

STATE OF CALIFORNIA
CALIFORNIA ENVIRONMENTAL PROTECTION AGENCY
AIR RESOURCES BOARD

**CALIFORNIA'S INFORMAL
PARTICIPATION
IN THE PARTICLE
MEASUREMENT
PROGRAMME (PMP)
LIGHT DUTY
INTER-LABORATORY
CORRELATION
EXERCISE (ILCE_LD)**

FINAL RESEARCH REPORT

October 2008

(This Page Intentionally Blank)

State of California
California Environmental Protection Agency
AIR RESOURCES BOARD

The technical staff of the California Air Resources Board (CARB) is pleased to share with the Transport and Air Quality Unit of the Institute for Environment and Sustainability at the European Commission – Directorate General - Joint Research Center (EC-DG-JRC or JRC) the findings from our emissions evaluation of the PMP's Golden Vehicle (GV). Under a Memorandum of Understanding (MOU) for research collaboration¹, our agencies agreed that CARB's informal participation in the ILCE_LD was mutually beneficial. Thus, the GV and the golden particle measurement system (GPMS) were shipped to California for testing in October of 2006.

CARB staff wishes to thank JRC for the opportunity to carry out this research, and our technical curiosities were fulfilled. The opportunity to compare our light-duty clean diesel emissions laboratory capabilities against those of the PMP participating laboratories was invaluable. Our results were all in good general agreement with the PMP results.

CARB accepts the responsibility of being a leading environmental steward. Our widely recognized low emission vehicle (LEV) programs require that we stay abreast of all of the latest technical developments in motor vehicle emission measurements. The PMP is one of the most notable efforts in recent times for advancing the regulatory control of vehicle emissions so that only the cleanest vehicles, diesel or gasoline, make it onto our roads. The experience we gained from this effort has policy relevance that will bear fruits for many years to come. We were impressed by the PMP protocol for solid particle number emission determination. Our findings in this report are for informational purposes only. There is no expectation that they would bear merit for consideration in your official United Nations-sanctioned PMP.

The exercise helped advance our understanding of the PMP program and its many merits. We look forward to our continued technical exchange. As you embark in the PMP heavy-duty program, California will remain watchful and engaged. We hope that you find our research findings for your GV informative and helpful.

DOCUMENT AVAILABILITY

Electronic copies of this document can be found at:
<http://www.arb.ca.gov/research/veh-emissions/pmp-ld/pmp-ld.htm>

¹ Memorandum of Understanding for research collaboration between the EC-DG-JRC and CARB, signed on October 5, 2005 in Sacramento, California, U.S.A.



Principal Investigators

Alberto Ayala¹, Sherry Zhang², John Collins¹, Tao Zhan¹, Harry Dwyer^{1,*}, Tao Huai¹
Jorn Herner¹ and Wilson Chau³

Contributors

Paul Rieger⁴, M.-C. Oliver Chang⁴, Ronald Haste², Sharon Lemieux², Wayne
McMahan², and Keshav Sahay²

¹Research Division

²Mobile Source Control Division

³Mobile Source Operations Division

⁴Monitoring and Laboratory Division

*Special Consultant to CARB and Retired Professor of Mechanical and Aeronautical
Engineering, University of California, Davis

Contact Information:

Alberto Ayala
Research Division
California Air Resources Board
1001 I Street
Sacramento, CA 95812
aayala@arb.ca.gov
(916)327-2952

<http://www.arb.ca.gov/homepage.htm>

<http://www.arb.ca.gov/research/veh-emissions/veh-emissions.htm>

The statements and opinions expressed in this report are solely the authors' and do not represent the official position of the California Air Resources Board. The mention of trade names, products, and organizations does not constitute endorsement or recommendation for use.

ACKNOWLEDGMENTS

CARB staff wishes to extend its appreciation to JRC staff for the opportunity to conduct this research. Of special note are the helpful interactions with Dr. Penny Dilara, Mr. Barouch Giechaskiel, and Mr. Giorgio Martini.

Dr. Qiang Wei of Horiba, Inc. is specially acknowledged for providing in-kind an SPCS unit for this research. Dr. Wei's technical input and participation was critical for the emission measurement comparisons in this project.

We thank Mr. Jon Andersson of Ricardo and Mr. Chris Parking of the UK's Department for Environment, Food and Rural Affairs for their expert advise during this work.

We also thank Ms. Emma Sandbach from AEA Energy & Environment for calibration of the GPMS and TSI, Inc. for the loan of particle counters.

The assistance with logistics for shipping the Golden Vehicle from Europe to California and back by Dr. Whitney Leeman and Dr. Pablo Cicero-Fernandez of CARB and Dr. Tom Durbin of the University of California, Riverside was greatly appreciated.

The University of Wisconsin played a vital part in this study by their preparation and analysis of the filters for PM and metal determination.

The authors also wish to thank all of the CARB laboratory personnel, management, and executive staff for the support for this research and for the California-EC collaboration.

ACRONYMS

CARB – California Air Resources Board
CPC – Condensation Particle Counter
CVS – Constant Volume Sampler
DPF – Diesel Particle Filter
DPM – Diesel Particulate Matter
DQO – Data Quality Objectives
EC – European Commission
ET – Evaporation Tube
EUDC – European Driving Cycle
FBC – Fuel Borne Catalyst
FTP – Federal Test Procedure
GPMS – Golden Particle Measurement System
GV – Golden Vehicle
HC - Hydrocarbon
HDE – Heavy Duty Engine
ILCE_LD – Inter-laboratory Correlation Exercise
JRC – Joint Research Center
LDV – Light Duty Vehicle
LEV – Low Emission Vehicle
MLD – Monitoring and Laboratory Division
MOU – Memorandum of Understanding
NEDC – New European Driving Cycle
OC/EC – Organic and Elemental Carbon
PM – Particulate Matter
PMP – Particulate Measurement Programme
PND – Particle Number Diluter
PZEV – Partial Zero Emission Vehicle
SHED – Sealed Housing for Evaporative Determination
SOP – Standard Operating Procedure
SPCS – Solid Particle Counting System
SRM – Standard Reference Material
TAC – Toxic Air Contaminant
THC – Total Hydrocarbons
UDDS – Urban Dynamometer Driving Schedule
ULSD – Ultra Low Sulfur Diesel
UN-ECE-GRPE - United Nation’s Economic Commission for Europe - Group of Experts
on Pollution and Energy
UW – University of Wisconsin
VT SHED – Variable Temperature SHED

TABLE OF CONTENTS

ACKNOWLEDGMENTS.....	ii
ACRONYMS	iii
TABLE OF CONTENTS	iv
LIST OF TABLES.....	v
LIST OF FIGURES.....	vi
EXECUTIVE SUMMARY.....	vii
1 INTRODUCTION.....	1
1.1 Overview.....	1
1.2 Background	1
2. EMISSION TESTING	5
2.1 Equipment	5
2.1.1 The Golden Vehicle.....	5
2.1.2 The Golden Particle Measurement System.....	5
2.1.3 CARB Particle Measurement Systems.....	6
2.1.4 CARB Exhaust Test Cell	9
2.1.5 CARB Evaporative Emissions System	9
2.2 Analytical Methods.....	10
2.2.1 Particulate Matter Mass	10
2.2.2 Organic and Elemental Carbon	10
2.2.3 Trace Metals	10
2.3 Pretest Procedures	11
2.3.1 Fuel Refilling Procedures	11
2.3.2 Regeneration.....	11
2.4 Evaporative Emission Test Procedures	12
2.4.1 Vehicle Precondition Procedures	12
2.4.2 One-Hour Hot Soak and Two-Day Diurnal Test Procedures	12
2.5 Exhaust Emission Test Procedures	15
2.5.1 Test Weight and Road Load Coefficients.....	15
2.5.2 Driving Cycles and Emission Measurement and Analyses	15
2.5.3 Engine Conditioning	15
2.5.4 Lubricating Oil	15
2.5.5 Fuel.....	15
2.5.6 Fuel Borne Catalyst.....	16
2.6 Quality Assurance / Quality Control	16
3. TEST RESULTS.....	17
3.1 Evaporative Emission Test Results	17
3.2 Tailpipe Emission Testing Results	19
3.2.1 Comparison between Cell 7 and PMP Participating Laboratories	20
3.3.2 Vehicle Soak Time and Preconditioning Study.....	23
3.3.3 Particle Sampling and Counting Systems Comparison	24
3.3.4 Particle Emissions as a Function of Time	27
3.3.5 Chemical Characteristic of Particle Mass Emissions.....	33
4. CONCLUSIONS.....	38
5. REFERENCES.....	40
APPENDIX A. MISCELLANEOUS INFORMATION ABOUT THE GV AND TESTING..	42

APPENDIX B. EMISSIONS DURING A REGENERATION EVENT 45
 APPENDIX C. TEST CYCLES 50
 APPENDIX E. EVAPORATIVE EMISSION TEST SUMMARIES 54
 APPENDIX F. TRACE METAL ANALYTICAL PROCEDURES 56
 APPENDIX G. TRACE METAL BLANK AND UNCERTAINTY IN UNITS OF MG/MILE 60

LIST OF TABLES

Table 2-1 Instruments for Measuring Particle Concentrations..... 8
 Table 3-1. Emission test and preconditioning sequence 19
 Table 3.2: Comparison of Emission Results from Haagen Smit Laboratory Cell 7 and
 Other PMP Participating Laboratories 22
 Table 3.3: Trace Metal Emission Rates..... 36

LIST OF FIGURES

Figure 1-1 The Golden Vehicle	3
Figure 1-2 CARB’s Haagen Smit Laboratory, Test Cell 7.....	4
Figure 2-1 : The PMP GPMS Top Panel: Picture. Bottom Panel: Schematic.....	7
Figure 2-2 Schematic of typical sampling setup during CARB emission testing.....	8
Figure 2-3 Filters before regeneration and including a DPF Regeneration	12
Figure 2-4 Sequences for evaporative emission testing. The left hand path, two-day-diurnal, was followed for the Golden Vehicle test.....	14
Figure 3-1 Temporal Variation of THC Mass during One-Hour Hot Soak Test.....	17
Figure 3-2 Temporal Variation of THC Mass during Two-Day-Diurnal Soak Test.....	18
Figure 3-3 Emissions over five NEDC tests with overnight soak and no pre-conditioning	21
Figure 3-4 Average and standard deviation of emissions over five NEDC tests with overnight soak and no pre-conditioning.....	21
Figure 3-5 Comparison of the average and standard deviation of emissions between CARB and PMP laboratories	22
Figure 3-6: Emissions over NEDC for various soak and preconditioning options.....	23
Figure 3-7: Emissions over FTP for various soak and preconditioning options.....	24
Figure 3-8: NEDC particle number emissions using Horiba SPCS and the GPMS CPCs.	25
Figure 3-9: Comparison of Solid Particle Concentration by Seven Different Instruments	26
Figure 3-10: Comparison of Solid Particle Average Concentration by Five Different Instruments	27
Figure 3-11: Particle Number Concentrations from Multiple Particle Counters during Tunnel Background.....	28
Figure 3-12: Comparison of Particle Number Concentrations from Multiple Particle Counters during Test NEDC-32.	29
Figure 3-13: Comparison of Integrated EEPS Number Concentration with Total and Solid Particle Number Concentrations during Test NEDC-32.	29
Figure 3-14: Particle Number Concentrations during Test FTP-12	31
Figure 3-15: Particle Number Concentrations during Five Repeat NEDC Cycles with the Horiba SPCS.....	31
Figure 3-16: Particle Number Concentrations during Five Repeat FDP Cycles with the Horiba SPCS.....	32
Figure 3-17: EEPS particle size during cold start	32
Figure 3-18: EEPS particle concentration and size during a regeneration event	33
Figure 3-19: Emission rates of Organic and elemental Carbon during the European Cycle where the notation P1, P2, and P3 denotes the parts or phases of the NEDC and FTP cycles, such as cold, transient, and warm	34
Figure 3-20: Emission rates of trace metals during Steady State at 120 kph	37

EXECUTIVE SUMMARY

This research report describes the results of the California Air Resources Board's (CARB) participation in an international investigation of emissions from a European trap-equipped light-duty clean diesel vehicle and of various instruments used to carry out those measurements. The CARB investigation was centered on a new solid particle number emission measurement protocol developed under the **Particulate Measurement Programme** (PMP). The PMP was launched under the auspices of the United Nation's Economic Commission for Europe - Group of Experts on Pollution and Energy (UN-ECE-GRPE). In addition to solid particle number, CARB investigators conducted measurements of regulated emissions, evaporative emissions, and the chemical characterization of particle mass emissions. The PMP methodology has been shown to be 20 times more sensitive than traditional gravimetric methods, and it is planned to be an important complementary element to measure and analyze diesel and gasoline particle mass and number emissions for new vehicles to be certified for emissions compliance in Europe in the near future. The participation by CARB adds new information to the findings by the nine international laboratories that participated in PMP and that extensively tested the clean diesel vehicle that served as a reference standard, the Golden Vehicle (GV).

The present program was carried out under a Memorandum of Understanding (MOU) between CARB and the Joint Research Center (JRC), and it was anticipated that CARB's informal participation would be highly beneficial to both agencies. CARB's interests and experiences in PMP are part of past and future efforts to drastically lower particulate matter from all mobile sources, both gasoline and diesel, and it is expected that the PMP will be one of the major tools for future regulatory actions throughout the world. Due to the importance of this program, CARB extended the GV testing to include the influence of vehicle preparation and pre-conditioning, and this extension is a unique and informative contribution to the international effort. In addition to the GV investigation CARB has completed detailed PMP studies for Heavy Duty vehicles (HD), which involved both laboratory and on road testing with the use of the PMP methodology. Therefore, the GV program has advanced our knowledge of particulate matter, and it will be very helpful in our future plans and actions.

The GV and the Golden Particle Measurement System (GPMS) for particle number measurement were shipped to a CARB emission laboratory in Los Angeles from the Institute for Environment and Sustainability at the European Commission – Directory General – Joint Research Center (JRC). The present interaction between international laboratories is an excellent step to establish world clean air standards for diesel engines, and it will lead to an improvement of our air quality and environment.

The California testing of the PMP on the GV occurred between November 2006 and May 2007, and the testing was done at CARB's Haagen Smit Laboratory. There were some minor problems with the GV measurement system that was shipped to CARB, and slight modifications of the measurement system were made. The modifications consisted of changes in the locations of the sampling ports, and the substitution of a

CARB measurement system for the GPMS measurement system. The particle measurement instruments consisted of both CARB and GPMS particle counters, and a comparison of the instruments was carried out. The Horiba SPCS was used extensively for these measurements.

In order to get a complete picture of the emissions from the new light-duty clean diesel vehicles, CARB enhanced its testing program to include evaporative emissions from Ultra Low Sulfur Diesel (ULSD) fuels. The testing followed the standard preconditioning procedures for LEV II, and it requires the use of the Federal Test Procedure (FTP) cycle. The test result shows that the emission of the Total Hydrocarbons (THC) from the GV with no evaporative emission controls was very low, as expected for diesel fuels. The emission of THC was 260 mg, and this result is below the 350 mg level required for gasoline vehicles to be certified as a Partial Zero Emission Vehicle. The temporal variation of THC mass during the study was not typical of CARB's previous experiences, and further studies of evaporative emissions on ULSD fuels may be considered in the future.

The development of the PMP methodology as a new measurement tool was the primary focus of the investigation, but a detailed investigation of tailpipe emissions from the GV was also carried out. The important tasks were the following: (a) Compare CARB laboratory test results for criteria gases, particle mass, and particle number with results from PMP participating laboratories; (b) Evaluate the effects of soak time on PM and particle number results; (c) Evaluate the effects of pre-conditioning cycles on PM and particle number results; (d) Compare various particle sampling instruments; and (e) Determine some chemical characteristics of the PM emissions. The determination of the chemical characteristics of the PM emissions was again a CARB enhancement of the testing carried out by the international laboratories, and it is an area that CARB needs to further study in the future.

The regulated emissions and particle number emissions from several cold start New European Driving Cycles (NEDC) were compared to the results of the PMP participating laboratories, and the inter-laboratory variations were of major interest. In general, regulated emissions measured by CARB were within the range of other PMP results, except for CO, whose average is approximately three times higher. A possible explanation for this result was the slightly lower Cetane number for the ULSD fuel used by CARB. The Horiba SPCS employed in this study counted somewhat fewer particles than the results reported by other PMP laboratories for none pre-conditioned tests.

In order to better understand the sensitivity of the particle number measurement to the choice of the sampling instrument, cycle, and vehicle preparation, CARB carried out extended testing. In general, soak time and pre-conditioning did not have a substantial influence on gas phase and PM measurements, however pre-conditioning did increase particle number emissions from the Horiba SPCS to the same level as GPMS instruments during a NEDC cycle. The pre-conditioning investigation was posed by JRC to CARB, since JRC did not carry out this type of study in the international program, and the CARB results represent a unique contribution to the PMP methodology. Additional

testing of the particle number emissions was carried out for FTP cycles, and an increased sensitivity to pre-conditioning was observed. However, pre-conditioning for the FTP cycle decreased particle number emissions, and a strong conclusion cannot be made from these results. Therefore, it is recommended that the effects of vehicle preparation be studied further in the future.

Seven consecutive NEDC cycles were carried out and simultaneous measurements were made with five correctly functioning instruments (Two of the instruments did not function properly). All of the instruments, including both CARB and GPMS instruments, showed similar trends and they gave magnitudes in reasonable agreement. An unusual aspect of the test results was that there was a significant decrease in particle number emissions as the test progressed. A possible explanation of this result was that the tests were performed immediately before a regeneration event was scheduled to be performed on the GV Diesel Particle Filter (DPF). If the DPF is dramatically increasing particle capture near regeneration, this behavior should be accounted for in future developments in the particle number methodology.

NEDC and FTP cycles tests were used to study the real time particle number emissions. In terms of capturing the peaks of the particle numbers during the cycles the results are in good qualitative agreement, however the logarithm scale of the plots hides some of the quantitative variability of the particle number counts. In general there is a significant Coefficient of Variation, COF, for particle number emissions among all of the participating international laboratories, but the accuracy of the new PMP methodology is much better than traditional methods. The exact causes of the variability between repeat cycles cannot be determined at the present time, and there is a need to refine the measurement methodologies of ultrafine particles. New research and development for particle measurement systems, pre-conditioning systems, and cycle choice should be considered, since we need to better understand particle counting systems and methodologies.

An extension of the CARB study was to investigate the particles generated during trap regeneration, and these particles are considerably smaller than typical diesel emissions. The results show a strong peak in concentration for particles in the 10 nm range during the regeneration part of the test. The particle concentrations have significant values for sizes between 6 and 40 nm, and these concentrations remain constant during most of the regeneration event. At the end of regeneration the particle concentrations have a maximum peak value in the 8 nm range.

Since diesel particles are a serious health concern, the CARB testing program was extended to include the chemical characteristics of the particle mass emissions. Particle emission samples for organic and elemental carbon were collected and analyzed over both the NEDC and the FTP cycles. The total carbon emissions were less than 0.3 mg/km, and this is very low compared to the current US standard of 6.23 mg/km. During the cold start portion of the NEDC cycle the elemental carbon content was 50%, and it was less than 10% during the warm phase. For the FTP tests the percentage of elemental carbon was considerably lower. Trace metal samples were collected for

steady state driving, and thirty-two species were able to be measured with good accuracy and signal to noise ratio. For example, the cerium emissions rates from the DPF were 100 times higher than background levels, however the overall rates were very low during the NEDC cycles and they are not a likely health concern. Many of the trace metal species were related to emissions from the lubrication oil.

It is expected that the number of diesel light-duty vehicles will be increasing in the US during the coming years. Since the diesel DPF industry has not standardized on a single technology, there is a need to apply the PMP methodology to a wider class of vehicles. In fact, the entire after-treatment system of diesel engines is changing at a rapid pace, and both the regulated emissions and their chemical characteristics need to be studied in much more detail.

CARB accepts the responsibility of being a leading environmental steward. Our widely recognized low emission vehicle (LEV) programs require that we stay abreast of all of the latest technical developments in motor vehicle emission measurements. The PMP is one of the most notable efforts in recent times for advancing the regulatory control of vehicle emissions so that only the cleanest vehicles, diesel or gasoline, make it onto our roads. The experience we gained from this effort has policy relevance that will bear fruits for many years to come. We were impressed by the PMP protocol for solid particle number emission determination. Our findings in this report are for informational purposes only. There is no expectation that they would bear merit for consideration in your official United Nations-sanctioned PMP.

The exercise helped advance our understanding of the PMP program and its many merits. We look forward to our continued technical exchange. As you embark in the PMP heavy-duty program, California will remain watchful and engaged. We hope that you find our research findings for your GV informative and helpful.

1 INTRODUCTION

1.1 Overview

CARB and JRC have agreed to collaborate on a number of research areas of mutual interest under a MOU on *Emissions from Transport* signed on October 2005. One of the research topics of interest is the Particulate Measurement Programme (PMP) launched under the auspices of the United Nation's Economic Commission for Europe - Group of Experts on Pollution and Energy (UN-ECE-GRPE). The purpose of this California study was to conduct emission testing of the PMP's Golden Vehicle by CARB at its vehicle emission laboratory facilities in Los Angeles. The testing was a voluntary and informal participation by CARB in the Inter-laboratory correlation exercise (ILCE_LD) that PMP conducted formally under the auspices of the GRPE effort. The California testing of the PMP Golden Vehicle occurred between November 2006 and May 2007.

1.2 Background

Particulate matter (PM) from diesel engines is a known carcinogen that has been shown to cause various adverse health effects. It has been designated a Toxic Air Contaminant (TAC) in California, and in the Los Angeles area, 70% of the cancer risk by inhalation from known TACs is caused by diesel particulate matter (DPM), (CARB, 2000). Identification as a TAC requires the development and implementation of a mitigation plan to reduce human exposure to emissions from all sources to the maximum extent that is technically feasible and cost effective. One element of the response to the health threat has been to gradually reduce DPM emission standards for new engines. In California, the first DPM limits for heavy-duty engines (HDEs) were set in 1988 at 0.6 g/bhp-hr or 0.805 g/kW-hr. Since then, this standard has been made gradually more stringent and is currently at 0.01 g/bhp-hr or 0.0134 g/kW-hr. The LEV II standards for light-duty vehicles (LDVs) also require passenger cars (gasoline or diesel) to emit less than 0.01 g/mile or .00622 g/km for the first 120,000 miles of operation. Similar steps have been taken in many parts of the world, and in Europe the EURO1 standard was introduced in 1992 and required diesel passenger cars to meet a 0.14g/km of PM limit. The current EURO5 PM standard took effect this year at 0.005 g/km and for the first time applies to certain gasoline passenger cars. Europe has a very large fraction of diesel passenger cars, which is not the case in California. Diesel engines dominate the heavy duty fleet both in California and in Europe.

The developments in clean diesel engine technology that have complied with the increasing stringency of the DPM emission standards over the past two decades has been a tremendous success for the environment. Industry deserves recognition for developing the engine technology that continues to meet this challenge. CARB and other authorities are interested in continually enhancing the understanding of emissions, how to measure them accurately, and how to reduce them to near zero levels. Until the present time PM emission standards have been mass based, and emissions are collected on filter media and weighed. Emissions are expressed in mass per unit

distance travelled for LDVs or mass per energy output for HDEs. The determination of emissions is accomplished using dynamometer testing of a vehicle or engine with a Constant Volume Sampler (CVS) full-exhaust dilution tunnel and subsequent collection under controlled conditions of a diluted DPM sample on filter media. The filter is weighed prior to the test and then post-weighed after the test to determine the mass emissions. The detection limit of this methodology is sufficiently low to determine compliance with current emission standards, thanks in great part to improvements to the method for HDE certification that were developed in a collaborative approach by government, industry, and academia. However, meeting the accuracy requirements for the gravimetric PM measurement is quite challenging with the very low emission levels seen for US07/EURO5-compliant HDEs. Additionally, research indicates that a current and properly working diesel particle filter (DPF) can reduce emissions significantly below the current US07 PM standard², and this level will further challenge the gravimetric method.

Due to these developments there is a need to explore new and improved methods for the measurement of PM emissions from low emission engines and vehicles. A promising and complimentary methodology for measuring PM mass is counting particles, which may be significantly more accurate and precise at very low emission levels than the gravimetric method. Recognizing the need for an alternative or complimentary method for vehicle emission class approval, Europe launched an extensive and multi-nation research initiative as part of the UN-ECE-GRPE-PMP. The research is coordinated by JRC and has included an extensive investigation into the practicability of a particle number standard to compliment the existing particle mass standard. The result of the significant international effort led by Europe has been the identification of instrumentation and methodologies for the counting of solid particles for emission certification. This solid particle measurement is now included in the EURO5/6 directive since "*The particle number measurement procedure is suitable for regulatory use*" (GRPE-PMP-17-1, Ispra, 12SEP06).

Extensive testing of the newly proposed PMP sampling protocol was accomplished in Europe and Asia to verify the applicability and practicality of the proposed methodology at different laboratories. The Golden Vehicle shown in Figure 1.1 was used as a reference and was shipped to laboratories in Italy, Sweden, United Kingdom, Germany, Greece, Japan, Korea, and France in a round-robin testing exercise completed in the summer of 2006. A set of particle counting instruments, the GPMS, was sent along with the GV. A 'Golden Engineer' was also commissioned to help with initial setup, troubleshooting, quality assurance, and expert oversight. In this manner, the PMP has been able to isolate inter-laboratory variations expected with the new metrology. The program concluded that the particle number measurement is 20 times more sensitive than the mass measurement [Working paper No. GRPE-PMP-15-2].

The GV was sent to Los Angeles in October 2006 for testing at the CARB's Haagen Smit Laboratory, Cell 7. This is a new test cell dedicated to clean vehicle testing (Figure

² Coordinating Research Council, Project E-66 has demonstrated that a 1998 DDC Series 60 with a Johnson-Mathey CRT can deliver PM emissions that are at about 5% of the US07 standard or approximately 0.0005 g/bhp-hr (CRC, 2005). <http://www.crao.com/publications/emissions/E-66%20Exec%20Summary.pdf>

1.2). The testing by CARB provides JRC an additional data point for its inter-laboratory correlation exercise. For CARB, this exercise has offered the unique opportunity to gain important experience with the PMP methodology and to compare our laboratory capabilities to other laboratories from around the world.

The testing of the GV was the culmination for a number of initial pilot investigations completed by CARB to assess the PMP protocol for other vehicle classes (Zhang et al., 2008; Ayala et al., 2007a and b; Robertson et al., 2007; Herner et al., 2007; Ayala and Herner, 2006; Herner *et al.*, 2006). The most recent investigation of the PMP method for HDEs was conducted in partnership with researchers from the University of California Riverside, the University of Minnesota, Matter Engineering, TTM, and Ricardo (Durbin *et al.*, 2008; Jung et al., 2008).

Besides the need to study diesel engine emissions, there are other diesel vehicle emission areas, which need to be investigated. Currently, diesel-fueled motor vehicles in California are exempt from existing evaporative emission standards, and there is very little information about these emissions. Past and limited exploratory testing by CARB on a diesel-fueled passenger car yielded hydrocarbon (HC) emissions above the “zero-fuel” evaporative emission demonstration level of 54 mg/test, but below the “whole vehicle” evaporative emission level of 350 mg/test required for Partial Zero Emission Vehicle (PZEV) certification. However, only a single evaporative emissions test was conducted and the testing did not include a demonstration of useful-life durability. Since more information is needed on diesel evaporative emissions, we took advantage of the opportunity and conducted limited evaporative emissions testing of the GV.



Figure 1-1 The Golden Vehicle



Figure 1-2 CARB's Haagen Smit Laboratory, Test Cell 7

2. EMISSION TESTING

The equipment, measurement systems, and test procedures will now be described for the two types of testing that were performed. In the first part of the testing the GV vehicle was investigated for evaporative emissions in one of CARB's sealed housing for evaporative determination (SHED) facilities. Upon completion of the evaporative emission tests, the GV vehicle was tested for tailpipe emissions on a chassis dynamometer. In general, our tests followed the protocols prescribed in the PMP Laboratory Guide (Ricardo, 2005). Deviations from the protocol are noted.

2.1 Equipment

2.1.1 The Golden Vehicle

The Golden Vehicle is a Peugeot 407 Saloon 2.0 HDi 136 SE equipped with an uncoated DPF and cerium-based fuel borne catalyst. Some of its specifications and past testing load provided by JRC are presented in Appendix A. The vehicle was shipped from Genoa, Italy, to Los Angeles, California. Once it arrived at the Port of Los Angeles on October 25th, 2006, it was transported to CARB's Haagen Smit Laboratory on a flat bed truck.

2.1.2 The Golden Particle Measurement System

The GV was shipped with portions of the GPMS instrumentation in the back seat, however it had to be returned immediately to AEA in the UK for final calibration. Those components and the remainder of the GPMS were received by CARB after final calibration approximately two weeks after receipt of the GV. The first stage of the GPMS is a cyclone provided by Ricardo, with a design flow rate of 90 lpm and a size cut-point of 2.5 μm . The GPMS system did not include a pump for the cyclone, therefore CARB used their own pump with a flow rate of 90 lpm. The cyclone is followed by a secondary dilution system (a modified MD-19 rotating disc diluter by Matter Engineering), an evaporation tube or volatile particle remover (VPR), a tertiary dilution stage, two Condensation Particle Counters (CPCs) (TSI model 3010) and pumps. Figure 2.1 shows a picture and a schematic of the GPMS. Additional pictures showing individual components are found in Appendix A.

The schematic in Figure 2-1 shows how the GPMS is intended to be used. Note that the MD-19 diluter (shown in the dashed box) in the GPMS has been modified to include a sample port downstream of the rotating disk diluter and upstream of the evaporator, PND1 in figure. The GPMS Reference CPC is intended to sample from that port, and the GPMS Golden CPC samples downstream of the tertiary dilution, PND2. Initial plans were to compare results from the GPMS with results from a similar system implemented by CARB. However, due to problems with the GPMS MD-19, the GPMS system never functioned on its own. Instead the CARB MD-19 system was used in combination with

various CARB and GPMS particle counters to obtain some particle measurement comparisons. The CARB MD-19 does not include the sample port modification to allow sampling after the rotating disk diluter and before the evaporator. Therefore, all particle sampling was conducted after the cyclone and before the rotating disk denuder or after the tertiary dilution stage.

2.1.3 CARB Particle Measurement Systems

CARB used the cyclone provided with the GPMS, replaced the GPMS MD-19 with its own MD-19, and operated a number of particle measurement instruments, configured as shown in Figure 2-2. Note that there is no CPC in the GPMS “Reference” position.

Matter Engineering MD-19 and ASET15-1 Measurement System

The measurement system provides secondary dilution (the CVS tunnel provides primary dilution), particle evaporation, and tertiary dilution. The secondary diluter was controlled at 150 C, and the evaporator was controlled at 300 C. The design dilution ratios of the GPMS system are 17:1 in the rotating disk diluter and 10:1 in the tertiary diluter, for a combined dilution ratio of 170:1. The CARB system was operated with dilution of 25:1 in the rotating disk diluter and 6.8:1 in the tertiary diluter for a combined dilution ratio of 170:1. The CARB MD-19 system worked correctly throughout the course of the experiments.

Horiba SPCS

A Horiba solid particle counting system (SPCS) was loaned to CARB for this study by Horiba. This instrument drew sample from a manifold directly after the cyclone. It provides counts of solid particles analogous to the Golden CPC in the GPMS setup. This system included a calibrated aerosol generator and diluter system to generate test aerosols used to perform linearity checks on the SPCS. The SPCS system worked correctly throughout the course of the experiments.

EEPS

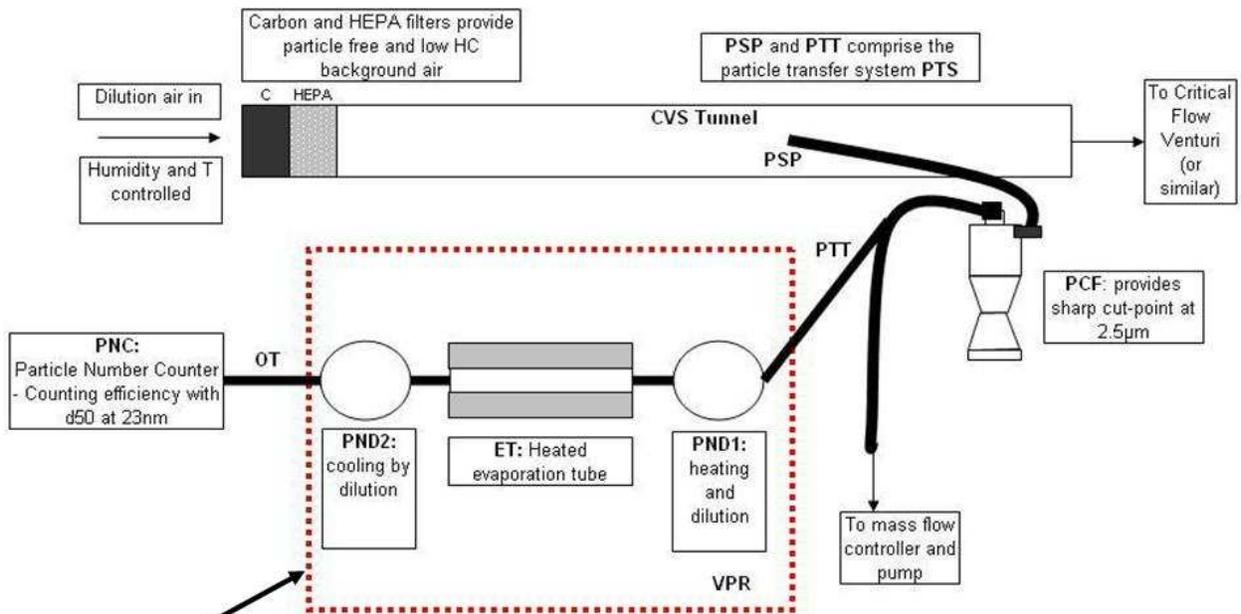
CARB owns a TSI model 3090 EEPS. This system drew sample from the manifold directly downstream of the cyclone. This system worked correctly throughout the course of the experiments, but was operating near or below its detection limit.

CPCs

CARB had on loan a TSI 3010 and a TSI 3790 (which is an updated 3010D). The TSI 3010 and TSI 3790 each drew sample from the manifold downstream of the cyclone. The TSI 3010 worked correctly during the course of the experiments, but the TSI 3790 developed problems early in the study.

CARB owns a GRIMM model 5.403 CPC and also had the GPMS Reference and GPMS Golden CPCs, each a TSI 3010D. These were operated in parallel on a manifold downstream of the MD-19. The Golden CPC developed problems early in the study and

gradually deteriorated. The Grimm CPC and the Reference CPC worked correctly throughout the course of the experiments. It appears from the present investigation that the current CPCs are not robust, and they tend to fail during testing. There should be a concerted effort to make these devices more robust in the future. A summary of all the particle measurement systems that were used in the investigation is shown in Table 2.1. It should also be noted that the systems that developed problems are shown in the table.



Matter Engineering ASET15-1 and MD19 Components

Figure 2-1 : The PMP GPMS Top Panel: Picture; Bottom Panel: Schematic.

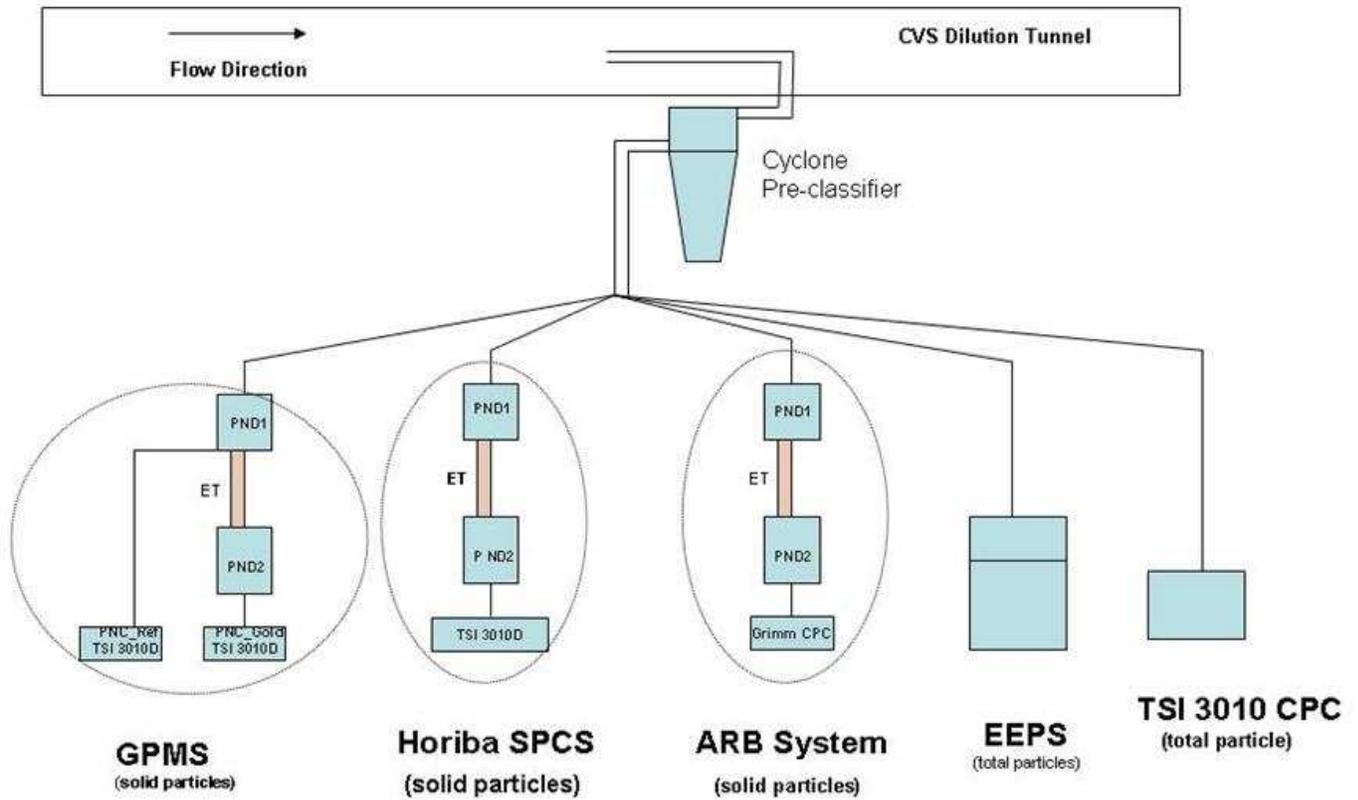


Figure 2-2 Schematic of typical sampling setup during CARB emission testing

Table 2-1 Instruments for Measuring Particle Concentrations

Instrument	Detectable Size limit	Sampling Location	Particle Type	Problem
Gold CPC	23 nm	CARB MD-19	Solid	errors
Ref. CPC	23 nm	CARB MD-19	Solid	none
Grimm CPC	5 nm	CARB MD-19	Solid	none
Horiba SPCS	23 nm	Cyclone	Solid	none
3010 CPC	10 nm	Cyclone	Solid & Volatile	none
3790 CPC	23 nm	Cyclone	Solid & Volatile	errors
EEPS	5.6 nm	Cyclone	Solid & Volatile	noisy

2.1.4 CARB Exhaust Test Cell

Exhaust emission tests were conducted in CARB's Haagen Smit Laboratory Test Cell 7 for clean diesel testing. The sampling system, calculations, calibrations, and quality control for Cell 7 conform to the requirements of 40 CFR 86³. Sampling and calculations for PM mass on TX40 and Teflon filters conforms to 40 CFR 1065⁴. Some features are described below.

The cell is equipped with a 1.22 m single-roll electric dynamometer and a driver's aid. The primary dilution system is a full-flow CVS. The main tunnel is .254 meters in diameter, and the total tunnel flow rate is controlled by a bank of critical flow venturis. Dilution air is room air filtered through a pre-filter, charcoal filter, and HEPA filter. Total tunnel air flow was controlled at 420 SCFM, 11.8 m³/min, for all the experiments in this study. Criteria gases (HC, NO_x, CO) and CO₂ are analyzed using a Horiba analytical bench. PM mass is collected on TX40 filters at 47 +/- 5 °C. The TX40 filters used for this study were Pallflex 47 mm dia. TX40 filters (MFAB) glass fibre bound, in conformance with PMP guidelines.

In addition to sampling for the regulated pollutants, CARB collected samples for analysis of OC/EC and metals. Quartz fiber filters were collected at ambient temperature and submitted to CARB's Monitoring and Laboratory Division (MLD) for determination of OC/EC. A selection of the Teflon filters used to determine PM mass were also analyzed for metals using ICPMS at the University of Wisconsin (UW).

2.1.5 CARB Evaporative Emissions System

The CARB Haagen Smit Laboratory is equipped to perform mobile source evaporative emission testing with three similarly configured Model #101000-100, variable volume/variable temperature Sealed Housings for Evaporative Determinations, manufactured by Webber EMI, Ontario, CA. These SHEDs are provided with top-hinged, pneumatically operated vehicle doors, which use an inflatable, channel-mounted seal to ensure sealing integrity. They are designed to withstand an internal-to-external SHED pressure differential of ± 5.08-cm (H₂O) without deformation or other negative effect. The interior dimensions are approximately: 2.37 m. (height), 3.05 m. (width), and 6.49 m. (length). The nominal inside volume is approximately 46.9 cu. m., and the expansion volume is approximately 7.56 cu. m. Each SHED is equipped with a Horiba Ltd. analytical bench for measuring emissions of CO, CO₂, THC, and CH₄.

³Code of Federal Regulations: PART 86--CONTROL OF EMISSIONS FROM NEW AND IN-USE HIGHWAY VEHICLES AND ENGINES 86.084-40, Automatic expiration of reporting and recordkeeping www.access.gpo.gov/nara/cfr/waisidx_04/40cfr86_04.html

⁴Code of Federal Regulations: PART 1065--CONTROL OF EMISSIONS FROM NEW AND IN-USE HIGHWAY VEHICLES AND ENGINES 1065.084-40, Automatic expiration of reporting and recordkeeping www.access.gpo.gov/nara/cfr/waisidx_04/40cfr1065_04.html

2.2 Analytical Methods

2.2.1 Particulate Matter Mass

Samples for determination of PM mass were collected on Teflon coated glass fiber filters (Pall Corp, PallFlex TX40) at a nominal flow rate of 60 lpm, and the filters were in a temperature controlled secondary dilution and filter collection system operating at 47°C +/- 5°C. The sample collection system meets the requirements of 40 CFR 1065. Gravimetric determinations are made following requirements also specified in 40 CFR 1065.

2.2.2 Organic and Elemental Carbon

Samples for analysis of organic and elemental carbon (OC/EC) were collected from the primary dilution tunnel at a nominal flow rate of 60 lpm at ambient temperature, which is nominally maintained between 20°C and 30°C. The samples are submitted to CARB's MLD for analysis. MLD reports OC/EC filter mass to MSCD for calculation of emission rates.

Total carbon analysis follows MLD Standard Operating Procedure (SOP) 139⁵ using the IMPROVE_A thermal protocol, with the DRI Thermal/Optical Carbon Analyzer Model 2001. The sampling media are 47mm quartz fiber filters (Pall Corp, Tissuequartz fiber 7202). The filters are prebaked in the lab at 900°C for 4 hours, and then cooled naturally overnight before use. Prior to sampling, 5-10% of the baked filters are analyzed to make sure that the carbon background (laboratory blank) is below the reporting limit (1.49 ug C/cm²).

2.2.3 Trace Metals

Metals were collected on Teflon filters under two conditions: One set was collected directly from the primary tunnel at ambient temperature without pre-screening or secondary dilution. A second set was collected in parallel with the first set, but they were taken after a 2.5-um cyclone separator onto filters controlled at 47 °C, and again without secondary dilution. The filters were pre-washed at University of Wisconsin to ensure low blank levels. After sampling, selected filters were submitted to the University of Wisconsin, Madison State Laboratory of Hygiene and Environmental Chemistry & Technology Program for analysis. The samples at UW are extracted by microwave-assisted acid digestion in miniature Teflon bombs using an automated, temperature and pressure-regulated system specifically designed for trace analyses (Milestone Ethos+). Extracts are then nebulized using an ESI low-flow (80 µL min⁻¹) Teflon micro-concentric nebulizer and analyzed with a magnetic sector Inductively-Coupled Plasma Mass Spectrometer (HR-ICPMS; Finnigan Element 2). Samples are quantified in triplicate using external standards with internal normalization.

Additional detail on trace metal analytical procedures is provided in Appendix F.

⁵ *Standard Operating Procedure No. MLD 127. Revision 2.0. July 2003. Organic Analysis Section. SLB MLD www.arb.ca.gov/testmeth/slb/slb127_rev_2.pdf*

2.3 Pretest Procedures

2.3.1 Fuel Refilling Procedures

The vehicle arrived with an empty fuel tank, and fuel tank filled with ULSD diesel fuel. The DPF in the Golden Vehicle requires a fuel borne catalyst (FBC), and the FBC is stored in an on board tank, which was full on arrival. The FBC is added to the fuel automatically. The JRC provided CARB with the following procedure for refueling of the Golden Vehicle:

- 1) Fill up the tank with approximately 50 liters (13 gallons) of diesel fuel.
- 2) Turn the ignition key On but do NOT start the engine. Leave the ignition key in the On position for 2-3 min.
- 3) The car then determines the amount of FBC needed and adds the appropriate amount to the tank.
- 4) Turn the key off.
- 5) Conduct a PMP preconditioning run: 120 km/hr for 20 min + 3 European Driving Cycles (EUDCs).
- 6) Soak the vehicle at least 12 hours.
- 7) Conduct one New European Driving Cycle (NEDC).

These procedures are needed to allow the on-board diagnostics to add the required FBC to the fuel tank. It was important for CARB staff to remain cognizant of these instructions as the GV was fuelled during both evaporative and emission testing.

2.3.2 Regeneration

Regeneration of the DPF occurs as discrete events. During regeneration there are elevated gaseous and PM mass emissions, particle number emissions and temperature (see Appendix B for an illustration). Generally, emission testing for the program should not take place during a regeneration event, and any imminent regeneration should be triggered prior to any testing. The engine should not be turned off when regeneration occurs. Instead, the NEDC cycle currently underway should be continued until it is completed. It was estimated that regeneration occurred every 1000km, and it was imminent upon the GV's arrival in California

When the regeneration is over, "regeneration conditioning" is required before starting additional testing. After regeneration the DPF loses efficiency until a soot layer has deposited on the walls. This regeneration conditioning consists of driving the vehicle on the dynamometer at 80 km/hr for 300 km followed by at least two NEDC cycles. A regeneration event was completed before evaporative emission testing, and regeneration events occurred twice more during the study. Figure 2-3 show filter loadings collected during a regeneration event compared with normal, pre-generation operation, and it is clear that the regeneration event does influence the filters. Data from tests with regeneration events were not included in calculation of mass emission rates, but they are reported for some particle number tests and trace metals tests.



Figure 2-3 Filters before regeneration and including a DPF Regeneration

2.4 Evaporative Emission Test Procedures

2.4.1 Vehicle Precondition Procedures

The test vehicle followed the standard vehicle preconditioning procedures for LEV II Two-Day Diurnal plus Hot Soak tests (CARB, 2007). The LEV II procedures require the use of the Federal Test Procedure (FTP) cycle. The special refueling procedures specific to the fuel borne catalyst were not performed for the evaporative testing.

- 1) Drain the windshield wiper fluid tank and flush with water.
- 2) Drain and fill vehicle with commercial diesel fuel to 40% of nominal fuel tank capacity.
- 3) Soak the vehicle for at least 6 hours after being refueled.
- 4) Following this soak period, place the vehicle on a chassis dynamometer and precondition by driving a Urban Dynamometer Driving Schedule (UDDS), which is part of a FTP emission certification test.
- 5) Following the preconditioning drive, drain fuel tank and fill to 40% of nominal capacity.
- 6) Soak vehicle for 12 to 36 hours prior to the exhaust emission test.

2.4.2 One-Hour Hot Soak and Two-Day Diurnal Test Procedures

- 1) Following the period of 12 to 36 hours soak, push vehicle onto a chassis dynamometer and secure.
- 2) Drive a cold-start and enhanced FTP cycle. Use Cell 7 if exhaust emission data is to be collected. Use Cell 1 if no exhaust emission data is needed.
- 3) Upon completion of the FTP cycle, place the vehicle in a variable volume, variable temperature SHED (VT SHED) and conduct the One-Hour Hot Soak Evaporative Emission Test within 7 minutes of ending the Emission Control diesel fuel test. The hot soak test should be performed at an ambient temperature range of 20°C to 30°C. The hydrocarbon mass data analyzed from the hot soak test will be used in evaporative emission calculations.

- 4) Upon completion of the hot soak test, soak vehicle for no less than 6 hours or more than 36 hours. The vehicle should be soaked at $65^{\circ}\text{F} \pm 3^{\circ}\text{F}$.
- 5) After the 6-hour to 36-hour soak, complete the two-day diurnal test consisting of two 24 hour test cycles during which time for each day the temperature is cycled from 18.3°C at time zero to 40.5°C at 12 hours and back to 18.3°C at 24 hours.
- 6) The evaporative emission result for the hot soak test is calculated as the total hydrocarbon (THC) (g) at time 60 minutes minus THC(g) at time 0 minutes.
- 7) The evaporative emission result for the two-day-diurnal soak test is calculated as the maximum of the following two values. THC(g) at time 1440 minutes minus THC(g) at time 0 minutes and THC(g) at time 2880 minutes minus THC(g) at time 1440 minutes.
- 8) The evaporative emission result from the two-day-diurnal test is calculated as the sum of the one-hour hot-soak emission and the maximum of the two 24-hr emissions measured during the two-day-diurnal test.

The test sequences for the two-day-diurnal and for three-day-diurnal tests are shown in Figure 2.4. The two-day test (left hand branch of the figure) was used in this study.

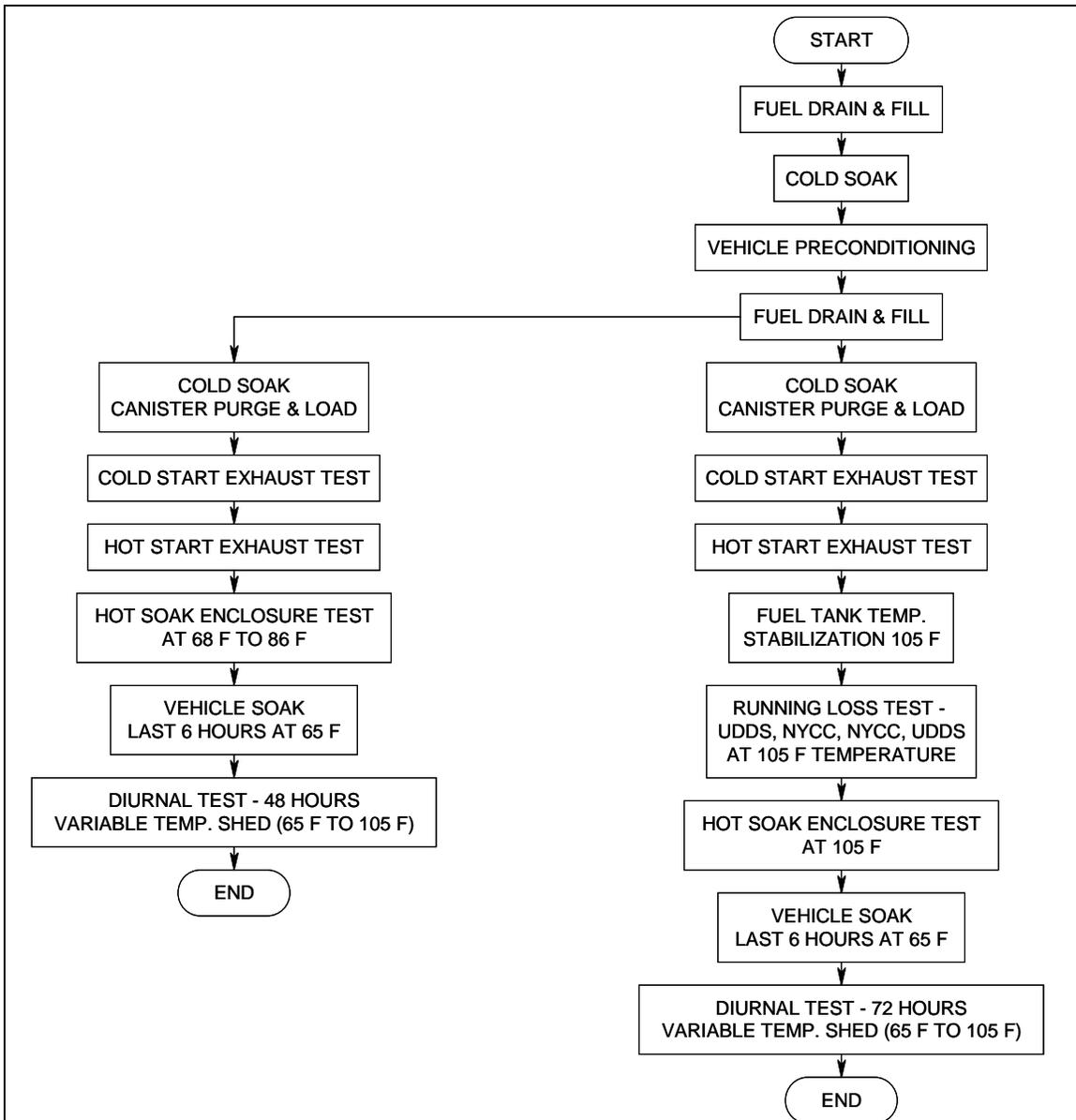


Figure 2-4 Sequences for evaporative emission testing. The left hand path, two-day-diurnal, was followed for the Golden Vehicle test.

2.5 Exhaust Emission Test Procedures

2.5.1 Test Weight and Road Load Coefficients

Equivalent test weight and Target road load coefficients were provided by JRC. CARB conducted their own dynamometer coast-downs in order to determine the dynamometer Set coefficients following procedures described in SAE Standard J2264.

2.5.2 Driving Cycles and Emission Measurement and Analyses

Except for the steady state testing, the three driving cycles used in testing program are shown in Appendix C and are the following:

- 120 kph steady state
- EUDC
- NEDC
- FTP

2.5.3 Engine Conditioning

Engine conditioning prior to running an NEDC cycle consists of 20-min-running at 120 km/hr followed by three EUDCs. Engine conditioning for the remaining cycles were carried out according to standard CARB procedures and determined by the test engineer. This is the same conditioning used after refueling.

2.5.4 Lubricating Oil

The GV was sent without engine lubrication oil. The JRC sent the required lubricating oil and oil filter for the testing in California after the arrival of the GV. The engine oil was added and the oil filter installed prior to testing.

2.5.5 Fuel

Diesel fuel was not sent with the GV. Commercially available California ULSD was used to fuel the engine. The specifications of the fuel used in previous GV testing can be found in Appendix D. For comparison, a table showing typical results for a California ULSD is also shown in Appendix D. During exhaust emission testing, the filling instructions provided in 2.3.1 were followed after each refueling to ensure proper addition and conditioning of the fuel borne catalyst.

2.5.6 Fuel Borne Catalyst

The GV arrived with sufficient FBC in the FBC tank to complete the testing in California. The filling instructions provided in 2.3.1 were followed after each refueling to ensure proper addition and conditioning of fuel borne catalyst.

2.6 Quality Assurance / Quality Control

The CARB's operating protocols for quality assurance and quality control implemented in this study are rigorous and designed to produce certification quality data. Each participating laboratory has standard operating procedures in place, and these procedures were applied to the testing of the Golden Vehicle. The evaporative emission laboratory protocols implement the requirements of 40 CFR parts 86. The exhaust emission test cell protocols implement the requirements of 40 CFR parts 86 and 1065. The gravimetric analysis protocols implement the requirements of 40 CFR part 1065. The analytical laboratory for OC/EC analysis follows standard operating procedures implementing the IMPROVE_A method for OC/EC. The QC includes pre-analysis checks, internal standards, blank media checks, and replicate analyses every tenth sample. The analytical laboratory for trace metals analysis implements a comprehensive program of contamination control to avoid sample contamination and to achieve method low blank levels. Samples are analyzed in batches typically consisting of 22 unknowns, 6 standard reference materials (SRMs), 4 matrix blanks, 2 method blanks, and 2 matrix spikes. A QA/QC program following EPA QA guidelines is in place including Standard Operating Procedures (SOPs) and Data Quality Objectives (DQO). Additional information can be found in appendix F and in Shafer and Overdier 1996.

3. TEST RESULTS

3.1 Evaporative Emission Test Results

Two rounds of evaporative testing were conducted, and the initial testing was deemed unreliable due to contamination of the test vehicle by residual windshield wiper fluid. The original tests were discarded and the vehicle was re-tested. The re-test produced the temporal emission profile shown in Figure 3-1 for the One-Hour Hot Soak test. The total hydrocarbons in the cell were 145 mg at the beginning and 202 mg at the end of the test, for a net emission of 57 mg.

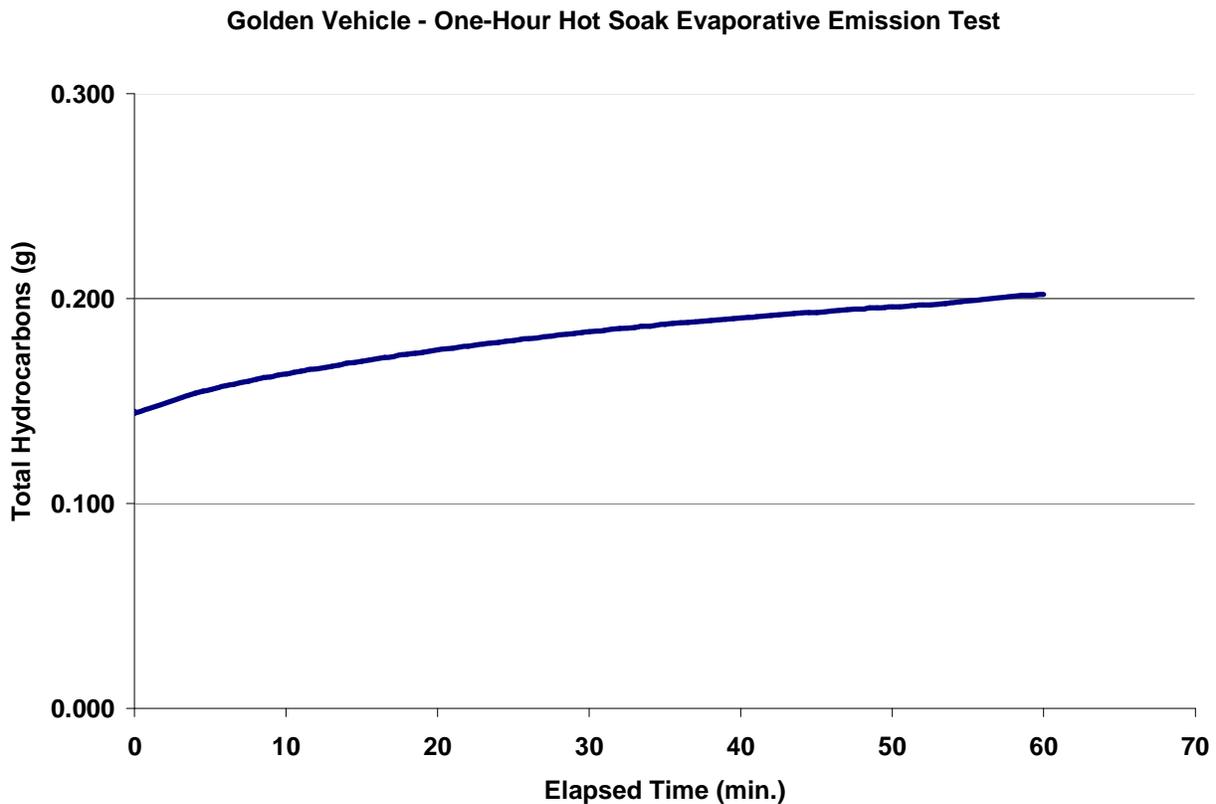


Figure 3-1 Temporal Variation of THC Mass during One-Hour Hot Soak Test

During the succeeding Two-Day-Diurnal Test, a clear diurnal pattern occurred as seen in Figure 3.2. The THC mass was 116 mg at the beginning and 319 mg after 24 hours for a net emission of 203 mg. At the end of the second day THC mass was 442 mg for a net emission of 123 mg on that day. Thus, the two-day diurnal emissions were determined to be 203 mg, in accordance with the test procedures described in 2.3.3.

Golden Vehicle - Two-Day Diurnal Evaporative Emission Test

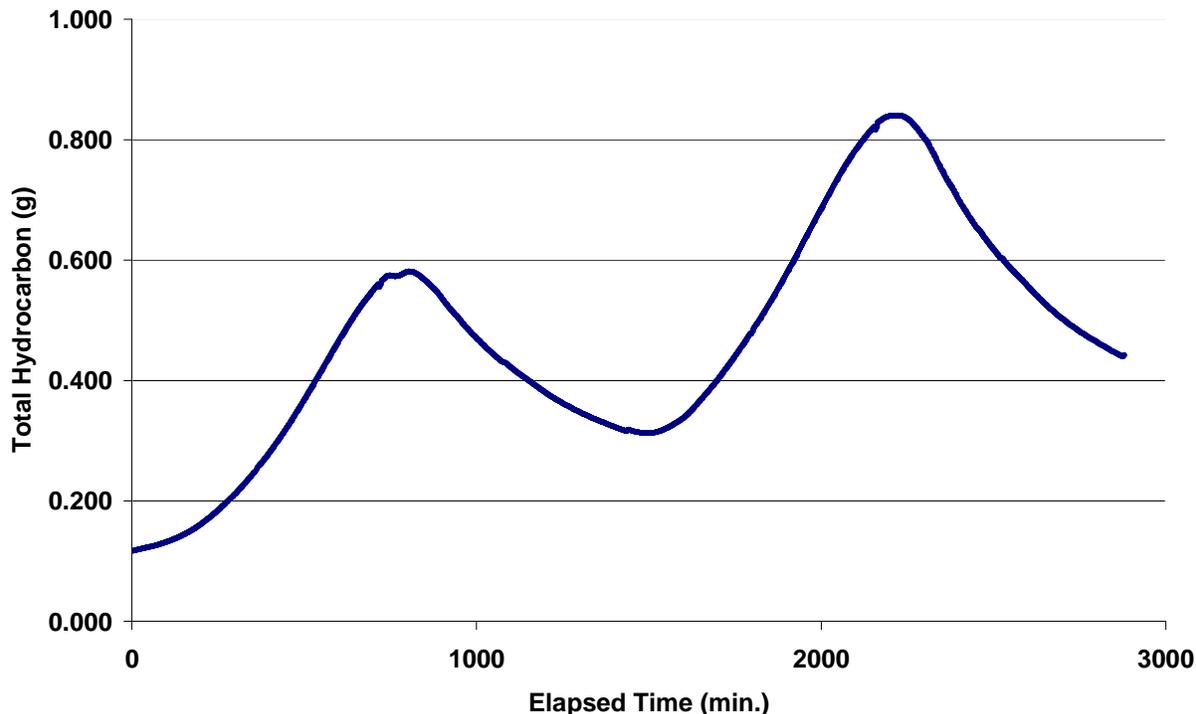


Figure 3-2 Temporal Variation of THC Mass during Two-Day-Diurnal Soak Test

The total emission calculated following standard procedures is the sum of the 1-hr and 2-day emission results, which is 260 mg. The summary of the two emission tests is presented in Appendix E. The California total evaporative emission standard for the same test on a gasoline-fueled passenger car certified as a Partial Zero Emission Vehicle (PZEV) is 350 mg. The test result shows that the emission of THC from this diesel vehicle with no evaporative emission controls was very low. This result is expected for diesel fuels. For comparison, CARB has results for an evaporative emission test on another vehicle completed in December, 2005. The 1-hr hot soak result was 34 mg and a 1-day diurnal emission of 235 mg for a total emission of 269 mg was determined.

The THC concentration pattern peaks in Figure 3-2 at approximately 13 hours and 37 hours when temperatures are slightly past their maximum, and then drops by 50% to 75% from its peak increase during the day. Laboratory staff reviewed the QC data surrounding this test (mass recovery, mass retention, and volume constancy), and they determined that the data are valid and describe a THC loss phenomenon within the cell. A much smaller drop is sometimes seen for gasoline vehicles and it is considered normal. Diesel vehicles are not normally tested for evaporative emissions, and a prior test of a different diesel vehicle showed a drop of about 20% from peak to trough. Therefore, given the very low emission levels, these small drops have not been of concern, however the THC drop for GV is a large fraction of the peak. At the present

time the “lost” THC are not counted during the CARB test, however if they were counted, then the GV diesel with no evaporative emission controls moves from below PZEV to above the PZEV standard.

3.2 Tailpipe Emission Testing Results

Exhaust emission tests were conducted to study a number of issues, and a list of the important issues is the following:

- compare CARB laboratory test results for criteria gases, particle mass, and particle number with results from PMP participating laboratories,
- evaluate the effects of soak time on PM and particle number results
- evaluate the effects of pre-conditioning cycles on PM and particle number results
- compare various particle sampling instruments
- determine some chemical characteristics of the PM emissions

The study of pre-conditioning effects was a specific request by JRC, and their goal was to obtain additional information for the ILCE-LD. The sequence of exhaust emission tests conducted is shown in Table 3.1, and the results and comparisons with other JRC tests are discussed in the sections that follow.

Table 3-1. Emission test and preconditioning sequence

Test #	Date	Time	Cycle	Prior Cycle	Soak Prior to test
NEDC-19	3/15/2007	(AM)	NEDC	NEDC	Overnight
NEDC-20	3/15/2007	(PM)	NEDC	NEDC	6 hr
NEDC-21	3/16/2007	(AM)	NEDC	NEDC	Overnight
NEDC-22	3/20/2007	(AM)	NEDC	PMP precond	Overnight
	3/20/2007	(AM)	PMP precond		
NEDC-23	3/20/2007	(PM)	NEDC	PMP precond	6 hr
NEDC-24	3/21/2007	(AM)	NEDC	NEDC	Overnight
NEDC-25	3/21/2007	(PM)	NEDC	PMP precond	6 hr
NEDC-26	3/22/2007	(AM)	NEDC	NEDC	Overnight
NEDC-27	3/22/2007	(PM)	NEDC	NEDC	6 hr
NEDC-29	3/27/2007	(PM)	NEDC	PMP precond	6 hr
EC1-7	3/29/2007	(PM)	FTP	FTP	6 hr
EC1-8	3/30/2007	(AM)	FTP	FTP	overnight
EC1-9	4/04/2007	(AM)	FTP	FTP precond	overnight
EC1-10	4/04/2007	(PM)	FTP	FTP	6 hr
EC1-11	4/05/2007	(AM)	FTP	FTP	overnight

EC1-12	4/05/2007	(PM)	FTP	FTP precondition,	6 hr
EC1-13	4/06/2007	(AM)	FTP	FTP	overnight
NEDC-30	4/10/2007	(AM)	NEDC	PMP precondition	overnight
NEDC-31	4/10/2007	(PM)	NEDC	NEDC	6 hr
NEDC-32	4/11/2007	(AM)	NEDC	NEDC	overnight
NEDC-33	4/11/2007	(PM)	NEDC	NEDC	6 hr
NEDC-34	4/12/2007	(AM)	NEDC	NEDC	overnight
NEDC-35	4/12/2007	(PM)	NEDC	NEDC	6 hr
NEDC-36	4/13/2007	(AM)	NEDC	NEDC	overnight

3.2.1 Comparison between Cell 7 and PMP Participating Laboratories

A major purpose of the current study is to examine inter-laboratory variations. The regulated emissions and particle number emissions from several cold start NEDC cycles are shown in Figure 3-3. The tests were run in the morning with overnight soak, no pre-conditioning, and with the NEDC as the last cycle of the prior evening. Figure 3-4 show the average and standard deviation of five CARB tests, and the specific values of the tests are given in Table 3-2. Also presented at the bottom of Table 3-2 are the range of average emission values from the PMP participating laboratories, and these averaged results were obtained from 11 tests in 9 countries and laboratories [GRPE-PMP-18-2, 2007].

A graphical summary of the CARB and PMP laboratory averages is presented in Figure 3-5. In general, regulated emissions measured in CARB HSL Cell 7 were within the range of other PMP results, except for CO, whose average value is about three times higher. It should be noted the average value of Cetane number for California ULSD fuel is slightly lower than the fuel used for PMP testing, see Appendix D, and this could be a possible contributor to increased CO levels. The Horiba SPCS employed in this study counted somewhat fewer particles than the results reported by other PMP laboratories, which is consistent with a instrument comparisons shown later in this report.

New European Driving cycle (NEDC)

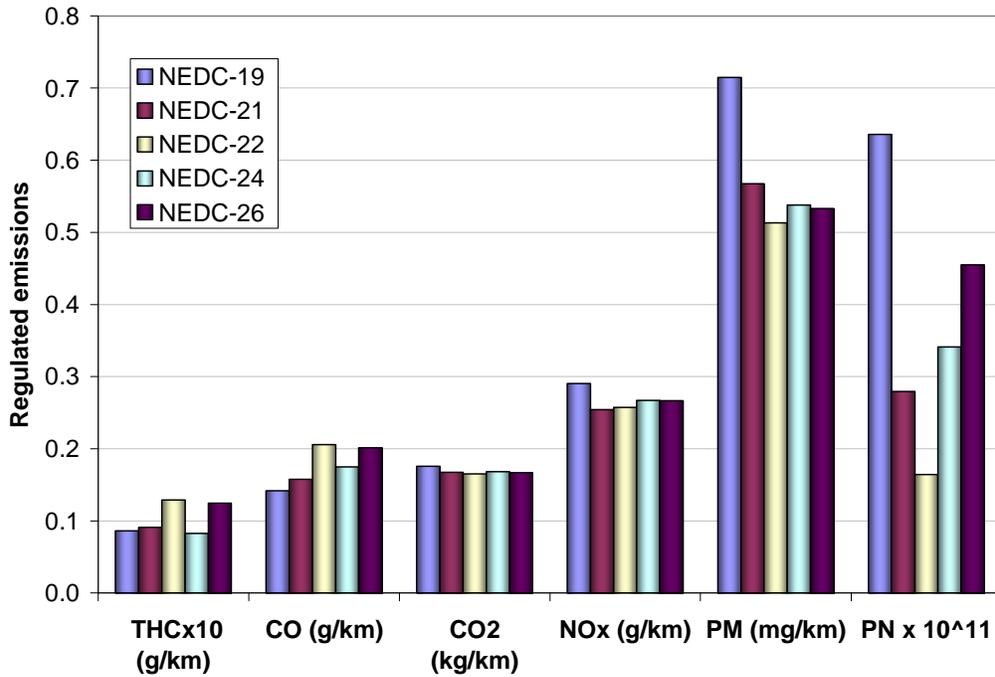


Figure 3-3 Emissions over five NEDC tests with overnight soak and no pre-conditioning

New European Driving cycle (NEDC)

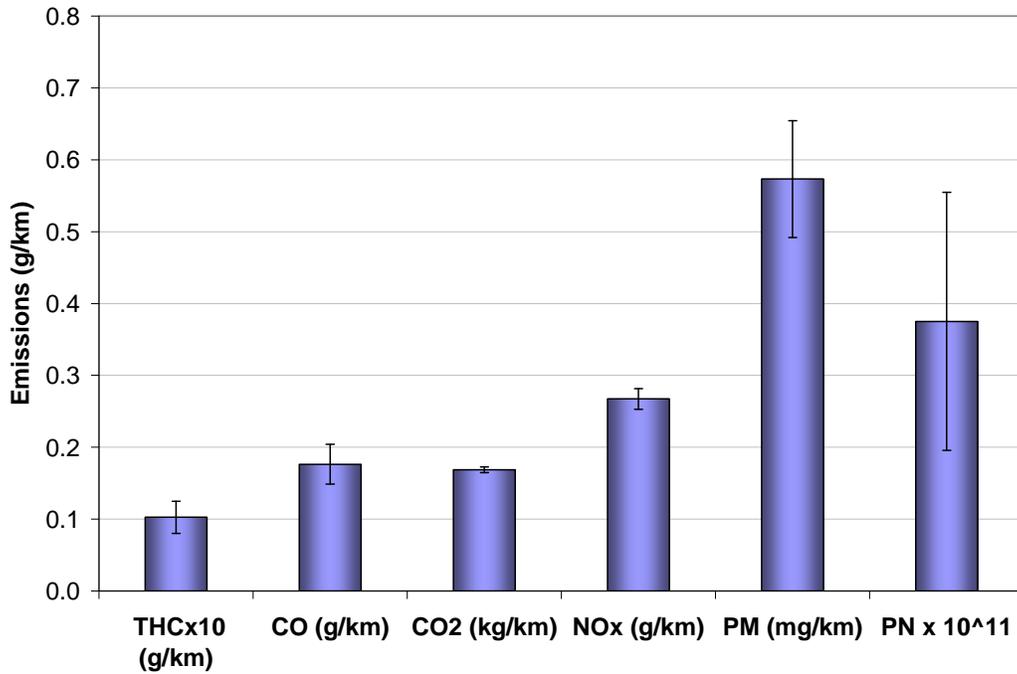


Figure 3-4 Average and standard deviation of emissions over five NEDC tests with overnight soak and no pre-conditioning.

Table 3.2: Comparison of Emission Results from Haagen Smit Laboratory Cell 7 and Other PMP Participating Laboratories

Test Type	Test Date	Prior Cycle	Soak Time	THC (g/km)	CO (g/km)	CO2 (g/km)	NOx (g/km)	PM (mg/km)	Filter Mass (mg)	Horiba SPCS (#/km)
NEDC-19	3/15/2007 (AM)	NEDC	Overnight	0.009	0.141	175.828	0.291	0.715	0.0389	6.36E+10
NEDC-21	3/16/2007 (AM)	NEDC	Overnight	0.009	0.158	167.545	0.254	0.567	0.0308	2.79E+10
NEDC-22	3/20/2007 (AM)	NEDC	Overnight	0.013	0.206	164.875	0.257	0.513	0.0279	1.64E+10
NEDC-24	3/21/2007 (AM)	NEDC	Overnight	0.008	0.175	168.079	0.267	0.538	0.0294	3.41E+10
NEDC-26	3/22/2007 (AM)	NEDC	Overnight	0.012	0.201	167.094	0.267	0.533	0.0292	4.55E+10
Avg.				0.010	0.176	168.684	0.267	0.573	0.0312	3.75E+10
COV (%)				21.69	15.72	2.48	5.36	14.21	14.11	47.90

JRC Report	Range	0.002-0.01	< 0.1	150-170	0.19-0.27	0.2-0.6	0.005-0.06	5E+10-1.3E+11
Avg.			0.056	161		0.57		8.70E+10
COV (%)			5-50	< 3	2-10	10-65		12-72

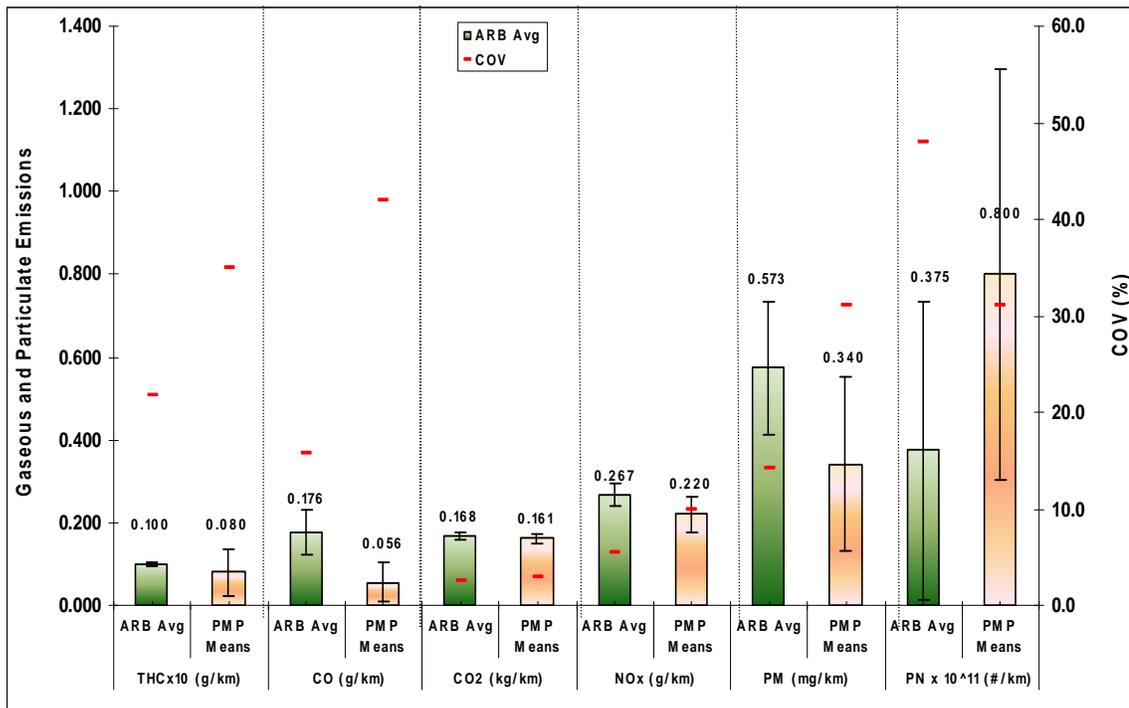


Figure 3-5 Comparison of the average and standard deviation of emissions between CARB and PMP laboratories.

3.3.2 Vehicle Soak Time and Preconditioning Study

The NEDC test procedures specify a minimum soak time of 6 hours, whereas the US FTP procedures specify a minimum soak time of 12 hours. The impact of soak period and preconditioning on criteria emissions and particle number emissions was studied for both the NEDC and the FTP cycles. Some results are presented in Figures 3.6 and Figure 3.7, and the soak period did not appear to have a substantial effect on emissions. The preconditioning of the GV vehicle does not seem to have substantially affected gas phase or PM mass emissions, however particle number emissions appear to be sensitive to preconditioning. Preconditioning appears to have increased particle number emissions over the NEDC cycle but decreased them over the FTP cycle. However, the large variability in particle number emissions shown in Figures 3-6 and 3-7 precludes any strong conclusions, and the pre-conditioning effects should be considered for additional study.

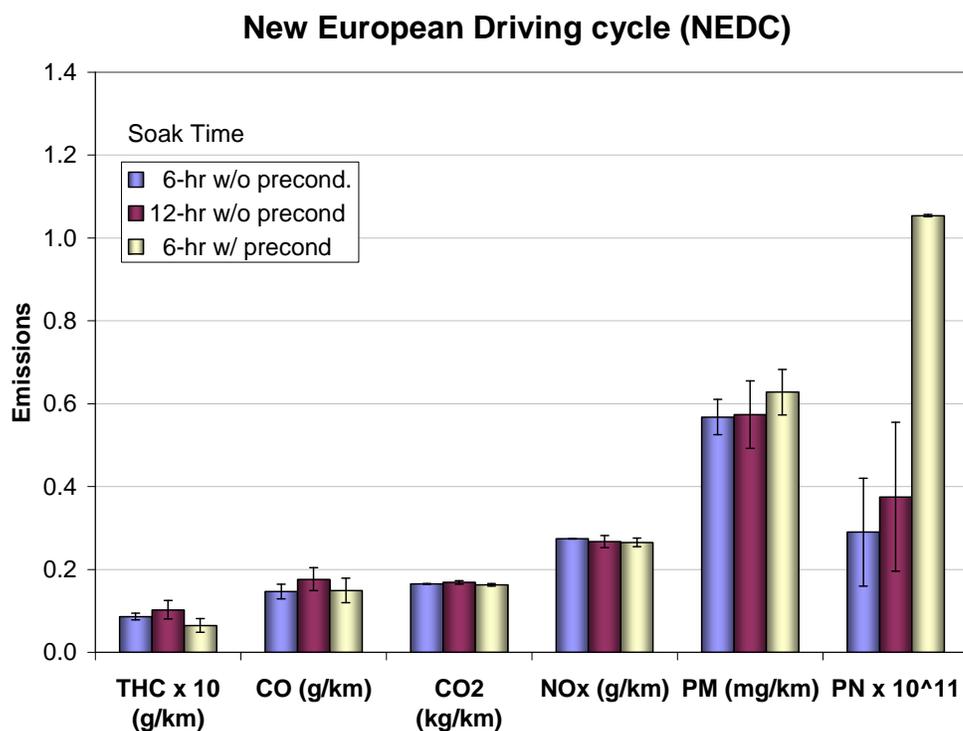


Figure 3-6 Emissions over NEDC for various soak and preconditioning options

U. S. Federal Test Procedure (FTP)

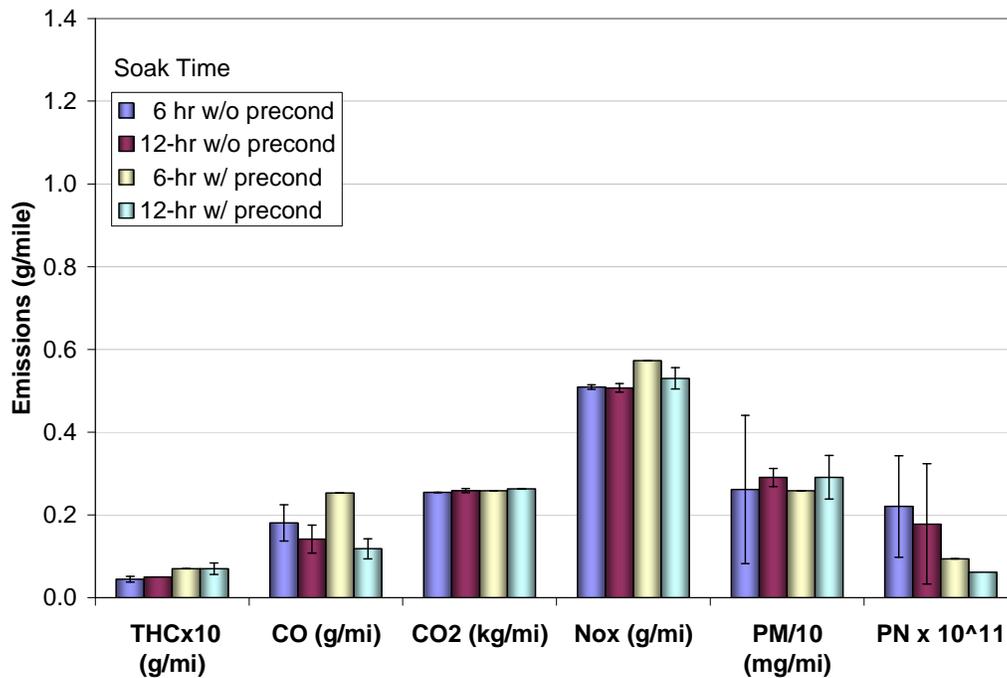


Figure 3-7: Emissions over FTP for various soak and preconditioning options

3.3.3 Particle Sampling and Counting Systems Comparison

The sensitivity of the particle number measurement to the choice of sampling instrument was tested over the NEDC. NEDC-25 followed a 6-hour soak, and NEDC-26 followed an overnight soak. Figure 3.8 compares solid particle number emissions measured using the GPMS CPCs with solid particle number emissions measured using the Horiba SPCS, and the instruments were configured as described in section 2.1 The Horiba SPCS was sampling downstream of the cyclone at the primary dilution ratio, the Reference CPCs sampled downstream of the first dilution stage in the GPMS MD-19, and the Gold CPC sampled downstream of the second dilution stage in the GPMS MD-19, i.e. downstream of the tertiary dilution stage. Unfortunately after these two tests, the GPMS MD-19 stopped functioning, and all tests involving a MD19 used the CARB MD-19.

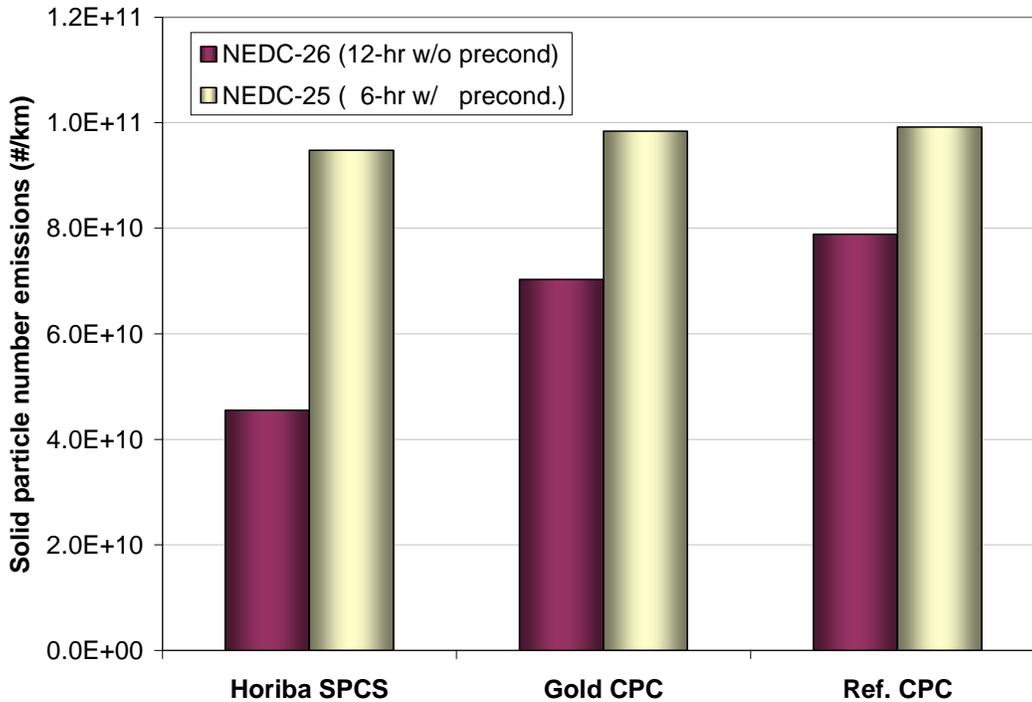


Figure 3-8: NEDC particle number emissions using Horiba SPCS and the GPMS CPCs.

All three systems gave very similar results for the 6-hour soak test with pre-conditioning, however the Horiba SPCS gave substantially lower results than the GPMs CPCs for the 12-hour soak test without pre-conditioning.

In order to compare the different particle instruments a series of seven NEDC cycles were run to with all of the particle instruments running simultaneously. The results are presented as number of particles per kilometer, however no formal attention was paid to soak time or to pre-conditioning. Figure 3-9 shows the results from seven different instruments, and the instruments shown in parentheses had developed problems during the testing problems. The Gold CPC had a low temperature error displayed on its front panel. At the beginning of the testing the Gold CPC was working and responding similar to the Reference CPC, but it gradually deteriorated during the course of the study. The TSI 3790 instrument displayed flow rate and concentration errors, while the EEPS was working correctly, however the particle concentrations were near or below instrument noise levels.

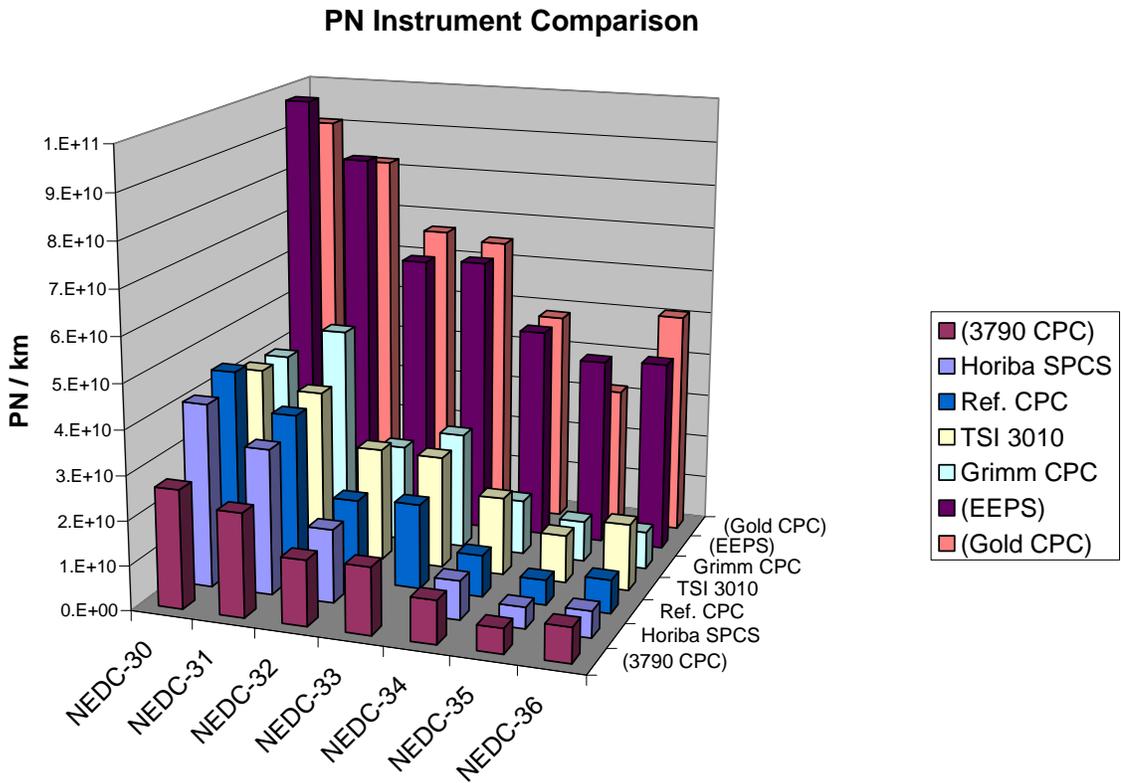


Figure 3-9: Comparison of Solid Particle Concentration by Seven Different Instruments

All systems showed similar trends from test to test, even the systems with instrumentation problems. The five correctly functioning systems (central five rows in the figure) are TSI 3010, Grimm, Ref, Horiba, and EEPS. The TSI 3010 and EEPS measured total particles while the other three systems measured solid particles. Except for the EEPS four of these systems show reasonable agreement with each other in magnitude as well as trend, especially when compared with test to test variability. The cause of the downward trend for all systems from test to test has not been determined. Variability of this magnitude should be a significant concern when trying to establish a particle number “standard” for testing a vehicle for compliance with the “standard”. It should be mentioned that the seven consecutive NEDC cycles used for Figures 3-9 and 3-10 were performed before a regeneration event was scheduled to occur for the Golden Vehicle. If the GV DPF is very sensitive as shown in Figure 3-9 near the regeneration event, then this behavior should be addressed in future studies. An average of all seven of the NEDC tests is shown in Figure 3-10, and all instruments exhibited a large standard deviation due to the downward trend from test to test.

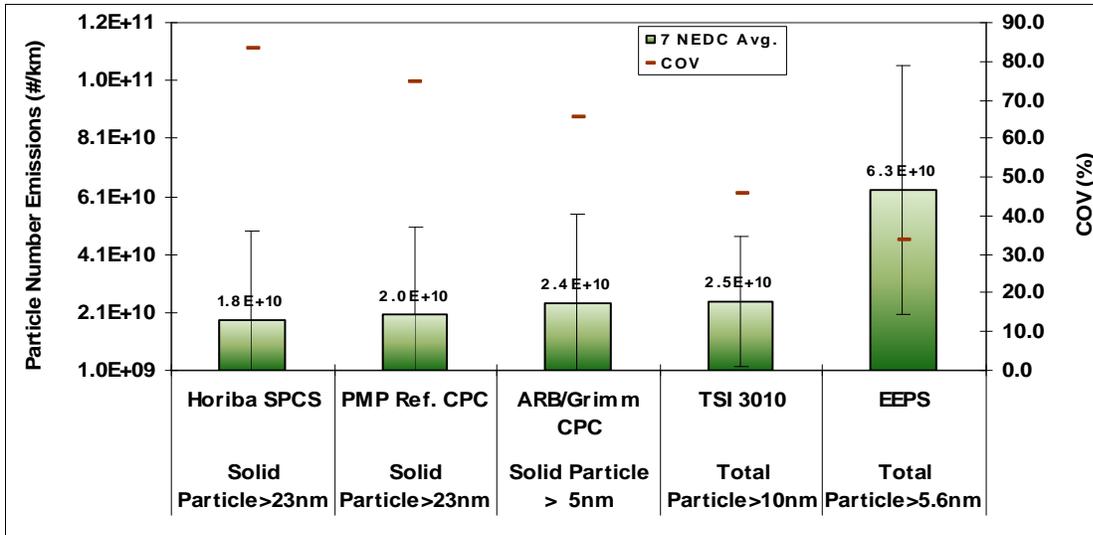


Figure 3-10: Comparison of Solid Particle Average Concentration by Five Different Instruments

3.3.4 Particle Emissions as a Function of Time

Another important part of the CARB investigation was to study real time particle emissions, and these results will now be presented. Due to the low magnitude of the particle numbers the particle number concentrations were measured during a tunnel blank run before the start of the testing program, and the results are shown in Figure 3-11. It should be noted that different instruments have different background counts. The Reference CPC and the Horiba SPCS both measure 23 nm large solid particles and both average near 200 particles per cm^3 . The average background measured by the Grimm CPC is near $300/\text{cm}^3$, which is consistent with its smaller cut-point of 5 nm. The TSI 3010 measures total particles (solid + volatile) and averages about $550/\text{cm}^3$. The EEPS has a higher noise level and higher background, averaging about $1350/\text{cm}^3$.

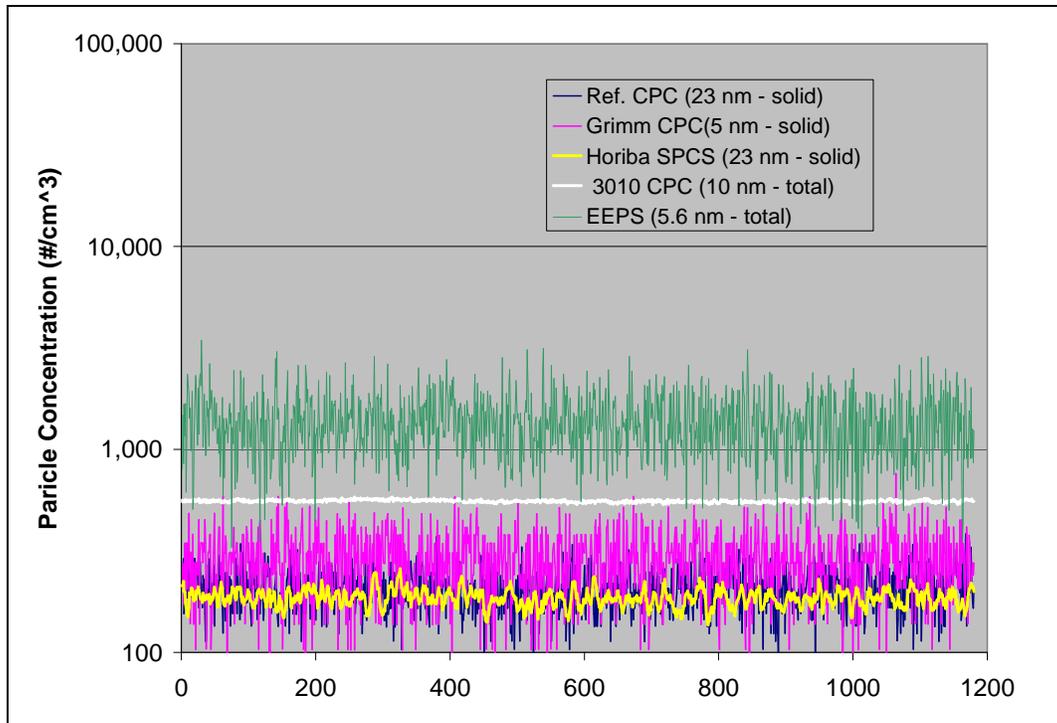


Figure 3-11: Particle Number Concentrations from Multiple Particle Counters during Tunnel Background

The particle number emissions as a function of time during an NEDC cycle are shown in Figures 3-12 and 3-13. The ordinate in the figures is presented on a log scale, and the majority of the emissions occur during the first 300 seconds of the cycle at the 2nd and 3rd acceleration periods. After the first 300 seconds of the NEDC cycle in Figure 3-12, particles measured from multiple particle counting systems are close to tunnel background. All CPCs overlap each other during parts of the cycle, but the TSI 3010 has a higher baseline level. In order not to obscure the data in Figure 3-12, the noisy EEPS data is shown along with the Horiba SPCS and the TSI 3010 data in Figure 3-13. The EEPS follows the same trend as the CPCs, but it has higher noise and higher baseline concentrations than the CPCs..

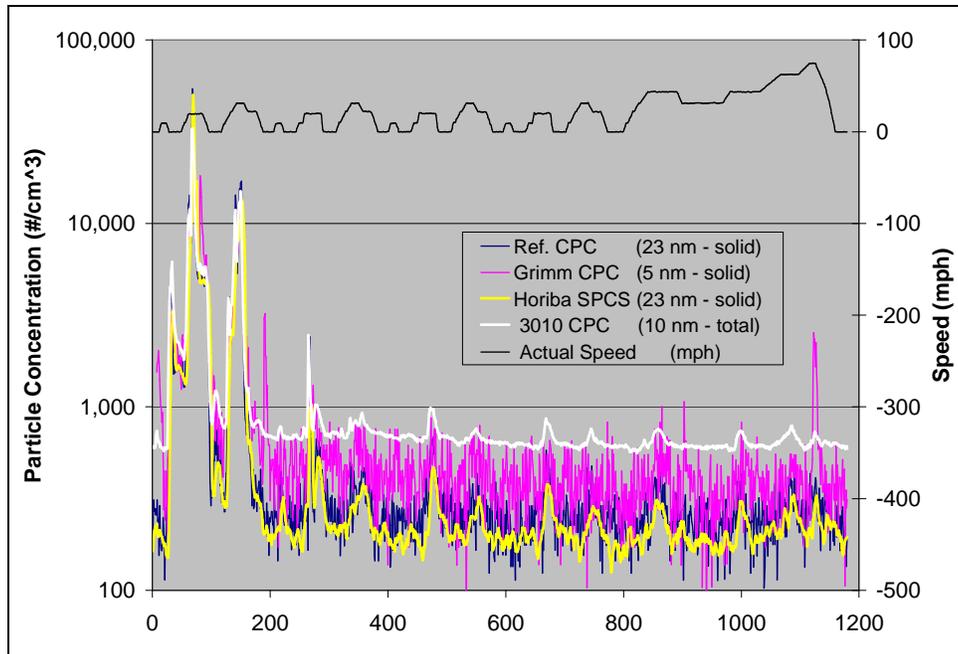


Figure 3-12: Comparison of Particle Number Concentrations from Multiple Particle Counters during Test NEDC-32

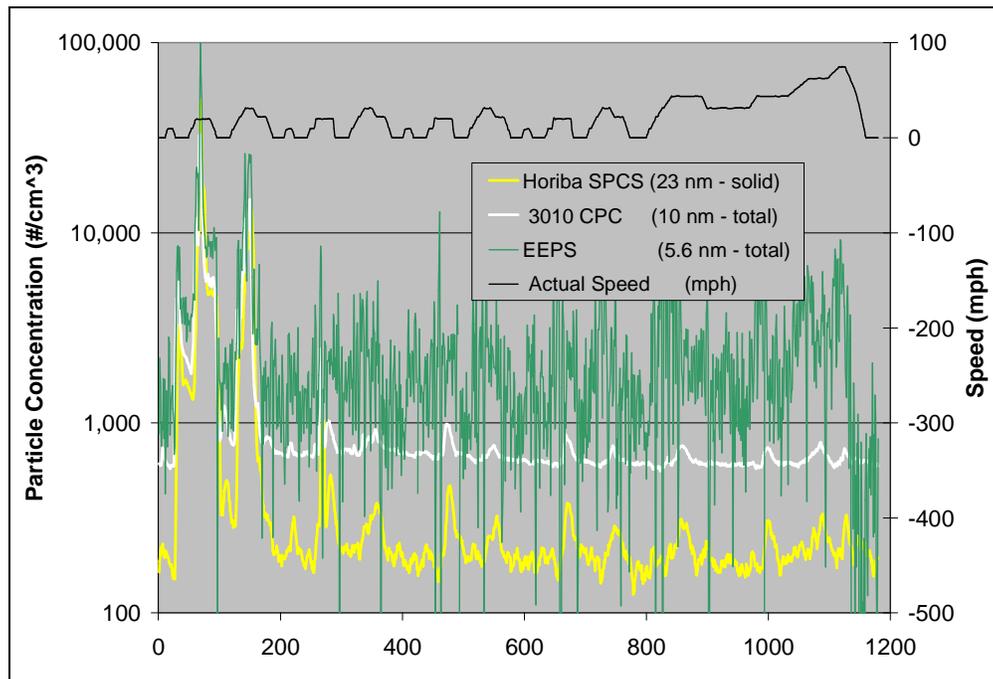


Figure 3-13: Comparison of Integrated EEPS Number Concentration with Total and Solid Particle Number Concentrations during Test NEDC-32

The particle number concentrations during a FTP cycle are shown in Figure 3-14, and the concentrations are similar in trend to the NEDC cycle. At the beginning of the cycle there are some spikes of solid particles, and then the concentrations remain very low throughout the rest of the test. However, the concentrations for the FTP are lower than for the NEDC, and the concentrations for the FTP were below baseline noise levels for the EEPS during the initial spikes of solid particles. Figure 3-14 also demonstrates the very close agreement between the Horiba SPCS system and the best simulation of the GPMS that was available for this study (the Reference CPC sampling from the tertiary dilution stream of the CARB MD-19).

Another interesting and important aspect of our particle number study was to investigate the repeatability of the results during different cycles with the same instrument. Shown in Figures 3-15 and 3-16 are five repeats of the NEDC and FTP cycles with the use of the Horiba SPCS counter. In terms of capturing the peaks of particle numbers during the cycles the results are in good qualitative agreement, however the logarithm scale of plots hides some of the quantitative variability of the particle number counts. In terms of the average particle number per kilometer, PN/km, the NEDC repeats had a COV of 48% while the JRC participating laboratories had COVs ranging from 12% to 72%, Table 3.2.

The exact causes of the variability between repeat cycles cannot be determined at the present time, and there is a need to refine the measurement methodologies of ultrafine particles. New research and development for particle measurement systems, pre-conditioning systems, and cycle choice should be considered, since we need to better understand particle counting systems and methodologies.

Although the EEPS data is at noise levels during the majority of the tests, the EEPS collects sufficient particles to generate size distributions during the initial few hundred seconds of the test cycle. These particles are solid particles with diameter of about 80nm at peak concentration. Shown in Figure 3-17 is the size spectra at the time of peak concentration, and significant values of particle diameters are in the size range from 40 to 200 nm.

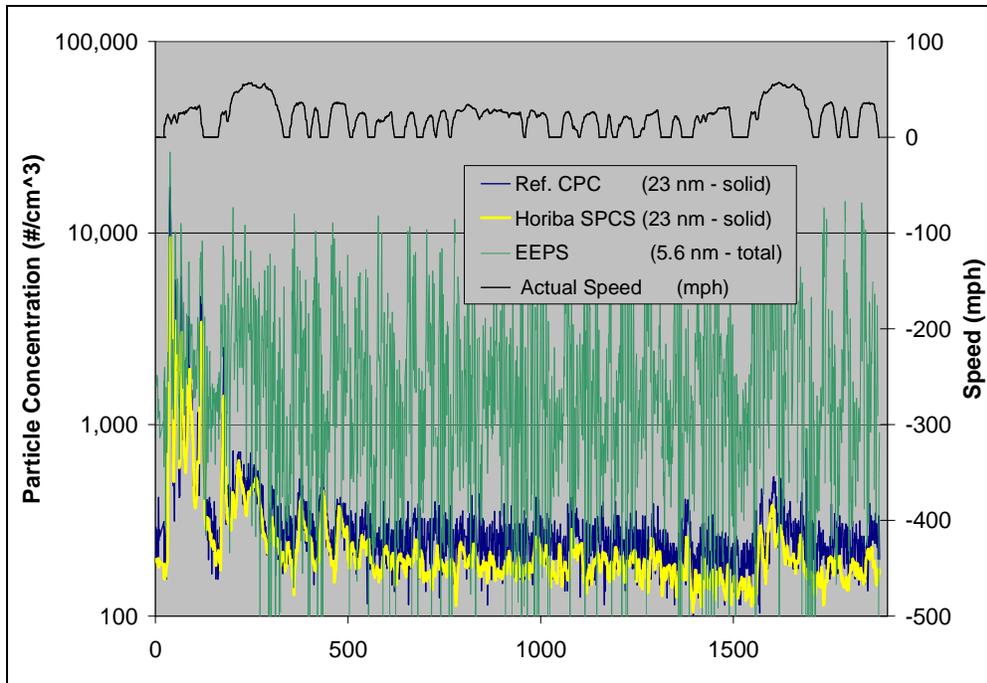


Figure 3-14: Particle Number Concentrations during Test FTP-12

5 Repeat NEDC Cycle-Phase 1

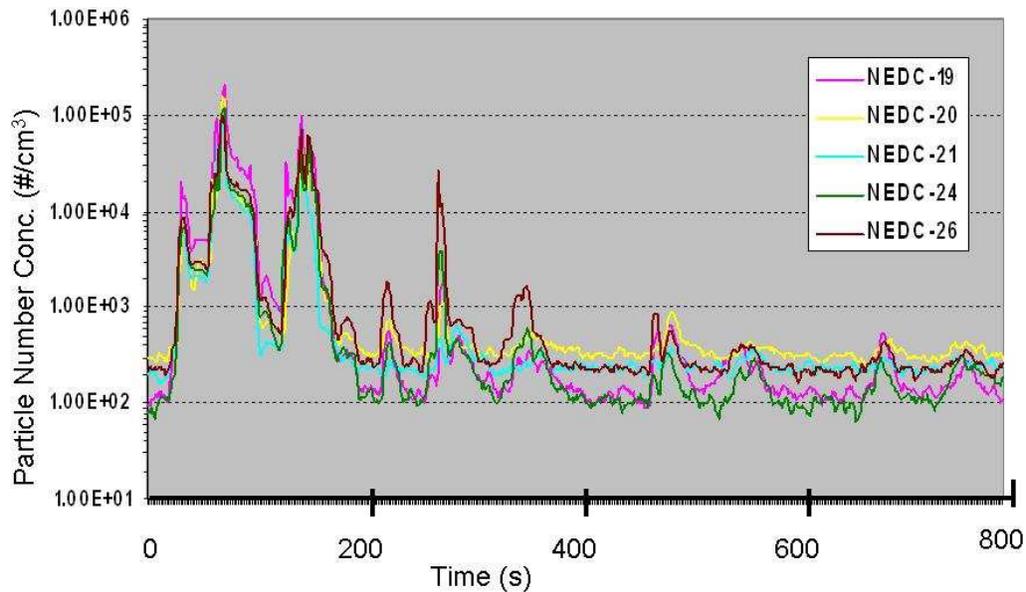


Figure 3-15: Particle Number Concentrations during Five Repeat NEDC Cycles with the Horiba SPCS

5 Repeat FTP Cycles- Phase 1

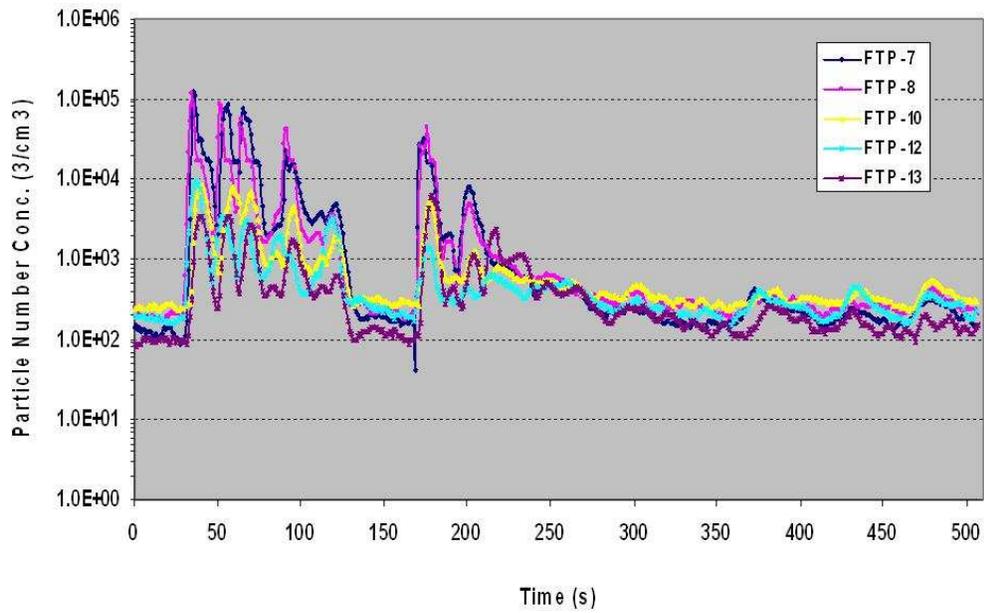


Figure 3-16: Particle Number Concentrations during Five Repeat FDP Cycles with the Horiba SPCS

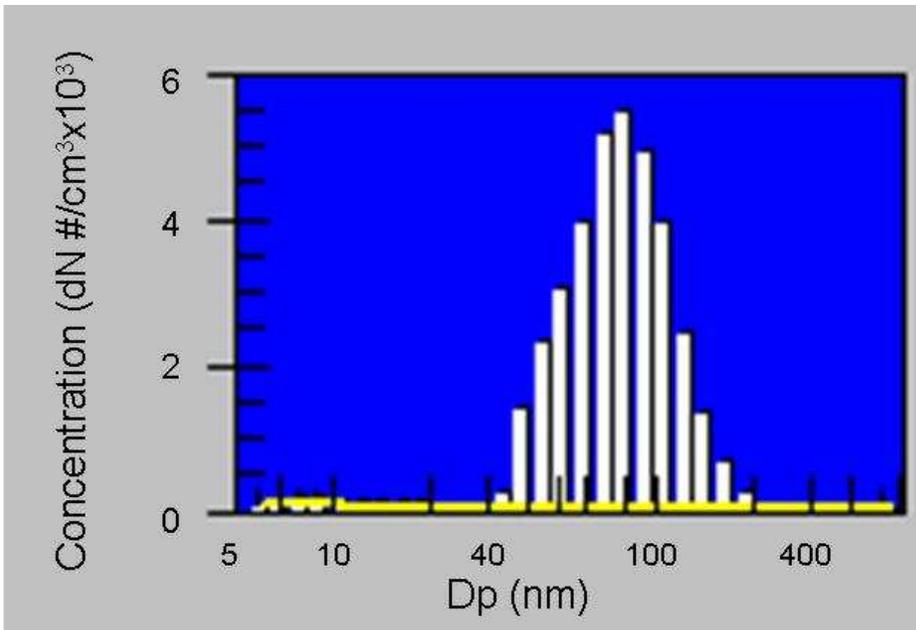


Figure 3-17: EEPS particle size distribution during cold start

An extension of the study was to investigate the particles generated during the regeneration event, and these particles are considerably smaller than typical diesel emissions. Contours of particle concentration versus time and particle size are shown in Figure 3-18 during a regeneration event and the color bar at the top of the figure presents the particle concentrations. The plot shows a strong peak in concentration for particles in the 10 nm range at 10 minutes before the end of the test cycle. The particle concentrations have significant values for sizes between 6 and 40 nm, and these concentrations remain constant during most of the regeneration event. At the end of regeneration the particle concentrations have a maximum peak value in the 8 nm range.

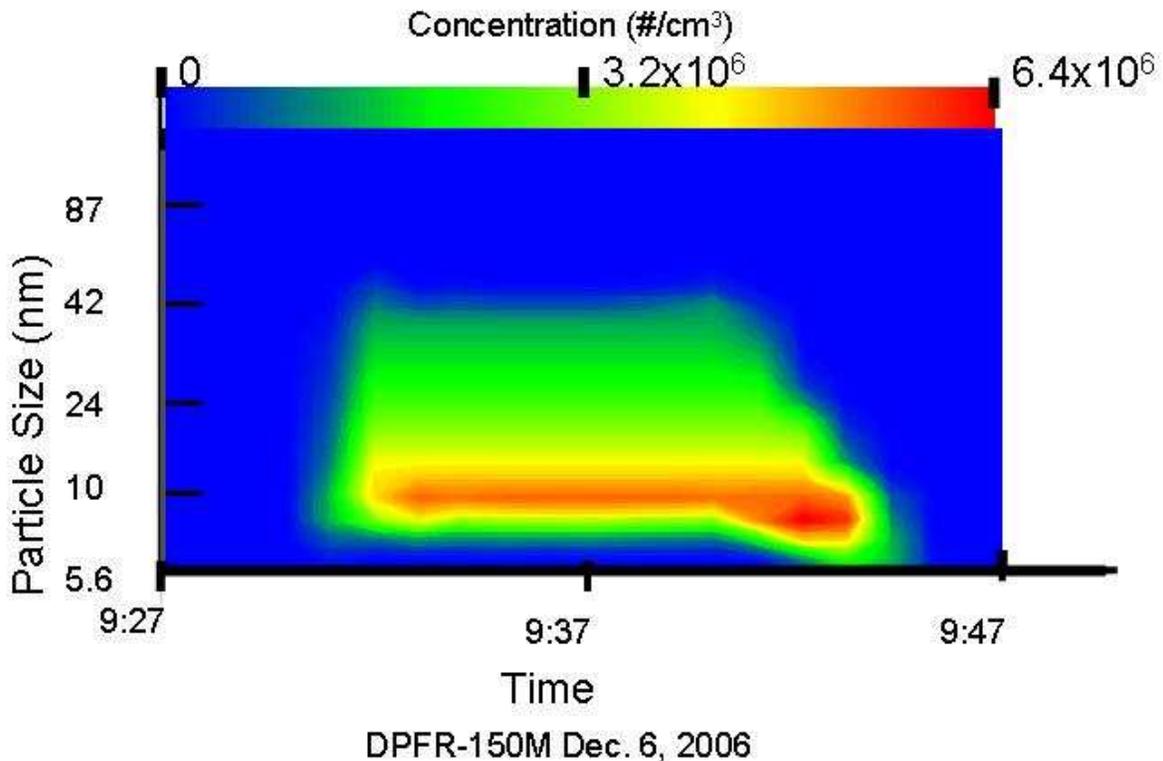


Figure 3-18: EEPS particle concentration and size during a regeneration event.

3.3.5 Chemical Characteristic of Particle Mass Emissions

Since diesel particles are a serious health concern, the CARB testing program was extended to include the chemical characteristics of the particle mass emissions. Particle emission samples for organic and elemental carbon were collected and analyzed over both the NEDC and the FTP cycles. Emissions from 22 cold start tests were composited onto quartz filters for the NEDC cycle, and emissions from 8 cold start tests were composited for the FTP cycle. The results are shown in Figure 3-19, and total carbon emissions are less than 0.3 mg/km (0.5 mg/mi). For comparison the current US standard is 10 mg/mi or 6.23 mg/km. The total carbon content in phase one of the NEDC cycle consists of approximately 50% organic carbon and 50% elemental carbon, while during the warm phase the carbon content is almost 80% organic carbon. For the

FTP cycle, the percentage of carbon in the organic fraction is much higher ranging from 80% during the cold start phase to over 95% during the warm start phase.

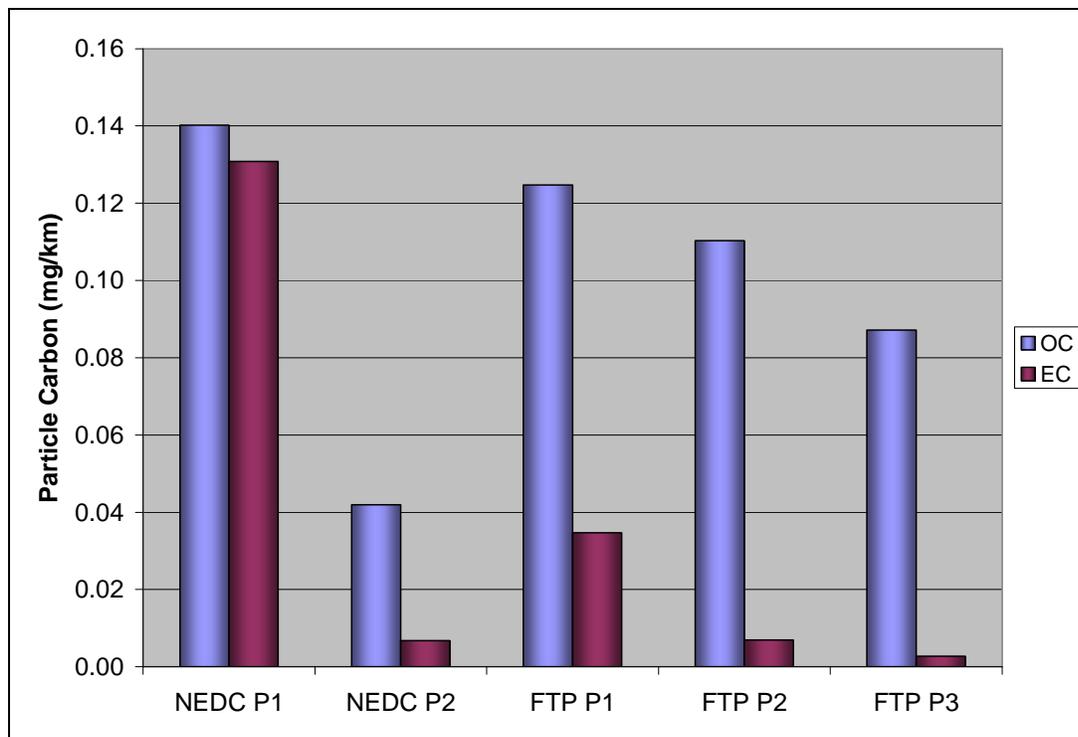


Figure 3-19: Emission rates of Organic and elemental Carbon during the European Cycle where the notation P1, P2, and P3 denotes the parts or phases of the NEDC and FTP cycles, such as cold, transient, and warm.

As part of the enhancement of our investigation trace metals samples were collected for steady state driving at 120 km/hr (10 twenty-minute cycles composited onto 1 sample set.) and for the NEDC cycle (4 cycles composited onto one sample set). The list of all species analyzed is shown in Appendix G in table form, and the table provides analytical results and uncertainty for the trip blanks expressed in terms of nanograms per mile for each of the two sampling cycles. A trip blank is an unexposed filter that was sent to the analytical laboratory without ever being used to collect a sample. Blank mass per mile was calculated using the sample volumes and distances for the steady state and NEDC cycles. Because the samples for the Steady State test were collected over more volume and distance than for the NEDC testing, the blank levels expressed in ng/mile are about nine times lower for the Steady State than for the NEDC. The Steady State testing included a regeneration event during one of the 20-minute cycles; the NEDC testing did not include a regeneration event.

The emission rates for selected species are shown in Table 3.3, and the species were selected by including only species for which the sample was at least three times the

blank or at least three times the uncertainty in at least one sample. Thirty two species survived this screening, primarily on the basis of results for PM10 from the steady state testing. The species are sorted from highest to lowest emission rates in the table, and the species emission rates cover over seven orders of magnitude. The results are shown on a log scale for the steady state testing in Figure 3-20.

Various features of the data set include the following:

- For the Steady State test the PM10 sample is over five times higher than the PM2.5 sample. This result highlights the importance of including a size cut pre-screening device in the sample train. The high values for PM10 could be due to a very small number of coarse particles shaking loose from the exhaust system or tunnel sampling system. These particles may not be representative of emissions that remain suspended in the atmosphere for very long period of time.
- The difference between PM10 and PM2.5 is much less evident for the NEDC cycle, and may indicate that the large particles for the steady state test are associated with the regeneration event.
- Very few species were significantly above noise level for the NEDC tests.
- Despite reaching very small absolute magnitudes, the signal to noise ratio remains significant for many species.
- Cerium emission rates are only about 1 to 12.5 ng/km. However, the cerium emissions for steady state are still over 100 times higher than cerium in the blank. As can be seen in Figure 3-20, the signal to noise ratio for cerium is stronger than for nearby species. This result could be due to the presence of cerium in the fuel borne catalyst.

Table 3.3: Trace Metal Emission Rates

Species	SS PM10 ng/mile	SS PM2.5 ng/mile		NEDC PM10 ng/mile	NEDC PM2.5 ng/mile
S32	20,026.93	9,983.40		0.01	693.16
Fe56	8,436.71	1,688.23		3,531.23	1,057.29
Ca44	1,547.78	234.27		591.54	585.09
Cu63	1,002.53	217.18		473.80	146.10
Al27	705.97	88.35		389.18	177.98
Cr52	628.15	106.98		179.79	43.13
Na23	503.12	89.52		0.01	16.75
Zn66	366.53	75.12		136.40	13.02
Sn120	304.30	66.94		379.57	178.19
Ni60	267.92	1.41		43.85	0.01
K39	123.90	22.43		0.01	182.78
Mn55	133.58	18.16		38.93	0.01
Mg25	121.90	17.50		0.01	0.01
P31	35.08	0.00		0.01	0.01
Ti49	34.39	2.32		0.01	0.01
Ba138	32.59	13.27		88.10	46.11
Mo95	28.94	3.39		15.64	5.12
Ce140	16.19	9.01		1.17	0.68
Pb208	11.46	1.48		5.05	0.01
Sr88	6.47	0.95		4.84	8.42
Co59	4.41	0.18		0.29	0.51
Sb121	3.83	0.77		1.33	0.01
V51	4.06	1.47		9.40	9.57
Cd111	0.91	0.92		0.14	0.01
Ga71	0.28	0.00		0.39	0.04
La139	0.24	0.03		0.01	0.01
Pt195	0.19	0.04		0.01	0.01
Nd146	0.20	0.00		0.01	0.01
Pr141	0.03	0.00		0.01	0.01
Rh103	0.02	0.00		0.01	0.01
Cs133	0.02	0.00		0.04	0.01
U238	0.01	0.00		0.01	0.01

Steady State @ 75 mph

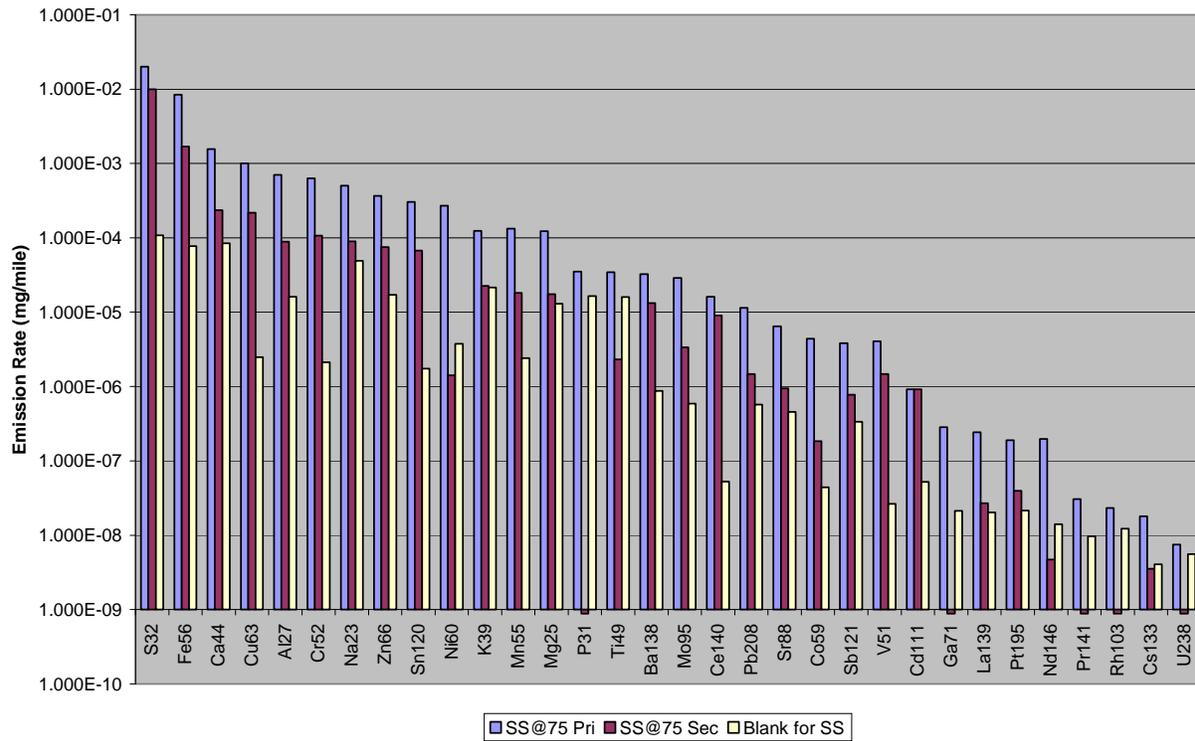


Figure 3-20: Emission rates of trace metals during Steady State at 120 kph.

4. CONCLUSIONS

The California Air Resources Board has successfully conducted a research program for emissions testing with the PMP's Golden Vehicle. The research program was similar to test performed at other International Laboratories, however the CARB testing was expanded to include evaporative emissions, particle counting instrumentation, and the chemical composition of particle mass emissions. The major conclusions of the research program are the following:

- The comparisons of regulated gas emissions with PMP participating laboratories were in a similar range, except for CO, whose nominal result was three times higher.
- PM mass emissions, mg/km, were also very similar, however the Horiba SPCS counted fewer particles than the results from other PMP laboratories. Much of the difference between particle number emissions was removed with the use of preconditioning.
- During the testing some of the particle counting instruments developed problems and displayed errors. All of the instruments showed similar trends during seven consecutive NEDC cycles, however there was a significant downward trend in particle numbers from test to test. This variability occurred immediately before the need to DPF regeneration, and this behavior could be a concern when trying to establish a particle number standard.
- Real time measurements of particle number concentration during other FTP and NEDC cycles showed less variability than the consecutive NEDC cycles. All measurements were made with the Horiba SPCS, and they captured the peaks in particle number concentration with good qualitative agreement. However, these measurements did show significant variability in the average PN/km from test to test.
- Although further research is needed to refine and understand particle instruments, the method appears to be much more sensitive than mass measurements.
- There were significant differences in organic and elemental carbon levels between the NEDC and the FTP cycles. During phase one of the NEDC cycle the organic carbon was 50%, while the FTP levels of organic carbon were always larger than 80%.
- NEDC and Steady State cycles were performed to determine the emissions of selected trace metals. Despite reaching very small absolute magnitudes the measurements achieved good accuracy in many cases.

- The evaporative emissions tests showed that the THC emissions from the Golden Vehicle were very low, even though there were no evaporative emissions controls on the vehicle.

5. REFERENCES

CARB, 2000. "Risk Reduction Plan to Reduce Particulate Matter Emissions from Diesel-Fueled Engines and Vehicles," October, 2000, California Air Resources Board, Sacramento, CA, 2000.

CARB, 2007. "California Evaporative Emission Standards and Test Procedures For 2001 And Subsequent Model Motor Vehicles". Adopted: August 5, 1999, Amended: October 17, 2007. California Air Resources Board, Sacramento CA.

Ayala and Herner, 2006. "Evaluation Of Ultrafine Particle Measurement Instruments And The European PMP Protocol On A California Trap-Equipped Diesel Truck." Presented to the 16th CRC On-Road Vehicle Emissions Workshop, San Diego, CA. March 2006. Coordinating Research Council, Alpharetta, GA. 2006.

Ayala, A., Zhang, S., Herner, J.D., and Robertson, W., "A California Preliminary Assessment of PMP for Determination of Diesel Particle Emissions" Proceedings of the 11th ETH Conference on Combustion Generated Particles, Zurich, Switzerland, August 2007a.

Ayala, A., Herner, J.D., Zhang, S., Robertson, W., Frodin, B., Huai, T., Haste, R., McMahan, W., and Lemieux, S., "Experiences from the CARB PMP-based Program," International Conference on Transport and Environment: A Global Challenge, Technical and Policy Solutions, Milan, Italy, March 19 – 21, 2007b.

CRC, 2005. "2007 Diesel Particulate Measurement Research, Final Report, Phase I," May 2005. CRC Report No. E-66-1, Coordinating Research Council, Alpharetta, GA. 2005.

Durbin, T., et al., "Evaluation of the Proposed New European Methodology for Determination of Particle Number Emissions and its Potential in California for In-Use Screening", Final Report Submitted to CARB, 2008.

GRPE-PMP-18-2, 2007, "Particle Measurement Program (PMP) Light-duty Inter-laboratory Correlation Exercise (ILCE_LD) Final Report, 2nd Draft.

Herner, Robertson, and Ayala, 2006. "Nanoparticle Formation In The Emissions from A Trap-Equipped Heavy Duty Diesel Truck.: Presented to 7th International Aerosol Conference, St. Paul, Minnesota, September 2006. American Association for Aerosol Research, Mt. Laurel, NJ.

Herner, Robertson, and Ayala, 2007, "Investigation of Ultrafine Particle Number Measurements from a Clean Diesel Truck Using the European PMP Protocol", SAE Technical Paper 2007-01-1114.

Herner, J.D., Zhang, S., Frodi, B., Leeman, W., Ayala, A., Johnson, T., and Wei, Q., "Emissions Measurements from the Golden Vehicle – A Light Duty Diesel Vehicle Used During Validation of the European PMP Protocol" Proceedings of the 17th CRC On-Road Vehicle Emissions Workshop, San Diego, CA, March 26-28, 2007.

Jung, H., Johnson, K.C., Durbin, T.D., Chaudhary, A., Cocker, D.R., Herner, J.D., Robertson, W.H., Huai, T., Ayala, A., and Kittelson, D., "Evaluation of the European PMP Methodologies during On-road Testing," 2008 Spring WSS/Ci Meeting Organized by the Western States Section of the Combustion Institute and Hosted by the University of Southern California, March 17-18, 2008.

Ricardo, 2005. "UN-GRPE PMP Phase 3, Inter-laboratory Correlation Exercise: Framework and Laboratory Guide", Working Paper No. GRPE-PMP-14-1, Ricardo Consulting Engineers, Shoreham by Sea, West Sussex, UK, November 25, 2004. (<http://www.unece.org/trans/doc/2005/wp29grpe/PMP-2005-14-01e.pdf>).

Robertson, W.H., Herner, J.D., Ayala, A., and Durbin, T.D., "Investigation of Ultrafine Particle Emissions from Clean Heavy Duty Vehicles using the European PMP Method," Proceedings of the 13th Diesel Engine Emissions Reduction Conference, Detroit, Aug., 2007.

Shafer and Overdier 1996; Analysis of Surface Waters for Trace Elements by Inductively-Coupled Plasma Mass Spectrometry, Revision 5, 1996 (University of Wisconsin-Madison).

Zhang, S., McMahon, W., Wei, Q., Huai, T., and Ayala, A., "Final Results from CARB's Assessment of the European Reference Vehicle from the Particulate Measurement Programme," Proceedings of the 18th CRC On-Road Vehicle Emissions Workshop, San Diego, CA, March 31-April 2, 2008.

APPENDIX A. MISCELLANEOUS INFORMATION ABOUT THE GV AND TESTING

This appendix contains additional information obtained from the JRC. The information includes the vehicle specifications and load, and some pictures of the components of PMP GPMS taken in JRC.

GV Specification and Load

	Emission Test Facility VELA 2	CD Programma PMP 2004-JRC Peugeot 407 2.0 Hdi Fap 100kw Pag.1 di 1																																																
ROAD Load Derivation based on ECE																																																		
Vehicle n° Vehicle type: Dyno inertia: Highway values: mt: A_i: B_i: C_i:	PT004 Peugeot 407 2.0 Hdi Fap 100kw 1590 kg 1590 kg 208.0 N 0.0 Nh/km 0.03220 Nh ² /km ²																																																	
ROAD Load Derivation																																																		
Dyno Load A_s/B_s/C_s	<table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 10%;">RUN</th> <th style="width: 15%;">A_s [N]</th> <th style="width: 15%;">B_s [Nh/km]</th> <th style="width: 15%;">C_s [Nh²/km²]</th> <th style="width: 15%;">max. error [%]</th> </tr> </thead> <tbody> <tr> <td>1</td> <td>104</td> <td>0</td> <td>0.0322</td> <td>-14.77</td> </tr> <tr> <td>2</td> <td>99.4</td> <td>-1.0206</td> <td>0.03494</td> <td>3.37</td> </tr> <tr> <td>3</td> <td>99.4</td> <td>-1.0206</td> <td>0.03494</td> <td>4.73</td> </tr> </tbody> </table>	RUN	A _s [N]	B _s [Nh/km]	C _s [Nh ² /km ²]	max. error [%]	1	104	0	0.0322	-14.77	2	99.4	-1.0206	0.03494	3.37	3	99.4	-1.0206	0.03494	4.73																													
RUN	A _s [N]	B _s [Nh/km]	C _s [Nh ² /km ²]	max. error [%]																																														
1	104	0	0.0322	-14.77																																														
2	99.4	-1.0206	0.03494	3.37																																														
3	99.4	-1.0206	0.03494	4.73																																														
Last Run																																																		
	<table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 10%;">Interval</th> <th style="width: 15%;">v-max [km/h]</th> <th style="width: 15%;">v-min [km/h]</th> <th style="width: 15%;">t-actual [s]</th> <th style="width: 15%;">t-target [s]</th> <th style="width: 15%;">error [%]</th> </tr> </thead> <tbody> <tr> <td>1</td> <td>125.00</td> <td>115.00</td> <td>6.723</td> <td>6.573</td> <td>2.28 [5.0]</td> </tr> <tr> <td>2</td> <td>105.00</td> <td>95.00</td> <td>8.600</td> <td>8.329</td> <td>3.25 [5.0]</td> </tr> <tr> <td>3</td> <td>85.00</td> <td>75.00</td> <td>11.095</td> <td>10.659</td> <td>4.09 [5.0]</td> </tr> <tr> <td>4</td> <td>65.00</td> <td>55.00</td> <td>14.194</td> <td>13.632</td> <td>4.12 [5.0]</td> </tr> <tr> <td>5</td> <td>55.00</td> <td>45.00</td> <td>15.895</td> <td>15.303</td> <td>3.87 [5.0]</td> </tr> <tr> <td>6</td> <td>45.00</td> <td>35.00</td> <td>17.599</td> <td>17.009</td> <td>3.47 [5.0]</td> </tr> <tr> <td>7</td> <td>25.00</td> <td>15.00</td> <td>20.921</td> <td>19.977</td> <td>4.73 [5.0]</td> </tr> </tbody> </table>	Interval	v-max [km/h]	v-min [km/h]	t-actual [s]	t-target [s]	error [%]	1	125.00	115.00	6.723	6.573	2.28 [5.0]	2	105.00	95.00	8.600	8.329	3.25 [5.0]	3	85.00	75.00	11.095	10.659	4.09 [5.0]	4	65.00	55.00	14.194	13.632	4.12 [5.0]	5	55.00	45.00	15.895	15.303	3.87 [5.0]	6	45.00	35.00	17.599	17.009	3.47 [5.0]	7	25.00	15.00	20.921	19.977	4.73 [5.0]	
Interval	v-max [km/h]	v-min [km/h]	t-actual [s]	t-target [s]	error [%]																																													
1	125.00	115.00	6.723	6.573	2.28 [5.0]																																													
2	105.00	95.00	8.600	8.329	3.25 [5.0]																																													
3	85.00	75.00	11.095	10.659	4.09 [5.0]																																													
4	65.00	55.00	14.194	13.632	4.12 [5.0]																																													
5	55.00	45.00	15.895	15.303	3.87 [5.0]																																													
6	45.00	35.00	17.599	17.009	3.47 [5.0]																																													
7	25.00	15.00	20.921	19.977	4.73 [5.0]																																													
Coast down times																																																		
	<table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 15%;">delta-v [km/h]</th> <th style="width: 15%;">t-target [s]</th> <th style="width: 15%;">t-actual1 [s]</th> <th style="width: 15%;">t-target2 [s]</th> <th style="width: 15%;">t-target3 [s]</th> </tr> </thead> <tbody> <tr> <td>125.0-115.0</td> <td>6.573</td> <td>5.801</td> <td>6.659</td> <td>6.723</td> </tr> <tr> <td>105.0 - 95.0</td> <td>8.329</td> <td>7.275</td> <td>8.509</td> <td>8.600</td> </tr> <tr> <td>85.0 - 75.0</td> <td>10.659</td> <td>9.165</td> <td>10.939</td> <td>11.095</td> </tr> <tr> <td>65.0 - 55.0</td> <td>13.632</td> <td>11.619</td> <td>13.984</td> <td>14.194</td> </tr> <tr> <td>55.0 - 45.0</td> <td>15.303</td> <td>13.049</td> <td>15.645</td> <td>15.895</td> </tr> <tr> <td>45.0 - 35.0</td> <td>17.009</td> <td>14.559</td> <td>17.308</td> <td>17.599</td> </tr> <tr> <td>25.0 - 15.0</td> <td>19.977</td> <td>18.172</td> <td>20.650</td> <td>20.921</td> </tr> </tbody> </table>	delta-v [km/h]	t-target [s]	t-actual1 [s]	t-target2 [s]	t-target3 [s]	125.0-115.0	6.573	5.801	6.659	6.723	105.0 - 95.0	8.329	7.275	8.509	8.600	85.0 - 75.0	10.659	9.165	10.939	11.095	65.0 - 55.0	13.632	11.619	13.984	14.194	55.0 - 45.0	15.303	13.049	15.645	15.895	45.0 - 35.0	17.009	14.559	17.308	17.599	25.0 - 15.0	19.977	18.172	20.650	20.921									
delta-v [km/h]	t-target [s]	t-actual1 [s]	t-target2 [s]	t-target3 [s]																																														
125.0-115.0	6.573	5.801	6.659	6.723																																														
105.0 - 95.0	8.329	7.275	8.509	8.600																																														
85.0 - 75.0	10.659	9.165	10.939	11.095																																														
65.0 - 55.0	13.632	11.619	13.984	14.194																																														
55.0 - 45.0	15.303	13.049	15.645	15.895																																														
45.0 - 35.0	17.009	14.559	17.308	17.599																																														
25.0 - 15.0	19.977	18.172	20.650	20.921																																														

Pictures of the PMP GPMS Components

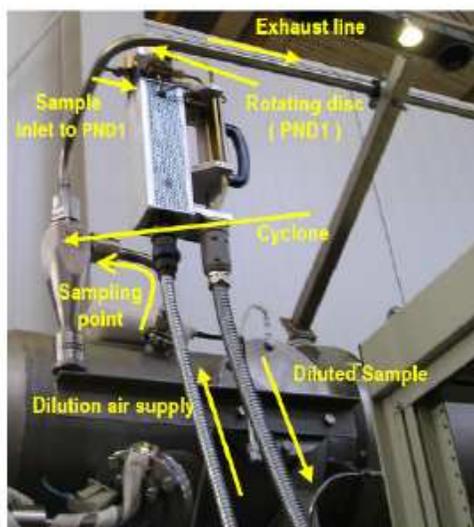


Figure A.1: Particle Number Diluter (PND1)

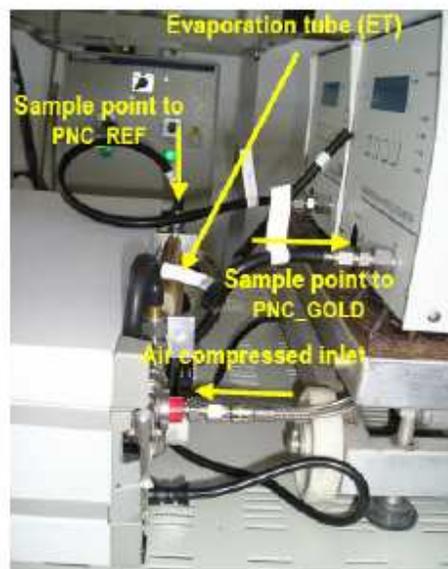


Figure A.2: Evaporation Tube (ET) and Samples Point for the CPCs



Figure A.3: Control Unit of the GPMS and CPCs (CPC_GOLD and CPC_REF)

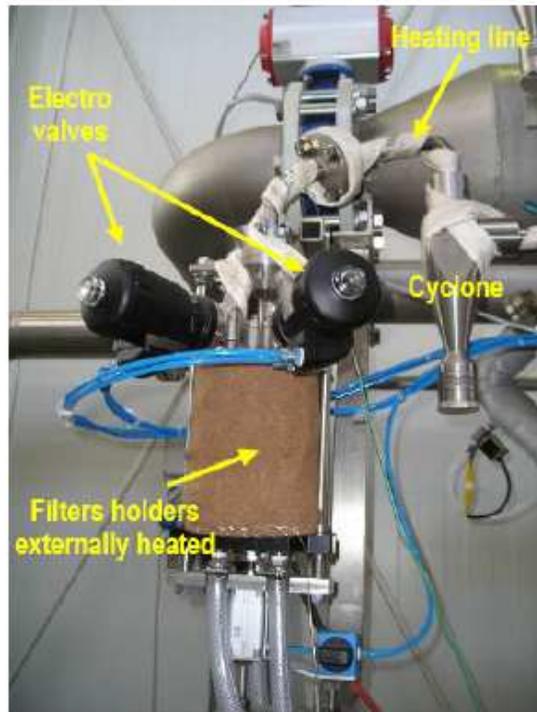
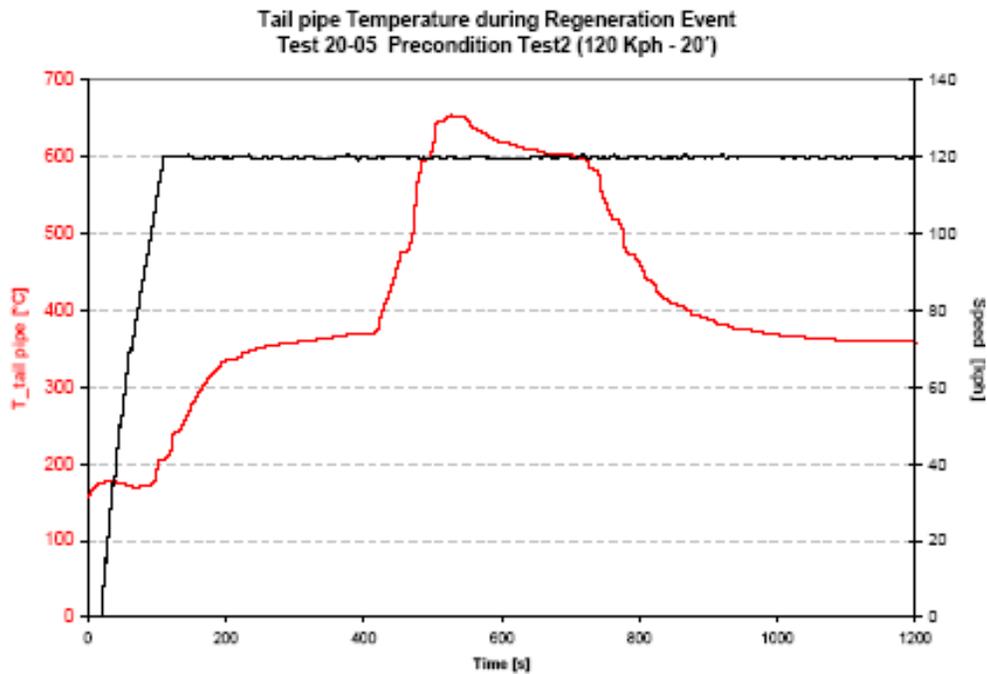
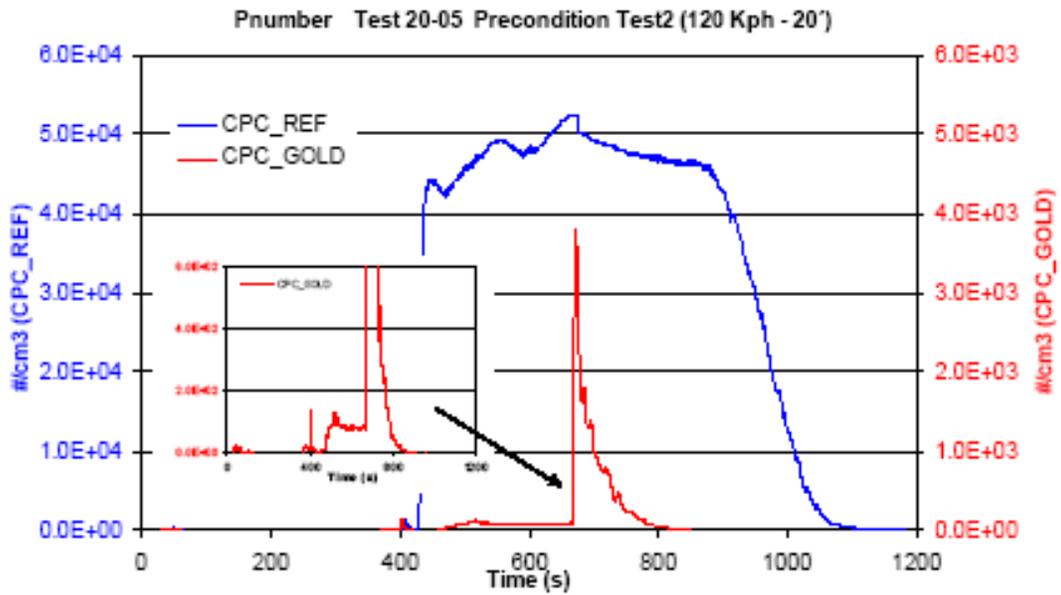


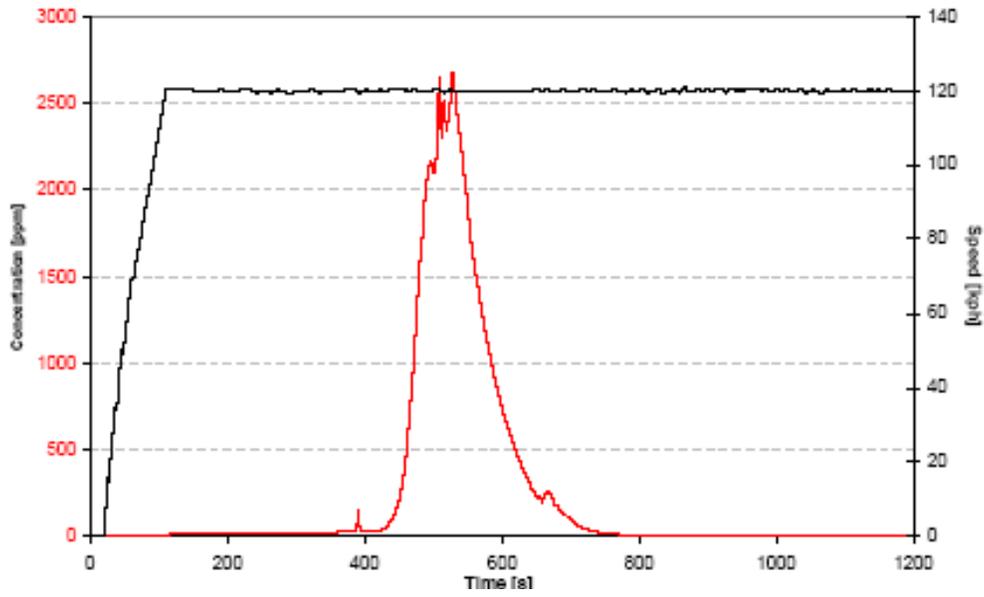
Figure A.4: Particulate Mass System Heated Externally

APPENDIX B. EMISSIONS DURING A REGENERATION EVENT

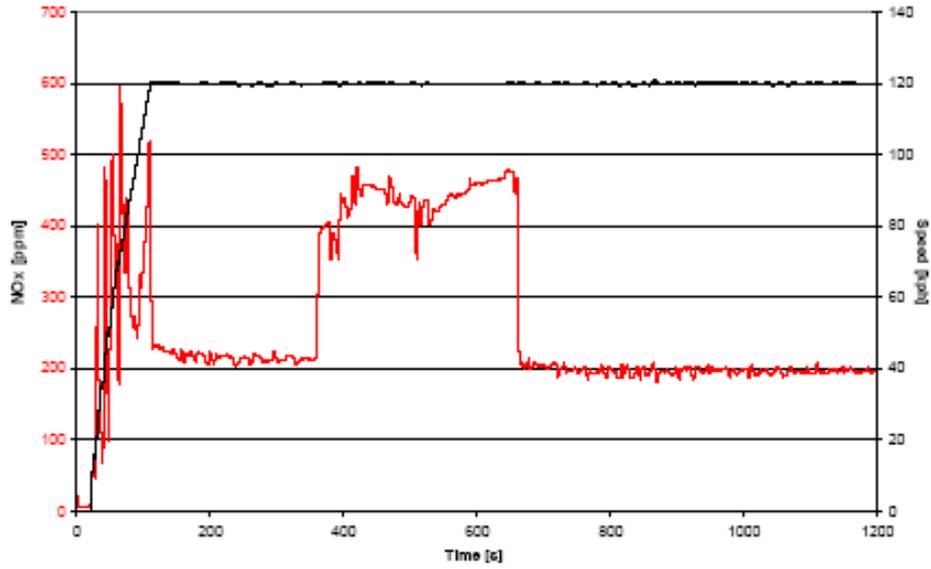
The following figures illustrate the particle and gaseous emissions during a regeneration event when the GV is preconditioned at 120 km/hr for 20 min.



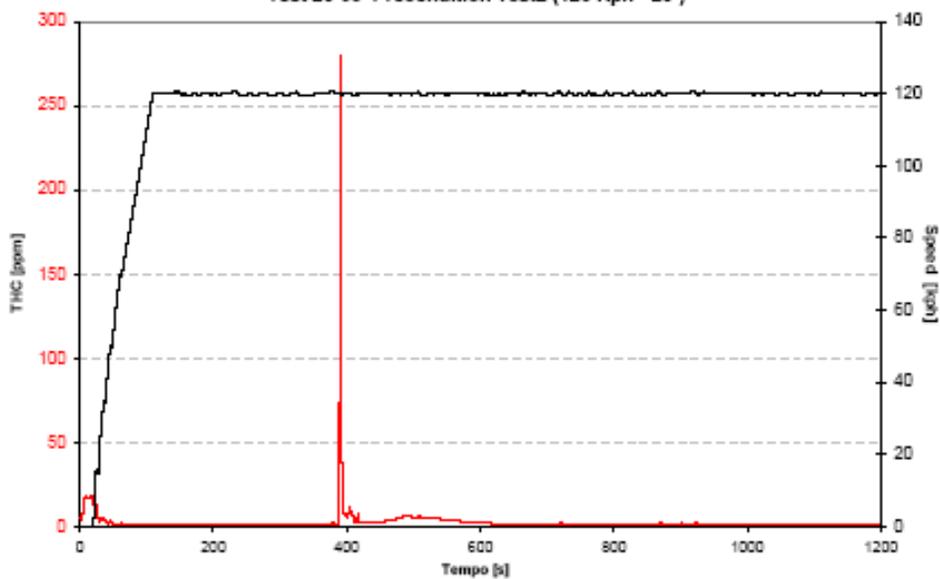
Carbon Monoxide Emissions during Regeneration Event
Test 20-05 Precondition Test2 (120 Kph - 20')



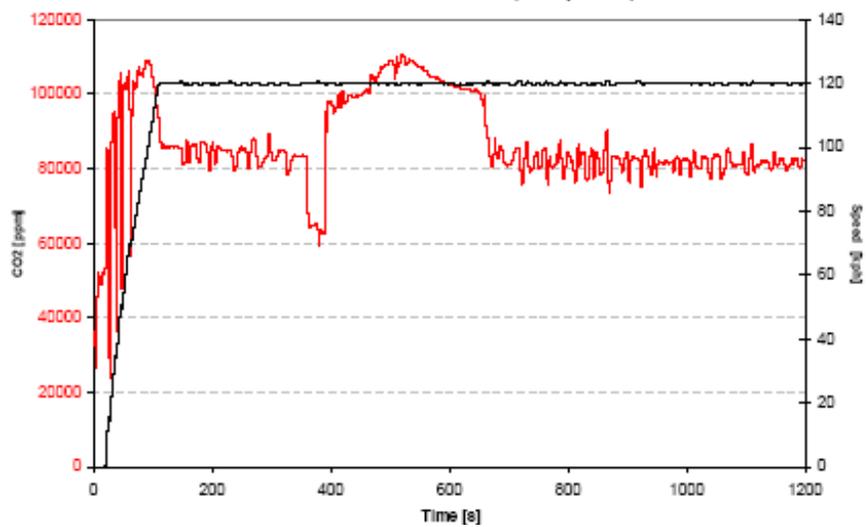
Nitrogen Oxides Emissions during Regeneration Event
Test 20-05 Precondition Test2 (120 Kph - 20')



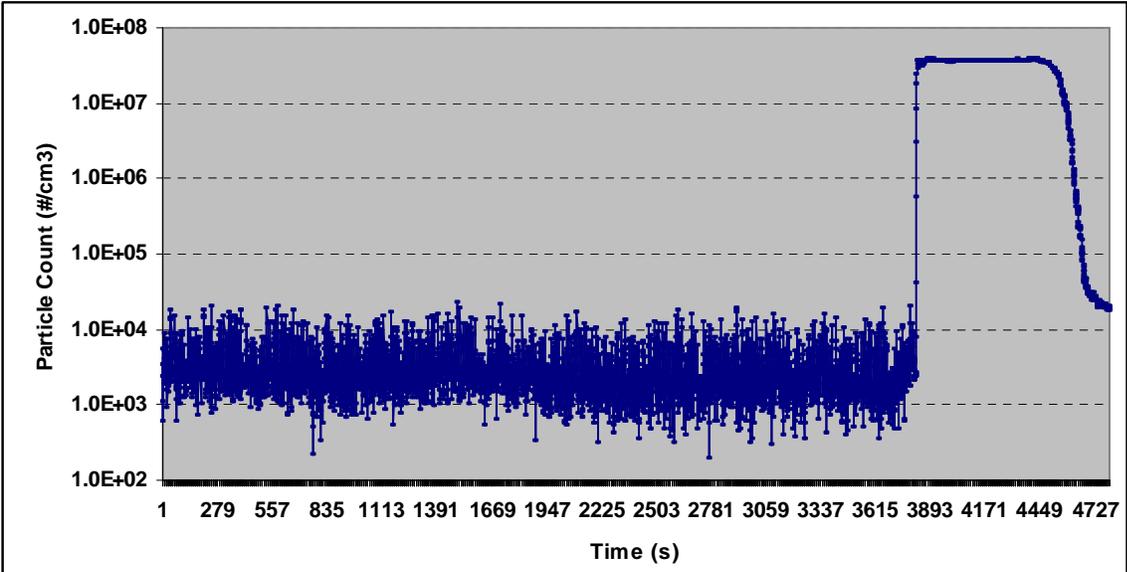
Total Hydrocarbons Emissions during Regeneration Event
Test 20-05 Precondition Test2 (120 Kph - 20')



Carbon Dioxide Emissions during Regeneration Event
Test 20-05 Precondition Test2 (120 Kph - 20')

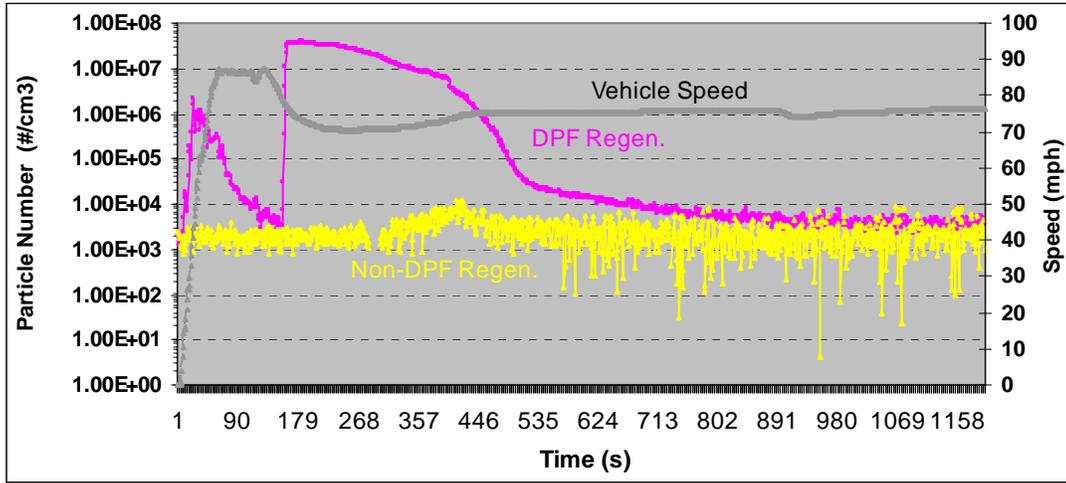


Particle Number Emissions during DPF Regeneration Measured from EEPS, Real-time Particle Number Concentrations

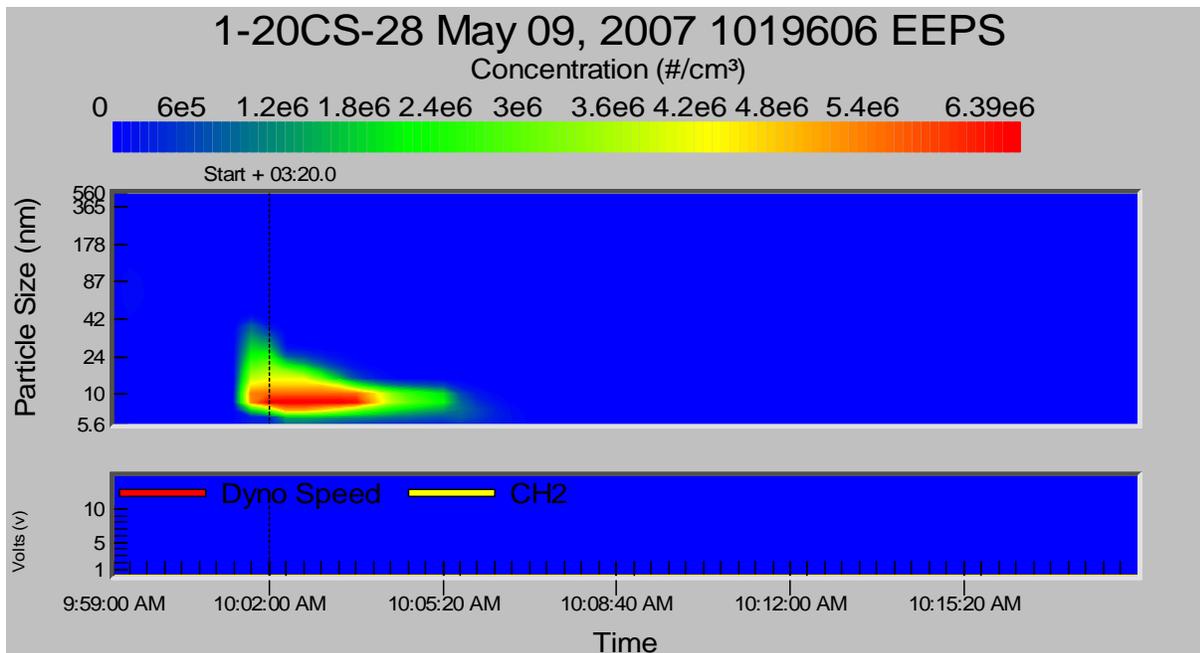


Particle Number Emissions from 20CS tests during and post DPF regeneration.

(a) Real-time Particle Number Emissions

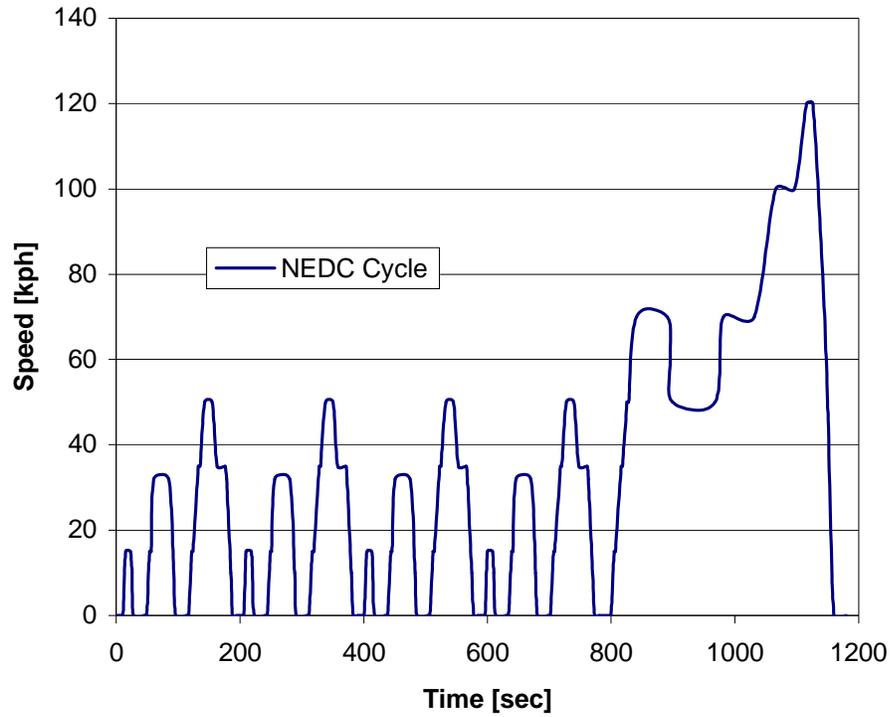


(b) 2-D Contour Graph

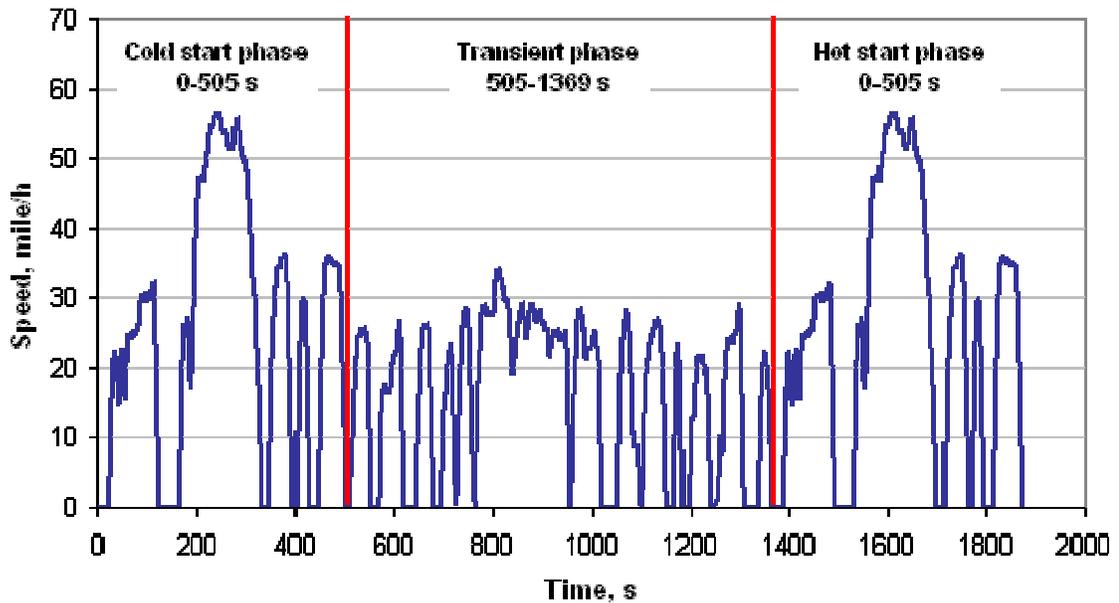


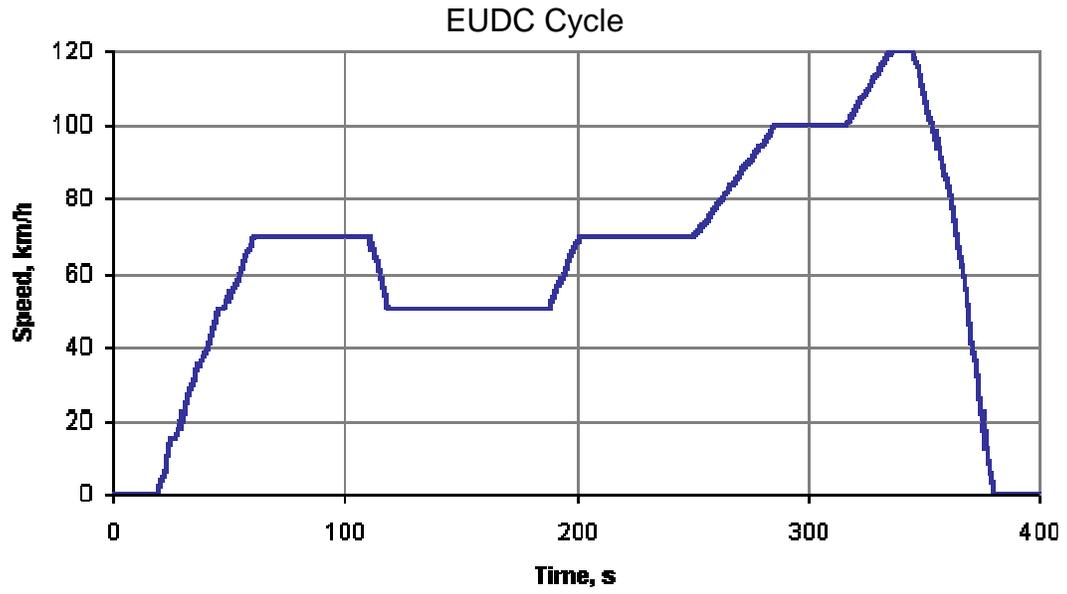
APPENDIX C. TEST CYCLES

NEDC Cycle



FTP 75 Cycle





APPENDIX D. FUEL SPECIFICATION



Direction Additifs et Carburants Spéciaux

Chemin du canal - BP 22 - 69360 Solaize France
Tél: +33 4 78 02 60 64 - Fax: +33 4 78 02 60 91

APPELLATION : GAZOLE TYPE CEC RF 06-03			Référence analyse : 6160	
GAZOLE INDUSTRIE		N° de lot : B7274081		Date : 03/09/2004
CERTIFICAT DE CONFORMITE <input checked="" type="checkbox"/>			BULLETIN D'ANALYSES <input type="checkbox"/>	
GAZOLE	SPECIFICATIONS	UNITE	RESULTATS	METHODES
DONNEES PHYSIQUES				
Masse Volumique 15 °C	833 à 837	kg/m3	835	ASTM D 4052
Viscosité à 40°C	2.3 à 3.3	mm2/s	2,7	ASTM D 445
DISTILLATION				
PI		°C	185	ASTM D 86
5 % Vol		°C	201	ASTM D 86
10 % Vol		°C	208	ASTM D 86
20 % Vol		°C	219	ASTM D 86
30 % Vol		°C	233	ASTM D 86
40 % Vol		°C	251	ASTM D 86
50 % Vol	245 mini	°C	274	ASTM D 86
60 % Vol		°C	293	ASTM D 86
70 % Vol		°C	309	ASTM D 86
80 % Vol		°C	320	ASTM D 86
90 % Vol		°C	333	ASTM D 86
95 % Vol	345 à 350	°C	346	ASTM D 86
PF	370 maxi	°C	356	ASTM D 86
E 250 °C		%Vol	39.6	ASTM D 86
E 350 °C		%Vol	96	ASTM D 86
E 370 °C		%Vol	96.5	ASTM D 86
INDICE DE CETANE				
Cétane calculé		index	53.5	ASTM D 4737
Cétane mesuré	52 à 54	index	53	ISO 5165-98
Point Eclair	55 mini	°C	75	EN 22719
COMPOSITION				
Aromatiques Totaux		%Mass	21.8	IP 391
Poly-Aromatiques	3.0 à 6.0	%Mass	4.4	IP 391
TENUE AU FROID				
Point de trouble		°C	-9	ASTM D2500
TLF	-5 maxi	°C	-18	EN 116, NF M 07042
COMBUSTION				
Pouvoir Calorifique Inférieur (G)		MJ/kg	43.355	ASTM D 4868
%C, %H, %O		%Mass	87.4/11.4/<0.5	GC / Calculated
DONNEES COMPLEMENTAIRES				
Stabilité à l'Oxydation	25 maxi	g/m3	10	ISO 12205
Corrosion Cuivre 3H, 50°C	C1	merit	1a	ASTM D 130
Soufre	10 maxi	mg/kg	8	ISO 4260 / ISO 8754
Carbone Conradson sur résidu 10% Vol	0.2 maxi	%m/m	0	ISO 10370
Teneur en cendres	0.01 maxi	%m/m	0,01	ISO 6245
Indice d'acide	0.02 maxi	mg KOH/g	0	ASTM D 974
Teneur en sédiments		mg/kg	2	ASTM D 2276
Teneur en esters méthyliques d'acides gras	néant	%Mass	0	
Teneur en eau	200 maxi	mg/kg	55	EN ISO 12937
Pouvoir Lubrifiant à 60°C	400 maxi	um	360	ISODIS 12155
Observation :				
VALIDATION LABO le 24/09/2004 par Metin KELLE 		Document confidentiel. Diffusion extérieure soumise à l'accord de RM/SPE/ACS L'interprétation des résultats des mesures relève de la norme NF EN ISO 4259 Fiche de données de sécurité : 80030000 DE / EN / ES / FR / IT		
Date specs : 26/06/2003 Rév: 0				

24/09/2004

**Comparison of PMP Fuel
With Average California ULSD**

Property	CARB ¹ ULSD	PMP Fuel
API Gravity	38.5	38.0
Sulfur (ppm)	4.4	8.0
Freeze Point (°F)		
Smoke Point (mm)		
Naphthalenes (vol%)		
Aromatics (vol%)	17.6	21.8
Polynuclear Aromatics (vol%)	2.2	4.4
Cetane Number	51.3	53.0
Pour Point (°F unadditized)	0.9	-0.4
Distillation (°F)		
IBP	341.8	365.0
T10	390.6	406.4
T30	426.9	451.4
T50	479.3	525.2
T70	524.1	588.2
T90	605.8	631.4
FBP	659.2	672.8

1. Average Diesel Fuel Properties, All Refineries, Summer 2006
 "California Refinery Survey", California Energy Commission, Sacramento, CA 2006

APPENDIX E. EVAPORATIVE EMISSION TEST SUMMARIES

Evaporative Emission Summary



TEST TYPE: H686 TEST DESCRIPTION: Hot Soak at 68-86 Deg for 1 Hour

Evaporative Test Date: 19-DEC-06	Vehicle ID: 1004300	SHED No: 2
Project No: 2R0615	Manufacturer: PEUGEOT	DynostopTime: 19-DEC-06 07:57:58
Vehicle No: 1	Division: PEUG	EngineOffTime: 19-DEC-06 07:59:39
Test No: 2	Model Year: 2004	Seal Time: 19-DEC-06 08:00:46
Evaporative TestID: 1018750	Model: 407	Seven Min Lag: PASS (ST-DST) < 7min
Dyno TestID: 1018748	License No: N/A	Two Min Lag: PASS (ST-EOT) < 2min
DR Sequence: 1	Engine Family:	Evap End Test: 19-DEC-06 09:00:46
Reason: B	Evaporative Family:	THC K Factor: 2.9747
Fuel Type: DN02	VIN: VF36DRHRH21028953	CH4 K Factor: 3.328
Batch ID: 5	Odometer (mi.): 13103	SHED Operator: Hettigoda / Chau
Sample ID: 1	Vehicle Vol. (cu ft): 50	Max Error: 0
Alcohols (Y/N): N		Control Code: E
Speciation (Y/N): N		

Time [min]	CH4 Conc [ppm]	CH4 Full Scale [%]	CH4 Range [ppm]	THC Conc [ppmCl]	THC Full Scale [%]	THC Range [ppmCl]	CH4 Z/S QC [P/F]	THC Z/S QC [P/F]	Av Wall Temp [degF]	Baro Press [inHg]	SHED Vol [cuft]	CH4* [gram]	THC* [gram]	Net CH4* [gram]	Net THC* [gram]
0.0	3.332	33.32	10	4.733	9.466	50	PASS	PASS	70.63	29.96	1829.4	.115	.145	-----	-----
60.0	3.397	33.97	10	6.605	13.21	50	PASS	PASS	75.73	29.97	1838.3	.116	.202	.001	.057

Comments:
Baseline.

Errors:
0 No Error

* Based on FID readings from hydrocarbon/methane analyzers, uncorrected for oxygenate response.
 This report printed at 08-JAN-07 07:12:53

Evaporative Emission Summary

TEST TYPE: D48V TEST DESCRIPTION: Diurnal 48 hour Variable Test

Evaporative Test Date: 19-DEC-06	Vehicle ID: 1004300	SHED No: 2
Project No: 2R0615	Manufacturer: PEUGBOT	DynoStopTime:
Vehicle No: 1	Division: PEUG	EngineOffTime: N/A
Test No: 2	Model Year: 2004	Seal Time: 19-DEC-06 16:46:33
Evaporative TestID: 1018749	Model: 407	Seven Min Lag: N/A
Dyno TestID:	License No: N/A	Two Min Lag: N/A
DR Sequence: 1	Engine Family:	Evap End Test: 21-DEC-06 16:46:33
Reason: B	Evaporative Family:	THC K Factor: 2.9747
Fuel Type: DN02	VIN: VF36DRHRH21028953	CH4 K Factor: 3.328
Batch ID: 5	Odometer(mi.): 13103	SHED Operator: Chau
Sample ID: 1	Vehicle Vol.(cu ft): 50	Max Error: 0
Alcohols (Y/N): N		Control Code: E
Speciation (Y/N): N		

Time [min]	CH4 Conc [ppm]	CH4		THC Conc [ppmCl]	THC		CH4 Z/S QC [P/F]	THC Z/S QC [P/F]	Av Wall Temp [degF]	Baro Press [inHg]	SHED Vol [cuft]	CH4* [gram]	THC* [gram]	Net CH4* [gram]	Net THC* [gram]
		Full Scale	Range		Full Scale	Range									
0.0	2.068	20.68	10	4.141	8.282	50	PASS	PASS	65.03	29.92	1651.6	.065	.116	-----	-----
1439.1	2.455	24.55	10	11.41	22.82	50	PASS	PASS	65.13	29.90	1647.4	.077	.319	.012	.203
2880.0	3.06	30.6	10	15.87	31.74	50	PASS	PASS	64.93	29.85	1646.5	.095	.442	.018	.123

Comments:
Baseline.

Errors:
0 No Error

* Based on FID readings from hydrocarbon/methane analyzers, uncorrected for oxygenate response.
 This report printed at 08-JAN-07 07:16:18

APPENDIX F. TRACE METAL ANALYTICAL PROCEDURES WISCONSIN STATE LABORATORY of HYGIENE BRIEF SUMMARY of HR-ICP-MS METHODS and QUALITY ASSURANCE

Accurate trace element analyses of filter-collected aerosols depends critically upon successful application of a comprehensive program of contamination control. Our laboratory has been in the forefront in developing and applying compatible sampling and analysis methods for trace species in environmental matrices (Shafer et al. 1999; Hurley et al. 1996). The practical, achievable, lower limits of detection of trace metals using modern Q-ICPMS and HR-ICP-MS techniques are controlled by method blanks. To this end, proper filter preparation, filter handling and sampler operations, and strict trace-clean laboratory protocols are critical to achieving the desired detection levels. All preparation steps (equipment cleaning), aerosol leaching, and analyses are performed in HEPA filtered, dedicated trace element clean labs by personnel with extensive experience in trace level techniques. Our two clean labs were purpose-built for trace metal analyses from non-metallic materials. Filter substrates are handled with Teflon forceps in gloved hands. Critical sample and equipment handling (bottle/vial drying, sub-sampling, and dilutions) are performed under polypropylene/acrylic laminar-flow benches. Extreme precautions are taken to minimize contamination during chemical extractions. Commercially available salts of the highest purity are further cleaned-up on Chelex columns. High purity acids are further purified in-house by sub-boiling point distillation in quartz/Teflon stills. Samples contact only trace metal compatible materials (TFE, FEP, PFA -Teflon, polypropylene, or polyethylene), exhaustively prepared in multi-step acid leachings. Equipment/supplies are protected by double-bagging in plastic, and field manipulations are minimized by pre-packaging field supplies.

Particulates are typically collected on Teflon-based substrates. Teflon filters were selected because of their relatively low blank levels and compatibility with the various extraction and rigorous bomb-digestion procedures. On Teflo® substrates, the encircling polypropylene ring is removed prior to digestion. To ensure the lowest possible method detection levels, trace contaminants in the Teflon filters are removed via a cleaning protocol incorporating sequential flow-through leaches with 2N HCl, 2N HNO₃ and MQ water. Where required (to minimize filter mass) or desired (to provide sample replicates or splits), filters are halved or quartered using a ceramic knife. The whole filter and individual sections were carefully weighed to allow for normalization of elemental data to complete filter.

Total dissolution of particulates, either bulk, or collected on pre-cleaned Teflon membranes is effected by microwave-assisted acid digestion in miniature Teflon bombs. An automated, temperature (and pressure)-regulated, trace analysis microwave system (Milestone Ethos+) is utilized. The acid chemistry employs a small volume mix of ultra-high purity acids (1.0 mL 16N HNO₃, 0.25 mL 12N HCl, 0.1 mL 28N HF) to realize very low blanks and completely solubilize traditionally difficult elements (Cr, noble metals, platinum group) and compounds (aluminosilicates, quartz). The method is efficient and rapid, with digestion of a 36 sample batch completed in less than one hour (microwave program: 15 minute temperature ramp to 200 °C followed by a 30 minute hold at 200 °C). A low final dilution volume (15 mL) enhances signal to noise for subsequent ICP-

MS analysis. A typical batch consists of 22 unknowns, 6 standard reference materials (SRMs), 4 matrix blanks, 2 method blanks, and 2 matrix spikes. The SRMs used to monitor digestion performance were selected to represent phases that represent actual aerosols or significant aerosol components. These included the NIST SRMs: Recycled Auto Catalyst (#2556), Urban Dust (#1649a), and San Joaquin Soil (#2709). We maintain a suite of additional NIST SRMs for use with samples with unique matrices.

Elements are quantified with a magnetic sector Inductively-Coupled Plasma Mass Spectrometer (HR-ICPMS; Finnigan Element 2). The magnetic sector instrument provides several important advantages over quadrupole-based ICP-MS in this application: (a) the superior sensitivity and noise characteristics result in greatly enhanced S/N metrics, enabling accurate quantitation of ultra-trace elements in PM; (b) the high mass resolution capability virtually eliminates molecular isobars, ensuring accurate elemental identification even in the most complex PM and acid digest matrices. Multiple isotopes (where feasible) of many of the target elements were acquired as part of the overall data quality assessment.

The Finnigan Element 2 (with fast scanning magnet and Pt guard electrode), is interfaced to an ESI low-flow ($80 \mu\text{L min}^{-1}$) Teflon micro-concentric nebulizer. Configured in this manner the sensitivity ranged from 1500 to 4000 MHz/ppm (low resolution mode) with backgrounds typically less than 0.5 cps. Three internal standards (gallium, indium, iridium) were spiked into the diluted digests prior to HR-ICP-MS analysis. Quantification is performed using external standards with internal normalization. Isotopes are acquired in peak jumping mode. We commonly run unknown samples at several mass resolution settings to confirm the absence of molecular isobars. A minimum of three replicate 180 second analyses are performed on each sample after a 45 second uptake and stabilization period. A long (360 second) rinse with 2% high purity nitric acid is performed between samples to virtually eliminate carry-over and to recondition the sampler cone. Instrumental detection limits (3-sigma) are in the range of 0.01 to 10 ng L^{-1} . QA/QC samples analyzed along with each batch of PM samples includes: NIST SRMs (see above), digestion spike recoveries, sample spike recoveries, analytical and sample replicates, method blanks, and isotope and resolution checks.

A comprehensive QA/QC program is in place for our ICP-MS and HR-ICP-MS metals analyses. Standard operating procedures (SOPs) are clearly documented and available for review. Data Quality Objectives (DQO) are summarized in Table below. A typical MCN-ICP-MS batch will include 25 actual samples, several field method blanks, 2 matrix spikes, 6 SRM's, 3 matrix blanks and a set of check blanks (CCB's) and calibration verification checks (CCV's) that are run at frequent intervals during the batch sequence. A detailed discussion of our routine ICP-MS quality assurance plan can be found in the EPA document: Shafer and Overdier 1996; Analysis of Surface Waters for Trace Elements by Inductively-Coupled Plasma Mass Spectrometry, Revision 5, 1996 (University of Wisconsin-Madison).

DQO Summary: HR- ICP-MS with Microwave-Assisted Acid Digestion

Analyte	Isotopes	Units	Hold Time	MDL	Precision	Accuracy	Completeness
Aluminum	27	ng m ⁻³	12 months	17	±15%	70-120%	95%
Antimony	121, 123	ng m ⁻³	12 months	0.4	±15%	70-120%	95%
Arsenic	75	ng m ⁻³	12 months	1	±20%	70-120%	95%
Barium	135, 137	ng m ⁻³	12 months	0.6	±15%	70-120%	95%
Beryllium	9	ng m ⁻³	12 months	0.02	±15%	70-120%	95%
Cadmium	111, 114	ng m ⁻³	12 months	0.02	±15%	70-120%	95%
Calcium	40, 44	ng m ⁻³	12 months	1.4	±15%	60-120%	95%
Cerium	140	ng m ⁻³	12 months	0.06	±15%	70-120%	95%
Cesium	133	ng m ⁻³	12 months	0.05	±15%	70-120%	95%
Chromium	52, 53	ng m ⁻³	12 months	0.15	±15%	70-120%	95%
Cobalt	59	ng m ⁻³	12 months	0.15	±15%	70-120%	95%
Copper	63, 65	ng m ⁻³	12 months	0.6	±15%	70-120%	95%
Iridium	191, 193	ng m ⁻³	12 months	0.02	±20%	70-120%	95%
Iron	54, 56	ng m ⁻³	12 months	0.2	±15%	70-120%	95%
Lanthanum	139	ng m ⁻³	12 months	0.05	±15%	70-120%	95%
Lead	206, 208	ng m ⁻³	12 months	0.01	±15%	70-120%	95%
Lithium	7	ng m ⁻³	12 months	0.06	±15%	70-120%	95%
Magnesium	24, 25, 26	ng m ⁻³	12 months	0.3	±15%	70-120%	95%
Manganese	55	ng m ⁻³	12 months	0.05	±15%	70-120%	95%
Molybdenum	95, 98	ng m ⁻³	12 months	0.5	±15%	70-120%	95%
Nickel	60, 62	ng m ⁻³	12 months	0.4	±15%	70-120%	95%
Palladium	105, 108	ng m ⁻³	12 months	0.1	±20%	70-120%	95%

Platinum	194, 195	ng m ⁻³	12 months	0.04	±20%	70-120%	95%
Potassium	39	ng m ⁻³	12 months	0.8	±15%	70-120%	95%
Rhodium	103	ng m ⁻³	12 months	0.02	±20%	70-120%	95%
Rubidium	85	ng m ⁻³	12 months	0.4	±15%	70-120%	95%
Silver	107, 109	ng m ⁻³	12 months	0.02	±20%	70-120%	95%
Selenium	78, 82	ng m ⁻³	12 months	0.5	±20%	60-130%	95%
Sodium	23	ng m ⁻³	12 months	1.3	±15%	70-120%	95%
Strontium	88	ng m ⁻³	12 months	0.5	±15%	70-120%	95%
Thallium	205	ng m ⁻³	12 months	0.3	±15%	70-120%	95%
Tin	118, 120	ng m ⁻³	12 months	1.7	±20%	60-130%	95%
Titanium	47, 50	ng m ⁻³	12 months	0.4	±15%	60-130%	95%
Tungsten	182, 184	ng m ⁻³	12 months	0.1	±20%	70-120%	95%
Uranium	238	ng m ⁻³	12 months	0.02	±15%	70-120%	95%
Vanadium	51	ng m ⁻³	12 months	0.8	±15%	70-120%	95%
Zinc	66, 68	ng m ⁻³	12 months	1.1	±15%	70-120%	95%

MDL = Method Detection Limit (ng m⁻³; 3 sigma). Based on 14 m³ samples collected on pre-cleaned 47 mm Teflon membrane substrates.

Note: Both accuracy and precision criteria apply to concentrations >5x the MDL.

Reference Shafer, M., Schauer, J., Copan, W., Peter-Hoblyn, J., Sprague, B., and Valentine, J. "Investigation of platinum and cerium from use of a fuel-based catalyst." SAE 2006 Transactions Journal of Fuels and Lubricants, 2006-01-1517:491-503.

APPENDIX G. TRACE METAL BLANK AND UNCERTAINTY IN UNITS OF MG/MILE

Species	Twenty Steady State @ 75 mph		Four NEDC Cycle	
	Blank ng/mile	+/- ng/mile	Blank ng/mile	+/- ng/mile
Li7	0.135	0.111	1.176	0.962
Na23	49.149	11.643	427.814	101.345
Mg25	12.938	2.992	112.620	26.041
Al27	16.168	21.911	140.736	190.727
P31	16.374	1.551	142.526	13.503
S32	107.343	2.526	934.366	21.988
K39	21.428	3.957	186.517	34.442
Ca44	84.379	53.996	734.476	470.009
Sc45	0.155	0.071	1.348	0.620
Ti49	15.948	2.586	138.819	22.507
V51	0.027	0.038	0.232	0.327
Cr52	2.125	0.096	18.493	0.834
Mn55	2.422	0.166	21.080	1.448
Fe56	76.995	1.091	670.202	9.494
Co59	0.044	0.021	0.385	0.179
Ni60	3.736	1.214	32.518	10.564
Cu63	2.474	0.234	21.538	2.035
Zn66	17.166	1.248	149.426	10.867
Ga71	0.021	0.030	0.185	0.260
Se82	2.464	5.608	21.445	48.817
Rb85	0.682	0.175	5.940	1.523
Sr88	0.454	0.026	3.953	0.226
Y89	0.115	0.031	1.003	0.272
Nb93	0.941	0.543	8.195	4.730
Mo95	0.590	0.162	5.136	1.414
Ru101	0.021	0.012	0.183	0.104
Rh103	0.012	0.004	0.107	0.033
Pd108	0.528	0.195	4.595	1.698
Ag109	0.520	0.174	4.530	1.512
Cd111	0.052	0.024	0.455	0.211
Sn120	1.744	0.276	15.182	2.406
Sb121	0.337	0.022	2.935	0.192
Cs133	0.004	0.002	0.035	0.014
Ba138	0.873	0.080	7.599	0.693
La139	0.020	0.008	0.177	0.067
Ce140	0.052	0.008	0.456	0.066
Pr141	0.010	0.004	0.085	0.037
Nd146	0.014	0.014	0.123	0.118
Sm152	0.009	0.004	0.080	0.034
Eu153	0.006	0.004	0.052	0.037
Dy163	0.004	0.002	0.031	0.021
Ho165	0.008	0.002	0.067	0.022
Yb174	0.023	0.032	0.196	0.275
Lu175	0.004	0.002	0.036	0.015
Pt195	0.022	0.025	0.188	0.215
Tl205	-0.001	0.005	-0.007	0.046
Pb208	0.575	0.010	5.002	0.089
Th232	0.512	0.586	4.453	5.097
U238	0.006	0.002	0.049	0.017

(This Page Intentionally Blank)