SAE TECHNICAL PAPER SERIES

2000-01-2213

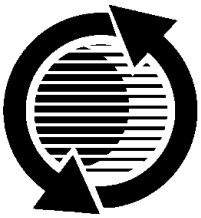
Particulate Emissions from a Pre-Emissions Control Era Spark-Ignition Vehicle: A Historical Benchmark

John M. E. Storey, C. Scott Sluder and Douglas A. Blom
Oak Ridge National Lab (ORNL)

Erin Higinbotham
Automotive Testing Lab, Inc.

The Engineering Society For Advancing Mobility Land Sea Air and Space®
INTERNATIONAL

Government/Industry Meeting
Washington, D.C.
June 19-21, 2000



ISSN 0148-7191

2000-01-2213

Particulate Emissions from a Pre-Emissions Control Era Spark-Ignition Vehicle: A Historical Benchmark

John M. E. Storey, C. Scott Sluder and Douglas A. Blom
Oak Ridge National Lab (ORNL)

Erin Higinbotham
Automotive Testing Lab, Inc.

ABSTRACT

This study examined the particulate emissions from a pre-emissions control era vehicle operated on both leaded and unleaded fuels for the purpose of establishing a historical benchmark. A pre-control vehicle was located that had been rebuilt with factory original parts to approximate an as-new vehicle prior to 1968. The vehicle had less than 20,000 miles on the rebuilt engine and exhaust. The vehicle underwent repeated FTP-75 tests to determine its regulated emissions, including particulate mass. Additionally, measurements of the particulate size distribution were made, as well as particulate lead concentration. These tests were conducted first with UTG96 certification fuel, followed by UTG96 doped with tetraethyl lead to approximate 1968 levels. Results of these tests, including transmission electron micrographs of individual particles from both the leaded and unleaded case are presented.

The FTP composite PM emissions from this vehicle averaged 40.5 mg/mile using unleaded fuel. The results from the leaded fuel tests showed that the FTP composite PM emissions increased to an average of 139.5 mg/mile. Analysis of the particulate size distribution for both cases demonstrated that the mass-based size distribution of particles for this vehicle is heavily skewed towards the nano-particle range. The leaded-fuel tests showed a significant increase in mass concentration at the <0.1 micron size compared with the unleaded-fuel test case. The leaded-fuel tests produced lead emissions of nearly 0.04 g/mi, more than a 4-order-of-magnitude difference compared with unleaded-fuel results. Analysis of the size-fractionated PM samples showed that the lead PM emissions tended to be distributed in the 0.25 micron and smaller size range.

INTRODUCTION

Recent concerns about direct-injection spark-ignition (SI) and compression-ignition (CI) exhaust emissions have focused attention on fuel properties, such as sulfur content and its effect on emerging exhaust emissions control technologies. The presence of sulfur in motor fuels is in many ways analogous to the presence of lead in gasoline in the 1960s and early 1970s. During that time, many were concerned about removing lead from gasoline both because of potential engine longevity issues and the lack of economically viable alternatives for lead alkyl antiknocks. However, the presence of lead in gasoline represented a health concern as well as a barrier to implementation of relatively new catalytic exhaust emissions control technologies. Many of the advances that have been made in reducing the emissions from gasoline-powered vehicles have been possible because of advances in fuel formulation.

Similarly, in the case of diesel fuel, fuel sulfur enhances lubricity which in turn prolongs engine life. Also, in economic terms, the removal of sulfur from fuel represents a monumental investment for our nation's refineries. However, the deleterious effect of sulfur on both present-day and emerging exhaust emissions control technologies has been well-documented. (1-4)

Concerns about the health effects from PM produced by direct-injection engines (whether CI or SI) have caused a number of studies to be initiated. Many of these are ongoing. Health effects concerns about PM have focused both on the toxicity of the compounds present as well as the effective diameter of the particles. In examining the potential health effects of modern, direct-injection engine PM, it is useful to examine historical PM emissions as a basis for comparison. A number of studies

have put forward data that show the PM emissions of vehicles during the 1980s and 1990s (5,6), however, the PM emissions from earlier vehicles in proper operating condition are a relative unknown. This is due largely to the lack of advanced instrumentation during the period. This study aims to provide a historical perspective on emissions from a gasoline pre-emissions control vehicle using both leaded and unleaded fuel to augment available data. Although the gaseous emissions from vehicles of this era are well-documented, newer technologies for the characterization of particulate emissions make it worthwhile to revisit the particulate emissions of vehicles of the pre-control era.

EXPERIMENTAL METHODS

SELECTION OF TEST VEHICLE – In order to best represent the emissions from a new vehicle in the 1960s, a near-pristine vehicle from this era was required. Most vehicles of this age have accrued a larger-than-desirable amount of mileage; hence, a vehicle was sought that had recently undergone an engine re-build using only factory replacement parts. Based on these criteria, a 1967 Chrysler 300 was identified. This vehicle (Figure 1) had 94,000 original miles on the chassis. The engine and exhaust system were rebuilt with factory replacement parts at 74,000 miles. The spark timing, carburetor tune, and other pertinent parameters were brought within factory specifications. The vehicle was equipped with a 6.3-liter (383 cubic-inch-displacement) V-8 engine. The carburetor was a factory unit, but was not necessarily exactly the same as the original unit. Prior to testing, the exhaust system was leak-checked. In addition, two full Federal Test Procedure (FTP) tests were performed to prepare the vehicle for reportable tests.

Figure 1. 1967 Chrysler 300 test vehicle

EVALUATION PROCEDURE – In order to determine the differences in the vehicle's emissions characteristics when operating on leaded and unleaded fuel, the vehicle was subjected to repetitive FTP tests. Three tests were performed with each fuel, beginning with unleaded fuel (UTG96). The leaded fuel was produced by adding appropriate levels of tetraethyl lead (TEL) to the unleaded base fuel. The lead level was raised to approximate the lead levels in gasoline in the late 1960s (0.8 grams/liter). The aromatic content of the base fuel was 32.2%. This was slightly lower than the aromatic content during the late 1960s. However, since both fuels had relatively high aromatics, the authors do not believe that significant differences in the PM emissions resulted from this small difference in aromatic content. No engine re-tuning was performed during the evaluations.

In addition to regulated gaseous emissions, the particulate (PM) emissions of the vehicle during each of the tests was measured. Both PM mass and mass-based size distribution were investigated. Samples for transmission electron microscopy (TEM) were collected as well. The TEM samples were collected using carbon-film grids temporarily attached to impactor substrates. This allowed TEM analysis of the PM emissions in a size-fractionated fashion. The elemental composition of the PM samples was determined by both energy dispersive X-ray spectroscopy (EDS) and inductively-coupled plasma mass spectroscopy (ICP-MS). FTP tests and sample collection were performed by Automotive Testing Laboratories, Inc. (ATL) of East Liberty, Ohio. ATL's emissions-grade test cell utilizes a Horiba AC electric dynamometer and Horiba analytical emissions sampling bench. Supplemental analyses of particulate samples were conducted by Oak Ridge National Laboratory (ORNL).

RESULTS

The results showed a large effect of lead in the fuel on PM emissions, but not on gaseous emissions. Figure 2 shows the composite emissions results for hydrocarbons (HC), oxides of nitrogen (NOx) and carbon monoxide (CO). The data are for an average of three tests. Note the similarity in the results for each of the species. Figure 3 shows the PM mass emissions for the composite cycle as well as each individual bag averaged over three runs. Overall, the PM emissions were much higher for the leaded fuel. The data show the high and variable PM results for Bag 1, the cold start portion of the FTP. This is to be expected as a large displacement engine with a carburetor will have relatively poor control of fuel delivery especially during cold start conditions. The PM values for Bags 2 and 3 were much less variable.

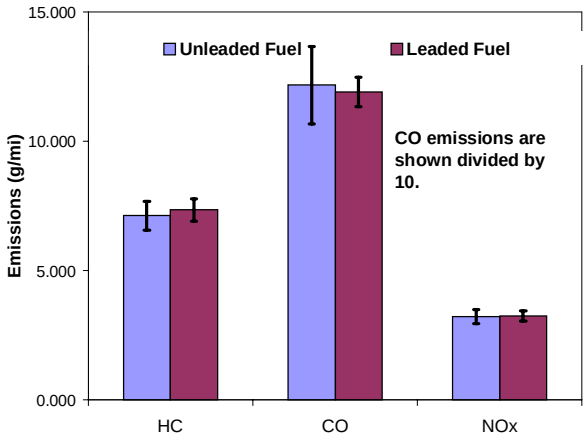


Figure 2. Gaseous pollutant emissions for the FTP

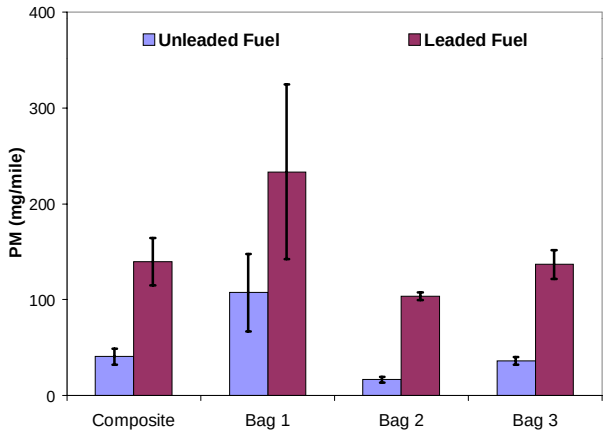


Figure 3. FTP PM emissions results

The size distribution of the PM was determined by Micro-Orifice Uniform Deposit Impacter (MOUDI). This technique measures the weight of PM accumulated on 9 stages and an after-filter (7). The stages represent different size ranges as illustrated in Table 1. Because of the very low amounts of PM generated by a spark-ignited (SI) vehicle, the MOUDI samples were an accumulation taken during three individual tests to produce one size-distribution measurement per fuel. As such, the distribution was an average over three tests. Figure 4 illustrates the results for the unleaded and leaded fuels. Some impaction techniques have shown a tendency for particles to bounce, then be re-entrained in the sample flow rather than deposited upon their representative stages. Use of a silicone impactor coating can minimize this problem. An impactor coating was not used for this study because of concerns that the silicon EDS spectra might interfere with other elemental responses preventing meaningful analysis of the collected PM sample. The emissions increased overall for the leaded fuel and in particular at the 3 lowest PM size cutpoints. The MOUDI device also utilizes a backup filter to trap particles too small to be size fractionated using this device. Although these backup filters were not analyzed for lead content, the mass of PM trapped on the backup filter for the leaded-fuel test case was 2.5 times higher than the mass of PM trapped on the filter for the unleaded-fuel test case.

PM LEAD ANALYSES – The filters were analyzed for lead to determine the lead contribution to the PM mass emissions. The filters were digested and analyzed with ICP-MS specifically for lead. The MOUDI substrates for stages 7, 8, and 9 were analyzed by EDS.

Table 1. MOUDI instrument stage cutpoints

MOUDI Stage Number	Particle Size Midpoint (Diameter in microns)
1	10
2	7
3	2.5
4	1.4
5	0.78
6	0.43
7	0.25
8	0.14
9	0.07
10 (Backup Filter)	0.02

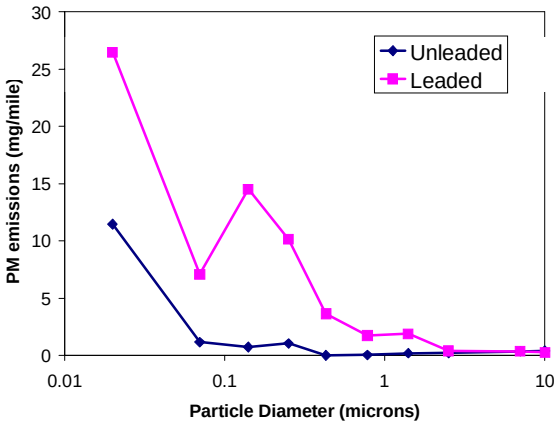


Figure 4. MOUDI PM size fractionation results

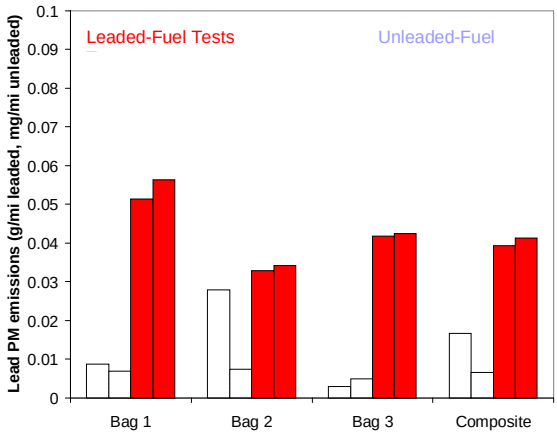


Figure 5. ICP-MS filter analysis results

The blank corrected ICP-MS results for the unleaded and leaded fuel are shown in Figure 5. There was a 4-order-of-magnitude difference in the PM lead emissions for the leaded and unleaded tests.

Figure 4 showed a large increase in the PM mass on MOUDI stages 7, 8, and 9 with leaded fuel compared with those stages for unleaded fuel. As a result, stages 7, 8, and 9 from both fuels were investigated using EDS. This technique produces a weight percentage for specific elements that are present on the sample substrates. Figure 6 shows these results for three specific elements (chlorine, carbon, and lead) for both fuels. In addition, bromine was detected, however there was interference in this measurement caused by the aluminum foil substrate.

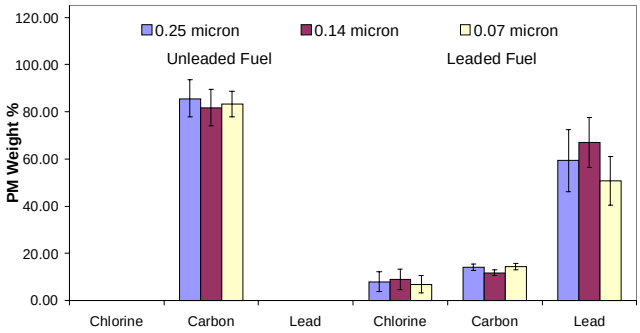


Figure 6. EDS results for substrates 7, 8, and 9

Chlorine and bromine (as ethylene dichloride and ethylene dibromide) were often added during the leaded-fuel era to scavenge lead from the combustion chambers of the engine to reduce combustion chamber deposit formation (8). Lead bromochloride, lead bromide, and lead chloride are formed during combustion and emitted as PM. The remaining measured weight percent of the PM not accounted for by lead, chlorine, or carbon likely consisted of oxygen, hydrogen, and trace elements.

The particulate matter from the unleaded fuel had a consistent composition for all three MOUDI stages. The overwhelming majority of the PM consisted of carbon and oxygen, although some iron and silicon were also detected. No lead was detected for the unleaded fuel samples. Using leaded fuel resulted in at least 50% of the weight of the collected PM being due to lead for all three sizes of particulate matter. Additionally, chlorine appeared in the PM from leaded fuel. Carbon and oxygen, while minor on a weight basis, still accounted for the majority of atoms present in the particulate matter. Again, minor amounts of the silicon and iron were seen in some, but not all, of the spectra. The lead concentration in the PM appeared to vary slightly with average particle size. PM from stage 8 had the most lead, while stage 9 PM had the least.

TEM CHARACTERIZATION RESULTS – The morphology, structure, and composition of PM is also of concern. TEM analyses can allow investigation of these characteristics of individual particles. PM was collected during both a hot-start event and a cruise condition In order to examine individual particles, short time sampling of the exhaust stream was performed. TEM grids were mounted on top of MOUDI substrates for stages 7 - 9. Analytical grade dodecane was used to provide adhesion between the aluminum foil substrate and the TEM grids. A Hitachi HF-2000 200 KV field emission transmission electron microscope was used for the analysis.

Figure 7 shows a micrograph of typical particulate matter generated by the vehicle when running on leaded gasoline. The particulate was a complex chain-like morphology made up of small spheres of carbonaceous material. This morphology is also typical of PM emitted by modern SI vehicles. The dark areas of the particle were more electron dense than the the light areas. In this case, EDS analysis indicated that the dark regions were lead rich areas of the PM. There was a significant bromine signature in the EDS of individual particles, and, in this case, there was no aluminum substrate to interfere with the bromine signal. Thus, the particle consisted of carbon, oxygen, silicon, bromine, lead and chlorine.

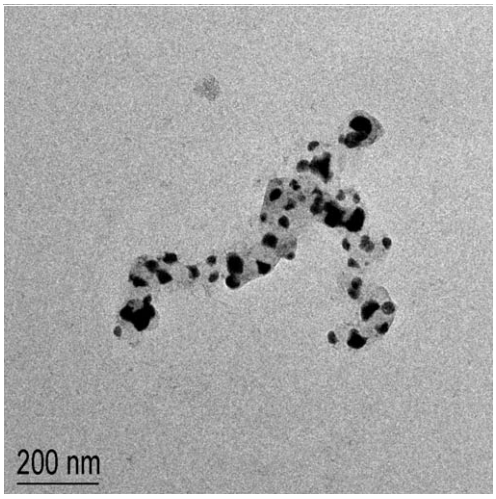


Figure 7. Micrograph of a typical particle emitted by the vehicle using leaded fuel.

PM generated by the vehicle on unleaded gasoline is shown in Figure 8. This PM demonstrated morphology similar to the leaded-fuel PM, but it lacked the large dark areas that correspond to the heavy element fraction of the PM (lead). EDS indicated that this particle consisted only of carbon, oxygen, silicon, and a small quantity of sulfur.

DISCUSSION OF RESULTS

Overall, the PM characterization supports the notion that the lead was distributed throughout the particle size range. However, the majority of the PM mass for the unleaded fuel occured in the nano-particle size range (less than 0.05 microns). The mass-based size distribution for unleaded fuel showed a large amount of PM mass at sizes less than 0.07 microns. Because these small particles individually were less massive than larger particles of the same composition, there must have been

many more small particles than large particles in order to affect the mass-based size distribution in this way. Thus, although number-based particle size distribution was not performed, the results imply that the number-based size distribution was likely skewed towards the nano-particle range as well. This same trend in the number-based size distribution has been seen in other studies(9). It is possible, however, that particle-bounce has skewed the results towards smaller mean-diameters than were actually present. The leaded-fuel case, however, showed a mass-based PM size distribution that was skewed towards the 0.1 to 0.3 micron size range. However, as addition of lead to the PM causes an increase in the density of individual particles, it is not clear that the number-based size distribution would be any different from the unleaded-fuel test case.

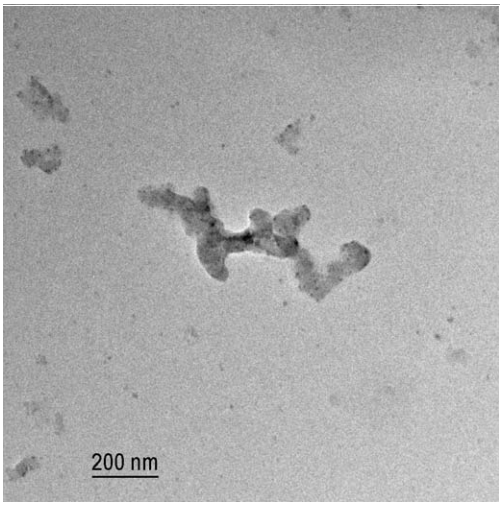


Figure 8. Micrograph of a typical particle emitted by the vehicle using unleaded fuel.

ACKNOWLEDGEMENTS

The authors would like to gratefully acknowledge the support of the U.S. Department of Energy, Office of Heavy Vehicle Technologies, and in particular Dr. Jim Eberhardt for this project. We would also like to thank Dr. Linda A. Lewis for performing the ICP-MS analyses for this study and Dr. Lisa Lanning of ATL for PM sample handling.

REFERENCES

1. "The Impact of Gasoline Fuel Sulfur on Catalytic Emissions Control Systems." Manufacturers of Emissions Controls Association, September 1998.
2. "The Impact of Sulfur in Diesel Fuel on Catalyst Emission Control Technology." Manufacturers of Emissions Controls Association, March 1999.
3. C. H. Schleyer, R. A. Gorse, R. F. Gunst, G. J. Barnes, J. Eckstrom, K. D. Eng, J. Freel, M. Natarajan, and A. M. Schlenker. "Effect of Fuel Sulfur on Emissions in California Low Emission Vehicles." SAE #982726. Society of Automotive Engineers, 1998.
4. "Diesel Emissions Control Sulfur Effects (DECSE) Program – Phase 1 Interim Data Report Number 2: NOx Adsorber Catalysts." U. S. Department of Energy, Engine Manufacturers Association, and Manufacturers of Emissions Controls Association. October 1999.
5. S. H. Cadle, P. A. Mulawa, R. A. Ragazzi, K. T. Knapp, J. M. Norbeck, T. D. Durbin, T. J. Truex, and K. A. Whitney. "Exhaust Particulate Matter Emissions from In-Use Passenger Vehicles Recruited in Three Locations: CRC Project E-24." SAE # 1999-01-1545. Society of Automotive Engineers, 1999.
6. Z. D. Ristovski, L. Morawska, N. D. Bofinger, and J. Hitchins. "Submicrometer and Supermicrometer Particulate Emissions from Spark Ignition Vehicles." Environmental Science & Technology, Volume 32 Number 24. American Chemical Society, 1998.
7. V. Marple, K. Rubow, G. Ananth, and H. J. Fissan. "Micro-Orifice Uniform Deposit Impactor." Journal of Aerosol Science, Volume 17, Number 3. Pergamon-Elsevier Science, 1986.
8. B. Harrison, J. R. Taylor, A. F. Diwell, and A. Salathiel. "Lead Species in Vehicle Exhaust: A Thermodynamic Approach to Lead Tolerant Catalyst Design." SAE # 830268. Society of Automotive Engineers, 1983.
9. B. R. Graskow, D. B. Kittelson, I. S. Abdul-Khalek, M. R. Ahmadi, and J. E. Morris. "Characterization of Exhaust Particulate Emissions from a Spark Ignition Engine." SAE #980528. Society of Automotive Engineers, 1998.