

LASER MICROPROBE MASS SPECTROMETRY MICROANALYSIS OF POLYCYCLIC AROMATIC HYDROCARBONS IN FLAMES, IN DIESEL FUELS AND IN DIESEL EMISSIONS

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Introduction

Diesel fuels and emissions are composed of numerous hydrocarbon species. Combustion generated or pyrogenic polycyclic aromatic hydrocarbons (PAHs) derived from premixed and diffusion flames often consists of the most stable benzenoid PAHs. In contrast, diesel fuels from the UK, [1] US [2] and the current work contain petrogenic alkyl-PAHs with high hydrogen content. Laser microprobe mass spectrometry (LMMS) and gas chromatography/mass spectrometry (GC/MS) are used in a complementary manner to differentiate the (PAHs) originating in the fuel from those produced by engine combustion in particulate emission samples.

Diesel emissions from circa 1990s engines (a NIST SRM 1650a and ambient roadway tunnel samples) display the full mass range of PAHs from 128 u to 376 u including both the benzenoid PAHs and alkyl-PAHs. The chemical nature and absence of petrogenic species larger than 206 u facilitates their detection and delineation from pyrogenic PAHs by mass spectrometry.

Experimental Section

A commercial laser microprobe mass spectrometer is used to analyze particles produced from diesel engine exhaust, pure ethene flame and micro quantities of diesel fuel. The instrument is described in detail by Denoyer et al. 1982 [3]. This is a time-of-flight mass spectrometer that utilizes a single pulsed laser operating in the UV to simultaneously ablate and ionize the sample (in a single irradiation). The laser microprobe has transmission geometry with respect to the laser beam and the time-of-flight mass spectrometer as shown in Figure 1.

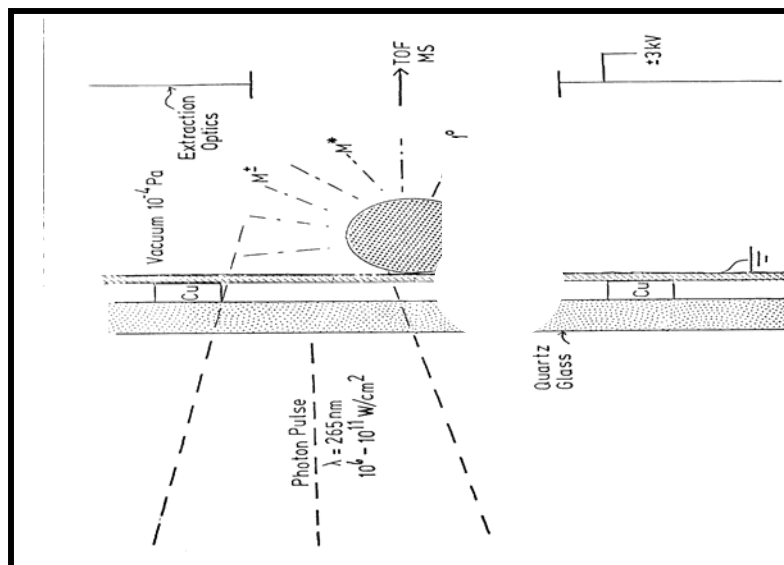


Figure 1. Schematic of laser desorption/ionization by a focused laser beam and subsequent mass analysis by time-of-flight mass spectrometry.

Carbonaceous particles were collected from the interior domain of a pure ethene diffusion flame by a thermophoretic sampling method previously described in detail [4]. The particles were collected on copper TEM grids that were cleaned by an oxygen plasma ashing process.

Diesel emission particles were obtained from the Fort McHenry Tunnel in Baltimore, Maryland from the predominately diesel truck route. The samples were collected on pre-fired quartz coverslips using an eight stage low-pressure aerosol impactor.

Standard Reference Material (SRM) 1650a, Diesel Particulate Matter, is intended for evaluating analytical techniques to determine trace concentrations of PAHs and nitro-polynuclear aromatic hydrocarbons (N-PAHs). SRM 1650a has certified values for 17 PAHs and nitro-PAHs and reference values for an additional 25 PAHs, 3 nitro-PAHs and 9-fluorenone. A small amount of particles were taken directly from the issued bottle and were mounted onto either a cleaned quartz coverslip or a cleaned uncoated copper transmission electron grid. No chemical extractions were made.

A small quantity of SRM 1624c, an uncut diesel No. 2-D distillate fuel, was also analyzed by LMMS and a larger aliquot by gas chromatography/mass spectrometry. The later analysis employed isotopically labeled standards for relative quantitation of PAHs in the fuel.

Results and Discussion

Comparison of two typical positive ion mass spectra for pure ethene and for diesel particulate collected in the Baltimore tunnel are shown in Figure 2. The flame spectra contain virtually no small peaks that correspond to PAHs below 202 u while the diesel spectrum contain peaks that represent PAHs from 128 u to over 376 u. Similar spectra were obtained for the diesel SRM 1650a. Since the flame PAHs are derived from pure ethene gas, they are unquestionably pyrogenically derived. The mass range for these predominately benzenoid PAHs is from 200 u to 450 u [5].

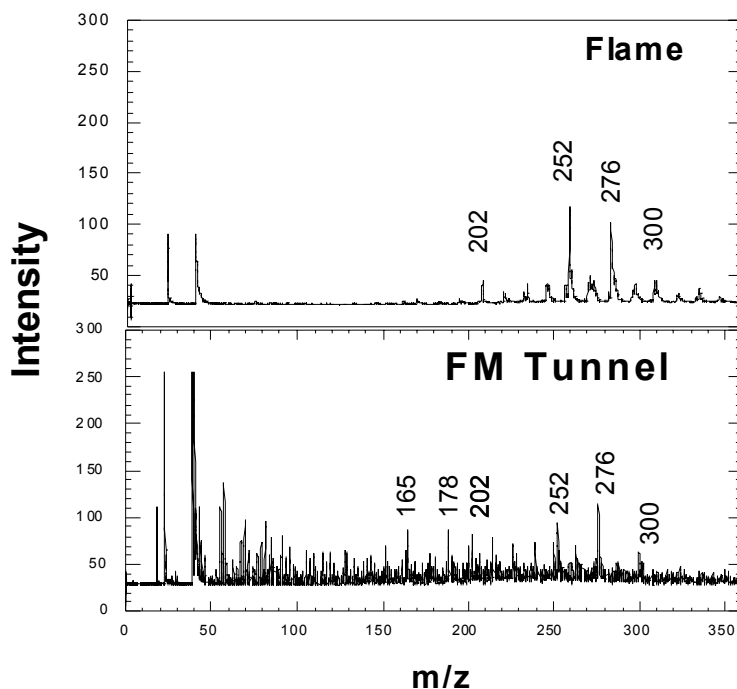


Figure 2. Two positive ion mass spectra of carbonaceous particles collected from an ethene diffusion flame (top) and Fort McHenry Tunnel.

The PAH relative distributions found for the diesel particulate matter from both SRM 1650a and Baltimore tunnel as well as the ethene flame particles is summarized in Figure 3. The ethene peaks are primarily in the large mass region and the peaks associated with the diesel sources are in the small mass domain.

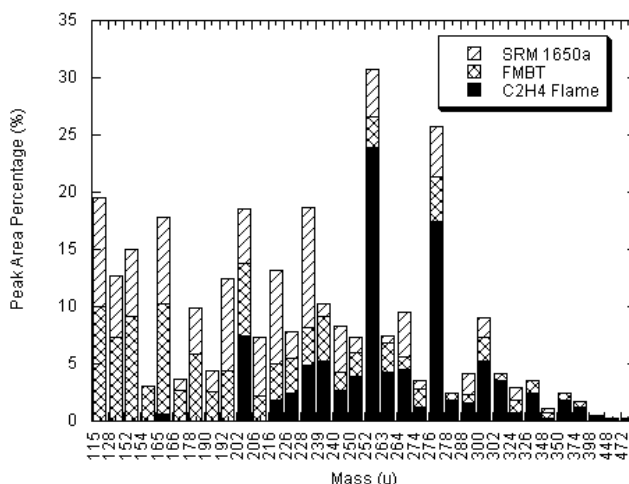


Figure 3. Relative abundance of mass peaks found for Fort McHenry Baltimore Tunnel, SRM 1650a (diesel) and ethene flame.

There is evidence for the origin of the small mass peaks in the PAH distribution of the typical diesel fuel. Other researchers and our work have shown that the small mass, alkyl-PAHs are found in diesel fuel and are thus from petrogenic sources. A summary of the analysis is presented in Table 1.

Table 1. Relative Abundances of Mass Peaks Observed from LMMS of Ethene Flame, Baltimore Tunnel, SRM1650a and SRM 1624c Oil

m/z	Possible Formula	Ethene Flame	Tunnel	SRM 1650a	SRM 1624c Fuel (GC/MS)	SRM 1624c Fuel (LMMS)
116	C ₉ H ₈		2.3	0.9		
128	C ₁₀ H ₈		7.2	3.7	2.8	+
132	C ₁₀ H ₁₂		5.0	9.6		
134	C ₁₀ H ₁₄		5.0	8.7		+
142	C ₁₁ H ₁₀		3.3	0.3	20.7	
152	C ₁₂ H ₈		8.5	4.0		+
154	C ₁₂ H ₁₀		2.6	0.3		
156	C ₁₂ H ₁₂		2.3	3.1	23.6	
166	C ₁₃ H ₁₀		2.4	0.7	2.7	
170	C ₁₃ H ₁₄		3.4	5.4	25.3	
178	C ₁₄ H ₁₀		5.4	2.6	4.3	+
180	C ₁₄ H ₁₂		6.0	11.6	0.4	
190	C ₁₅ H ₁₀		2.3	0.8		
192	C ₁₅ H ₁₂		3.3	5.7	9.9	
194	C ₁₅ H ₁₄		2.9	3.4		
202	C ₁₆ H ₁₀	9.4	5.6	3.4	0.5	+
206	C ₁₆ H ₁₄		2.0	3.2	9.6	
216	C ₁₇ H ₁₂	2.4	2.6	5.5		

220	C ₁₇ H ₁₆		0.9	0.7		
226	C ₁₈ H ₁₀	3.0	2.8	1.5		+
228	C ₁₈ H ₁₂	6.1	3.1	7.1	0.05	
240	C ₁₉ H ₁₂	3.4	1.4	2.7		
250	C ₂₀ H ₁₀	+	+	+		
252	C ₂₀ H ₁₂	29.9	2.6	2.8		
264	C ₂₁ H ₁₂	5.6	1.0	2.6		
274	C ₂₂ H ₁₀	+	+	+		
276	C ₂₂ H ₁₂	21.9	3.9	3.0		
288	C ₂₃ H ₁₂	2.0	0.6	1.2		
300	C ₂₄ H ₁₂	6.6	1.9	1.2		
302	C ₂₄ H ₁₄	4.4	0.8	0		
324	C ₂₆ H ₁₂	+	+	+		
326	C ₂₆ H ₁₄	3.1	0.9	0.1		
350	C ₂₈ H ₁₄	2.3	0.7	0		
376	C ₃₀ H ₁₆	+	0.1	0		

+ Indicates peak observed

LMMS analysis in the positive ion mode also provides information on the nitro-PAH species that can be formed in combustion processes. This is based on analysis of pure nitro-PAHs that have characteristic fragmentation patterns [6]. In the case of 2-nitrofluorene, C₁₃H₉NO₂, the spectra contain the following mass fragments which along with the principal positive ion [M]⁺ = 211 u; are [M-O]⁺ 195 u; [M-NO]⁺ 181 u; [M-NO₂]⁺ 165 u; and [M-NO-CO]⁺ 153 u. The [M-NO₂]⁺ ion produces the relatively strongest spectral peak [6]. This nitro-PAH forms a fingerprint of positive ion fragments indicative of the compound. A similar fragmentation pattern was observed in the LMMS analysis of the Baltimore truck tunnel samples.

Two other nitro-PAH compounds, 9-nitroanthracene, and 1-nitropyrene, were found to have similar mass fragmentation patterns as given above [6]. In each case the stronger mass peak associated with the [M-NO]⁺ ion was detected. These mass peaks were also found in the Baltimore tunnel. In each case, there may be mass interferences that could account for the observed peaks warranting additional study for nitro-PAHs determination by the LMMS technique.

Summary

We have used LMMS to analyze and subsequently compare the mass spectra of pure ethene flame particles, diesel emission particles and diesel fuel. Gas chromatography with mass spectrometry was used to determine the PAH content of a diesel fuel material. From our analysis, we conclude that the PAH associated peaks found in mass spectra of diesel particulate are derived from two sources; the low mass alkylated peaks come from unburned PAHs native to the fuel (petrogenic) as evidenced from several fuel analyses and the large mass benzenoid PAHs are pyrogenic in nature and derived primarily from the combustion process.

References

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