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General Motors Corporation and Pacific Northwest Laboratory Staff Exchange: Instrumentation for Rapid Measurement of Automotive Exhaust Emissions

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July 1995

Prepared for U.S. Department of Energy
under Contract DE-AC06-76RLO 18306

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GENERAL MOTORS CORPORATION AND PACIFIC NORTHWEST LABORATORY STAFF EXCHANGE: INSTRUMENTATION FOR RAPID MEASUREMENT OF AUTOMOTIVE EXHAUST EMISSIONS

Staff exchanges such as the one described in this report are intended to facilitate communication and collaboration among scientists and engineers at Department of Energy (DOE) laboratories, in U.S. industry, and academia. Funding support for these exchanges is provided by the DOE, Office of Energy Research, Laboratory Technology Transfer Program. Funding levels for each exchange typically range from \$20,000 to \$40,000. The exchanges offer the opportunity for the laboratories to transfer technology and expertise to industry, gain a perspective on industry's problems, and develop the basis for further cooperative efforts through Cooperative Research and Development Agreements (CRADAs) or other mechanisms.

Information in this report on the staff exchange of Pacific Northwest Laboratory (PNL) staff with the AIGER Consortium (General Motors, Ford, Chrysler, Navistar, the Environmental Protection Agency, and the California Air Resources Board) includes the purpose and objectives, a summary of activities, significant accomplishments, significant problems, industry benefits realized, recommended follow-on work and potential benefits from that work, and two appendices. Appendix A is a brief description of the fast gas chromatography and infrared spectroscopy chemometric technologies and their application to the rapid characterization of automobile exhaust emissions. Appendix B is a list of key contacts and the schedule of activities pertaining to the staff exchange.

PURPOSE/OBJECTIVE

The objectives of this project were as follows:

- to establish a sound working relationship with the AIGER consortium so that joint projects on the development of exhaust emissions instrumentation could proceed smoothly
- to familiarize the AIGER consortium members with the capabilities of PNL in the areas of rapid hydrocarbon identification and quantification, infrared spectroscopy, and chemometrics
- to familiarize PNL staff with the capabilities of the AIGER members, and with the requirements for developing rapid measurements for exhaust emission measurements

SUMMARY OF ACTIVITIES PERFORMED

This staff exchange began in September, 1993 with a visit to the General Motors Vehicle Emissions Laboratory at the GM Proving Ground in Milford, Michigan by Dr. Tom Sloane and Mr. Bill Robins of PNL. They attended a meeting of the AIGER Board to discuss the proposed project to develop two instruments for rapid vehicle exhaust measurements. They then held detailed discussions of PNL's capabilities in the area of fast gas chromatography, and the approach PNL would take if the project were funded. They also visited the vehicle test area to become familiar with the constraints imposed by the need for rapid, routine analysis of vehicle exhaust. Mr. Robins also visited the Ford emissions facility, and conducted extensive discussions with both GM and Ford staff on the requirements for decreasing the time needed to analyze a bag sample of auto exhaust from the current one hour down to five minutes.

PLANT TOURS

On April 25, 1994 Paul Rieger of the California Air Resources Board visited PNL to discuss our progress on the development of an instrument to measure the ozone-forming reactivity of vehicle exhaust. Paul is the designated AIGER champion for this joint AIGER/PNL project. He had provided exhaust emissions data performed at CARB that included both the mid-infrared spectrum and gas chromatographic speciation of exhaust samples taken from the test vehicles. Paul visited PNL to get a first-hand look at our capabilities, and to assist with the analysis of the data he provided.

Jeff Loo of GM also visited PNL from June 13-15, 1994 as part of this exchange. During this visit several important issues were addressed: 1) refined definition of the emissions instrumentation problem being addressed; 2) scope and priority of PNL R&D activities that would be of most benefit to AIGER; 3) prioritization of target chemical species in exhaust; 4) overview of PNL R&D activities completed to date on CRADA Project PNL 93012; 5) overview of future R&D activities; and 6) administrative matters relating to R&D information. A high priority was placed on near-term (1-2 years) technology enhancements that will allow U.S. auto companies to meet the regulatory demands using their current chemical analysis support structure. New prototype instruments that function outside the current structure were described as important longer-term (> 1-2 years) priorities.

EXPERIMENTS

A number of experiments were carried out at PNL during the visit of Dr. Jeff Loo on June 13-15, 1994. Various chromatographic separation and injection methods were evaluated, using auto exhaust samples which Dr. Loo brought with him. As a result, a clearer picture of the required fast gc techniques has emerged. In particular, the low concentration of exhaust hydrocarbon species will require some preconcentration of the sample prior to injection onto the chromatographic column. Either a cryogenic or room-temperature adsorption method will be required. Steps will also need to be taken to prevent undue deterioration of the columns resulting from the presence of a large amount of water vapor in the samples.

SIGNIFICANT ACCOMPLISHMENTS

The staff exchange has stimulated close cooperation between AIGER and PNL on the development of rapid exhaust-emissions measurement instrumentation. A CRADA project has been funded by the DOE ER-LTA program at a level of \$340K per year for three years to conduct this development work at PNL. The AIGER consortium will contribute an equal amount over the three-year period, as work-in-kind. The staff exchange has facilitated a better understanding of industry needs and PNL capabilities among the CRADA participants, so that the project can proceed more efficiently, as described below.

- 1) A refined definition of the emissions sampling and measurement problem has been developed. More emphasis will be placed on development of a fast GC instrument that can be used at a central emissions laboratory. Also, less emphasis will be placed on the analysis of oxygenated species in the exhaust.
- 2) Since all U.S. auto companies employ a central laboratory for their emissions-testing programs, the maximum value of PNL work will be to develop methods and instrumentation modification "kits" that will allow existing laboratory capabilities to be retrofitted for the significantly more rapid chemical-analysis approaches. The development of a new prototype instrument becomes a longer-term objective.
- 3) Using the experience and perspective of Dr. Loo, the most important and troublesome species (from the perspective of current analysis methodology) were identified.
- 4) An update of completed experiments and on-going experiments was presented, and Dr. Loo was able to provide suggestions for further work.
- 5) Anticipated research plans for the next few months were reviewed, including evaluation of various chromatographic columns, operating parameters, injection and sampling methods, and various detector evaluations. Dr. Loo concurred with the outlined plans.
- 6) An understanding was reached regarding the need for coordinating technical information releases among all parties within AIGER, particularly the auto companies.

SIGNIFICANT PROBLEMS

No significant problems occurred during the staff exchange. The ability to carry over funds from FY93 into FY94 allowed a reasonable degree of flexibility in determining how the exchange proceeded. The significant issue that made this flexibility highly desirable was the rumored introduction of a commercial fast gas chromatographic instrument at the PITTCON analytical chemistry conference in

March, 1994. Commercial availability of such an instrument could have a significant impact on the desired course of action by AIGER and PNL. It became clear at the March, 1994 PITTCON that such an instrument was not going to be introduced during FY94, so the exchange and the CRADA project could proceed as originally planned.

INDUSTRY BENEFITS REALIZED

AIGER now has a much better understanding of PNL capabilities and the quality of PNL staff working on the emissions instrumentation development CRADA project. An excellent working relationship has been established so that the project will proceed in a manner that is carefully attuned to the requirements of the AIGER partners. It is expected that this relationship will be enduring and long-term, focused on the near- and long-term emissions-measurement needs of AIGER.

RECOMMENDED FOLLOW-ON WORK

The principal recommendation resulting from the staff exchange is to carry out the ER-LTA-funded CRADA project as quickly and as efficiently as possible. Close cooperation with a commercial instrumentation manufacturer has also been recommended. Preliminary contacts have been made with Andros, Inc. as one potential commercial partner. Hewlett-Packard has recently announced that they plan to introduce a new commercial high-speed gas chromatograph at the 1995 PITTCON meeting. PNL may be involved in the testing and adaptation of this new instrument to the needs of AIGER.

POTENTIAL BENEFITS FROM PURSUING FOLLOW-ON WORK

The concentration of hydrocarbons in the exhaust of automobiles that are being developed to meet stricter emissions regulations will be very low. More measurements of exhaust emissions will therefore be needed to achieve the desired precision. The ability to make these measurements more rapidly will greatly reduce the time and cost needed to develop vehicles for emissions certification.

APPENDIX A

**Brief description of the fast gas chromatography and
infrared spectroscopy chemometric technologies and their application
to the rapid characterization of automobile exhaust emissions**

APPENDIX A

The AIGER consortium has requested that a number of instruments for more rapid analysis of vehicle-exhaust emissions be developed. PNL has been funded by the DOE-ER-LTA program to develop two rugged, reliable prototype instruments for rapid automotive-emissions analysis. One will identify and quantify all the major organic components as specified by the Environmental Protection Agency and the California Air Resources Board with a batch-analysis cycle time of five minutes or less. The second instrument will perform rapid (one-second time resolution), direct measurement of emissions ozone-forming reactivity. The work will be a joint effort between the Pacific Northwest Laboratory (PNL), a DOE laboratory, and the Environmental Research Consortium (ERC), a consortium comprising General Motors, Ford, Chrysler, and Navistar.

These instruments are needed because in the near future, vehicle manufacturers and regulatory agencies will need much more sophisticated emissions-test equipment than is currently commercially available so as to be able to meet and enforce new regulations of vehicle emissions. The regulations present new measurement challenges which center around two principal factors: 1) requirements to measure extremely low concentration levels of emissions; and 2) requirements to more completely and more rapidly identify and quantify (speciate) hydrocarbon and oxygenated hydrocarbon emissions, compared to existing capabilities. This greater measurement capability requirement is due in part to the need to assess not only the mass of vehicle emissions, but also the ozone-forming reactivity of these emissions. The industry and regulatory agency needs based on these requirements have been circulated widely among instrument manufacturers, with insufficient positive response that the required instruments can be developed and supplied. The vehicle manufacturers themselves cannot devote the necessary resources to satisfy their needs in a timely fashion, because they are tied up certifying vehicles to current regulations. The DOE laboratories provide a viable avenue for the development of the required instrumentation through a partnership with the AIGER consortium.

A complete analysis of emissions samples in five minutes or less may require a combination of measurement techniques. Initial experiments, however, will concentrate on high-speed gas chromatography with the aim of developing the simplest system that will perform this task. Throughout all the project work, the data obtained will be analyzed using chemometric techniques to extract the maximum amount of information from the measurements. Advanced methods for inter-calibration of instrument combinations will be utilized. The transfer of calibration models between instruments will also be considered.

High-resolution frequency-modulated near-infrared diode laser absorption spectroscopy, combined with chemometric data analysis, is proposed to rapidly measure the ozone-forming reactivity of automobile emissions. This method promises to achieve the intention of the fast "top fifteen" speciation analyzer for modal analysis, without necessarily measuring the absolute concentrations of individual exhaust components. The method is analogous to the determination of octane-number and properties of gasolines with chemometric analysis of near-IR spectra of the gasoline, in which quantification of the functional groups that are the basis for gasoline octane number substitutes for quantification of the individual gasoline components. Likewise, the idea behind the proposed project is the quantification of functional groups associated with high reactivity in automobile exhaust, in particular carbon-carbon double bonds, aldehydes, and aromatic rings. Modern biased regression methods will be used for calibration of the infrared reactivity measurement device.

APPENDIX B

Key Contacts and Schedule of Activities

Key Contacts

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Schedule of Activities

September, 1993

Visit to GM Proving Grounds in Milford, Michigan by Dr. Tom Sloane and Mr. Bill Robins of PNL

April 25, 1994

Visit to PNL by Paul Rieger of the California Air Resources Board

June 13-15, 1994

Visit to PNL by Dr. Jeff Loo of General Motors Corporation

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