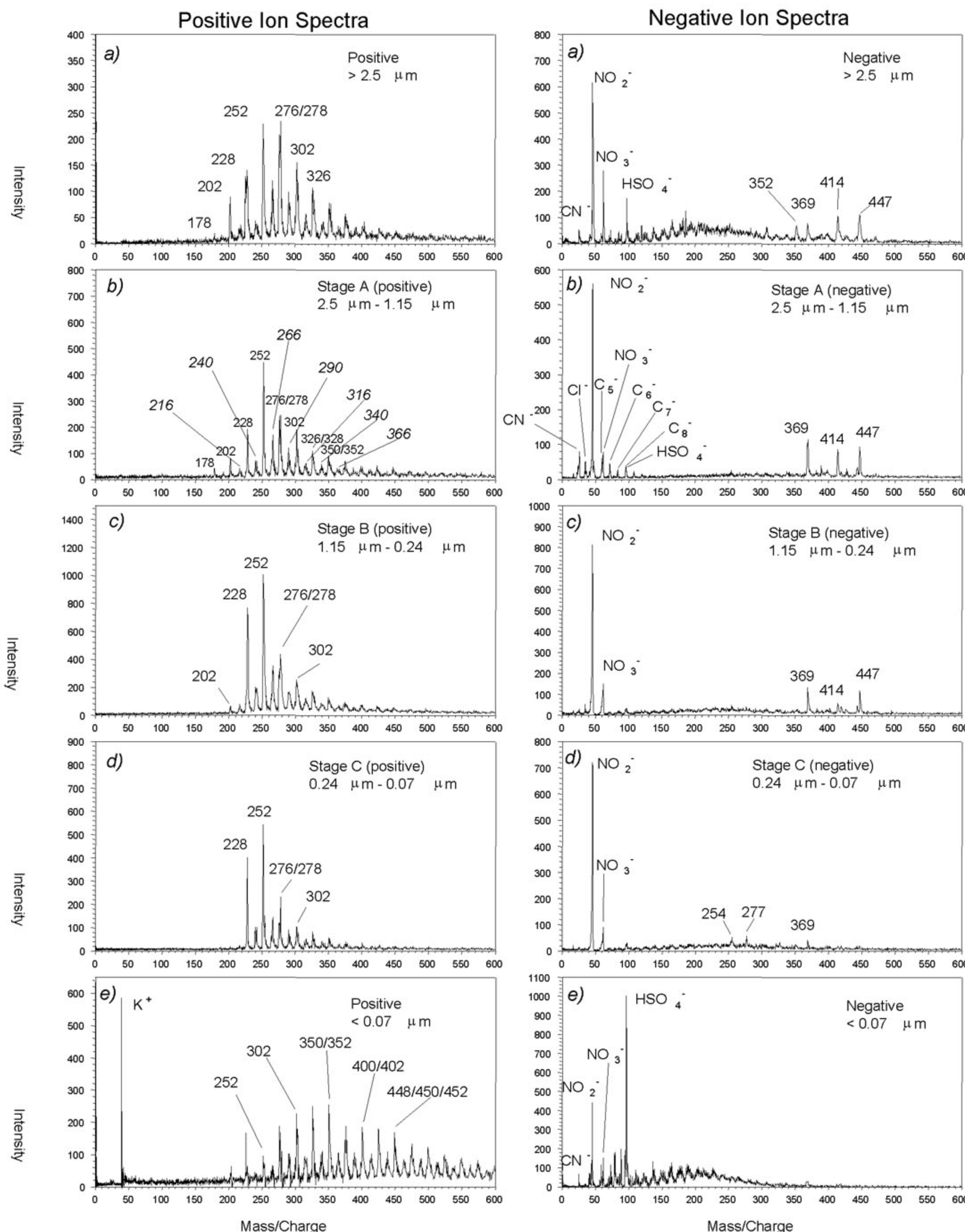
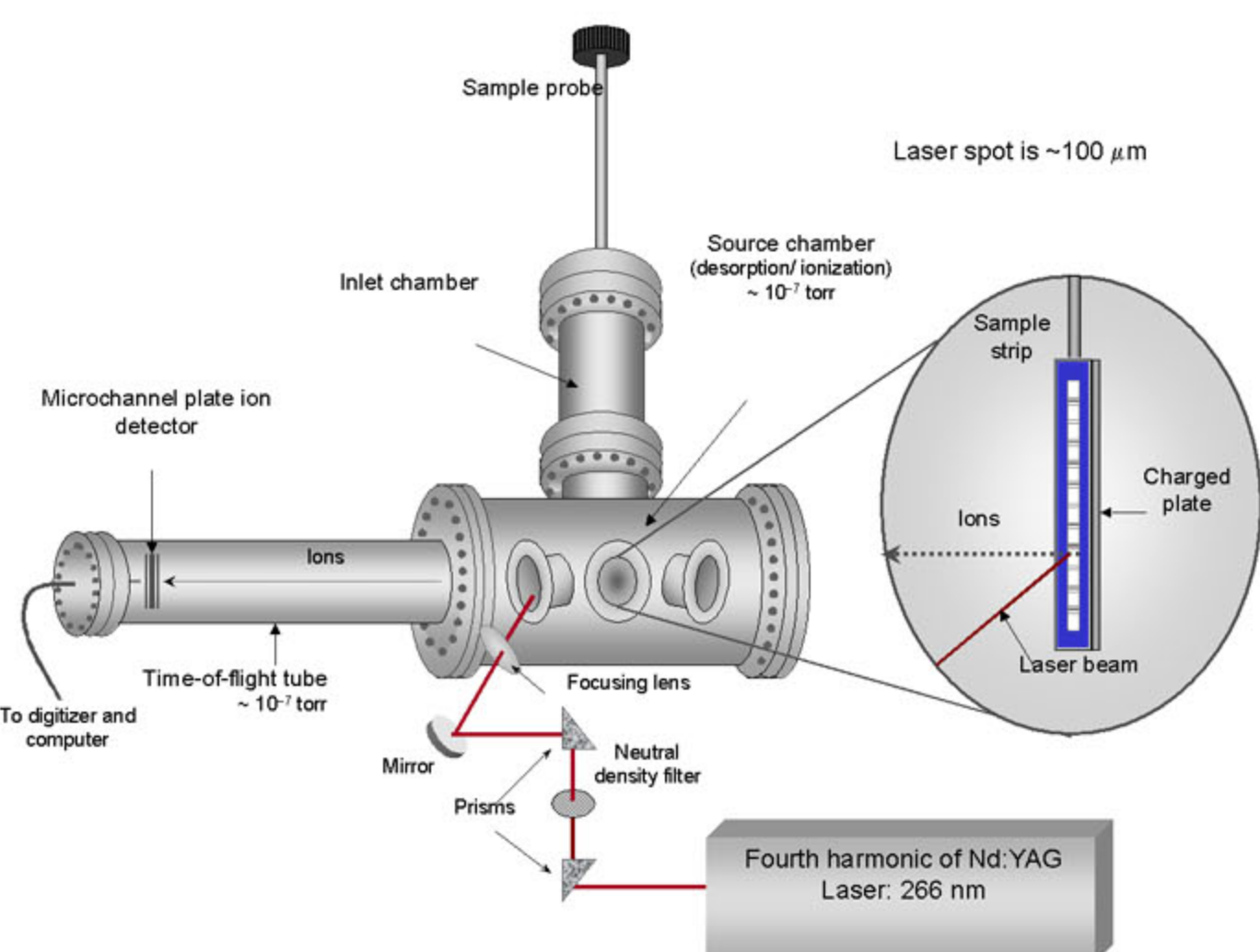
- Low mass PAHs are more abundant in $> 2.5 \mu\text{m}$ particles than $< 0.07 \mu\text{m}$, ultrafine particles.
- Only the smallest particles, $< 0.07 \mu\text{m}$ have significant amounts of PAH with mass greater than 400 Da.
- A large potassium signal is observed in the $< 0.07 \mu\text{m}$ particles.

Negative Ion Spectra

- Inorganic ions, OH^- , Cl^- , NO_2^- and NO_3^- are observed for all five particle size ranges.
- Ultrafine particles, $< 0.07 \mu\text{m}$, show significantly higher HSO_4^- than larger particles.
- The highest mass negative ions (m/z : 369, 414, and 447) are associated with the larger particles.

Diesel Soot Ultrafine Fraction

- Chemical analysis of the ultrafine particles yields the best information on initial nucleation.
- Both PAH > 400 Da. and KHSO_4 (hydrated) have lower vapor pressure, thus they are first to nucleate.

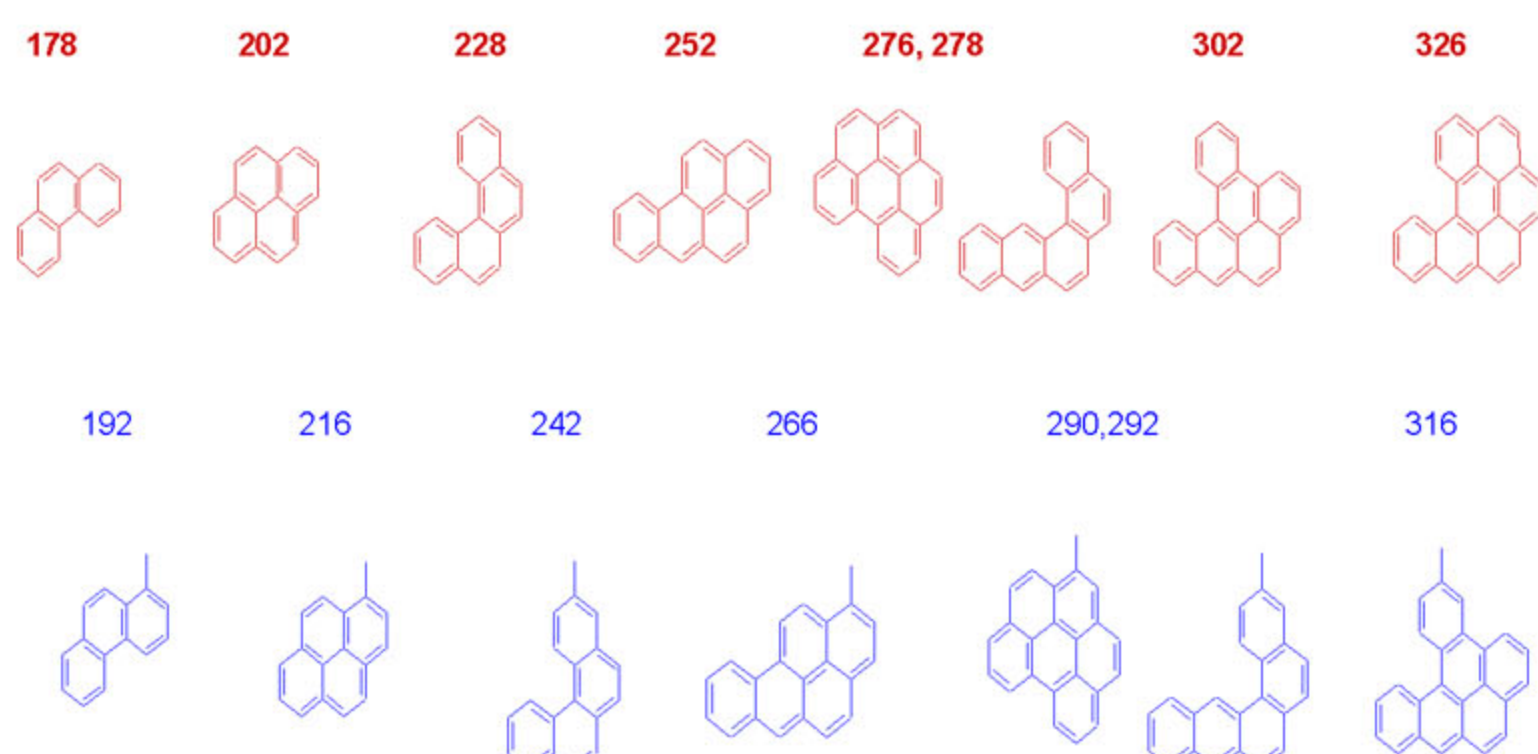


PAHs in diesel soot particle samples were detected using laser desorption ionization time of flight mass spectrometry (LDITOF/MS) coupled with a cascade impactor [1]. PAHs and PAH derivatives are of environmental concern due to their carcinogenic properties [2]. The particle size, coupled with chemical composition, is required for assessment of toxicity of the particulate matter. The greatest health risk is associated with particles in the ultrafine size range ($< 0.1 \mu\text{m}$) [3]. In the LDITOF/MS mass spectra, the observed change in mass distribution of PAHs identifies a change in chemical composition in the diesel soot particle samples for different size ranges. Our work demonstrates the use of a particle sizing impactor to obtain diesel soot particle samples for mass spectrometry. Impactor collection of the ultrafine particles allows examination of the particle size range that is inaccessible to the single particle TOF methods [4]. The large relative abundance of bisulfate anion in the ultrafine mass spectrum supports the theory that the formation of diesel soot particles involves nucleation and growth about sulfuric acid and water condensate [5]. In further application of LDITOF/MS, we will examine diesel engines under varying operating conditions.

Acknowledgements

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Formula	Mass (Da)	PAH	Formula	Mass (Da)	PAH
C ₁₀ H ₈	128	naphthalene	C ₁₈ H ₁₂	228	chrysene
C ₁₂ H ₈	152	acenaphthylene	C ₂₀ H ₁₂	252	benzo[a]pyrene
C ₁₃ H ₁₀	166	fluorene	C ₂₀ H ₁₂	252	benzo[e]pyrene
C ₁₄ H ₁₀	178	phenanthrene	C ₂₀ H ₁₂	252	benzo[k]fluoranthene
C ₁₆ H ₁₀	202	fluoranthene	C ₂₀ H ₁₂	252	perylene
C ₁₆ H ₁₀	202	pyrene	C ₂₂ H ₁₂	276	benzo[ghi]perylene
C ₁₈ H ₁₂	228	benz[a]anthracene	C ₂₂ H ₁₂	276	indeno[123-cd]pyrene