GS-MS Determination of Volatile Organic Compounds in Gasoline and Diesel Emissions

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Abstract: In light of environmental concerns over volatile organic compounds (VOCs) in the atmosphere, we investigated those found in gasoline and diesel emissions using gas chromatography-mass spectrometry (GC-MS). We took tailpipe samples from two gasoline and three diesel vehicles for 4 minutes after cold-start ignition. Two sampling methods were compared in this study: pumping exhaust through an absorbent charcoal tube and directly collecting VOCs via solid phase microextraction (SPME). SPME was determined to be more effective than pump sampling as it afforded longer sample retention times and higher chromatogram quality. Of the twenty chromatograms analyzed in this study, gasoline emissions contained higher abundances of the lower-boiling aromatic hydrocarbons, such as benzene, toluene, ethylbenzene, styrene, 1,2,4-trimethylmethylbenzene, than diesel. Large n-alkane derivatives of decane, undecane, and hexadecane were detected in diesel exhaust. Vegetable oil was also analyzed and found to contain compounds similar to diesel. Compounds identified in all three fuel emissions correlated with those detected from headspace analysis of pure standards.

Introduction

This paper investigates the emission of volatile organic compounds (VOCs) in the exhaust of three fuels: gasoline, diesel, and waste vegetable oil.

Gasoline and diesel fuels are derived from petroleum, a product of decomposed plants and animals. Hydrocarbons in the fuel react with oxygen in the air to form carbon dioxide (CO_2) and water (H_2O) by the following combustion reaction:

$$C_{X}H_{V}(g) + O_{2}(g) \rightarrow CO_{2}(g) + H_{2}O(g)$$

This reaction is exothermic and has the capability to power motor vehicles. Since combustion does not always proceed to completion, poisonous gases such as carbon monoxide (CO) and volatile organics are emitted. In addition, sulfur (S₂) in the fuel and nitrogen (N₂) in the air react in the engine to form sulfur oxides (SO_x)—a major contributor to acid rain—and nitrogen oxides (NO_x)—a cause of ground-level ozone and smog. The emissions from motor vehicles contribute significantly to the air pollution problem in most large cities.

Gasoline mostly contains hydrocarbons in the range of C7-8 while diesel is composed of heavier petroleum fractions of C9-10. In addition to containing simple alkanes, both fuels also include cycloalkanes, benzene, and other aromatic hydrocarbons. Since gasoline contains more lower-molecular weight components, it has a lower boiling point than diesel fuel (1). Diesel engines tend to be more powerful than gasoline engines and are often used in heavy-duty vehicles such as buses, trucks, ships, and locomotives. Despite its advantages as a source of SPRING 2006 power, diesel is considered to be dirtier than gasoline and produces large amount of soot (2). Studies have shown that soot can cause respiratory problems such as chronic bronchitis, asthma, and cancer (3).

In order to reduce gasoline emissions of poisonous gases, modern cars are equipped with catalytic converters that produce rather benign products by the following reactions (1):

$$\begin{aligned} & 2\text{CO}(g) + \text{O}_2(g) \rightarrow 2\text{CO}_2(g) \\ & \text{NO}_x(g) \rightarrow \text{O}_2(g) + \text{N}_2(g) \\ & \text{C}_x\text{H}_v(g) + \text{O}_2(g) \rightarrow \text{CO}_2(g) + \text{H}_2\text{O}(g) \end{aligned}$$

Catalytic converters use sensors to ensure that there is a stoichiometrically equivalent presence of oxygen relative to products in the exhaust. Once the catalytic converter warms up, usually to 300 °C, it is very effective at driving the above reactions to completion. In fact, around 80%of all vehicular emissions occur in the first few minutes after ignition, before the catalytic converter is ready (1). As a cleaner alternative fuel, vegetable oil has received significant attention (4). Although its combustion properties are very similar to those of diesel fuel, vegetable oil cannot be injected directly into an engine because of its high viscosity. Sunflower oil, for example, is one of the most popular choices for this substitution (4). At 27 °C its viscosity is 58.5 mm²/s, while that of diesel is 4.3 mm2/s at the same temperature (5). Heating the oil immediately before it passes through the engine can solve this problem and diesel engines can easily be reconfigured to accept vegetable oil with the addition of a new, heated fuel tank (6, 7, 8). Another

possibility is to chemically convert the vegetable oil into less viscous compounds by cracking it, performing a transesterification, blending it with other fuels, or creating a micro-emulsification (5).

As for the environmental consequences of burning vegetable oil as fuel, studies have shown that it emits lower levels of particulate pollutants than diesel (4). However, some studies show a general tendency for vegetable oil based fuels to emit more nitrogen oxides (NOx) (4), while other studies (5) have shown a slight decrease in NOx emissions. Recycling waste vegetable oil may offer the benefits of being inexpensive and renewable, but its environmental effects must be further investigated.

Among the numerous air pollutants in auto exhaust, this study focuses on volatile organic compounds such as benzene, toluene, and o, m, p-xylenes. VOCs react with sunlight and nitrogen oxides to produce groundlevel ozone, which causes lung and tissue damage upon prolonged exposure (9, 10). In addition, acute inhalation of VOCs may lead to irritation of the eyes, nose, and throat, gastrointestinal effects, eye irritation, and neurological effects in humans. Chronic inhalation can adversely interfere with the central nervous system, causing headaches, dizziness, fatigue, tremors, and loss of coordination (11).

In this study, two methods were used to collect VOCs n car exhaust: solid phase microextraction (SPME) and activated carbon in the form of charcoal. The SPME procedure can be used in the field to sample VOCs from air. SPME samplers, which retain samples for up to three days when stored at -4 °C, are easily transported to lab for direct injection into a gas chromatograph (GC) (12). The SPME fiber is coated with a 75 _m layer of CarboxenTM/ polydimethylsiloxane (PDMS) and can be retracted behind a septum to prevent contamination (12). The second method involves the use of activated charcoal to trap organic molecules. Exhaust is pumped across charcoal in glass tubes which can be sealed and transported to lab (13). Before the samples are injected into the GC, they must be desorbed from the charcoal with an appropriate solvent-in this study, carbon disulfide (CS₂) was used.

Vehicle	Mileage/	Sampling	Ambient	Sample ID	Sampling
1999 Ford Taurus	Fuel Type 200,590mi/	Date 18 Jul 05	Temperature 33 °C	Tau1A, Tau1B,	Duration 4 min; 8 min
SE	Reg. Gasoline	10 941 05		Tau2A, Tau2B 3A, 3A2, 3A3,	4 11111, 0 11111
		25 Jul 05	29 °C	3B1, 3B2, 3C, S2A, R2A	4 min
		28 Jul 05	25 °C	S4A, R4A, 4A, 4B	4 min
		12 Aug 05	32 °C	S5A, R5A, 5A, 5B	4 min
1990 Volvo 240DL	116,376mi/ Reg. Gasoline	01 Aug 05	30 °C	RV1, SV1, V1, V2	3 min 30 s
2004 Coach Bus	150,000/ Diesel	04 Aug 05	35 °C	SD1	30 s
1984 Mercedes 190D	190,162mi/ Diesel	05 Aug 05	30°C	SMDO1	4 min
	190,162mi/ Vegetable Oil	05 Aug 05	30 °C	RMO1	4 min
Diesel Truck International 4700 T444E	Diesel	09 Aug 05	35 °C	RT1, ST1, T1, T1B, T1C, T2	3 min 30 s; 4 min
Standard	Condition	Sampling Date	Ambient Temperature	Sample ID	Sampling Duration
Diesel	New	11 Aug 05	21 °C	RDIESEL2	10 min
Gasoline	New	11 Aug 05	21 °C	RGAS2	10 min
Vegetable Oil	New	12 Aug 05	150 °C	SNEWOIL1	10 min
	Used	12 Aug 05	150 °C	RWSTEOIL	5 min

Table I: Sample Sources, Conditions and Methodology

Experimental Procedure

Tailpipe Sampling for Pump and SPME

An Escort®LC Pump (MSA) was calibrated with a Buck Mini-CalibratorTM (A.P. Buck, Inc.) to 210 ± 5 cc/min. For the collection of tailpipe emissions, the pump was connected to the tailpipe via 180 cm of Tygon® tubing (Fisher Scientific, 3/16 in. ID) with a hollow, metal terminus that hooked on to the tailpipe. An ORBOTM 32 standard charcoal tube (Supelco) was incorporated into the length of the tubing. Samples were collected for approximately 4 minutes after igniting the engine from a cold start. The charcoal tube was immediately capped after sampling.



SPME and pump sampling techniques.

Image courtesy of the authors.

A Solid-Phase Microextraction (SPME) (Supelco) field sampler was concurrently introduced into the tailpipe during the sampling process for 4 minutes.

Carbon Disulfide Preparation for Charcoal

The contents of each charcoal tube were transferred to a 2 ml amber glass vial (National Scientific). The vials were crimped with Teflon-faced Neoprene® Septa (Supelco). 1.0 ml of carbon disulfide (99+% redistilled, Aldrich) was injected into the vial and the vial was placed on ice for at least 30 minutes before GC-MS analysis.

Standards for Gasoline, Diesel and Vegetable Oil

Standard chromatograms of pure gasoline, diesel, and vegetable oil were generated from sampling headspace volatiles by SPME. Gasoline and diesel samples were obtained courtesy of C. Ciambra. Unused and waste vegetable oil samples were provided by the Dartmouth Dining Services' Courtyard Café. 5.0 ml of each standard was transferred to a 20 ml EPA amber vial (Fisher Scientific), capped with a septum seal, and stirred for 20 minutes. Vegetable oil samples were heated to 150 °C.

Headspace volatiles were collected via SPME for an additional 10 minutes.

GC-MS Analysis

GC-MS analyses were performed on a HP 5890 Series 2 gas chromatograph and a HP 5971 mass selective detector (Hewlett Packard, Avondale, PA, USA). Helium, with a linear velocity of 30 cm/s, was used as a carrier gas for the 30.0 m x 0.25 mm x 1 _m film thickness capillary column (Supelco). The MS was maintained at 4.8 x 10-5- torr. For the pump samples, 1 _1 of the carbon disulfide solution was injected into the GC injector port at 250 °C. SPME samples were introduced to the injector port at 275 °C. Peaks were computer-integrated at their apexes and mass spectra were automatically compared to those spectra in the NBS75K library for identification purposes.

Results and Analysis

Commonly integrated compounds identified by GC-MS analysis are summarized in Table II for gasoline, diesel, and vegetable oil emissions. The samples in each category were compared to standard "un-combusted" samples containing pure gasoline, diesel, or waste vegetable oil. Since fuel samples come in a variety of different hydrocarbon mixtures, the compounds in the standards do not necessarily correspond to the compounds in the emissions. However, these pure standards still provide a frame of reference for which candidate compounds are likely to appear in the exhaust samples.

The most common compounds observed in the various gasoline samples were benzene, toluene, and isomers of xylene. None of the diesel samples exhibited significant levels of these volatile organics with the exception of the Mercedes diesel sample, which may have been contaminated by vegetable oil in the engine. However, the diesel standard indicates that a sizeable percentage of all three compounds were likely to have been present in the original diesel fuel. The results, although curious, can be explained by the fact that the tailpipe temperatures of the larger diesel vehicles far exceeded the temperatures of the smaller gasoline automobiles, thereby volatizing the more lower-boiling compounds before they reached the sampling devices. This assumption is supported by the diesel chromatograms, in which no significant peaks appear until after 14 minutes, while larger n-paraffins and iso-paraffins such as undecane and decane were detected in abundance.

Higher-boiling, aromatic derivatives of benzene containing two, three, or four extra carbons were prevalent in gasoline and diesel samples, but not found in the vegetable oil. The most common of these derivatives detected were 1,2,4-trimethyl-benzene, 1,2,3-trimethyl-benzene, 1-ethyl-2-methyl-benzene, 1-ethyl-4-methyl-

Gasoline Vehicle Emissions		Gasoline Standard				
Toluene	7.07 - 21.44%	Xylene	22.26%			
Xylene	5.88 - 21.42%	1,2,4-Trimethylbenzene	15.46%			
1-Ethyl-2-methyl-benzene	8.06 - 12.49%	Toluene	10.82%			
1,2,4-Trimethylbenzene	1.29 - 11.64%	1-Ethyl-2-methyl-benzene	9.27%			
Benzene	1.37 - 6.74%	Ethylbenzene	6.04%			
1-Ethyl-2,3-dimethyl-benzene	6.14%	Benzene	2.82%			
1,2,3-Trimethylbenzene	4.04 - 5.90%					
Ethylbenzene	2.74 - 4.57%					
1-Ethyl-4-methylbenzene	4.23%					
Naphthalene	3.20%					
Styrene	1.80%					
Benzaldehyde	1.24 - 1.67%					
Indane	1.48 - 1.50%					
Diesel Vehicle Emission	115	Diesel Standard				
Benzene	0.50 - 9.79%	Xylene	11.23%			
3,6-Dimethyl-undecane	7.43%	3,9-Dimethyl-undecane	10.79%			
Phenol	1.42 - 6.08%	Toluene	8.75%			
1,2,3-Trimethylbenzene	6.04%	1,2,4-Trimethylbenzene	6.55%			
Benzocycloheptatriene	4.49%	1-Ethyl-2,3-dimethyl-benzene	1.19%			

1.23 - 4.33%

2.16 - 3.65%

2.24 - 2.96%

4.01% 1.49 - 3.86%

3.45%

3.03%

2.80% 2.71%

1.97%

Benzene

4,6-Dimethyl-undecane	1.49%		
Vegetable Oil Vehicle Emissions	Vegetable Oil Standard		
Phenol	14.12%	2,4-Hexadienal	9.67%
Benzene	6.08%	Toluene	6.35%
Styrene	4.73%	p-Xylene	4.80%
Toluene	3.11%	Hexanal	4.29%
		Benzaldehyde	2.06%
		Ethylbenzene	1.36%
		Benzene	0.77%

Table II: List of VOCs Identified by GC-MS Analysis by Increasing Peak Area Percentages

benzene, 1-ethyl-2,3-dimethyl-benzene, and styrene. Oxidized derivatives of benzene (benzaldehyde, benzoic acid, phenol) and polycyclic aromatic hydrocarbons (PAHs) (naphthalene, indane, azulene, phthalan) were also detected, though in lower abundance levels, for gasoline and diesel samples.

In the remainder of this section, a descriptive summary of select chromatograms is given.

1990 Volvo 240DL

SPME: Benzene (1.39%, 6.07 min), toluene (14.83%, 8.98 min), p-/m-xylene (24.43%, 11.84 min), styrene (1.80%, 12.28 min), 1,3-dimethyl-benzene (3.91%, 12.43 min), benzaldehyde (1.24%, 13.76 min), 1-ethyl-4-methyl-benzene (4.23%, 14.20 min), 1,2,4-trimethylbenzene (11.64%, 15.05 min).

Pump: Benzene (4.35%, 6.15 min), toluene (21.44%, 9.53 min), o-/m-/p-xylene (7.09%, 11.71 min; 16.14%, 11.88 min), ethylbenzene (4.40%, 12.34 min).

0.60%

Decane

Azulene Benzoic acid

Naphthalene

Undecane

Phthalan

2,6-Dimethyl-undecane

1,2-Dithiacyclopentane

2,6,7-Trimethyldecane

3-Methyl-hexadecane

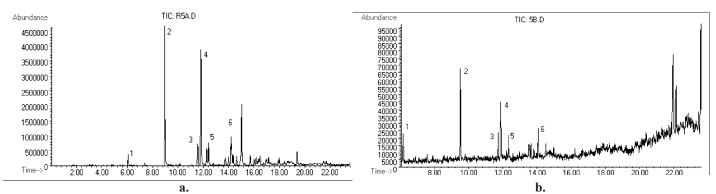


Figure I. Corresponding peaks in Taurus chromatograms collected by (a) SPME, and (b) pump. 1. Benzene 2. Toluene 3. Ethylbenzene 4. Xylenes 5. 1,2,4-Trimethylbenzene 6. 1-ethyl-2-methyl-benzene

2004 Large Coach Bus

SPME: 1,2,3-trimethylbenzene (6.04%, 14.99 min), 1-methyl-2,2-propenyl-benzene (1.37%, 18.65 min) naphthalene (4.04%, 19.37 min), benzocycloheptatriene (4.49%, 21.69 min).

International 4700 T444E Diesel Construction Truck

SPME: Benzene (0.50%, 6.08 min), phenol (1.42%, 14.11 min), phthalan (1.97%, 16.41 min), decane (4.33%, 17.55 min), benzoic acid (3.65%, 18.23 min), undecane (2.71%, 18.92 min), azulene (3.86%, 19.37 min), 3-methyl-hexadecane (2.80%, 19.69 min).

1984 Mercedes 190D

SPME (Vegetable Oil): Benzene (12.21%, 6.08 min), toluene (3.11%, 8.95 min), styrene (4.73%, 12.28 min), phenol (5.38%, 14.12 min).

SPME (Diesel): Benzene (9.79%, 6.07 min), 2cyclopenten-1-one (1.76%, 10.10 min), 1,2dithiacyclopentane (3.45%, 13.73 min), phenol (6.08%, 14.13 min), 2,6,7-trimethyl-decane (2.96%, 15.74 min), decane (1.23%, 17.57 min), azulene (1.49%, 19.37 min).

1999 Ford Taurus SE

SPME: Benzene (1.84%, 6.07 min), toluene (8.96%, 15.44 min), ethylbenzene (4.57%, 11.56 min; 4.57%, 12.42 min), m-/p-xylene (21.42%, 11.82 min), benzaldehyde (1.67%, 13.73 m), propyl-benzene (1.60%, 14.00 min), 1,2,4-trimethylbenzene (2.19%, 14.36 min) 1-ethyl-4-methyl-benzene (1.71%, 14.64 min), 1-ethyl-2-methylbenzene (12.49%, 15.03 m; 2.09%, 15.70 min), indane (1.09%, 16.01 min), naphthalene (3.20%, 19.40 min).

Pump: Benzene (6.74%, 6.17 min), toluene (16.92%, 9.51 min), o-/m-/p-xylene (5.88%, 11.71 min; 17.14%, 11.87 min; 6.59%, 12.32 min), 1,2,3-trimethyl-benzene (5.90%, 14.06 min).

Gasoline Standard

SPME: Benzene (2.82%, 6.07 min), toluene (10.41%, 8.98 min), ethylbenzene (6.04%, 11.61 min), o-/p-xylene (11.96%, 11.90 min; 10.30%, 12.55 min), 1-ethyl-2-methyl-benzene (7.12%, 14.29 min; 2.15%, 14.34 min), 1,2,4-trimethylbenzene (2.50%, 14.47 min; 1.55%, 14.72 min; 9.91%, 15.17 min; 1.50%, 15.78 min).

Diesel Standard

SPME: Toluene (8.75%, 8.98 min), p-xylene (11.23%, 11.85 min), 1,2,4-trimethylbenzene (6.55%, 15.05 min), 3,9-dimethyl-undecane (10.79%, 17.66 min). Benzene (0.60%, 6.07 min) was detected in low quantities and with a low quality match of 58. Other less notable compounds with high quality matches included 1-ethyl-2,3-dimethyl-benzene (0.70%, 17.95 min; 1.19%, 18.03 min), 1,2,3,4-tetrahydro-naphthalene (1.18%, 18.97 min), parachlorophenol (1.37%, 19.43 min), cyclopropylbenzene (1.10%, 21.14 min).

Vegetable Oil Standard

SPME: Benzene (0.77%, 6.13 min), toluene (6.35%, 8.98 min), ethylbenzene (1.36%, 11.61 min), 1,3-dimethylbenzene (4.80%, 11.85 min), benzaldehyde (2.06%, 13.86 min), 2,4-hexadienal (9.67%, 15.04 min), hexanal (4.29%, 9.61 min).

Discussion

The ultimate goals of this investigation were to draw a comparison between the VOCs in gasoline, diesel, and vegetable fuel emissions, and to qualify the relative abundances of an array of hydrocarbon compounds. In the process of drawing these comparisons, two sampling methods were used to trap volatile organics in this approach: direct sampling of exhaust via SPME and pumping exhaust across a charcoal-containing tube for analysis. Sampling via SPME and pump was conducted concurrently for each vehicle, offering a basis of comparison for the two methods (Table I). Both methods were found to be reproducible, reliable, and, in respect to final data, almost analogous.

Figure I compares the chromatogram results from the sampling of a Ford Taurus via SPME and pump method. Both trials were sampled at the same time, and analyses were performed on the same day. While pump abundances were 50 times higher for SPME, the retention times and relative abundances of the peaks of the two chromatograms do correspond. The higher signal-to-noise ratio (S/N) and level baseline in the first chromatogram, however, allowed the analysis program to identify peaks with a higher quality match. Additionally, the baseline of the latter chromatogram increased in slope starting at 16 minutes, limiting the computer's ability to integrate the peaks which appear after 22 minutes (peaks which do not appear in the first chromatogram).

In general, SPME produced superior Ford Taurus chromatograms with higher S/Ns, more abundant

peaks, and a steady baseline for all samples. The nature of the SPME instrument also allows for injection into the GC-MS immediately after sampling, requiring no intermediate preparation step such as the carbon disulfide dissolution required for analyzing pump samples. In addition, it was demonstrated that the abundances of compounds collected via the pump method dissipated over time. This dissipation was not the case for SPME samples, which were shown to preserve abundances for at least 24 hours. The one advantage of pump sampling is its repeatability. Multiple injections can be analyzed from the same preparation of charcoal to produce duplicate results, provided that the user does not wait too long in between injections, which is not the case for singleinjection SPME. However, the overall advantages of SPME (higher efficiency, cleaner chromatograms, and longer sample life) make it a better sampling method for volatile organic exhaust.





Image courtesy of the authors

Three fuel types were examined over the course of this investigation: gasoline, diesel, and waste vegetable oil. As discussed previously, gasoline exhaust samples generally contained low-boiling point compounds that were not present in diesel sample. This trend is seen in the diesel and gasoline standards as well, perhaps indicating that the initial composition of the fuel has a direct consequence on which types of compounds may be found in its exhaust. By the same comparison, diesel exhaust samples contained many more high-boiling, higher molecular weight compounds than their gasoline counterparts. These larger compounds, however, do not appear in the pure diesel standard. There are two explanations which may account for this observation. The first is that when sampling the diesel standard, the diesel was not heated to the same temperatures as it would reach in an engine; thus, higher molecular weight compounds could not volatize and appear in the chromatogram. The second is that the high temperatures of a diesel engine promote

reactions between smaller hydrocarbon chains to form higher molecular weight organics.

Of the compounds which were detected in gasoline and diesel emissions, many pose serious health hazards after acute or chronic levels of exposure (11). According to the EPA, acute exposure to styrene, ethylbenzene, xylenes, naphthalene, benzaldehyde, and phenol can cause an assortment of neurological, respiratory and gastrointestinal conditions, as well as eye and dermal irritation. Benzene is also a known carcinogen. Toluene is found to be disruptive to central nervous system functions. Larger hydrocarbons present in diesel fuel, such as decane and undecane, have been found to cause dizziness and irritation. All of the above compounds were detected

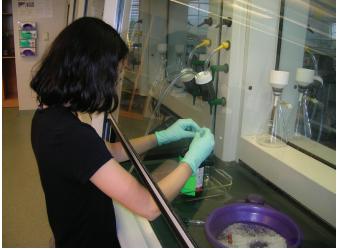
Volvo 240

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Image courtesy of the authors

by SPME and pump sampling methods and are listed in Table II.

As an attempt to mediate the emission levels of aromatic hydrocarbons, fuel additives such as oxygenates have been incorporated into different fuel types (14). Catalytic converters are another solution to lowering VOC concentrations in fuel exhaust. In this investigation, samples from repeated testing of a 1999 Ford Taurus with a catalytic converter and a 1990 Volvo with an older one were compared. Using the SPME method, the abundances from the Volvo samples were 2 to 4 times higher than the abundances for the Taurus samples. Although this discrepancy may likely have been due to inconsistencies in sampling method, it is not unreasonable to posit that significant differences in abundance are also due to advancements in catalytic converter technology.



Carbon disulfide preparation.

A third method for lowering VOC concentrations in fuel exhaust is to switch to vegetable oil as an alternative fuel source. Although Table II seems to suggest that the vegetable oil burns more cleanly than diesel fuel because less VOCs were detected in its emissions, this data may be misleading. In fact, the data is insufficient for drawing such a conclusion. Vegetable oil and diesel emissions sampled from the same Mercedes vehicle produced two similar chromatograms. In both chromatograms, 61 peaks were identified, and the abundance values were in the same range. However, due to a higher S/N in the diesel chromatogram, the computer was able to integrate more peaks above the quality threshold for that particular sample, giving the appearance that the diesel sample contained more VOCs than the vegetable oil sample. By just comparing the chromatograms alone and not the computer-generated analyses, the similarities in the two samples seem to suggest that cross-contamination of the two samples may have occurred in the engine. Therefore, it is reasonable to conclude that neither chromatogram represents a pure diesel or a pure vegetable oil sample. The waste vegetable oil standard shows that although vegetable oil contains aromatic hydrocarbons (namely

benzene, toluene, ethylbenzene, xylenes, benzaldehyde), the one advantage that it has over diesel is a lack of decane, undecane and other such long alkanes. The overall prospects for vegetable oil as an alternative fuel source seem promising, but further research is still needed to investigate exhaust from engines running solely on vegetable oil.

Conclusion

The scope of this investigation was large, comparing volatiles in exhaust from three different fuel types using two different sampling methods. Chromatograms produced by SPME sampling were generally easier to integrate than chromatograms produced by the pump and charcoal tubes method, and sample abundances could be preserved for longer periods of time before GC-MS analysis. Unless repeatability is an issue and a large number of SPME field samplers could not be obtained, then SPME is preferred over the pump method.

The VOCs identified in the exhaust via GC-MS depended largely on fuel type, purity of the sample, and the techniques used to obtain the sample. Many of the aromatics detected in the emissions have potential respiratory, neurological, gastrointestinal, or dermal consequences. Even vegetable oil, though hailed as an environmentally-safe alternative fuel source, has potential for harm. Further investigation is required in quantifying each of the VOCs identified, and expanding the study to a greater array of vehicles.

References

1. C. Baird and M. Cann. Environmental Chemistry, 3rd ed. (W.H. Freeman, New York, 2005).

2. Diesel Pollution. Available at http://www.sierraclub.org/cleanair/factsheets/diesel.asp (August 2005).

 J. L. Mauderly. Toxicol. Environ. Chemistry 49, 167-180 (1995).
M. Lapuerta, O. Armas, R. Ballestero, and J. Fernandez. Fuel 84, 773-780 (2005).

5. A. S.Ramadhas, S. Jayaraj, and C. Muraleedharan. Renewable Energy 29, 727-742 (2004).

6. Vegetable Oil-Kit. Available at http://www.diesel-therm.com/ veggie-kit.htm (August 2005).

7. Diesel to Vegetable Oil Engine Conversions. Available at http:// www.dieselveg.com (August 2005).

8. Vegetable Oil Conversion Kits. Available at http://www.fusel.com/kits.html (August 2005).

9. Q. Yang, Y. Chen, Y. Shi, R.T. Burnett, K.M. McGrail, and D. Krewski. Inhalation Toxicology 15, 1297 (2003).

10. P. J. Crutzen. Annual Review of Earth and Planetary Sciences 7, 443 (1979).

11. U.S. Environmental Protection Agency Air Toxics Website. Available at http://www.epa.gov/ttn/atw (August 2005).

12. Air Sampling of VOCs by SPME for Analysis by Capillary GC; Application Note 141; Supelco: Bellefonte, PA, 1998.

13. National Institute for Occupational Safety and Health.

Hydrocarbons, BP 36°-216 °C: Method 1500; NIOSH Manual of Analytical Methods, 4th ed.; Mar 2003.

14. K. E. Nord, D. Haupt. Environmental Science and Technology 39, 6260-6265 (2005).

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