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Technical Report

An Investigation of Photoacoustic Spectroscopy as a Technique for Measuring Diesel Particulate Emissions

by

Daniel P. Heiser

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Standards Development and Support Branch
Emission Control Technology Division
Office of Mobile Source Air Pollution Control
Office of Air, Noise and Radiation
U.S. Environmental Protection Agency

I. Introduction and Background

EPA is in the process of proposing a particulate emission standard for heavy-duty diesel vehicles. With this mandated requirement to regulate particulate emissions, EPA must propose a test procedure for the measurement of particulate emissions from diesel engines. A draft recommended practice for measuring particulate emissions from heavy-duty diesel engines has already been developed and described in a previous report.1/ In the draft recommended practice, the necessary additions and changes to the current Federal Test Procedure (FTP) were discussed and generally involved 1) the use of a dilution tunnel coupled with a constant mass sampler and 2) the use of filter media to collect the particulate matter over both the cold and hot start portions of the test. The latter of these two requirements (i.e., filter measurements) is of special interest here.

The method of measuring emitted particulate matter with filter media is believed to yield accurate results. Filter-based measurements are currently required for the certification of light-duty diesel vehicles,2/ and have also been accepted as the method of measurement in EPA's current program to determine heavy-duty diesel emissions over the transient cycle.3/ One major drawback in using filter media to measure particulate emissions is that the time needed to obtain results, or data processing time, is very slow, at least one hour after the end of the test.1/ In addition, there are also the disadvantages of being unable to analyze mass particulate emissions instantaneously as a function of the mode of engine operation, and of being unable to rapidly and effectively monitor the effects of minor engine adjustment with the engine operating. Also, filter measurements are subject to a number of errors during the filter stabilization period, such as changes in humidity, faulty handling procedures, etc.

The technique of photoacoustic spectroscopy may be an attractive alternative to filter measurements in that it would bring about instantaneous measurement and a short data processing time and thus help eliminate some of the problems mentioned above. Photoacoustic spectroscopy involves the use of a laser beam to heat particles in a cell. If a rapidly modulated laser beam is used, the particles heat and cool quickly, which in turn heat and cool the surrounding air resulting in pressure waves which are picked up by a spectrophone, which is a sensitive microphone with associated electronics. The response time is between 0.5 and 1.0 seconds4/5/ while the data processing time is less than one minute.6/

Photoacoustic spectroscopy is currently being used by Ford, General Motors, and possibly others for monitoring light-duty diesel particulate emissions. This report will investigate these present applications. This report will also discuss the feasibility of this technique as an alternative to filter measurements for certification testing of light-duty diesel vehicles and heavy-duty diesel engines.

II. Present Operation of Photoacoustic Spectroscopy

The photoacoustical effect can be used to measure the light absorption of airborne particulate matter in a suitable cell. In theory, the spectrophone response should be proportional to the amount of light absorbed which is in turn assumed to be proportional to the mass concentration of particles in the exhaust.

Measurement of particulate emissions from diesel exhaust has been attempted with photoacoustic spectroscopy.5/7/8/ The spectrophone measures only the portion of particulate which is elemental carbon, as elemental carbon is the only component of the particulate which absorbs light to a high enough degree.7/ This presents a problem with diesel particulate because it is composed of both elemental carbon and organic compounds that are attached to the carbon. If the elemental carbon to total mass ratio is known, then the airborne particulate concentrations can be determined. However, the fraction of attached organic material ranges from 10 to 70 percent of the total mass particulate,7/ depending on the type of engine and the operating conditions. Thus, the elemental carbon to total mass ratio must be approximated so that spectrophone correlations can be made.

Ford and General Motors appear to be doing the most research on the use of photoacoustic spectroscopy for measuring diesel particulate emissions. At present, photoacoustic spectroscopy is used by both Ford and GM for an "instant" readout of particulate emissions so that the process of modifying engine design as a function of particulate emissions can be done more rapidly and effectively than that possible with filter measurement. To better understand the present role of photoacoustic spectroscopy, the Ford and GM set-up and their most recent studies on monitoring of diesel particulate emissions will be examined in detail below.

A. Ford 5/7/9/

Ford uses an argon (Ar+) laser of 1.5 watts with a wavelength of 514.5 nanometers (nm) as the source of light. The laser beam is split into two beams. One beam serves as a reference and is detected by a photodiode (a device which converts a light beam into a usable electrical signal). The second beam is directed into a spectrophone cavity which intensifies the sound waves produced by the heated particulate in the cavity. The second beam is then detected by another photodiode. The output signals from the microphone are detected by amplifiers and sent to an appropriate instrument (ratiometer) to obtain the normalized spectrophone signal. Response time is approximately one second, while the data processing time is less than one minute.

Ford estimates the cost of their set-up to be about $10,000 for the laser, and $2,500 for the remaining equipment.10/

Ford's latest documented work of photoacoustic spectroscopy measurements involves a study of diesel particulate from a 1979 2.3 liter Opel diesel which could be run with two different rear axle ratios (3.89 or 2.70) and with or without exhaust gas recirculation (EGR).7/ In this experiment, the vehicle exhaust is diluted and mixed in a dilution tube that is about 30 feet long and 1.5 feet in diameter,11/ with samples being taken for both spectrophone and conventional filter analysis. The results of several tests performed on this Opel diesel show that the average spectrophone response (in MV) is proportional to the particulate mass loading (within reasonable accuracy) only under conditions where the ratio of elemental carbon to organic compound is fairly constant.

For example, one set of Ford's data shows that when the Opel diesel is run without EGR, the correlation between spectrophone response and particulate mass loading is accurate within ±5 percent.12/ The organic fraction in this case is believed to be constant at about 55 percent of total particulate mass.13/ Another set of Ford data on the Opel diesel, this time with EGR, also shows good correlation between spectrophone response and particulate mass loading, again within an accuracy of about ±5 percent. Again, the organic fraction is believed to be constant, this time about 35-40 percent of total particulate. However, this latter correlation has a slope (change in spectrophone response per change in particulate mass concentration) that is about 20 percent higher than the slope for the data without EGR.13/ Although good correlation exists for each case, a combined plot of these two sets of data yields a poor correlation between spectrophone response and particulate mass loading with an accuracy of roughly ±50 percent.13/ Thus, the Ford data indicate that the correlation of spectrophone response and particulate mass loading is poor for the combined results of the Opel diesel with and without EGR. Also, these test data show that the elemental carbon to organic ratio 1) must be known for an accurate correlation between spectrophone response and particulate mass loading to be developed, and 2) may vary greatly from one engine (or vehicle) design or operation to another.

In addition to the problem of determining the elemental carbon to organic ratio, another potential limitation with the photoacoustic spectroscopy system, as discussed by Ford, is that optical absorption per particle mass may not be independent of particle size. For carbon particles it has been shown that the absorption of light is constant per unit of mass only for particles with diameters much smaller than the incident wavelength of light (known as Rayleigh particles).14/ It is true that a laser beam of extremely long wavelength could bypass these small particles completely, with no absorption taking place. However, this would occur only at particulate concentrations much lower than those expected to be measured from light-duty diesels, even with particulate emission control devices. In the Ford set-up, the particle diameter may not be sufficiently less than the argon laser beam's wavelength of 514.5 nm (0.5 micrometer) to avoid this problem. This problem is also compounded by the fact that the particle size distribution may change under various vehicle operating conditions.

Ford has tried laser beams of longer wavelength in an effort to solve this problem involving particle size. For an argon laser, a wavelength of 514.5 nm is the longest possible wavelength.11/ Lasers other than argon with longer wavelengths may be used, but such lasers have difficulty producing the power output necessary to obtain sufficient spectrophone response (approximately 1 watt). For example, Ford tried using a krypton ion laser because of its longer wavelength, but the power of this laser was insufficient.11/ Ford also investigated the use of a carbon dioxide laser, which happens to be a laser with a wavelength in the infrared region that is powerful enough for spectrophone response. However, Ford found that the response to the carbon dioxide laser had to be corrected for gas phase absorption by both carbon dioxide and water, the concentrations of which both vary considerably in diesel exhaust. Also, absorption of the carbon dioxide laser may occur for some organic compounds. Thus, from Ford's published work, systems with lasers of longer wavelength appear to have as many of their own problems as the argon laser. (See discussion on GM set-up below.)

Thus, while Ford uses the photoacoustic spectroscopy method as an effective means to detect the relative effects of engine design on particulate emissions when the organic fraction is constant, they have not demonstrated at the moment that this technique can be used to measure absolute levels of particulate emissions with the accuracy necessary for certification work; an accuracy which is currently achievable with the filter technique.

B. General Motors (GM) 8/15/

According to GM's latest published report, photoacoustic measurements are made using a dual cell method in series. Both particulate and exhaust gases enter this apparatus at the second cell. The particulate is filtered after leaving the second cell, so that the first cell contains gases only. The particulate absorption signal can then be determined differentially. For diesel particulate measurements a carbon dioxide laser of 10.6 micrometer wave length is directed into the first cell and then into the second cell, operating at a power of 3.4 watts. (GM has used an argon laser of 514.5 nm wavelength for acetylene smoke measurements.)15/ With this high modulation frequency, background noise is neglible. In the second cell, the infrared absorption due to particulate plus gases (CO_2, H_2O, etc.) is measured, while in the first cell, the absorption of gaseous species only are measured. The particulate absorption is computed by electronically subtracting the response of the two photoacoustic cells. The spectrophones are placed in each cell midway between the open ends of the cells, to provide good coupling of both the laser and the microphone to the resonant mode. The response time is about 0.5 seconds.

GM estimates the cost of the whole unit to be about $35,000. 16/ This breaks down to $12,000 for the CO_2 laser, $4,000 - $5,000 for the optical bench, $10,000 - $12,000 for the electronics and amplifier, and about $4,000 for each of the two photoacoustic cells.

GM has used this system to measure diesel exhaust particulate concentrations from a 5.7 liter diesel engine. This engine was operated at various steady-state conditions and apparently was run without any modifications during the test program. Results indicate that for this diesel engine only, the photoacoustic signal is proportional to the diesel particulate mass concentration, within an overall accuracy of ± 15 percent. GM believes that by their measuring of particulate emissions in a cell sufficiently removed from the combustion source, the optical effects due to variation in the elemental carbon to organic compound ratio have been minimized for this test. However, they admit that data are too scattered (as shown on a plot of particle mass concentration vs. optoacoustic signal) to appreciably determine that the optoacoustic signal was not affected by variation in particle composition.

GM concludes from this study that the photoacoustic effect is a convenient and sensitive method for measuring mass emissions. However, GM states that there are problems involved with the photoacoustic spectroscopy method which may lead to inaccurate results. First, as mentioned above, the chemical composition of the particulate may vary and affect optical properties for a given mass concentration. Second, changes in particle size may still affect optoacoustical calibration in the visible light region somewhat because the wavelength is not sufficiently larger than particle size. This may be solved by using an infrared source (such as a carbon dioxide laser) of sufficiently long wavelength which should give measurements that are independent of particle size variations, if the particles are spheres. However, infrared light response can be affected by the shape of a particle if it is not spherical, which occurs frequently with diesel particulate emissions, where long chains of small particles tend to form.17/

In conclusion, GM uses photoacoustic spectroscopy to observe the effects of engine operating conditions on diesel particulate emissions. GM does not presently have data which compare photoacoustic spectroscopy to filter measurements over the Federal Test Procedure. At the moment they do not intend to use this technique as an alternative to conventional filter measurements for measuring exact amounts of particulate emissions, such as would be required in the Federal Test Procedure.

III. Future Applications of Photoacoustic Spectroscopy

Photoacoustic spectroscopy has been proven to be effective for relating changes in particulate emissions to changes in engine design and operating conditions of light-duty diesel vehicles, particularly if the organic fraction of the particulate is constant. This effectiveness is due to quick response (about 0.5 to 1.0 seconds) and data processing times (less than 1 minute) inherent in the system which allow it to show variations of emissions with driving conditions such as acceleration, steady highway speeds, and idles. However, the photoacoustic spectroscopy system can not be depended on for exact measurement of particulate emissions, as the overall accuracy of the correlation between spectrophone response and particulate mass loading is estimated to be about ±15 percent for the engine tested with no modifications by GM, and about ±50 percent for the Opel diesel engine tested with modifications (EGR) by Ford.

Because of this limited accuracy, photoacoustic spectroscopy should not be considered for certification application at this time. Also, photoacoustic spectroscopy has only been studied using a few light-duty diesel vehicles by Ford and General Motors. Given the problems already seen with this technique these few studies would not be adequate to show that the accuracy of the photoacoustical technique would not be affected to an even greater degree by different engines or vehicles. In other words, before photoacoustic spectroscopy could be considered for certification purposes the technique must correlate with the filter measurement technique for all types of light-duty diesel vehicles and heavy-duty diesel engines. Until data show otherwise, photoacoustic spectroscopy should not be allowed as an alternate certification technique for measuring particulate emissions.

Conclusion

Photoacoustic spectroscopy is currently used to monitor the effects of engine design and operating conditions on particulate emissions. Accurate measurements of the correlation between spectrophone response and particulate mass loading have not been obtained for particulate emissions because the absorption of the laser beam used in this technique seems to be affected by 1) particle size and shape and 2) particle composition. Thus, photoacoustic spectroscopy should be rejected at the moment as a technique for measuring particulate emissions during certification. Progress in photoacoustic spectroscopy should be monitored in the future as improvements may justify it as an alternative to the filter measurement test procedure.

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