

Extension of Analytical Methods for Detailed Characterization of Advanced Combustion Engine Emissions

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ABSTRACT

Advanced combustion strategies used to improve efficiency, emissions, and performance in internal combustion engines (IC) alter the chemical composition of engine-out emissions. The characterization of exhaust chemistry from advanced IC engines requires an analytical system capable of measuring a wide range of compounds. For many years, the widely accepted Coordinating Research Council (CRC) Auto/Oil procedure[1,2] has been used to quantify hydrocarbon compounds between C_1 and C_{12} from dilute engine exhaust in Tedlar polyvinyl fluoride (PVF) bags. Hydrocarbons greater than C_{12+} present the greatest challenge for identification in diesel exhaust. Above C_{12} , PVF bags risk losing the higher molecular weight compounds due to adsorption to the walls of the bag or by condensation of the heavier compounds. This paper describes two specialized exhaust gas sampling and analytical systems capable of analyzing the mid-range ($C_{10} - C_{24}$) and the high range (C_{24+}) hydrocarbon in exhaust. An automated gas chromatograph equipped with a mass spectrometer (GC-MS) sampling system was used to sample middle range hydrocarbons from raw exhaust. A separate sampling system consisting of a filter and XAD traps was used for the collection of particulate-phase and semi-volatile-phase hydrocarbons up to C_{24+} in dilute exhaust. After extraction, hydrocarbons trapped by the particulate filter and the XAD traps were speciated by a two dimensional gas chromatography mass spectroscopy (GCxGC-MS) technique. These two novel systems allowed more than 2000 compounds to be detected in the exhaust thus extended the analytical capacity in emission characterization.

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INTRODUCTION

Boosting the efficiency of IC engines through advanced combustion strategies has demonstrated that these strategies will alter the chemical composition of engine-out emissions. Changes in exhaust chemistry affect the performance of typical exhaust aftertreatment devices used to meet tailpipe emissions standards. As advanced combustion strategies are developed, new technologies for exhaust aftertreatment will need to be developed. Detailed chemical characterization of the exhaust is an essential for future exhaust aftertreatment design. Although the characterization for short chain volatile hydrocarbons between C_1 and C_{12} has been used widely for more than 25 years, the longer chain hydrocarbons (semi-volatile- and particulate-phase) present special analytical challenges. The CRC Auto/Oil method designed for hydrocarbons up to C_{12} does not allow for the identification and quantification of potential exhaust greater than C_{12} . [1]

Longer chain hydrocarbons in the exhaust are typically lost on the particulate filters or condense before the gas phase analyzers. The objective of the work described in this paper was to develop supplementary sampling and analytical systems to cover a larger range of hydrocarbons in the exhaust. Two specialized exhaust sampling and analytical systems were developed and validated. The first specialized automated exhaust gas sampling and analytical system was designed for characterization of middle range

hydrocarbons (from C_{10} through C_{24}). A GC-MS was used to identify these compounds. The system was also able to measure hydrogen (H_2), which is not one of the components typically identified on a regular basis. The quantification of H_2 was another important improvement necessary for the characterization of new technologies of advanced aftertreatment. Another important objective was to evaluate the effect of sample line temperatures on the quantification of hydrocarbons with high boiling points. Currently, 191°C is the required temperature for sample lines used to deliver exhaust from the engine to the gas analyzers. However, some of the hydrocarbons in diesel exhaust have a significantly higher boiling point than 191°C. The new chromatographic system was able to handle gases delivered by sample lines at 300°C. Therefore, it provided an opportunity to compare the efficiency of the currently accepted temperature for collection of hydrocarbons.

The second sampling system, consisting of a particulate filter and several XAD traps, was used for the collection of particulate and semi-volatile compounds. This system was capable of analyzing engine exhaust for heavier hydrocarbon compounds to about C_{40+} . After extraction, hydrocarbons trapped by the particulate filter and the XAD traps were speciated by GCxGC-MS. More than 2000 individual compounds were identified and separated by hydrocarbon class and carbon number. This paper describes these two novel sampling and analytical systems.

PART 1 - IN-SITU AUTOMATIC GC-MS GAS SAMPLING SYSTEM FOR DETAILED CHARACTERIZATION OF HYDROCARBON UP TO C₂₄

Method Development

To evaluate this analytical technique, a heavy-duty diesel engine (Engine 1) was installed in a state-of-the-art test cell compliant with the U.S. Code of Federal Regulations, Title 40, Part 1065.[3] Exhaust emissions were generated and collected using one of the test conditions taken from the ramped modal cycle (RMC) as specified in Title 40 Code of Federal Regulations (CFR) Part 86.1362(a).[4] The test condition was 1450 rpm at 195 Nm. Emission measurements included:

- Regulated emissions including total hydrocarbons (THC), carbon monoxide (CO), carbon dioxide (CO₂), and the oxides of nitrogen (NO_x)
- Speciation of hydrocarbon compounds above C₁₀
- H₂

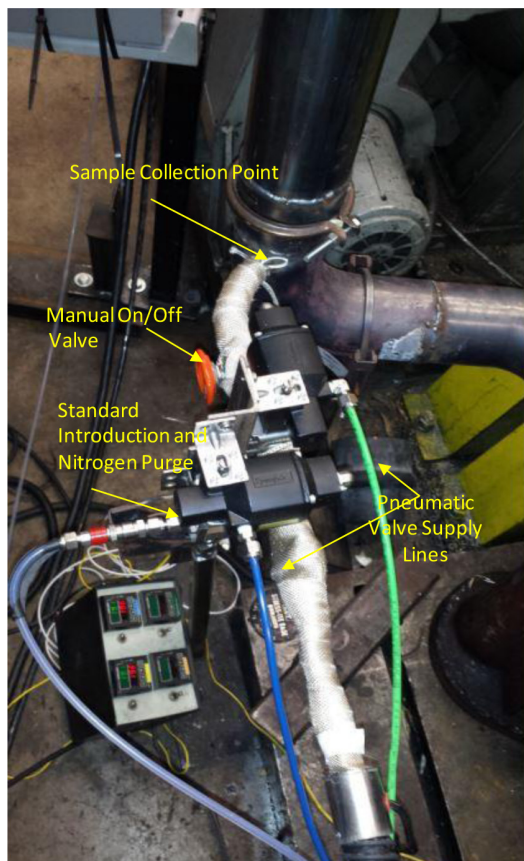


Figure 1. Assembled Valve System and Sample Port Used for Recovery Experiments

Raw exhaust sampling included a modified automated valve system and the sample distribution system that delivered two separate sample portions concurrently to two separate gas chromatography (GC) columns through a proprietary distribution system on the gas chromatograph. Consistent injections were conducted regardless of sample source, temperatures, and pressure. Figure 1 illustrates the

assembled valve system. Appendix Figure A1 illustrates the overall design of the GC-MS sampling system. An Agilent 6890 gas chromatograph was connected to the exhaust system through two extruded, stainless steel 1.6 mm (1/16 in.) tubes inserted inside a 9.5 mm (3/8 in.) stainless steel heated commercial heated sample line maintained at elevated temperatures. Sampling tubes were in contact with heated line (Unique Heated Product Inc., Part Number SII-C-6-300-S-E6-PRO-A-AK-D72-000, 300CMax). Temperatures were regulated by a proportional-integral-derivative (PID) controller. Two sampling temperatures were evaluated: 191°C (currently required for collection of regulated gaseous emissions) and 300°C (an elevated temperature expected to increase the heavy hydrocarbons transfer). 300 °C was maximum temperature for the commercial sampling line .

GC-MS Configuration

The chromatographic system used two detectors, a mass spectrometer (MS) to measure heavy hydrocarbon compounds and a thermal conductivity detector (TCD) to measure H₂, CO, oxygen (O₂), and CO₂. Different analytical columns were used for separation of the compounds of interest. The MS channel was used to detect the heavy hydrocarbon compounds. Initially, a 60m RTX-502.2 (Restek) column was used. Later, a 30m ZB-5MS (Phenomenex) column replaced to reduce the test time. Helium was used as the carrier gas. Since the hydrocarbon level was expected to be low, a 1 mL sample loop volume was used to inject the exhaust gas onto the MS analytical column.

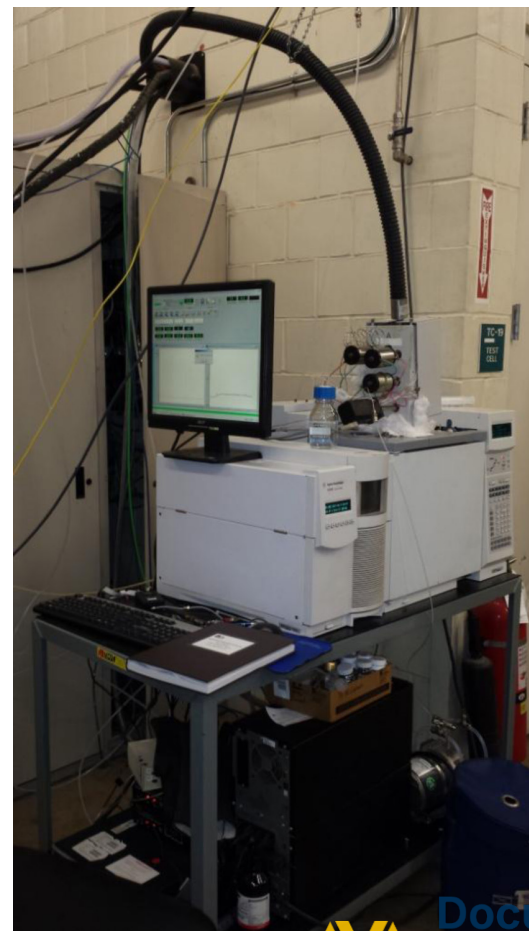


Figure 2. GC-MS System

The thermal conductivity detector was used to measure the H_2 , CO , O_2 , and CO_2 levels in the exhaust gas sample. The separation was performed using a 30m Poraplot-Q (Agilent) and a 2m ShinCarbon ST (Restek) column in series with nitrogen as the carrier gas. A 1mL sample loop was also used for this analysis in order to achieve a detection level of approximately 40 ppmv. Figure 2 illustrates a complete GC-MS system connected with an engine exhaust via heated line.

Method Validation

Linearity was measured by injection of the standards at different concentrations directly into the sample port of the GC-MS instrument. Figures 3 and 4 illustrate detectors responses for H_2 , CO_2 , CO , and O_2 . Repeat analysis of the hydrocarbons standards C_{10} - C_{13} introduced at the instrument produced Relative Standard Deviation (%RSD) of 5%. These results fall within range for routinely acceptable GC-MS instrument performance. One goal of this project was to demonstrate that the system was able to detect hydrocarbons up to C_{24} . Due to the high boiling point of $C_{24}H_{50}$ (tetracosane) at 391°C, there was no gaseous standard available for the program. A solution of tetracosane in carbon disulfide was injected into the instrument to determine if this compound could be sampled in the exhaust. Appendix Figure A2 illustrates that the method would detect this compound if it presents. Integrity of the entire sampling system was validated by comparison CO_2 results from TCD detector on GC-MS and a Non-Dispersive Infrared Detector installed in the Horiba MEXA7100DEGR bench during an engine tests. Based on the CO_2 results, both repeatability between triplicated tests from the on-line GC-MS and agreement between results from the on-line GC-MS and Horiba bench were sufficient to consider tests as valid tests and to confirm the integrity of the new sampling system. Table 1 includes CO_2 results from the triplicate engine tests from two analytical methods.

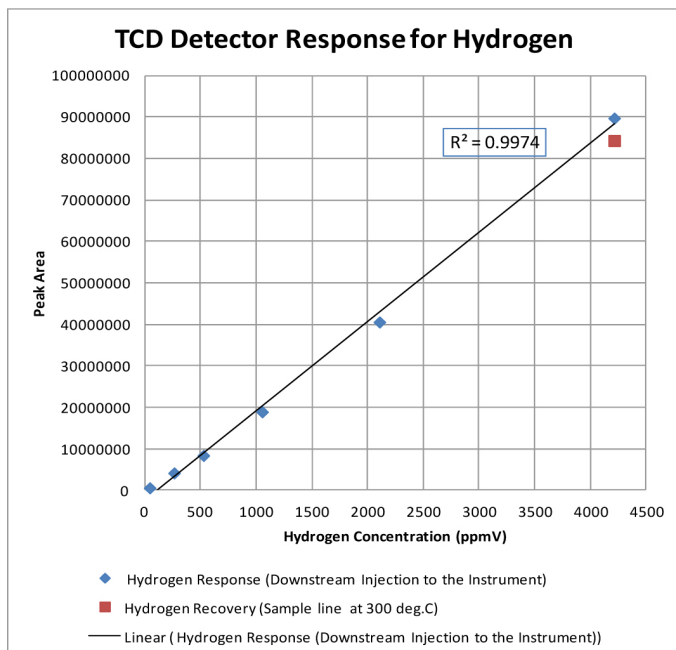


Figure 3. H_2 Response on TCD Detector

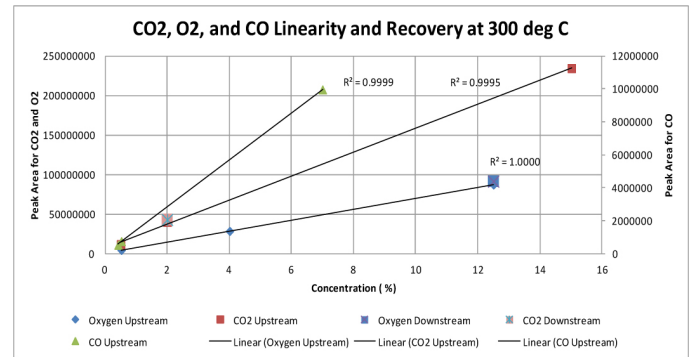


Figure 4. CO_2 , O_2 , and CO Response on TCD Detector

Table 1. CO_2 Results

TEST	CO_2 by GC-MS (%)	CO_2 by Horiba Bench (%)	% Difference Between Two Methods
Engine Sample 1	6.763	6.745	0.3%
Engine Sample 2	6.773	6.744	0.4%
Engine Sample 3	6.834	6.805	0.4%
Average Three Tests	6.790	6.765	
StDev	0.038	0.035	
% RSD	0.6%	0.5%	

Hydrocarbon recovery and sample line temperature effects were measured by the injection of standards upstream of the sample line. Hydrocarbon standards (at 1 ppmC levels) were connected through the quick connect to the sampling port and injected upstream of the sample line maintained at 191°C and at 300°C, respectively; and responses were compared with those obtained via direct injection to the GC-MS. Experiments showed that the recovery of the higher molecular weight hydrocarbons was 15-20 percent higher for the sample line maintained at 300°C than at 191°C. This difference increased with carbon number. Table 2 includes results of the recovery studies with sample lines at two different temperatures. In addition when the sample line was maintained at 300°C, better repeatability of the hydrocarbon composition was also observed (both total and individual hydrocarbons). Table 3 illustrates repeatability of the several consecutive hydrocarbon injections upstream of the sample line. Based on recovery and repeatability of the results at 300°C, engine emission tests for the GC-MS system were conducted at this temperature rather than 191°C.

Table 2. GC-MS Recovery for Hydrocarbons at Different Sample Line Temperatures

	Average Response on Instrument	Standard Recovery			
		Average Response Upstream at 300°C Sample Line	Recovery at 300°C, %	Average Response Upstream at 191°C Sample Line	Recovery at 191°C, %
C10	14557	12687	87	9650	66
C11	24087	17109	71	11826	49
C12	44104	26939	61	16007	36
C13	67139	48305	72	22389	33

Table 3. GC-MS Response for Hydrocarbons at Different Sample Line Temperatures

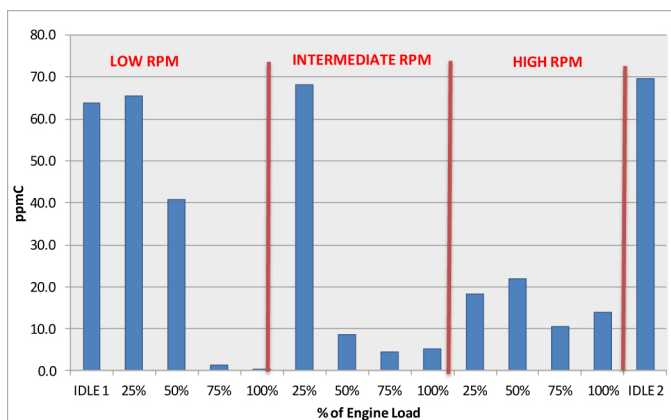
Injection Upstream of Sampling System (Sampling Line Temperature 300°C)								
	Std Conc, ppb	Response Factors						% RSD
		Injection 1	Injection 2	Injection 3	Injection 4	Avg	STDEV	
C10	109	13626	12444	11632	13047	12687	853	7%
C11	100	18089	17545	15615	17189	17109	1063	6%
C12	91	27142	28842	26462	25311	26939	1476	5%
C13	77	44790	52423	47074	48934	48305	3226	7%

Injection Upstream of Sampling System (Sampling Line Temperature 191°C)								
	Std Conc, ppb	Response Factors						% RSD
		Injection 1	Injection 2	Injection 3	Injection 4	Average	STDEV	
C10	109	11667	9504	9114	8314	9650	1433	15%
C11	100	14747	11241	11174	10143	11826	2011	17%
C12	91	20042	16541	14658	12787	16007	3096	19%
C13	77	25650	26080	21118	16710	22389	4402	20%

Table 4. Detailed Hydrocarbon Exhaust Composition (Sample Line at 300°)

Components	Engine Sample #1		Engine Sample #2		Engine Sample #3	
	Area Response	Conc (ppb)	Area Response	Conc (ppb)	Area Response	Conc (ppb)
1-Ethyl-3-methylbenzene	1254736	47.8	1292026	49.2	1244768	47.4*
1,2,3-Trimethylbenzene	382442	14.6	392096	14.9	370090	14.1*
Decane	69250	2.6	66393	2.5	65356	2.5
Undecane	81077	3.1	92165	3.5	82426	3.1
Naphthalene	1442721	54.9	1452793	55.3	1552174	59.1*
Dodecane	107100	4.1	139064	5.3	151227	5.8
Tridecane	109886	4.2	101340	3.9	129810	4.9
2-Methylnaphthalene	948519	36.1	874866	33.3	773604	29.5*
1-Methylnaphthalene	413557	15.7	368947	14.1	386445	14.7*
Tetradecane	155954	5.9	167921	6.4	150415	5.7
Pentadecane	173291	6.6	216465	8.2	180553	6.9
Eicosane	201240	7.7	255828	9.7	238647	9.1
Alkanes C10-C11	249525	9.5	248238	9.5	210588	8.0
Alkanes C11-C12	300845	11.5	276300	10.5	235860	9.0
Alkanes C12-C13	422563	16.1	388113	14.8	381522	14.5
Alkanes C13-C14	432547	16.5	529377	20.2	567177	21.6
Alkanes C14-C15	465396	17.7	612695	23.3	601702	22.9
Alkanes C15-C16	423826	16.1	472148	18.0	569898	21.7
Alkanes C16-C17	-	-	341385	13.0	629971	24.0
Alkanes C17+	-	-	573083	21.8	1222237	46.5

* Estimated based on Alkanes RF

Figure 5. Total Speciated C₁₀₊ THC and Detailed Speciation

To validate the entire sampling system, the new method was applied to the exhaust characterization for a single mode emission characterization during three separate days. Major hydrocarbon classes and some of individual hydrocarbons were quantified. The identified hydrocarbon types included aromatics, polycyclic aromatic

hydrocarbons (PAH), and various alkanes ranging from C₁₀ to C₂₀. The heavy hydrocarbons were coarsely estimated at ppbv levels based on available standards. Table 4 includes the results of these tests. The concentration of the heaviest hydrocarbons increased from run to run either due to their accumulation in possible cold spots in the sampling system or due to insufficient timing for the chromatographic method. Based on these results, thermo isolation of the entire sampling system was improved and sample purging time was increased. The fully validated method was later applied to emission characterization from a second engine, a 2015 medium size heavy-duty diesel engine (Engine 2), for all thirteen modes of the RMC. Figure 5 illustrates the total speciated hydrocarbons for the C₁₀-C₂₄ hydrocarbon range. Figure 6 includes detailed characterization distribution for the 25% load at intermediate rpm by carbon number, and Figure 7 shows the detailed polyaromatic hydrocarbon speciation on the range from C₁₀ through C₂₄ for the same mode. In addition, no hydrogen was detected above detection limits with either of the engines because both engines use traditional combustion strategies, and hydrogen in the exhaust was not expected.

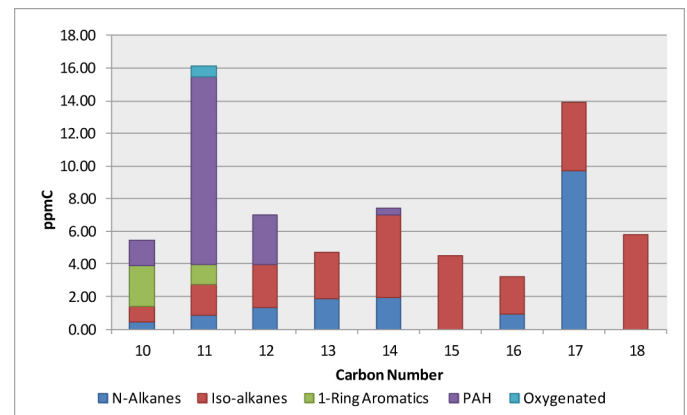


Figure 6. Hydrocarbon Distribution For 25% Load at Intermediate RPM

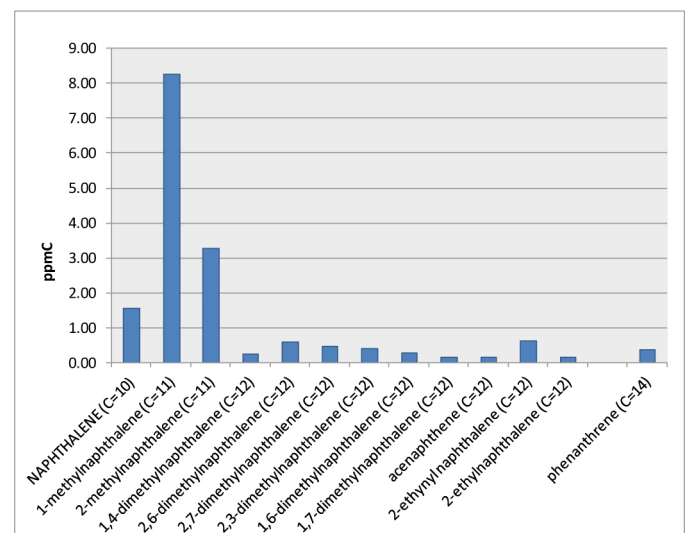


Figure 7. PAH Speciation for 25% Load at Intermediate RPM