

Kansas City PM Characterization Study

Final Report

Appendix AA

Quality Assurance Project Plan

(including revised Appendix A)

Assessment and Standards Division
Office of Transportation and Air Quality
U.S. Environmental Protection Agency

Sponsors:

National Renewable Energy Laboratory, U.S. Department of Energy
Federal Highway Administration, U.S. Department of Transportation
STAPPA-ALAPCO Emission Inventory Improvement Program
Coordinating Research Council Inc. (Project No. E-69)

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EPA Contract No. GS 10F-0036K

October 27, 2006
Revised April 2008 by EPA staff



United States
Environmental Protection
Agency

EPA420-R-08-009
April 2008

Quality Assurance Project Plan

Characterizing Exhaust Emissions from Light-Duty Gasoline Vehicles in the Kansas City Metropolitan Area

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August 1, 2006

QAPP REVISION HISTORY

Revision 1: April 15, 2004

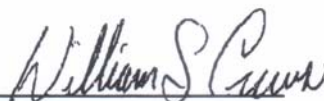
Revision 2: June 30, 2004


Revision 3: July 2, 2004

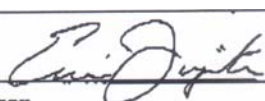
Revision 4 (current): August 1, 2006

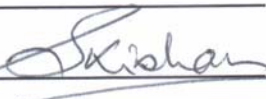
QUALITY ASSURANCE PROJECT PLAN

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Table of Contents

SECTION 1: PROJECT MANAGEMENT	7
1.1 Project/Task Organization - ERG	7
1.1.1 Problem Definition/Background	7
1.1.2 Project Task Description	8
1.2 Project/Task Organization - NuStats	8
1.3 Project/Task Organization - BKI	9
1.3.1 Problem Definition/Background	10
1.3.2 Project/Task Description	10
1.3.3 Quality Objectives and Criteria for Measurement Data	11
1.3.4 Special Training/Certification	12
1.3.5 Documents and Records	13
1.4 Project/Task Organization - DRI	13
1.4.1 Project and Task Organization	13
1.4.2 Problem Definition/Background	14
1.4.3 Project Task Description	14
1.4.4 Quality Objectives and Criteria	15
1.4.5 Special Training/Certification	21
1.4.6 Documents and Records	21
SECTION 2: SURVEY DATA ACQUISITION, PROCESSING, AND REPORTING	22
2.1 Data Acquisition Process	22
2.1.1 Sampling	22
2.1.2 Instrument Design	24
2.1.3 Response and Nonresponse	25
2.1.4 Data Acquisition Methods	26
2.2 Data Processing and Management (Review, Validation, and Verification)	26
2.2.1 Editing	26
2.2.2 Imputation	27
2.2.3 Estimation	27
2.2.4 Data Quality Evaluation	27
2.3 Data Reporting and Presentation	29
2.3.1 Disclosure Control	29
2.3.2 Data Analysis	29
2.3.3 Documentation	30
SECTION 3: DAY ONE VEHICLE INSPECTION AND CONDITIONING	32
3.1 Vehicle Inspection	33
3.2 Vehicle Repair	33
3.3 Vehicle Conditioning Run	34
SECTION 4: DAY TWO VEHICLE TESTING	36
4.1 Sampling Equipment	36
4.2 Calibration of Equipment	38
4.2.1 Dynamometer, CVS, and Gas Analysis Equipment	38
4.2.2 PEMS	47
4.3 Sampling Media Preparation and Certification	47
4.4 Testing, Inspection, and Maintenance of Equipment	49

4.4.1	Dynamometer and Associated Gas Analysis	49
4.4.2	PEMS	49
4.5	Obtaining Background Levels for Gas Analysis Equipment.....	49
4.6	Securing the Vehicle on the Dynamometer	50
4.7	Particulate and Toxics Sampling Methods.	51
4.7.1	Continuous PM Measurements	51
4.7.2	Collection of Time Integrated PM and Toxics Samples.....	52
4.8	Laboratory Analytical Methods	55
4.8.1	Protocol for Selection of Samples for Chemical Analysis.....	56
4.8.2	Mass Gravimetric Analysis.....	59
4.8.3	Elements by XRF.....	59
4.8.4	Elements by ICP-MS	59
4.8.5	Elemental and Organic Carbon	60
4.8.6	Ion Chromatographic Analysis for Chloride, Nitrate, and Sulfate	61
4.8.7	Semi-Volatile Organic Compounds.....	62
4.8.8	Gaseous Air Toxics.....	64
4.9	Quality Control	65
4.10	Sample Handling and Custody.....	67
4.11	Inspection/Acceptance of Supplies and Consumables.....	69
SECTION 5: DATA MANAGEMENT AND VALIDATION		70
5.1	Data Acquisition Requirements (Non-Direct Measurements).....	70
5.2	Reporting.....	71
5.3	BKI Data Review, Verification, and Validation.....	71
5.4	DRI Verification and Validation Methods.....	71
5.5	Verification and Validation for the PEMS.....	72
5.6	QC Calculations	73
5.7	MSOD Data Management.....	74
SECTION 6: ASSESSMENT AND OVERSIGHT.....		75
6.1	Assessment and Response Actions	75
6.2	Reports to Management	77
REFERENCES		78

List of Tables

Table 1-1.	Example Data Quality Objectives	12
Table 1-2.	Analysis List of Inorganic Species for the Kansas City LDGV Emission Characterization Study.....	15
Table 1-3.	Analysis List of Hydrocarbons and Carbonyl Compounds for the Kansas City LDGV Emission Characterization Study.....	17
Table 1-4.	Analysis List of Polycyclic Aromatic Hydrocarbons for the Kansas City LDGV Emission Characterization Study	18
Table 1-5	Analysis List of Hopanes, Steranes and Alkanes for the Kansas City LDGV Emission Characterization Study.....	19
Table 1-6.	Analysis List of Polar Organics for the Kansas City LDGV Emission Characterization Study.....	20
Table 2-1.	Sample Strata Specified in the Work Plan	22

Table 3-1. Vehicle Inspections	33
Table 4-1. Calibration and Performance Checks of Test Equipment and Analytical Instrumentation	41
Table 4-2. Standard Operating Procedures to Characterize Emissions	47
Table 4-3. Summary of Laboratory Related SOPs	55
Table 4-4. Number of Planned Chemical Analyses and Approximate Number of Composite Samples by Test Vehicle Category	58
Table 4-5. Composite Breakdown	59
Table 6-1. Schedule for QC Deliverable Outputs	77

List of Figures

Figure 2-1. Survey Instrument Data Flowchart	25
Figure 3-1. Summary of Daily Activities	32
Figure 4-1. CVS Sampling System Schematic	36
Figure 4-2. Kansas City Exhaust Measurement Flowchart	39
Figure 4-3. Testing Facility Layout	40
Figure 4-4. Sample Train of DRI Equipment	52

Appendix A Study Modifications made between Rounds 1 and 2

SECTION 1: PROJECT MANAGEMENT

1.1 Project/Task Organization - ERG

ERG is responsible for operation of the portable emission measurement systems (PEMS) devices. The PEMS devices are SEMTECH-G systems, manufactured by Sensors, Inc. of Saline, Michigan, and owned by EPA. EPA is responsible for providing the equipment and some of the consumable gases. ERG is responsible for installing, operating, and maintaining the equipment and providing most of the consumable gases.

As indicated in the bulleted list below, overall QA responsibility for the PEMS systems is in the hands of Sandeep Kishan. The task leader for PEMS installation is Andrew Burnette and Michael Sabisch will head most of PEMS operations in the field. Both Andrew Burnette and Michael Sabisch will report directly to Sandeep Kishan. QC/QA responsibilities to be implemented by ERG staff are described in detail in the QMP.

- Sandeep Kishan, Project Manager, ERG Project Manager
- Andrew Burnette, Engineer, PEMS Task Management
- Michael Sabisch, Engineer, PEMS Field Operations

During field testing ERG personnel are responsible for the installation, operation, and maintenance of the PEMS units. The WAM is EPA's principal contact. The EPA WAM determines the quality criteria on the basis of intended use of the results to be generated and communicates those criteria.

1.1.1 Problem Definition/Background

PEMS will be used in three ways:

- To record driving and emissions data during vehicle pre-conditioning of vehicles to be tested on the dynamometer (including on-road driving);
- To record driving and emissions during testing on the dynamometer; and,
- To collect on-road emissions and driving data on a randomly selected group of vehicles that have been tested on the chassis dynamometer. The purpose of collecting these data is simply to improve EPA's understanding of "real world" vehicle operations and emissions. Also the data will be added to the MSOD database, which EPA will use in the creation of the MOVES model.

ERG personnel will perform the first and third activities listed above and BKI personnel will perform the second activity. Both ERG and BKI personnel will assist each other, as necessary, during all PEMS activities.

1.1.2 Project Task Description

ERG personnel will install a PEMS device on each vehicle as it is prepared for pre-conditioning the day before testing on the dynamometer.

Owners of the selected vehicles will be instructed on their agreed duties while their vehicles have a PEMS unit installed. In summary, these owners will agree to drive their vehicles in the manner they normally would (as if the PEMS unit were not present on their vehicle). They will also be required to keep a log of significant events during the testing period (e.g., changes in vehicle load, such as passengers entering and leaving the vehicle).

After the device has been present on their vehicle for the prescribed time period, the owner will return to the project data collection location to have the PEMS/PAMS unit de-installed. The owner will receive an interview at that time to determine various data about their experience and events that occurred during their participation.

Quality Objectives and Criteria for PEMS Data

Quality assurance objectives for accuracy and precision have been developed specific to this project. These objectives are listed in the standard operating procedures and check lists developed by ERG for this project. Those documents are contained in Appendix A of this QAPP. If at any time it is noted that deviations in measured values exceed the objectives, testing will be stopped, equipment examined, and testing resumed after the problem has been corrected.

Special Training

ERG personnel (Andrew Burnette and Michael Sabisch) were trained in the proper use of SEMTECH equipment by the manufacturer. These personnel will train others on the proper use of the SEMTECH equipment during the course of the project, as needed. The manufacturer (Sensors, Inc.) has been retained as a subcontractor for technical help on an “as needed” basis.

Documents and Records

All maintenance, calibrations and data will be reported as specified in our standard operating procedures (Appendix A). Data input comes manually and automatically. Manual data include items such as vehicle description, calibration gas values, and testing notes. Automatic data are logged by the SEMTECH system. These data are combined in the SEMTECH electronic records during testing. Raw test records are downloaded after each test when possible, and will be archived at the end of each test day. The raw data are processed and plotted on site and given a visual quality check. The processed data are also archived for post processing and reporting offsite. Standard operating procedures (refer to Appendix A) detail how each of these documentation and recording processes is to take place.

1.2 Project/Task Organization - NuStats

Employees and managers at all levels in NuStats share a concern for, and pride in, quality. Acceptable quality is not achieved by managerial actions, edicts and checks. It is achieved

through understanding client needs and the sound application of knowledge and expertise at many levels. It requires motivated and competent human resources, and the effective development and management of these resources and their activities. To this end, NuStats has in place a series of human resource programs, together with the policies and procedures to promote, facilitate, and fortify activities and behavior consistent with the firm's central concern for quality.

- Mia Zmud, Project Manager, NuStats Project Manager
- Stacey Bricka, Project Scientist, Survey Instrument Development

1.3 Project/Task Organization - BKI

The QC/QA organization for the operation of the Transportable Dynamometer assigns overall QA responsibility to Mr. W.S. Crews, Project Manager of Bevilacqua Knight Inc. (BKI). Directly reporting to Mr. W.S. Crews in support of project quality assurance is Mr. Richard Snow, Project Scientist, for regulated emissions determinations, vehicle testing and data reporting.

- W.S. Crews, Project Manager, BKI Project Manager
- R.F. Snow, Project Scientist, Laboratory Simulations QC/QA

The key QC/QA responsibilities to be implemented by BKI staff are as follows:

QC Responsibilities

- Maintain up-to-date project records;
- Maintain sample chain-of-custody documentation;
- Follow and document deviations from established procedures/methods;
- Make data quality determinations based on QC data collected; and
- Reporting all problems and corrective actions.

QA Responsibilities

- Participate in the preparation of the Quality Assurance Project Plan;
- Ensure that all project participants read and follow the Quality Assurance Project Plan;
- Establish quality requirements with the EPA Work Assignment Manager (WAM);
- Train analysts to perform and evaluate QC measurements; and
- Verify that QC activities are performed and data quality is determined as required in the QA project plan, and document QC outputs.

As subcontractor to ERG the BKI Project Manager is ultimately responsible for the performance and coordination of the transportable dynamometer operation and vehicle testing during the project. The WAM is EPA's principal contact with ERG and ERG will relay to BKI information regarding the analysis requirements. The EPA WAM determines the quality criteria on the basis of intended use of the results to be generated and communicates those criteria. These criteria include the following:

QC Requirements

- Review data notebooks;
- Arrange for performance evaluation or audit samples (when applicable);
- Assist in scheduling audits; and
- Report data quality problems to Contracting Officer.

QA Requirements

- Ensure the development and approval of the Quality Assurance Project Plan;
- Ensure that SOPs are developed, reviewed and approved;
- Establish quality requirements with contractor staff;
- Ensure that required corrective actions are implemented; and
- Review project QC outputs.

The BKI Project Manager is responsible for all projects under this subcontract and for ensuring that all technical outputs meet the quality requirements of the contract.

1.3.1 Problem Definition/Background

BKI, as a subcontractor will support ERG and the United States Environmental Protection Agency (USEPA). BKI's support will be directed towards the maintenance, calibration, testing and reporting automotive data from mobile source emissions measurements for "Characterizing Exhaust Emissions from Light-Duty Gasoline Vehicles in the Kansas City Metropolitan Area". A transportable chassis dynamometer will be used to simulate engine load while the vehicle is operated over a representative highway transient driving cycle. Regulated emissions will be determined using prescribed driving cycles. All maintenance and QA performed with the transportable dynamometer will be done in accordance with the Transportable Dynamometer Standard Operating Procedure (SOP), (November 2002).

1.3.2 Project/Task Description

BKI, as a subcontractor, will support ERG and the USEPA, and will provide technical support for the calibration, operation, and maintenance of a transportable chassis dynamometer,

associated driver's aid, constant volume sampler (CVS), analytical bench, and data acquisition/reduction system. This system is used to obtain exhaust emission samples in the field. BKI will support the calibration, operation, and maintenance of other sampling and measuring equipment, as specified in the task descriptions. In addition, BKI shall implement the capability to collect particle matter and gaseous organic samples during field studies involving the transportable dynamometer. All tests will be performed as designated in the Standard Operating Procedure (SOP) or by technical direction through ERG as directed by the WAM.

1.3.3 Quality Objectives and Criteria for Measurement Data

Quality assurance objectives for accuracy and precision have been developed specific to this project, as described below. If at any time it is noted that deviations in measured values exceed the objectives, testing will be stopped, equipment examined, and testing resumed after the problem has been corrected (see Section C1). Performance objectives for vehicle emissions test systems and regulated emissions are based on procedures found in the Code of Federal Regulations (CFR 40 Part 86, Subpart B, 86.114 through 86.126). Accuracy determination of the regulated emissions analyzers is based on response to NIST gaseous standards. Accuracy determination of the vehicle test systems is based on comparisons of rigid initial calibrations to performance checks.

It is the responsibility of the EPA personnel to define the intended use of the data and to develop, in cooperation with the data users and BKI, the Data Quality Objectives (DQOs) appropriate to the project within the time and resources of the effort. These DQOs need to be conveyed to BKI as specifically as possible. DQOs are traditionally described in terms of precision, accuracy, completeness, representativeness, and comparability for all variables to be measured in this project. Development of DQOs must include the following steps.

- Define with specificity the objectives to be addressed.
- Establish guidelines for the types and quality of data needed to meet the objectives.
- Explain in quantitative terms the possible errors that may arise during the monitoring and measurement process.

DQOs will be established for each major measurement parameter. The measurements will be made so that results are representative of the media (i.e., air) and conditions being measured. An example of possible DQOs is summarized in Table 1-1. All data will be calculated and reported in units consistent with those used by other organizations reporting similar data to allow for comparability of data among organizations. The data quality objectives for accuracy and precision will be based on prior knowledge of the measurement system employed and methods validation studies using replicates, spikes, standards, calibrations, recovery studies, etc. Definitions of data quality parameters are discussed below.

Table 1-1. Example Data Quality Objectives

Parameter	Accuracy (%)	Precision (%)
THC Analysis	10	2
CO Analysis	10	2
NO _x Analysis	10	2
CO ₂ Analysis	10	2
Dyno Speed	5	5
Dyno Torque	5	5
PDP Counter	10	5
CVS Temperature	5	5
CVS Pressure	10	5

- A. Precision: Precision is a measure of mutual agreement among individual measurements of the same property, usually under prescribed similar conditions. Precision is best expressed in terms of the standard deviation. Various measures of precision exist depending upon the “prescribed similar condition”. Precision will be assessed by the collection of matrix spike and spike duplicate samples.
- B. Accuracy: Accuracy is the degree of agreement of a measurement (or an average of measurements of the same thing), X, with an accepted reference or true value. This term is a measure of the bias in a system. Accuracy will be assessed by the use of traceable reference standards and EPA-approved SOPs for all instrumentation.
- C. Representativeness: Representativeness is the degree to which data accurately and precisely represents the characteristics of a population, process, or environmental condition, or parameter variations at a sampling point. Representativeness will be assessed by the collection of appropriate sample numbers and the use of a statistically valid sampling design.
- D. Data Comparability: Comparability expresses the confidence with which one data set can be compared to another. Comparability of field sampling, monitoring, and analytical data will be ensured by using the standard sampling, analysis, and reporting methods. All data will be presented in specified and documented units and methods.
- E. Data Completeness: Completeness is a measure of the amount of valid data obtained from a measurement system compared to the amount that was expected to be obtained under normal conditions. Completeness will be assessed by reviewing field and laboratory data logs, sample custody forms, and field and laboratory logbooks to ensure that all data is certified and validated within established DQOs.

1.3.4 Special Training/Certification

No specialized training or certifications are required by personnel in order to successfully complete the project or task. However, instructions in sampling fuels and other safety courses may be held as required.

1.3.5 Documents and Records

Mr. William S. Crews, Project Manager of BKI's North Carolina operations, has 30 years of direct experience in conducting and monitoring QA activities for all aspects of performing research on investigating, characterizing, and reporting emissions from light-duty vehicles. Mr. Crews is responsible for the preparation of this Quality Assurance Project Plan for the Transportable Dynamometer and for ensuring the appropriate project personnel have the most current approved version of the QAPP, including version control, updates, distribution, and disposition.

Mr. Richard F. Snow, Project Scientist, has over 24 years of experience in conducting complex mobile source emissions projects and performing and directing all aspects of laboratory simulations, analytical methodology and emissions sampling for the determination of regulated and unregulated emissions. Mr. Snow is also thoroughly experienced in collecting and reporting batch and real-time data. Mr. Snow is accomplished in the QA requirements of the test facilities and equipment utilized in emissions testing. Mr. Snow is responsible for ensuring the appropriate operational personnel have the most current approved version of the QAPP, including version control, updates, distribution, and disposition

All maintenance, calibrations and data will be reported as specified by the US EPA. Data input comes in two forms, the data from the Vehicle Inspection team for initial vehicle data and the Operations team for regulated emissions and maintenance. Data from these two areas can be combined and final reports generated. The input includes a unique run number assigned by the systems analyst that identifies the research project, the testing cycle, and other parameters as required. As testing objectives change, the emissions database will be adapted to reflect those changes. BKI shall provide raw dynamometer vehicle emissions, fuels, and analytical data in electronic format for incorporation into spreadsheet models. The reports shall be structured so as to be easily imported into a database.

1.4 Project/Task Organization - DRI

- Eric Fujita, Project Manager, Principal Investigator
- William (Pat) Arnott, Project Manager, Co-Principal Investigator, Continuous PM, Photoacoustic, QCM, nephelometer
- David Campbell, Research Scientist, QA Support

1.4.1 Project and Task Organization

The QC/QA organization at Desert Research Institute assigns overall QA responsibility for this program to Dr. Eric M. Fujita, Principal Investigator. Dr. Fujita will be the primary contact at DRI and will coordinate project activities between field personnel and DRI's Organic Analytic Laboratory and Environmental Analysis Facility. He will be responsible for collection of integrated samples, validation of the integrated chemical data and analysis of the project results in relation to similar studies conducted in recent years. Dr. William P. Arnott will serve as co-Principal Investigator and will be responsible for operation of continuous PM instruments and

compilation and validation of the PA, QCM, and nephelometer measurements. Mr. David E. Campbell, Research Scientist, will support project quality assurance by conducting flow audits, coordinating sample shipping and receiving, coordinating identification of samples to be analyzed by the two DRI laboratories, and validating and preparing the database. The accompanying Quality Management Plan (QMP) delineates specific QC/QA responsibilities to be implemented by DRI field and laboratory personnel.

As a subcontractor to Eastern Research Group Inc. (ERG), the DRI principal investigator is ultimately responsible for sample collection and analysis during the project. The work assignment Manager (WAM) is EPA's principal contact with ERG and ERG will relay to DRI information regarding the analysis requirements. The EPA WAM determines the quality criteria on the basis of the intended use of the results to be generated and communicates those criteria.

1.4.2 Problem Definition/Background

The U.S. Environmental Protection Agency (EPA), U.S. Department of Transportation (DOT), Federal Highway Administration (FHWA), National Renewable Energy Laboratory, Coordinating Research Council (CRC), and the State and Territorial Air Pollution Program Administrators/ Association of Local Air Pollution Control Officials (STAPPA/ ALAPCO) are conducting a program to evaluate exhaust emissions from light-duty gasoline vehicles. The proposed program consists of measuring particulate matter (PM) and other toxic components in exhaust emissions of 480 randomly selected, light-duty vehicles in the Kansas City Metropolitan Area. A sampling plan has been developed that will allow for the determination of the distribution of particulate matter (PM) and other emissions in the sampled fleet as well as the identification of the percent of high emitters. Data obtained from this program will be used to evaluate and update existing and future mobile source emission models (MOBILE6 and MOVES), evaluate existing emission inventories and assess the representativeness of previous PM emissions studies. The project team consists of the prime contractor, Eastern Research Group (ERG), and the following subcontractors: Bevilacqua Knight Inc (BKI), Desert Research Institute (DRI) and NuStats Partners L.P.

1.4.3 Project Task Description

The work to be performed by the Desert Research Institute (DRI) provides the sampling and chemical analysis support for the EPA-sponsored study to characterize exhaust emissions from light-duty gasoline vehicles in the Kansas City Metropolitan Area. The sampling and analytical laboratory services include those in Task 3.2 (specialized sampling and analytical needs for vehicle testing) and Task 4 (chemical speciation) of the Statement of Work for U.S. EPA Solicitation No. PR-CI-03-10697. These services include the following.

1. Provide and prepare sampling equipment and sampling substrates required for the collection of the samples listed in Table 7 of the Solicitation.
2. Provide and operate real-time monitors for the measurement of fine particulate mass and fine particle elemental carbon as shown in Table 11 of the Solicitation.

3. Collect sample on each vehicle tested and conduct laboratory analyses of samples as shown in Table 7 of the Solicitation.
4. Perform sample analysis for integrated PM mass, EC/OC, elements, ions, semi-volatile organic compounds, and gaseous air toxics base on a percent of samples estimates shown in Table 7 of the Solicitation.

1.4.4 Quality Objectives and Criteria

DRI is fully committed to an effective quality assurance/quality control (QA/QC) program for this project. DRI will ensure that measurement data shall meet specific data quality objectives (DQOs). These DQOs are summarized in Tables 1-2 through 1-6. The data quality indicators that are typically used to characterize these measurements are listed below.

Precision: Precision is the degree of mutual agreement among individual measurements under prescribed conditions. Measurements, where possible, will be made of analytical precision and overall precision. The project goal for overall precision will be $\pm 10\%$ expressed as the coefficient of variation (CV) as determined from collocated instruments. The goal for analytical precision is $\pm 10\text{-}30\%$ for analytes that are present in concentrations greater than 10 times their detection limit. The goal for analytical precision of gravimetric mass is $\pm 5\%$ CV as determined from replicate weighings.

Bias: Bias is the systematic or persistent distortion of a measurement process that causes error in one direction. Bias may be determined through performance audits and or by inter-comparisons of the performance of similar instruments.

Accuracy: Accuracy is the correctness of data and refers to the degree of difference between a measured value and a known or “true” value. For particulate measurements, there are no known true values. Relative accuracy may be determined by comparing a measured value with a presumed reference or standard. Sampler accuracy will be measured by performance (flow rate) checks and audits between the sampler and a certified flow meter. The goal is $\pm 5\%$ relative percent difference (RPD) or better. Since no true reference samples exist for the chemistry of airborne particulate matter, the accuracy of other speciated atmospheric components cannot be inherently determined. Analytical accuracy of the analytes will be determined by analyzing known reference materials in the laboratory.

Table 1-2. Analysis List of Inorganic Species for the Kansas City LDGV Emission Characterization Study

Species	Analysis Method ^a	MDL ^b (µg/filter)	Species	Analysis Method ^a	MDL ^b (µg/filter)
Chloride (Cl ⁻)	IC	1.5005	Zinc (Zn)	XRF	0.0144
Nitrate (NO ₃ ⁻)	IC	1.5005	Gallium (Ga)	XRF	0.0259
Sulfate (SO ₄ ⁻)	IC	1.5005	Arsenic (As)	XRF	0.0230
			Selenium (Se)	XRF	0.0173
Organic Carbon (OC)	TOR	2.7590	Bromine (Br)	XRF	0.0144
Elemental Carbon (EC)	TOR	2.7590	Rubidium (Rb)	XRF	0.0144
			Strontium (Sr)	XRF	0.0144
Sodium (Na)	XRF	0.9533	Yttrium (Y)	XRF	0.0173
Magnesium (Mg)	XRF	0.3456	Zirconium (Zr)	XRF	0.0230
Aluminum (Al)	XRF	0.1382	Molybdenum (Mo)	XRF	0.0374
Silicon (Si)	XRF	0.0864	Palladium (Pd)	XRF	0.1526
Phosphorus (P)	XRF	0.0778	Silver (Ag)	XRF	0.1670
Sulfur (S)	XRF	0.0691	Cadmium (Cd)	XRF	0.1670
Chlorine (Cl)	XRF	0.1382	Indium (In)	XRF	0.1786
Potassium (K)	XRF	0.0835	Tin (Sn)	XRF	0.2333
Calcium (Ca)	XRF	0.0634	Antimony (Sb)	XRF	0.2477
Titanium (Ti)	XRF	0.0403	Barium (Ba)	XRF	0.7171
Vanadium (V)	XRF	0.0346	Lanthanum (La)	XRF	0.8554
Chromium (Cr)	XRF	0.0259	Gold (Au)	XRF	0.0432
Manganese (Mn)	XRF	0.0230	Mercury (Hg)	XRF	0.0346
Iron (Fe)	XRF	0.0202	Thallium (Tl)	XRF	0.0346
Cobalt (Co)	XRF	0.0115	Lead (Pb)	XRF	0.0403
Nickel (Ni)	XRF	0.0115	Uranium (U)	XRF	0.0317
Copper (Cu)	XRF	0.0144			

^a IC=ion chromatography. AC=automated colorimetry. AAS=atomic absorption spectrophotometry.

TOR=thermal/optical reflectance. XRF=x-ray fluorescence.

^b Minimum detectable limit (MDL) is the concentration at which instrument response equals three times the standard deviation of the response to a known concentration of zero.

Additional Notes

1. Boron (specified in Section 3.3.2.2 of RFP) cannot be done by XRF.
2. XRF can be replaced with ICP-MS with greater sensitivity. However, cannot measure Sulfur and Chlorine and cost twice as much as XRF. Three Teflon filters can be extracted together with ICP-MS to reduce cost.

Table 1-3. Analysis List of Hydrocarbons and Carbonyl Compounds for the Kansas City LDGV Emission Characterization Study

Hydrocarbons			Carbonyl Compounds
Sum C2s	2,4-DiMePentane	m/p-xylene	Formaldehyde
propene	223TriMeButane	2MeOctane	Acetaldehyde
propane	1MeCypentene	3MeOctane	Acetone
isoButane	Benzene	Styrene+heptanal	Acrolein
1Butene+iButylene	CycloHexane	o-xylene	Propionaldehyde
1,3-Butadiene	4MeHexene	Nonene-1	Crotonaldehyde
n-Butane	2MeHexane	n-Nonane	Methyl Ethyl Ketone
t-2-Butene	23DiMePentane	iPropBenzene	Methacrolein
c-2-Butene	Cyclohexene	iPropCyHexane	Butyraldehyde/Acrolein RP
3-Me-1-Butene	3MeHexane	26DiMeOctane	Benzaldehyde
isopentane	3EtPentane	alpha-pinene	Glyoxal
1-Pentene	1-Heptene	36DiMeOctane	Valeraldehyde
2-Me-1-Butene	224TrMePentane	nPropBenzene	m-Tolualdehyde
n-Pentane	t-3-Heptene	mEtToluene	Hexanaldehyde
Isoprene	n-Heptane	pEtToluene	
t-2-Pentene	244TMe-1-Pentene	135TriMeBenzene	
c-2-Pentene	MeCyHexane	oEtToluene	
2-Me-2-Butene	25DiMeHexane	beta-pinene	
22DiMeButane	24DiMeHexane	124TriMeBenzene	
CycloPentene	234TrMePentane	n-Decane	
CycloPentane	Toluene	iButBenzene	
23DiMeButane	23DiMeHexane	sButBenzene	
MTBE	2MeHeptane	123TriMeBenzene	
2-MePentane	4MeHeptane	Limonene	
22-DiMePentane	3MeHeptane	Indan	
3-MePentane	225TMHexane	13diethylbenzene	
2-Me-1-Pentene	Octene-1	14diethylbenzene	
1-Hexene	11DMeCyHexane	12diethylbenzene	
n-Hexane	n-Octane	2-propylToluene	
t-2-Hexene	235TriMeHexane+Bgr.	iPrToluene	
2-Me-2-Pentene	24DiMeHeptane	n-Undecane	
c-3-Me-2-Pentene	44DiMeHeptane	1245tetraMeBenzene	
c-3-Hexene	26DiMeHeptane	1235tetraMeBenzene	
c-2-Hexene	25DiMeHeptane	1234tetraMeBenzene	
t-3-Me-2-Pentene	33DiMeHeptane	Naphthalene+Decanal	
MeCyPentane	EtBenzene	n-Dodecane	

a. Canister/GC-FID or MS with MLD = 0.1 ppbC.

b. DNPH cartridge/HPLC-UV with MDL = 0.1 ppbv.

Acrolein RP - rearrangement product of acrolein coelutes with butyraldehyde.

Table 1-4. Analysis List of Polycyclic Aromatic Hydrocarbons for the Kansas City LDGV Emission Characterization Study

Polycyclic Aromatic Hydrocarbons (PAH) ^a		Nitro-PAH ^b
Naphthalene	Anthrone	1-Nitronaphthalene
2-methylnaphthalene	9-methylanthracene	2-Nitronaphthalene
1-methylnaphthalene	Anthraquinone	2-Nitrobiphenyl
Biphenyl	3,6-dimethylphenanthrene	3-Nitrobiphenyl
2-Methylbiphenyl	A-dimethylphenanthrene	4-Nitrobiphenyl
3-Methylbiphenyl	B-dimethylphenanthrene	1,3-Dinitronaphthalene
4-Methylbiphenyl	C-dimethylphenanthrene	1,5-Dinitronaphthalene
1+2ethylnaphthalene	D-dimethylphenanthrene	5-Nitroacenaphthene
2,6+2,7-dimethylnaphthalene	E-dimethylphenanthrene	2-Nitrofluorene
1,3+1,6+1,7dimethylnaphth	1,7-dimethylphenanthrene	9-Nitroanthracene
1,4+1,5+2,3-dimethylnaphth	Fluoranthene	4-Nitrophenanthrene
1,2-dimethylnaphthalene	Pyrene	9-Nitrophenanthrene
Acenaphthylene	9-Anthraaldehyde	3-Nitrophenanthrene
Acenaphthene	Retene	1,8-Dinitronaphthalene
Dibenzofuran	1-MeFl+C-MeFl/Py	2-Nitrofluoranthene
A-trimethylnaphthalene	B-MePy/MeFl	3-Nitrofluoranthene
B-trimethylnaphthalene	C-MePy/MeFl	1-Nitropyrene
C-trimethylnaphthalene	D-MePy/MeFl	2,7-Dinitrofluorene
E-trimethylnaphthalene	4-methylpyrene	7-Nitrobenz(a)anthracene
F-trimethylnaphthalene	1-methylpyrene	6-Nitrochrysene
2,3,5+1-trimethylnaphthalene	Benzonaphthothiophene	1,3-Dinitropyrene
J-trimethylnaphthalene	Benzo(c)phenanthrene	1,6-Dinitropyrene
2,4,5-trimethylnaphthalene	Benz(a)anthracene	1,8-Dinitropyrene
1,4,5-trimethylnaphthalene	Chrysene/Triphenylene	6-Nitrobenz(a)pyrene
Fluorene	Benzanthrone	
A-methylfluorene	Benz(a)anthracene-7,12-dione	
1-methylfluorene	5+6-methylchrysene	
B-methylfluorene	7-methylbenz(a)anthracene	
9-fluorenone	Benzo(b+j+k)fluoranthene	
Phenanthrene	BeP	
Anthracene	BaP	
Xanthone	Perylene	
Perinaphthenone	7-methylbenzo(a)pyrene	
Acenaphthenequinone	9,10-dihydrobenzo(a)pyrene-7(8H)-one	
A-methylphenanthrene	Indeno[123-cd]pyrene	
2-methylphenanthrene	Dibenzo(ah+ac)anthracene	
B-methylphenanthrene	Benzo(ghi)perylene	
C-methylphenanthrene	Coronene	
1-methylphenanthrene		

a. TIGF/XAD and GC/MS with MDL = 0.02 ug/sample

b. TIGF/XAD and GC/MS with MDL = 0.01 ug/sample

Table 1-5 Analysis List of Hopanes, Steranes and Alkanes for the Kansas City LDGV Emission Characterization Study

Hopanes and Steranes ^a	Alkanes ^b
C27-20S5a(H),14a(H)-cholestane	norfarnesane
C27-20R5a(H),14β(H)-cholestane	heptylcyclohexane
C27-20S5a(H),14β(H),17β(H)-cholestane	farnesane
C27-20R5a(H),14a(H),17a(H)-cholestane & C29-20S13β(H),17a(H)-diasterane	octylcyclohexane
C28-20S5a(H),14a(H),17a(H)-ergostane	nonylcyclohexane
C28-20R5a(H),14β(H),17β(H)-ergostane	norpristane
C28-20S5a(H),14β(H),17β(H)-ergostane	hexadecane
C28-20R5a(H),14a(H),17a(H)-ergostane	heptadecane
C29-20S5a(H),14a(H),17a(H)-stigmastane	decylcyclohexane
C29-20R5a(H),14β(H),17β(H)-stigmastane	pristane
C29-20S5a(H),14β(H),17β(H)-stigmastane	undecylcyclohexane
18a(H),21β(H)-22,29,30-Trisnorhopane	octadecane
17a(H),18a(H),21β(H)-25,28,30-Trisnorhopane	nonadecane
C29-20R5a(H),14a(H),17a(H)-stigmastane	phytane
17a(H),21β(H)-22,29,30-Trisnorhopane	dodecylcyclohexane
17a(H),21β(H)-30-Norhopane	tridecylcyclohexane
17b(H),21a(H)-30-Norhopane	tetradecylcyclohexane
17a(H),21β(H)-Hopane	eicosane
17β(H),21a(H)-hopane	heneicosane
22S-17a(H),21β(H)-30-Homohopane	pentadecylcyclohexane
22R-17a(H),21β(H)-30-Homohopane	hexadecylcyclohexane
17β(H),21β(H)-Hopane	docosane
22S-17a(H),21β(H)-30,31-Bishomohopane	triaosane
22R-17a(H),21β(H)-30,31-Bishomohopane	heptadecylcyclohexane
22S-17a(H),21β(H)-30,31,32-Trisomohopane	octadecylcyclohexane
22R-17a(H),21β(H)-30,31,32-Trishomohopane	tetracosane
	pentacosane
	hexacosane
	nonadecylcyclohexane
	eicosylcyclohexane
	heptacosane
	octacosane
	nonacosane
	triacontane
	hentriacontane
	dotriacontane
	tritriacontane
	tetratriacontane
	pentatriacontane
	hexatriacontane

a. TIGF/XAD and GC/MS with MDL = 0.02 ug/sample

a. TIGF/XAD and GC/MS with MDL = 0.1 ug/sample

Table 1-6. Analysis List of Polar Organics for the Kansas City LDGV Emission Characterization Study

Analytical Standards	Classification	Potential Organic Marker Type	MDL microgram/sample
hexanoic acid	alkanoic acid		0.05
heptanoic acid	alkanoic acid		0.05
methylmalonic	alkanedioic acid	secondary aerosol	0.05
guaiacol	methoxy phenol	wood smoke	0.05
benzoic acid	aromatic acid		0.05
octanoic acid	alkanoic acid		0.05
butenedioic (maleic) acid	alkenedioic acid	secondary aerosol	0.05
butanedioic (succinic) acid	alkanedioic acid	secondary aerosol	0.05
4-me-guaiacol	methoxy phenol	wood smoke	0.05
me-succinic acid	alkanedioic acid	secondary aerosol	0.05
nonanoic acid	alkanoic acid		0.05
4-ethyl-guaiacol	methoxy phenol	wood smoke	0.05
syringol	methoxy phenol	wood smoke	0.05
glutaric acid	alkanedioic acid	secondary aerosol	0.05
2-methylglutaric	alkanedioic acid	secondary aerosol	0.05
3-methylglutaric acid	alkanedioic acid	secondary aerosol	0.05
decanoic acid	alkanoic acid		0.05
4-allyl-guaiacol (eugenol)	methoxy phenol	wood smoke	0.05
4-methyl-syringol	methoxy phenol	wood smoke	0.05
hexanedioic (adipic) acid	alkanedioic acid	secondary aerosol	0.05
cis-pinonic acid	aromatic acid		0.05
3-methyladipic acid	alkanedioic acid	secondary aerosol	0.05
4-formyl-guaiacol (vanillin)	methoxy phenol	wood smoke	0.05
undecanoic acid	alkanoic acid		0.05
isoeugenol	methoxy phenol	wood smoke	0.05
heptanedioic (pimelic) acid	alkanedioic acid	secondary aerosol	0.05
acetovanillone	methoxy phenol	wood smoke	0.05
dodecanoic (lauric) acid	alkanoic acid		0.05
phthalic acid	aromatic diacid		0.05
suberic acid	alkanedioic acid	secondary aerosol	0.05
levoglucosan	carbohydrate	wood smoke	0.05
syringaldehyde	methoxy phenol	wood smoke	0.05
tridecanoic acid	alkanoic acid		0.05
isophthalic acid	aromatic diacid		0.05
vanillic acid	methoxy acid	wood smoke	0.05
homovanillic acid	methoxy acid	wood smoke	0.05
azelaic acid	alkanedioic acid	secondary aerosol	0.05
myristoleic acid	alkenoic acid	meat cooking	0.05
myristic acid	alkanoic acid		0.05
sebacic acid	alkanedioic acid	secondary aerosol	0.05
syringic acid	methoxy acid		0.05
pentadecanoic acid	alkanoic acid		0.05
undecanedioic acid	alkanedioic acid	secondary aerosol	0.05
palmitoleic acid	alkenoic acid	meat cooking	0.05
palmitic acid	alkanoic acid		0.05
isostearic acid	alkanoic acid		0.05
dodecanedioic acid	alkanedioic acid	secondary aerosol	0.05
heptadecanoic acid	alkanoic acid		0.05
traumatic acid	alkenoic acid		0.05
1,11-undecanedicarboxylic acid	alkanedioic acid	secondary aerosol	0.05
oleic acid	alkenoic acid		0.05
elaidic acid	alkenoic acid		0.05
stearic acid	alkanoic acid		0.05
1,12-dodecanedicarboxylic acid	alkanedioic acid	secondary aerosol	0.05
8,15-pimaradien-18-oic acid	resin acid	wood smoke	0.05
pimaric acid	resin acid	wood smoke	0.05
nonadecanoic acid	alkanoic acid		0.05
isopimaric acid	resin acid	wood smoke	0.05
dehydroabietic acid	resin acid	wood smoke	0.05
abietic acid	resin acid	wood smoke	0.05
eicosanoic acid	alkanoic acid		0.05
heneicosanoic acid	alkanoic acid		0.05
docosanoic acid	alkanoic acid		0.05
tricosanoic acid	alkanoic acid		0.05
tetracosanoic acid	alkanoic acid		0.05
cholesterol	sterol	meat cooking	0.05

Detectability: Detectability is the low range critical value that a method-specific procedure can reliably discern. DRI determines the minimum detection limit as 3 times the standard deviation of field blanks or 3 times the standard deviation of the noise of an instrument when subjected to clean air

Completeness: Completeness is the percentage of valid data compared to the total expected data. For this project, the completeness objective for all species and measurements is 75%.

Representativeness: Representativeness is the degree to which data accurately and precisely represents a characteristic of a population, parameter variations at a sampling point, a process condition, or an environment condition. For this project, spatial and temporal data representativeness will be achieved by assuring that criteria are met for site selection and setup, and that air quality measurements and statistics are compiled.

Comparability: Comparability reflects how confidently one data set can be compared with another. Using similar reporting units and measurement times may enhance comparability. For a research project that will be testing state-of-the-art instruments and methods, comparability becomes more difficult to estimate. Under such circumstance inferential methods are used to assess comparability. These may include comparisons of related, but dissimilar measurements such as measurements that may represent both the gaseous and particulate phases of a constituent with measurements of only the particulate phase of that constituent. In addition, trend analyses may be used including, but not limited to, regression analyses, agreement with model results such as stochastic chemistry, or typical ratios of atmospheric parameters.

1.4.5 Special Training/Certification

The Principal Investigators and QA Manager have appropriate degrees, background, and experience appropriate for their roles in the project. Laboratory personnel have appropriate degrees in scientific fields and experience in performing the tasks required by this project such as extracting, analyzing, and reporting field data and sample analysis results. Site operators have appropriate scientific and technical degrees and experience in operating and maintaining a field monitoring and sampling site. Additional guidance about actual site operations for this project is provided to the site operators in the form of checklists, forms, SOPs, and other material forming part of this QAPP.

1.4.6 Documents and Records

This QAPP summarizes planned measurements, defines data quality indicators, and specifies data quality objectives. Field and laboratory SOPs developed for the Kansas City vehicle characterization measurements are followed, and revised as needed, for the duration of the study. Revisions made to SOPs during the study period are noted and archived for traceability. Remedial actions taken as a result of field, laboratory, or data audits are also be documented. This information will be incorporated into a summary of quality assurance as part of final project report delivery to EPA.

SECTION 2: SURVEY DATA ACQUISITION, PROCESSING, AND REPORTING

2.1 Data Acquisition Process

2.1.1 Sampling

Sampling is the selection of a set of units from a target population. This set of units is referred to as the sample. The choice of the sampling design will take into account many factors, including the desired level of precision of the information to be produced, the availability of appropriate sampling frames, the availability of appropriate stratification variables, the estimation methods that will be used, and the available budgets. Decisions about the survey frame should conform to the target population and contain minimal undercoverage and overcoverage (avoiding duplication). Frame creation, use, maintenance and monitoring will be implemented within operational and cost constraints.

When determining sample size, the required levels of precision needed for the survey estimates, the type of design and estimator to be used, as well as both sampling factors (e.g., clustering) and non-sampling factors (e.g., nonresponse) will be taken into account.

The vehicle fleet samples associated with the MARC households as well as the RDD households that participated in the incentives test have been reviewed. The vehicles represented in those random sample had a different distribution than what was originally specified in the work plan (see Table 2-1). Since differences between the "real" distribution of vehicles compared to the originally estimated distribution affects the efficiency of data collection, we will monitor status by quota type daily during phases 1 and 2 of the study to confirm that we are meeting the strata goals specified. To support this, we will be using reports similar to the "Status by Cohort Day" and "Status by Sample Type" provided in Appendix A.

Table 2-1. Sample Strata Specified in the Work Plan

Stratum	Vehicle Class	Age Class	Total Vehicles Tested	Regular Responders	Refusers
1	Truck	Pre 1980	50	42	8
2	Truck	1980 – 1990	100	84	16
3	Truck	1991 –1995	70	58	12
4	Truck	1996 and newer	40	33	7
5	Car	Pre 1980	40	33	7
6	Car	1980 – 1990	50	42	8
7	Car	1991 –1995	80	66	14
8	Car	1996 and newer	50	42	8
Total			480	400	80

In addition, the Kansas vehicle registration data has recently been obtained. Combined with the Missouri vehicle registration data, this will provide a second fleet validation source. We are analyzing these databases to determine sample size allocations based on an "optimal" allocation

strategy, which effects a disproportionate allocation in order to increase statistical precision beyond that achievable through proportionate stratified sampling. During implementation of the sampling, the size and characteristics of the actual sample will be compared to what was expected. Monitoring the sampling process in this way helps in identifying and correcting errors that can occur.

Appropriate sample control procedures are in place for monitoring data collection operations. Such procedures track the status of sampled units from the beginning through the completion of data collection so that survey managers and clients can assess progress at any point in time. Sample control procedures and feedback from them are also used to ensure that every sampled unit is processed through all data collection steps, with a final status being recorded. These procedures include:

- Close monitoring of participants who meet the scheduled appointment with daily adjustments in scheduling goals. Nustats staff will initially over-book to minimize no-shows and adjust bookings daily until the right number is booked to ensure 5 vehicles are tested daily. Nustats will also work with onsite technicians daily to negotiate changes in test dates, in consultation with participants, to maximize testing.
- Establishing stratum specific sample size targets and daily monitoring both scheduling and testing status with regard to those targets.
- Daily communications with BKI and ERG using the projects online scheduling system (monitoring scheduled participants and testing status).
- Use of a "continuous improvement" operations model in which the early vehicle recruitment performance will be used to fine-tune the overbooking factor (and, if necessary, adjust incentive offerings).

As mentioned above, an online scheduling system will be developed that will facilitate transfer of information between NuStats and onsite testing staff. This system will allow for scheduling of vehicles for testing in order to ensure cohort sampling goals are met. For a given day, NuStats will be able to specify, at minimum, the following information for each vehicle:

- Vehicle License Plate
- Owner Name
- Owner Address
- Owner Phone Number
- Owner Alternate Phone Number
- Incentive Offered
- Last Contact Date
- Miscellaneous NuStats Comments

Onsite technicians will be able to access information on the system via the internet to assist with contact of participants as necessary. During the course of testing, onsite staff will be able to update the following information to reflect current testing status:

- Test Completion Status
- “Drive-away” PAMS information, if selected
- Incentive paid
- Miscellaneous Onsite Team Comments

Control systems are in place to ensure the security of data transmission and handling, with a network security system that prevents loss of information (and the resultant loss in quality) due to system failures or human errors. Information regarding quality on any given research project are used to signal that collection procedures or tools should be changed in future projects.

2.1.2 Instrument Design

Questionnaires are designed with the following in mind: the statistical requirements of the project, the administrative requirements of data collection organization, the requirements for data processing and the nature and characteristics of the respondent population (such as identifying the correct incentive level to ensure adequate participation). Good questionnaires impose low respondent burden while remaining both respondent and interviewer-friendly. Survey design will maximize the efficiency of data collection, with a minimum number of errors, while facilitating the coding and capture of data and minimizing the amount of editing and imputation that is required.

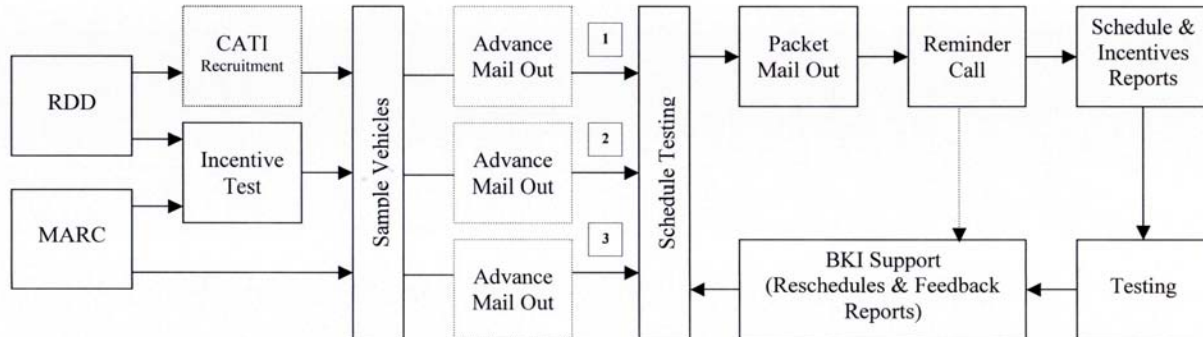
Introductions to the questionnaire will provide the subject of the research project, identify the sponsor or authority on whose behalf the project has been undertaken, explain the purpose, request the respondent’s cooperation, how the research data will be used, and what confidentiality protection will be afforded. The opening questions will be applicable to all respondents, easy and interesting to complete, and establish that the respondent is a member of the target population.

A wide range of methods will be used to test and evaluate the study instrument(s). In this case a pilot test was conducted to gain insight on the incentives that will be necessary to ensure participation in the vehicle testing. It also provided insight into how respondents react to the questionnaire (e.g., help identify poor question wording, errors in questionnaire layout or instructions, and problems caused by the respondents’ inability or unwillingness to answer the questions).

Even prior to conducting the pilot survey or the surveys in Phase I or II, a pretest was conducted for each (as part of interviewer training) that served as a “dress rehearsal” to observe how all the survey operations, including the administration of the questionnaire, worked together in practice.

A figure depicting data flow for the survey instrument is presented in Figure 2-1.

Figure 2-1. Survey Instrument Data Flowchart



2.1.3 Response and Nonresponse

Response patterns of two types are monitored under QA guidelines. Item response pertains to the number of data items answered by a respondent; unit response pertains to the number of sampled units that responded at all to the survey. Households will be considered non-responders if:

- they do not provide all vehicle information (year, make, model, and fuel type),
- they do not provide a mailable home address for delivery of the testing packet, or
- they miss more than two scheduled appointments.

Despite best efforts to maximize response, some nonresponse is virtually certain to occur. Nonresponse has two effects on the data: it contributes to an increase in the sampling variance of estimates as the effective sample size is reduced from that originally sought, and it contributes to bias of estimates when nonrespondents differ from respondents in the characteristics measured. For these reasons, response rates will be optimized to the degree that budget and time constraints allow.

To optimize response rates, research projects are designed to allow data to be provided using methods and formats that are convenient for respondents – not the survey organization. Since differences between respondents and nonrespondents can cause biases in the estimates, attempts are always made to determine if such differences exist. Although difficult to determine, this is done by linking to external data sources (for example, estimates from the U.S. Bureau of the Census), and by examining the responses of the nonrespondents who were converted with reluctance or during follow-up activities.

With client consent, one of two methods of compensating for nonresponse will be used: by means of sampling weight adjustment or through the use of imputation. For all projects, response and nonresponse rates will be reported using guidelines from established agencies (such

as the Council of American Survey Research Organizations or the American Association for Public Opinion Research).

2.1.4 Data Acquisition Methods

Data acquisition is any process whose purpose is to acquire or assist in the collection of data. Collection is often the most costly part of the survey process with significant influence on data quality. The effective use of available technology promotes improvement of the efficiency and quality of the data collection process. One example of this is the Computer Assisted Telephone Interviewing (CATI) technology that will be used in this study to interview respondents and collect data.

Interviewing is always done with surveyors who have the appropriate training and tools. As was addressed previously, prior to the initiation of the pilot study or either of the two phases of data collection, a training manual will be developed specifically for this study that includes background on the project, the objectives of the study, and a question-by-question guide that describes what will be asked of the respondents. This includes definitions of the incentives and other technical terminology. Each interviewer will participate in a training session that includes 2 hours conducting mock interviews before actually beginning the survey process. If the survey will be conducted in another language than English, interviewers will also participate in mock interviews in the alternative language as well. All training will be monitored and only those staff that exhibit mastery of the task will be allowed to conduct the survey.

Each data collection shift is monitored by an experienced data collection manager assigned to this project. These individuals track productivity, listen in and observe interviewers, and provide continual support to improve interviewer productivity. The EPA Project Manager or others are welcome to “listen-in” or visit the survey operations center to observe interviewing at any time.

Automated systems have been designed for measuring the quality and productivity of interviewing during every interviewing shift. Important data collection quality measures include refusal rates, interview completion rates, frequency of editing rejects, and number and type of corrections applied to the data. For this study, data review processes that provide feedback reports will be relied upon for managers and surveyors that contain information on frequencies of and causes of errors. Examples of these reports include daily productivity reports. So that the EPA Project Manager can adequately monitor the study’s progress on a daily basis during data collection, a password protected website can be set up for client access to monitor key productivity variables such as interview completion rates, cohort or quota completion, and other data.

2.2 Data Processing and Management (Review, Validation, and Verification)

2.2.1 Editing

Data editing is the application of checks that identify missing, invalid, or inconsistent entries or that point to data records that are potentially in error. In this study, the goals of editing are three-fold: to provide the basis for future improvements in survey designs and implementation (for

Phases I and II), to provide information about the quality of the survey data, and to tidy up the data for analysis.

While fatal errors (e.g., invalid or inconsistent entries) should be removed from the data sets in order to maintain our credibility and to facilitate further automated data processing and analysis, our culture guards against over editing which is not only costly in terms of financing, timeliness, and increased response burden, but can also lead to severe biases resulting from “changing” respondent reported information to fit some implicit model of data correctness.

Data is processed in a continuous fashion under a continuous data flow (CDF) model, which enables the moving of the editing step to the early stages of the survey process so that we can look upstream to reduce errors rather than cleaning up at the end. In editing data, automated procedures (such as edit check programs) are relied upon to the degree possible because with them editing can be done more expediently. Manual procedures are responsible for the high cost of editing, and we strive to find an appropriate balance between error detection and cost.

We typically work in conjunction with the client to identify the priorities for data editing, according to types or severity of errors or according to the importance of the variable or the reporting unit. We assign a high priority to learning from the editing process so that error prevention rather than error correction is the norm.

2.2.2 Imputation

Imputation is the process used to resolve problems of missing, invalid, or inconsistent responses identified during editing. This is done by changing some of the responses or missing values on the record being edited to ensure that a plausible, internally coherent record is created. Data will only be imputed with the client’s consent. Imputed values are flagged in the data set and clearly identify the methods and sources of imputation. The unimputed and imputed values of the record’s fields are retained for evaluation purposes.

2.2.3 Estimation

Estimation is the process that consists of assigning values to unknown population parameters using information from the data set. The parameters that are to be estimated can mostly be expressed as functions of population totals. Examples include simple descriptive statistics as well as more complicated analytical statistics such as regression coefficients. The quality of the computed estimates is in large part dependent on the preceding steps. Proper estimation conforms to the sampling design. To that end, sampling weights are incorporated in the estimation process. We attempt to keep statistical adjustments for nonresponse to a minimum because they may introduce a bias. Estimated standard errors or coefficients of variation are provided when reporting point estimates (e.g., a mean value) as a measure of precision. If appropriate, confidence intervals are provided.

2.2.4 Data Quality Evaluation

Data quality evaluation is the process of evaluating the final product in light of the original objectives of the statistical activity, in terms of the data’s accuracy and reliability. Such

information allows clients to make more informed interpretations of the survey results and is used to improve the way surveys are designed and implemented.

Data quality evaluations must meet the following minimum requirements: a measure of coverage error, a response rate and / or imputation rate, and measures of item nonresponse rates and / or sampling error for key characteristics. Managerial discretion is used to determine the appropriate amount of data quality evaluation for a given study. Factors considered include the uses of the data, the potential for error and its significance to the use of the data, the cost of the evaluation relative to the cost of the study, and whether or not the survey will be repeated or not.

Internal methods to evaluate data quality include:

- Checks of consistency with external sources of data,
- Internal consistency checks, for example calculation of ratios that are known to lie within certain bounds (e.g., sex ratios, trip rate estimates),
- Unit-by-unit reviews of the largest contributions to errors in estimates (e.g., geocoding precision),
- Calculation of data quality indicators such as nonresponse rates, imputation rates, and coefficients of variation,
- Debriefings with staff involved in the collection and processing of the data.

Sources of errors that are considered for evaluation include the following:

- Coverage errors, which consist of omission, erroneous inclusions, and duplications in the frame used to conduct the survey.
- Nonresponse errors, which occur when the survey fails to get a response to one, possibly all, of the questions.
- Measurement errors, which occur when the response received differs from the “true” value and can be caused by the respondent, the interviewer, the questionnaire, the mode of collection, or the respondent’s record-keeping system. Such errors can be random in nature, or can introduce a systematic bias into the results.
- Processing errors, which can occur at the subsequent steps of data editing, coding, capture, imputation, and tabulation.
- Sampling errors, which occur when the results of a survey are based on a sample of the population rather than the entire population.

2.3 Data Reporting and Presentation

2.3.1 Disclosure Control

Strict practices are observed to ensure and protect respondent data confidentiality. Team members adhere to practices advocated by the Council of American Survey Research Organizations and the American Association of Public Opinion Research. The following steps make up our confidentiality protection protocol:

- All project staff are given explicit training in the need to uphold confidentiality protocols and commitments. We train staff in reasons why this is such an important responsibility..
- All staff working on a given project (e.g., telephone supervisors and interviewers, application programmers, data processing staff, etc.) sign legally binding pledges of confidentiality as part of their employment contract.
- Only those personnel who have signed such pledges will have access to the confidential data, and then only on an as-needed basis.
- A unique number in the survey response database identifies each study participant so that names are not associated with responses to questions. Moreover, the data file containing the link between name and ID number will be stored separately from the data files containing question responses.
- Telephone numbers and all other potentially identifying information such as name, address, and SSN are purged from the data files and replaced with case identification numbers after interviewing and data processing have been completed.
- All confidential information will be stored in password-protected files by the holders of this information. Analytic files contain neither names, addresses, nor telephone numbers.
- During data collection and processing, access to all such files will be scrupulously controlled and we use a system of passwords to limit access to the files. These files are not accessible through Internet routes.
- We keep only a minimal amount of respondent-identifiable information is kept in the data files that are delivered.
- To maintain confidentiality and maximize respondent cooperation, all survey respondents will be assured that their survey answers will remain confidential and that no personal information that they give will be individually identified with them.

2.3.2 Data Analysis

Data analysis is the process of transforming raw data into useable information, often presented in the form of a published document (typically Microsoft Word) or presentation (typically

Microsoft Powerpoint), in order to add value to the statistical output. The basic steps in the analytic process consist of:

- examining the topic,
- asking meaningful questions,
- developing support for the answers, and
- communicating that story to the reader.

Quality Assurance is exercised in data analysis and reporting by:

- arranging ideas in a logical order and in order of relevance or importance;
- using headings, sub-headings, and sidebars to strengthen the organization of the report;
- keeping the language as simple as the subject permits;
- using graphs in preference to or in addition to text or tables to communicate the message; and
- helping readers understand the information in the charts by discussing it in the text.

When tables are used, special care is taken with the overall format, spacing, and the wording, placement, and appearance of the titles, row and column headings, and other labeling that contribute to the clarity of the data in the tables and prevents misinterpretation. All tables and graphs define the base used for the rates, and use only the number of significant digits that add to the utility of the data.

All reports and presentations are checked for consistency of figures used in the text, tables and charts, verification of the accuracy of external data, and simple arithmetic.

2.3.3 Documentation

Documentation constitutes a record of the statistical activity, including the underlying concepts, definitions, and methods used in the production of the data. It serves as a record for clients of what was done in order to provide a context for effective and informed use of the data. The level of detail provided in the documentation will depend on its intended audience, the type of data collection, the data sources, the analysis, range and impact of uses of the data, and the total budget of the study.

Documentation may include the following:

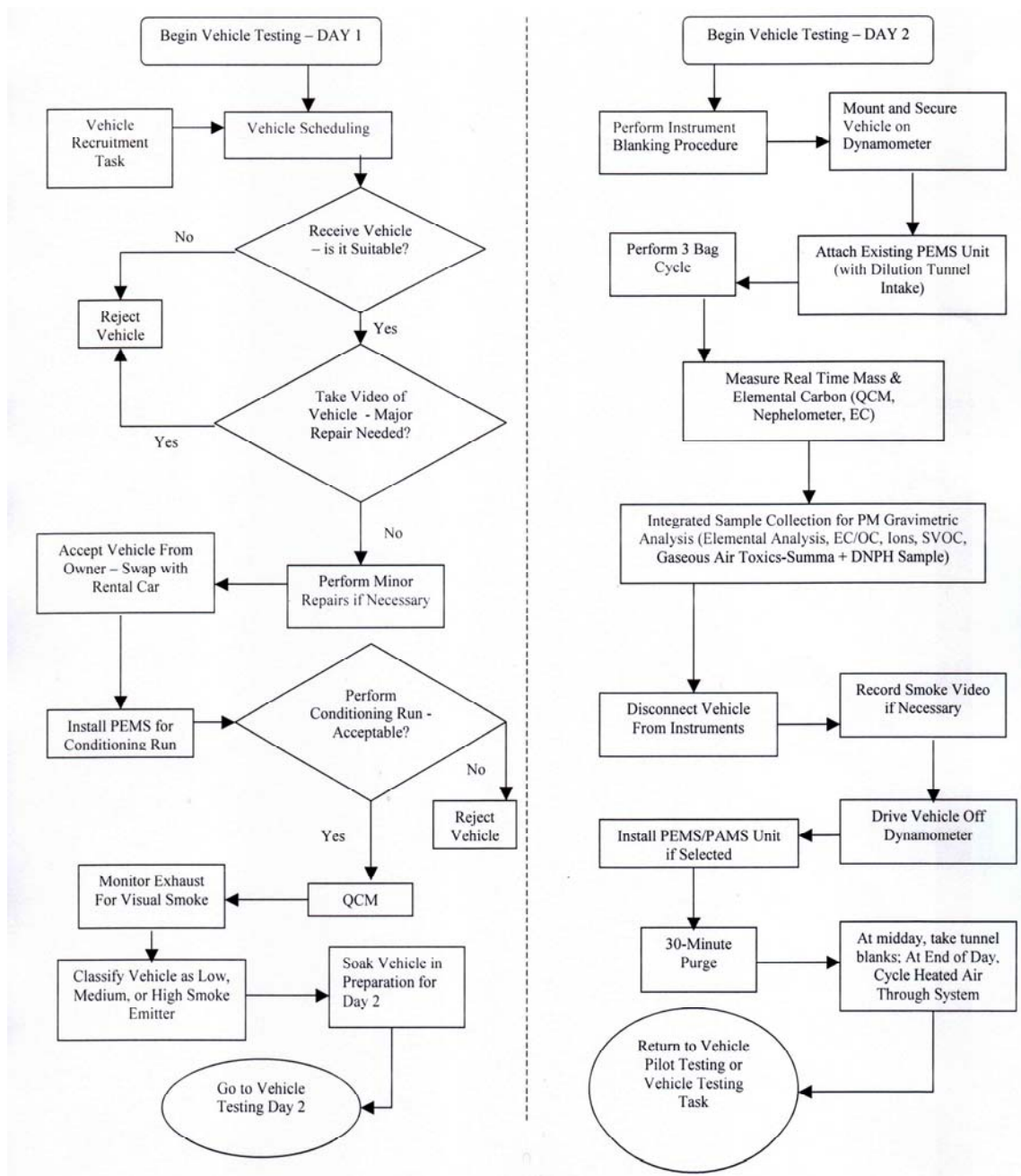
- Objectives;
- Content of the questionnaire;

- Tests of the questionnaire and the process;
- Methodological overview and discussion of technical issues;
- Data systems (data files structures, algorithms used to construct or define variables, weighting and expansion factors);
- Results of monitoring reports;
- Operations issues (training, feedback or debriefing reports;
- Implementation steps and challenges;
- Quality control indicators; and
- Data quality measures.

SECTION 3: DAY ONE VEHICLE INSPECTION AND CONDITIONING

The next two sections are organized temporally to follow an individual vehicle through the testing and analytical process. The flowchart presented in Figure 3-1 depicts the process.

Figure 3-1. Summary of Daily Activities



3.1 Vehicle Inspection

A number of vehicle inspections and vehicle data gathering activities are required to be performed during this study, in order to obtain vehicle information for the MSOD data table EQUIP_IN.dbf. Documentation for these activities may take the form of videotapes, interview questionnaires, checklists, hard copy data forms, and computer files. Each vehicle will receive a unique identification code which will be used to track documentation as it is gathered in the field.

While the vehicle is on site, all paper documentation generated will be maintained in a file folder inside the vehicle. Once the vehicle is returned to the owner, the vehicle documentation folder will be stored in a designated file cabinet located at the test site for the duration of the study, and at an offsite facility after the conclusion of the study. All vehicle data will be transferred to magnetic media to facilitate inclusion in the study database.

A staff member will be designated to co-ordinate all vehicle inspection procedures. The vehicle inspection coordinator will assign additional staff to perform many of the inspections. The coordinator will also review collected vehicle data to insure completeness and accuracy. Types of vehicle inspections to be performed are listed in Table 3-1.

Table 3-1. Vehicle Inspections

Inspection Type	Purpose
Initial Acceptance Inspection	To insure safety and test worthiness
Owner Questionnaire	Query for fuel and oil types
Video Tape	Document pre-existing damages
MSOD Compliant Vehicle Data Form	VIN, Engine family, Model, etc.
OBD Scan	OBD data
Visual	Smoke observations

Forms and checklists pertaining to the inspections listed above are provided in for reference Appendix A.

3.2 Vehicle Repair

Each test vehicle will be evaluated for repairs recently performed and for repairs which may need to be performed. The latter will serve primarily to ensure the vehicle can be safely operated on the road and dynamometer. If repairs are required, the vehicle owner will be notified and his/her permission will be obtained before repairs are performed. If the repairs cannot be performed by on-site personnel, the vehicle will be taken to a local repair shop by on-site personnel. Records of the repair will be maintained in the vehicle folder and a brief narrative of the repair will also be included. Repairs will also be documented in table sets associated with REPAR_IN.DBF in the MSOD. Following repair, the vehicle will be outfitted in the normal fashion, conditioned, and cued for testing.

Minor repairs that may be performed may include, but are not limited to, the following:

1. Replacement of unsafe, worn tires.
2. Replacement of belts or hoses.
3. Replenishment of fluids.
4. Brake service.
5. Replacement/repair of emission control components (oxygen sensor, EGR valve, etc.), so long as a short break-in period (approximately 100 miles) is feasible prior to testing.

Major repairs (either recently performed on the vehicle, or that the vehicle may require) that would cause us to exclude a vehicle from the test program may include, but are not limited to, the following:

1. Replacement of exhaust system. New exhaust systems would have to be conditioned for quite some time (> 300 miles) to remove cutting oils. These oils could bias the PM results.
2. Replacement of Catalyst. Conditioning of approximately 5000 miles would be required to age the catalyst.
3. Engine or engine component replacement or rebuild within the last 5000 miles (Including heads, valves, block, etc).

3.3 Vehicle Conditioning Run

Each test vehicle will be prepped the day before testing on a predetermined route that includes high speed accelerations, driving at freeway speeds, and driving at stop and go traffic patterns. This route is described in detail in Appendix A.

Prior to the conditioning run, a PEMS unit will be installed on the vehicle to monitor emission. The PEMS unit used for the preconditioning drive will undergo full a complete warm-up, zero and audit sequence to verify CO, CO₂, NO_x, and THC measurement accuracy. Calibrations will be performed as necessary to bring the PEMS into proper calibration. The concentrations and accuracy of all gasses used for auditing and calibrating will be recorded, and data files will be generated during all audits to preserve records of system accuracy and calibrations. All PEMS system flows and pressures will be verified and recorded, and ambient conditions as measured by the PEMS will be recorded and verified with independent measurements. A sample system leak check will be performed to verify sample system integrity, and a FID fuel leak check will also be performed. System temperatures (FID oven and chiller) will also be verified and recorded, and all sample rates and transport delay settings will be verified. Detailed installation guidelines, along with a checklist for the installation procedure, QC requirements are provided in Appendix A. This vehicle prep will be conducted for about 45 minutes. After the prep each vehicle will be soaked overnight for testing the next day. The dynamometer will be thoroughly warmed for at least 30 minutes and a coastdown will be performed at a specified load to check for

dynamometer load and inertia problems. Alternate vehicle prep and conditioning procedures may be used to meet specific field study goals. Inertia will be set before the vehicle is chained down. Both inertia and load for a particular vehicle model and year will be taken from tables supplied by EPA. Table inertia values will be rounded to the nearest available setting on the dynamometer.

SECTION 4: DAY TWO VEHICLE TESTING

4.1 Sampling Equipment

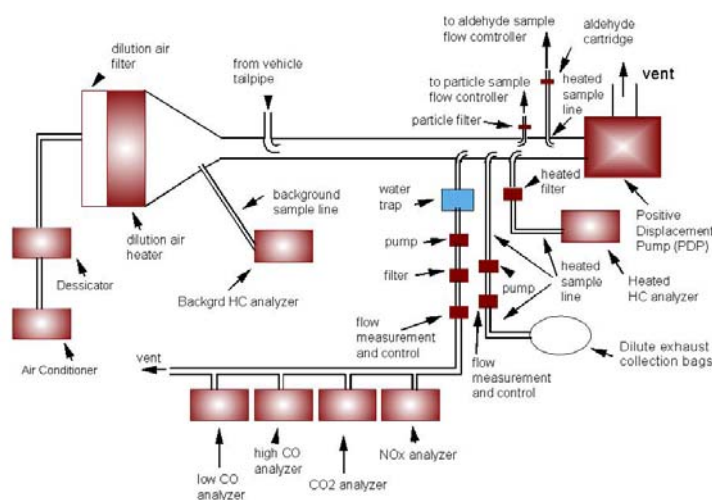
PEMS

Once the vehicle is mounted on the dynamometer, a PEMS unit will be installed on the vehicle to monitor undiluted emissions. Detailed installation guidelines, along with a checklist for the installation procedure, are provided in Appendix A.

Constant Volume Sampling (CVS)

Positive Displacement Pump-Constant Volume Sampling (PDP-CVS) system is used to dilute and transport the vehicle tailpipe exhaust to analyzers during the test. The PDP-CVS system employs an 8-inch diameter dilution tunnel with filtered dilution air. This system is graphically depicted in Figure 4-1. The CVS flow rate is sized to prevent water condensation over the range of ambient conditions and vehicle engine displacements encountered during testing. The existing test cell PDP is limited to about 540 SCFM. A spreadsheet model is available to accurately calculate second-by-second CVS water concentrations and dew points during transient speed tests. This model can be used to define the CVS system operating conditions (flow rates, temperatures) as a function of dilution air temperature and humidity, and vehicle emissions, that are necessary to avoid water condensation. A dilution air heater will also be used to avoid water condensation and loss of organic emissions in the sampling system. Condensed water will influence sampling system organic compound losses and can deteriorate sampling system flow control.

Figure 4-1. CVS Sampling System Schematic



The diluted exhaust is transported to the chemical analytical instrumentation through 1/4 inch O.D. tubing that is either heated (220° to 240°) to prevent water condensation, or when the compounds being analyzed are not water soluble (e.g., CO, NO), through a cryogenic water trap. The sample probes are located at least 10 tunnel diameters downstream from the position where the vehicle exhaust first encounters dilution air. Sample line flow rates must be adequate to achieve instrument response suitable for “real-time” measurement of the concentrations of the exhaust components of interest. Continuously integrated emission analyzers are required to have a response time of 1.5 seconds or less to 90% of a step change in concentration, where a step change is 60% of full scale or better. System response times between a step change at the sample probe position in the CVS tunnel and reading 90% of the change must be less than 10 seconds. Integrated bag samples may also be collected for each test phase permitting comparison of analytical results with those obtained by integration of the observed “real time” concentrations.

The potential for HC measurement artifacts exist resulting from absorption and subsequent release of HC from the dilution tunnel walls. As part of the dilution tunnel conditioning process, the dilution air heater and PDP are turned on at least 45 minutes prior to the days first test to purge the exhaust transfer line and dilution tunnel. Pumps at the analytical bench are also run to purge all sample lines. The PDP, dilution air heater and sample pumps run continuously (not shut down between tests) until conclusion of the days testing. Dilution tunnel HC concentrations are also monitored between tests to ensure that they return to ambient levels. Testing will not resume until dilution tunnel HC concentrations are within 15% of the ambient concentration.

CVS sample probes are designed to assure that continuous and adequate volume of sample is collected for analysis. Background and dilute exhaust sample line flows are monitored to assure no malfunction causing inadequate sample flow or analyzer response time deterioration such that time correlation for each emission constituent is no longer valid. The sample system will have an easily replaceable filter element to prevent particulate matter from reducing the reliability of the analytical system. The filter element will provide reliable sealing after filter element is changed. When the sample line is heated, the filter system is also heated.

The duct for transferring exhaust from the vehicle tailpipe to the CVS should be maintained as short as possible. The design should not cause static pressure in the tailpipe to change such that the emission levels are significantly affected. A change of ± 1.0 inch of water or less, as measured at the tailpipe, is acceptable. For dual exhaust systems, the design must insure that each leg maintains equal flow. Equal flow will be assumed if each leg is approximately equal in length ± 1 foot, and the area at the end of each leg is approximately equal.

All materials in contact with exhaust gas should be unaffected by and not affect the sample (i.e., the materials should not react with the sample, and neither should they taint the sample as a result of outgassing). Acceptable materials include stainless steel, Teflon®, silicon rubber, and Tedlar®.

Continuous Measurements

In addition to the regulated gas pollutants measured by BKI, DRI will provide continuous measurements of PM mass using an EPA-supplied Brooker Systems Model RPM-101 Quartz

Crystal Microbalance (QCM) and Thermo-MIE Inc. DataRam 4000 Nephelometer. Black carbon will be measured continuously with a DRI photoacoustic instrument and integrated samples will be collected and analyzed by DRI for PM gravimetric mass, elements, elemental and organic carbon, ions, particulate and semi-volatile organic compounds, volatile organic air toxics (benzene, toluene, xylenes, ethylbenzene, styrene, 1,3-butadiene, n-hexane, naphthalene, fo

The samples will be extracted from the BKI dilution tunnel through a low particulate loss 2.5 μ m cut point pre-classifier. The sample will be isokinetically partitioned among the continuous instruments and integrated air samples using a suitable sample distribution manifold. Separate Teflon and quartz filters will be collected for each of the three phases of the Unified Driving Cycle (UDC) using a sequential sampler. All other integrated samples will be collected over all three phases of the cycle, excluding the 10-minute soak period between phases 2 and 3.

The dynamometer dilution air will be dehumidified and heated to 47°C during testing. No residence chamber will be used for integrated samples and sampling streams will be maintained at 47°C. Photoacoustic instrument is an exception since it is designed to operate at below 35°C and black carbon concentrations should not be affected by temperature. The dilution tunnel will be purged between tests for a minimum of 30 minutes. PM mass will be monitored to ensure that background levels have stabilized after the prescribed purge period. A 60-minute dilution tunnel blank are collected once per day at the middle of the day.

Figure 4-2 presents a schematic of the sampling instrumentation.

4.2 Calibration of Equipment

Each piece of equipment or instrument will be calibrated and maintained to ensure accuracy within specified limits. Calibration and maintenance procedures are detailed in the Team Technical Standard Operating Procedures (SOPs) Manual. A copy of this and any other appropriate SOPs will be kept on-site. The equipment used by onsite personnel to collect samples will be calibrated according to Federal Register requirements (when applicable), manufacturer's procedures, or internal guidelines at recommended intervals. An equipment logbook will be kept on file that contains the calibration procedures and the results of each calibration, and will also serve as a permanent record of maintenance for the sampling equipment. This document will be available for review, if so requested.

4.2.1 Dynamometer, CVS, and Gas Analysis Equipment

SOPs for calibration are typically designated in the analytical methodology to be used but will be also be outlined in the laboratory's Quality Assurance Manual. Calibrations are also performed at regular intervals by onsite personnel. Calibrations to be performed for onsite equipment are presented in Table 4-1.

Figure 4-2. Kansas City Exhaust Measurement Flowchart

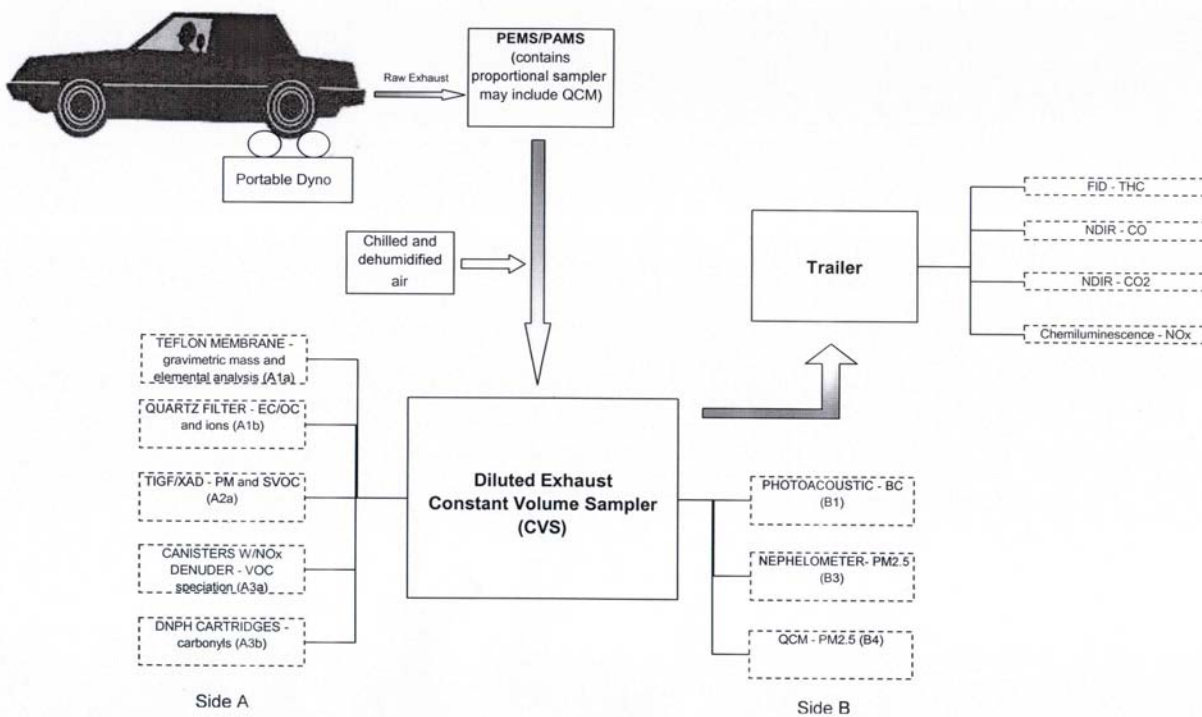


Figure 4-3. Testing Facility Layout

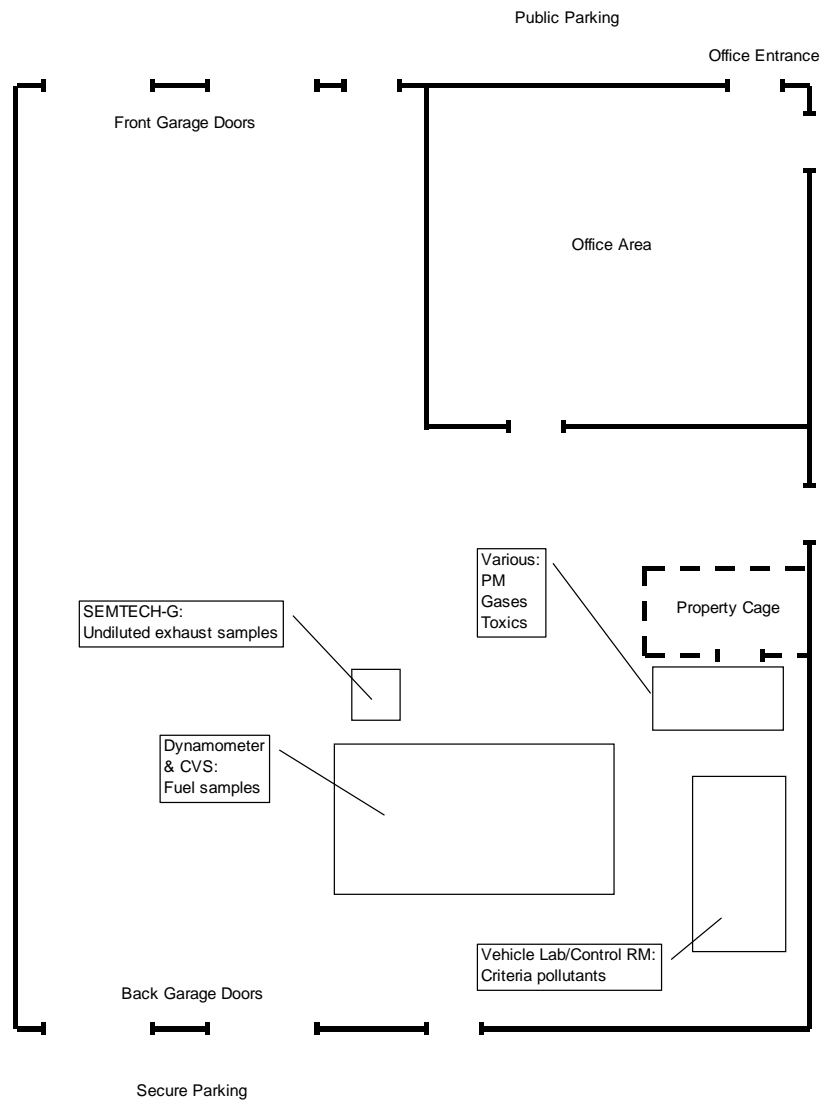


Table 4-1. Calibration and Performance Checks of Test Equipment and Analytical Instrumentation

Parameter	CFR Procedure	Time Period
DYNAMOMETER		
Calibration	86.118.78	Initial
Performance Check	86.118.78(b)	Daily
CONSTANT VOLUME SAMPLER (PDP-CVS)		
CVS system verification	86.119.90(c)	monthly
THC ANALYZER		
Response Optimization	86.121.90(a)	Initial
Multipoint calibration	86.121.90(b)	initial/monthly
Zero and Span Check	86.140-94	pre/post test
*Blind Audit Sample	-	as available
CARBON MONOXIDE ANALYZER		
H ₂ O and CO ₂ interference check	86.122-78(a)	Initial
Multipoint calibration	86.122-78(b)	Initial/monthly
Zero and Span Check	86.140.94	pre/post test
*Blind Audit Sample	-	as available
OXIDES OF NITROGEN ANALYZER		
Multipoint calibration	86.123-78(b)	Initial/monthly
Zero and Span Check	86.140.94	pre/post test
*Blind Audit Sample	-	as available
CARBON DIOXIDE ANALYZER		
Multipoint calibration	86.124-78	Initial/monthly
Zero and Span Check	86.140-94	pre/post test
* Blind Audit Sample	-	as available

* If available

When any of the parameters, accuracy and/or precision exceeds applicable boundaries (as specified in the CFR procedures listed above), then vehicle testing will cease and an investigation will be conducted to determine the cause of the problem. Testing will resume only when the problem is corrected and the parameter values are within the stated QC objectives. Instrument drift over a period of time, such as the time between calibration and sample analysis, is considered a component of measurement accuracy and must be reported. The precision is defined by evaluating the degree of mutual agreement among individual measurements made under prescribed like conditions.

The following narrative demonstrates SOPs and research protocol methods (RPMs) for some of the more critical instrumentation and test methods to be used in this project. The calibrations are included for the dynamometer operation, as well as calibrations for each of the instruments involved in the project.

Dynamometer Calibration

To ensure proper dynamometer simulation, speed and torque measurement and readout systems will be periodically calibrated. A suggested calibration schedule would include calibration just prior to transport to the field and then again just after initial setup in the field. In addition, calibrations shall be performed when daily coastdown tests so indicate the need.

Calibration of Dynamometer Roll Speed

Dynamometer speed will be calibrated using a Phototachometer to determine roll rpm. Using a vehicle to motor the dynamometer at a constant speed, the roll rpm shall be measured and the corresponding speed in mph determined. Simultaneous readings will be taken from the dynamometer's speed meter. Initial calibrations will be made at 10, 20, 30, 40, 50, and 60 MPH. Thereafter, daily calibration checks will be made at 50 MPH. Detailed instructions on speed signal calibration and adjustments are found in section 1.4.2 of the operator's manual.

Torque Cell Calibration

The dynamometer torque cell will be calibrated using the dead weight method as described in detail in section 1.4.3 of the operator's manual. A torque arm arbor and 3 weights are provided for this purpose.

Coastdowns

Coastdown tests are conducted for two purposes: 1) To establish a reference table of actual vs. indicated horsepower @ 50 MPH, and 2) to verify dynamometer calibration on a daily basis. A new reference table of actual vs. indicated horsepower @ 50 MPH will be made any time mechanical components of the dynamometer (including PAU fluid) are changed or altered. To construct the table, a series of coastdown tests will be performed at a variety of inertia and load settings. Coastdown times obtained are used to compute actual horsepower, which are in turn compared to indicate horsepower (by polynomial regression) to generate the table. Thereafter, coastdown tests will be performed on a daily basis (beginning of each day) on a thoroughly warmed up dynamometer. Daily coastdown times will agree within 1 second of reference times. If not, corrective action will be taken. As an initial step, speed and torque cell calibrations will be checked.

The coastdown test will be performed as outlined in the Code of Federal Regulations (CFR) 40 part 86. Speed trigger points of 55 and 45 mph are used. In order to perform a coastdown test, a vehicle will be used to motor the rolls to a speed above the high trigger point. At that time, the vehicle will be raised and the rolls allowed to coast down from 55 to 45 MPH. Coastdown time will be recorded and used to calculate horsepower absorbed @ 50 MPH. Detailed instructions on conducting the coastdown tests are given in Section 1.4.4 of the operator's manual.

For special high speed cycles, trigger points of 70 and 15 mph are used. In performing these special coastdown tests, a vehicle will be used to motor the rolls to a speed above the high trigger point, usually 73 mph. At that time, the vehicle is raised and the rolls allowed to coast down

from 70 to 15 mph. Coastdown time will be recorded and used to calculate speed vs. load curves for 70 to 15 mph.

Maintenance

Maintenance of the dynamometer will be carried out on a routine basis. Periodic checkups will occur at 1000-hour intervals or annually. Maintenance will be carried out in accordance with the Clayton Instruction Manual.

All laboratory equipment is on a preventative maintenance schedule. The most important preventative maintenance tool is the systematic performance check of the instruments. When an instrument is not performing to standards, the problem is investigated and corrected before it becomes significant.

All major laboratory equipment (GC/MSs, HPLC, ASE extractor) are on service contracts with the original manufacturer (Varian, Waters, Dionex, respectively). The contracts provide annual or biannual preventative maintenance by the manufacturer's service technician and immediate on-site response to any service call within 48 hours of notification of the manufacturer.

Several laboratory personnel have extensive experience working with all the major laboratory equipment, and extensive support facilities (electronics and machine shops, and QA lab with standard reference materials, etc.) are available. These personnel and facilities ensure the continued operation of all analytical laboratory instruments.

CVS Operation

The CVS system consists of an 8-inch dilution tunnel, particulate/charcoal inlet filter, and a positive displacement pump (PDP) operated to draw approximately 540 CFM of diluted exhaust gas through the system. Flow through the system during a test phase is a function of the volume swept per pump revolution, pump rpm, and the inlet pressure and temperature. Therefore, measurement of these four variables is needed to correctly calculate the flow.

Calibration of CVS

Volume per pump revolution, or V_o , is determined from propane injections that are conducted periodically in accordance with 86.119-78 paragraph (c) of 40 CFR July 1, 1983. Under normal circumstances, V_o , once determined, is not subject to change. The temperature and pressure measurements at the blower inlet will be taken using transducers which are periodically calibrated to insure accurate and precise values. PDP rpm will not be measured on a per test basis, but will be checked periodically (at least once daily) using a phototachometer.

Preventative Maintenance

The CVS dilution air filter pak will be changed whenever the pressure drop across the filter becomes excessive. This condition occurs when it is no longer possible to maintain exhaust line pressure within +/- 6 inches of water.

Driving Cycle Simulation

The test vehicle will be operated by a driver over a specified driving schedule on the dynamometer. The driver will follow a speed vs time trace on a driver's aid which establishes a speed error band within which vehicle speeds are controlled. Following the test, an indication will be given of the number of driver violations. A violation occurs when the vehicle speed is outside the error band for two or more seconds. Generally, violations resulting from inability of the vehicle to keep up with the test cycle will be disregarded.

Drivers Aid Speed Check

At the time the dynamometer speed calibration is carried out, indicated speed on the driver's aid will also be checked. Zero and span adjustments to the driver's aid will be made if the driver's aid speed signal does not agree with actual speed.

Measurement of Diluted Exhaust Gases

The four routinely measured automobile or truck exhaust emissions are HC, CO, CO₂, and NO_x. Concentrations of these gases will be measured in exhaust gas which has been diluted with a constant volume sampler (CVS). During the test, concentrations in diluted exhaust will be measured and logged on a real time basis (1 sample per second). At the conclusion of a test, with the vehicle's engine off, the ambient air will also be measured for background concentrations of HC, CO, CO₂, and NO_x. Average gaseous concentrations per test will be computed, background corrected and used per the CFR 40, for mass emission determination.

Calibration of Exhaust Gas Analyzer

All analyzers used in the measurement of HC, CO, NO_x, and CO₂ shall be calibrated in accordance with requirements 86.121-82, 86.122-78, 86.123-78, and 86.124-78 respectively, all of which can be found in 40 CFR July 1, 1983. These procedures include periodic multipoint calibrations using NIST gases and zero and single point span checks before each dynamometer test.

Operation and Maintenance of Exhaust Gas Analyzers

All analyzers shall be operated and maintained in accordance with their respective operating manuals. Deviations from these procedures will be documented in the Lab Notebook.

Analytical Gases

Analytical gases must meet the requirements of 86.114-94 of 40 CFR July 1, 1998. Accordingly, calibration gases in the laboratory are traceable within 1 percent of NIST gases, while span gases will be accurate to within 2 percent of true concentration (NIST gases). The reference followed for naming cylinder gases as calibration standards is EPA Protocol No. 2 which is entitled "Traceability Protocol for Establishing True Concentrations of Gases Used for Calibration and Audits of Air Pollution Analyzers", June 15, 1978.

Multipoint Calibrations

All regulated emissions instrumentation will be subjected to monthly multipoint calibrations to ensure response linearity. THC, FIDs, and NOX chemiluminescent analyzers are inherently linear over the analysis ranges normally used, while CO and CO₂ NDIRs are linearized by electronic methods and therefore subject to drift. Procedures for multipoint calibration are identical for each method. The response of each analyzer will be adjusted for appropriate response to zero gas and a full-scale calibration gas. With no further adjustments, down-scale concentrations will be introduced to the instrument and responses recorded. Down-scale concentrations of 90, 80, 70, 60, 50, 40, 30, 20, and 10% of full scale will be generated by dynamically diluting the full-scale calibration gas with a 10-point gas divider. Linear regression techniques will be used to define a best-fit linear curve to the data. Actual concentrations for each down-scale point will then be compared to concentrations calculated from instrument response and curve coefficients. If the calculated concentration deviates by more than 2% from the actual concentration, corrective action is required.

Zero/Span

Immediately before analysis of the CVS bags, each instrument will be zeroed and spanned by using appropriate zero and span gas. Span gases will be accurate to $\pm 2\%$ of true concentration (as referenced to NIST standards). Prior to zeroing and spanning, the CVS sample will be “sniffed” to ensure analysis will be done on the proper instrument range. Range control, zero/span, and analysis of the CVS bags are automated to reduce potential for operator error.

Analytical Systems

Prior to analysis, analytical systems (i.e., GC/ECD/FID, HPLC, GC/MS, and GC/IRD/MSD) are checked for purity and are certified clean (less than 0.1 ppbv of targeted compound). Quality control in the laboratory includes instrument calibration for each batch of samples analyzed, replicates of standards, and analysis of approximately 10% of the samples for estimate of analytical precision (historically less than 6%).

Primary reference standards are traceable to a NIST Standard Reference Material (SRM). For canister hydrocarbon speciation by GC/FID, a NIST SRM 1805 is used consisting of 254 ppb of benzene in nitrogen. In addition, NIST SRM 2764 (245 ppb of propane in air) is used for calibrating the light hydrocarbon analytical system. For halogenated compound measurements, a NIST-traceable standard mixture of 39 compounds is purchased from Scott Specialty Gases and diluted for calibration. For VOC measurements by the GC/MS system, a 74 compound mixture in low ppb level (Air Environmental, Inc., Denver, CO), traceable to the NIST SRM 1805, is used for calibration. For PAH measurements, a NIST SRM 1647 with the addition of other compounds not present in the mixture is used.

Gas cylinders of helium, nitrogen, hydrogen, and ultra zero air (all UHP grade from best sources available) are used for the analytical systems. From a single analysis, the GC/IRD/MSD system gives three dimensions of data for positive compound identification: retention times, infrared spectra, and mass spectra. Unknown compounds are identified by matching corresponding data

of known standards. The current inventory of reference samples consists of over 250 single- and multi-component reference samples and includes most of the compounds of interest in this project.

The analytical systems are calibrated initially by multipoint calibration (i.e., three levels plus humid zero air) and checked regularly by a one-point calibration using appropriate NIST SRM or other standard. The day-to-day reproducibility of $\pm 10\%$ is acceptable for either standard. Control charts are used for assessing analytical system performance.

Samples that fall outside the calibration range are diluted until bracketed by the calibration curve. Instrument responses to calibration standards for each parameter are analyzed using a least squares linear regression. The calibration must generate a correlation co-efficient (R^2) of 0.99 to be acceptable.

During the course of analysis, calibration standards are routinely analyzed to ensure that the instrument response has not changed. The criterion of $\pm 10\%$ of the expected response is used by the analyst to determine whether the instrument must be recalibrated. Retention time windows for each analyte are established prior to analysis and re-established continuously throughout the course of the analytical period.

The QA Manager conducts a field and laboratory systems audits, a laboratory performance audit and/or interlaboratory comparisons, and four field performance audits. Systems audits examine all phases of measurement and data processing to determine that the SOPs are followed and that operational staff is properly trained. The systems audit is intended to be a cooperative assessment resulting in improved data, rather than a judgmental activity. Performance audits establish the extent to which data specifications are being achieved in practice and evaluate measurement accuracy against independent standards. The field systems audit is conducted at the beginning of the project after all equipment is installed and operating. It will be followed by the first field performance audit. These audits will identify deficiencies and implement remedial actions. Subsequent field performance audit results will be used to define accuracy of field measurements.

Laboratory audits present standards with known concentrations to each laboratory process. These standards are analyzed according to normal procedures and the results will be compared with the standard values. In some cases, however, NIST standards are not available (e.g., elemental carbon, organic carbon). In such cases, interlaboratory comparisons are an effective audit tool. Audit strategies, issues, and procedures are described in detail in respective SOPs.

In the case of a failure of a performance or technical systems audit, written notification including the details of the recommended corrective action will be sent from the audit team to the project PI and to the QA Manager. The PI - in collaboration with the QA Manager - will determine the party responsible for taking corrective action and will verify any work completed. All audits will be reported in the Quality Assurance Final Report, which will be submitted as an attachment to the Project Final Report.

Analytical procedures that may be required for the accomplishment of the Statement of Work tasks are listed in Table 4-2. All QC requirements designated in these methods will be met. For

required tasks not described in an EPA- or ASTM-approved method, SOPs will be required and archived. A summary of the SOPs currently in use for these studies is provided in Table 4-2. These SOPs are stand- alone documents and are not included with this document.

Table 4-2. Standard Operating Procedures to Characterize Emissions

Analytical Measurement	Standard Operating Procedure
Regulated Emissions	<u>Federal Register</u> : Standards for Emissions
CVS Water Condensation	Procedures for Determining Constant Volume Sampling System Water Condensation
Thermocouples	Procedures for Calibration of Thermocouples

Mr. Richard Snow is responsible for the analytical equipment for the Transportable Dynamometer system should a failure occur. In the case of an electronic malfunction in the analytical equipment, the usual repair method is for an onsite technician to contact the equipment or instrument manufacturer. With the assistance of the manufacture's service departments, Mr. Snow has successfully performed troubleshooting and repair of analytical equipment. The assistance of an electronic engineer(s) for troubleshooting instrument problems and diagnosing individual component problems that may need replacing, such as diodes, resistors, circuit boards and capacitors, etc is available if necessary. In extreme cases, the manufacturer's service representative will be required to travel onsite to make the required repairs. The repair of any analytical equipment will be recorded in the instrument laboratory maintenance logbook. The entry will describe the problem and remedy.

4.2.2 PEMS

A PEMS unit will be used to concurrently measure vehicle exhaust emissions during dynamometer testing. This unit will undergo a complete verification, audit, and calibration sequence (calibration only as necessary), for each vehicle tested. This sequence will be identical to that as described in Section 3.4. All audit and calibration information will be recorded on data collection sheets, as shown in Appendix A.

4.3 Sampling Media Preparation and Certification

Teflon and Quartz Filters

Teflon filters are equilibrated for weighing only after they pass acceptance testing by XRF. The filters are equilibrated for a minimum of four weeks before performing initial weights. At least two filters from each lot (typically 100 filters) received from the manufacturers are analyzed for species to verify that pre-established specifications have been met. Lots are rejected if they do not pass this acceptance test. Each filter is individually examined over a light table prior to use for discoloration, pinholes, creases, or other defects. In addition to laboratory blanks, 5 to 10% of all filters will be designated as field blanks to follow handling procedures, except for actual sampling.

Quartz fiber filters absorb organic gases from ambient air and organic artifacts from the manufacturing process. By pre-firing the quartz filters before sampling, these absorbed gases and artifacts are reduced to constant insignificant levels. The filters are pre-fired in preparation for thermal/optical reflectance carbon (TOR) analysis, which is a thermal desorption process subjecting the filters to temperatures between 25°C through 800°C. Therefore, the filters are pre-fired at 900°C to remove all possible interferences with the TOR analysis. Sets of filters with levels exceeding 1.5 mg/cm² for organic carbon and 0.5 mg/cm² for elemental carbon are re-fired or rejected. Pre-fired filters are sealed and stored in a freezer prior to preparation for field sampling.

PUF/XAD/PUF Cartridge and Filter

DRI will also acceptance test TIGF filters and XAD-4 resin packs. XAD-4 is placed in a Buchner funnel and rinsed with distilled water three times followed by technical grade methanol 3-4 times, and again three times with distilled water. It is then further cleaned by Soxhlet extraction for 48 hours with methanol, followed by Dionex ASE extraction for 15min/cell with ~170 mL of dichloromethane (CH₂Cl₂) and acetone at 1500 psi and 100 C. The XAD-4 is then dried in a vacuum oven at -15 to -20 in Hg and 50° C. Cleaned XAD-4 is transferred to clean 1L glass jars and stored in aluminum cans with activated charcoal. The TIGF filters will be cleaned by sonification in CH₂Cl₂ for 30 minutes, followed by another 30-minute sonification in methanol. Then they will be dried, placed in aluminum foil, and labeled. Each batch of precleaned XAD-4 resin and ~10% of precleaned TIGF filters. The XAD-4 resins are assembled into glass cartridges (50 g of XAD between two screens), wrapped in aluminum foil and stored in a clean freezer prior shipment to the field. This procedure is described in detail in the DRI Standard Operation Procedure: Analysis of Semi-Volatile Organic Compound by GC/MS.

Carbonyl DNPH Cartridges

For commercial 2,4-dinitrophenylhydrazine (DNPH) cartridges (Waters Sep-Pak XpoSure Aldehyde Sampler), DRI will analyze 5% of the purchased cartridges to ascertain the blank variability. Another 5% will be analyzed if the initial data show that the blank variability is marginally acceptable (at or slightly higher than 1/3 of the desired lower quantifiable limits (LQL)). This is necessary because unless cartridges are prepared in-house there is no other indication of the quality of the product, such as reagent and blank cartridge purity. In carbonyl measurements, the blank variability is the single most important factor in determining the lower quantifiable limit of the measurement; other factors such as flow rate, and analytical variability are secondary in importance.

Canister Cleaning and Preparation

Prior to sampling, the canisters will be cleaned by repeated evacuation and pressurization with humidified zero air, as described in the EPA document "Technical Assistance Document for Sampling and Analysis of Ozone Precursors" (October 1991, EPA/600-8-91/215). Six repeatable cycles of evacuation to ~0.5 mm Hg absolute pressure followed by pressurization with UHP humid zero air to ~15 psig is used. Our method differs from the EPA method by heating the canisters to 140°C during the vacuum cycle. At the end of the cleaning procedure, one

canister out of the six per lot is filled with humidified UHP zero air and analyzed by the GC/FID method. The canisters are considered clean if total NMOC concentrations are less than 20 ppbC.

Sampling System Cleaning

Sampling systems with internal surfaces upstream of the collection media (e.g., canister sampler) must be cleaned and certified for cleanliness prior to sampling. The canister sampling systems are cleaned prior to field sampling by purging with humidified zero air for 48 hours, followed by purging with dry UHP zero air for one hour. Each canister sampling system is certified clean by the GC/FID analysis of humidified zero air collected through this sampling system. The system is considered clean if the concentration of any individual targeted compound is less than 0.2 ppbv, and total NMOC concentration is less than 10 ppbC. In addition, a QA sample consisting of a blend of organic compounds of known concentration in clean humidified zero air is collected through the sampling system and analyzed by the GC/FID method. The sampling system is considered non-biasing if recoveries of each of the QA compounds are in the range of 80-120% (EPA document EPA/600-8-91/215).

4.4 Testing, Inspection, and Maintenance of Equipment

4.4.1 Dynamometer and Associated Gas Analysis

Prior to deployment in the field, each instrument is bench-tested and inspected in the laboratory. Maintenance frequency varies depending on instrument. Instrument and equipment testing, inspection, and maintenance requirements are discussed in detail in the SOPs.

Procedures and schedules for preventive maintenance of field sampling equipment are the responsibility of onsite personnel. Maintenance procedures and calibrations will be performed periodically on each piece of analytical laboratory equipment to ensure accuracy within DQOs. These procedures and frequency of performance are designated in the individual instrument manuals or in the laboratory Quality Assurance Manual.

4.4.2 PEMS

Prior to project deployment, current firmware will be downloaded onto all PEMS units, and all host computers will be updated with current operating software. Sampling system filters will be checked and replaced as necessary. All systems will undergo a full audit and calibration sequence to ensure they are operating within allowable limits. All system operating parameters will be monitored throughout testing, as listed in Section 3.4 and detailed in Appendix A. PEMS units will be removed from service if any out “out of range” operating conditions are identified, and all “out of range” conditions will be corrected prior to placing the unit back into service. All pertinent audit, verification, and calibration information will be recorded on data collection sheets included in Appendix A.

4.5 Obtaining Background Levels for Gas Analysis Equipment

THC background levels used for emission rate calculations are measured continuously during all test phases with a dedicated FID. Carbon Monoxide, CO₂, and NO_x background levels used for

emission rate calculations are measured during the engine-off soak period between phases 2 and 3 for multi phase cycles or after completion of the test for single phase cycles, using the same instrumentation that measures diluted exhaust during the test phases.

Background levels are also monitored prior to each test to ensure reasonable ambient conditions exist at the start of the test. Background THC, CO, NOx, and CO2 concentrations in the dilution tunnel are recorded by the regulated emissions bench operator within 2 minutes prior to the start of the day's first test. These are designated background reference concentrations. These reference levels should be at or below typical ambient levels for the area. Backgrounds are measured before each subsequent test and compared to the reference concentrations. If these measured concentrations are greater than 15% above the reference concentrations, corrective action must be taken. If the increase in background concentration is due to an increase in the ambient background level (not influenced by station exhaust or spillage) and cannot be corrected, a new set of background reference concentrations may be established and testing may resume.

4.6 Securing the Vehicle on the Dynamometer

The transportable test cell includes a Clayton model CTE 50-0 water brake chassis dynamometer mounted on a Freuhauf trailer. The dynamometer is coupled to a Clayton direct drive variable inertia flywheel system allowing vehicle testing at inertia weights of 1750, 2000, 2250, 2500, 2750, 3000, 3500, 4000, 4500, 5000, and 5500 pounds. Vehicle road load (Hp @ 50 MPH) is manually set using the driver's pendant switch.

All utilities necessary for dynamometer operation (compressed air, cooling water, and electrical power distribution) are self-contained on the trailer. A compressor provides compressed air for operation of the dynamometer's roll brake, vehicle lift, and flywheel clutches. Compressed air is also available at each corner of the trailer via quick-disconnect fittings for adjusting test vehicle tire pressure. A closed-loop water system provides the dynamometer's power absorption unit with both cooling and load water. The water system includes a SPA pump, a 12-gallon storage tank, and a liquid to air heat exchanger. The water system is normally filled with a 50/50 mixture of water and antifreeze to prevent freeze damage in colder weather. The air compressor and water system are electrically wired into the test cell's electrical power distribution box. Electrical outlets, also wired to the power distribution box, are located underneath the trailer for miscellaneous equipment with either 110 VAC and 220 VAC power requirements.

The vehicle is maneuvered onto the dynamometer with the drive wheels positioned and laterally stabilized on the dynamometer rolls. The vehicle's hood is opened and an auxiliary cooling fan is positioned in front of the vehicle. Testing does not begin until this system is positioned and activated. The cooling system is positioned to direct air to the vehicle cooling system, but shall not be directed at the catalytic converter. The vehicle must be restrained to assure that it cannot leave the dynamometer rolls during acceleration and braking. The parking brake should be set for front wheel drive vehicles prior to the start of the test. The parking brake need not be set for vehicles that release the parking brake automatically when the transmission is put in gear. A detailed SOP describing the securing a vehicle on the dynamometer is presented in Appendix A.

Several equipment systems are required to fulfill the objectives of this project. The dynamometer and its constant volume sampling (CVS) system are used to simulate roadway conditions in a stationary setting. Undiluted vehicle exhaust gases are sampled by a SEMTECH before the exhaust enters the CVS. Diluted exhaust is sampled from the CVS by several types of measurement systems that continuously quantify particulate, carbon dioxide, carbon monoxide, oxides of nitrogen, hydrocarbons. Other systems remove a “batch” or an “integrated” sample throughout a given vehicle’s test for storage and later analysis (e.g., fuels and some toxic gases). The sketch in Figure 4-3 gives an overview of the facility layout and the physical relationship between the various instrument systems.

Figure 4-3. Overview of Facility and Equipment Layout

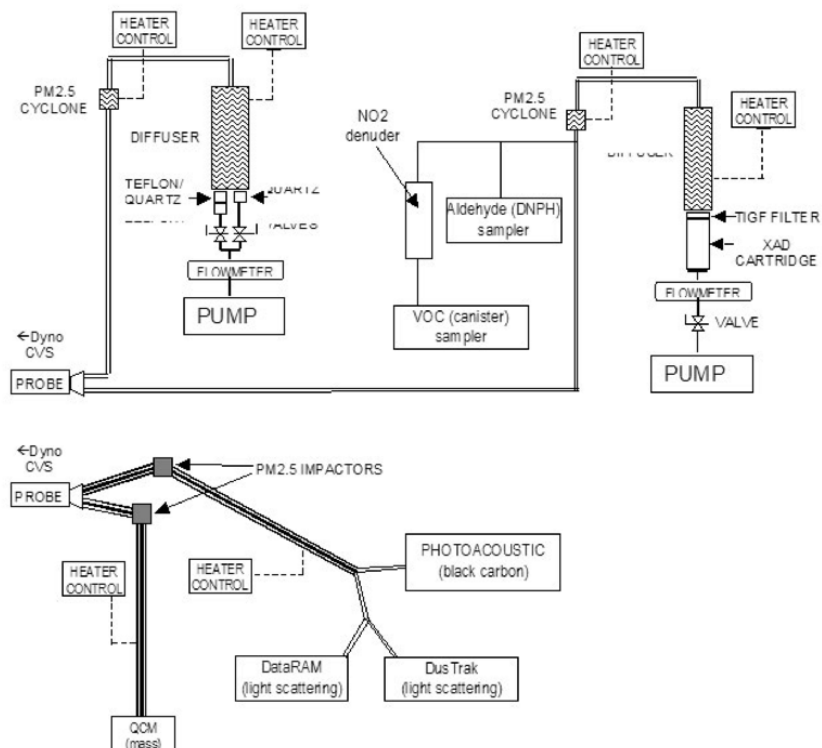
4.7 Particulate and Toxics Sampling Methods.

DRI will install and operated a suite of instruments to provide continuous PM analysis and to collect batch samples of particle and gaseous exhaust components for later analysis. These instruments collect sample air from the dynamometer dilution system via two isokinetic probes, provided by BKI, inserted prior to a 90-degree bend in the dilution tunnel. Figure 4-4 illustrates the sample train as it was installed for the pilot study. Heated conductive lines carried air from the probes to the continuous instruments. Insulated copper tubing was used to carry sample air to the time-integrated samplers.

4.7.1 Continuous PM Measurements

Continuous measurements include a Brooker Systems Model RPM-101 Quartz Crystal Microbalance (QCM) and Thermo-MIE Inc. DataRam 4000 Nephelometer for PM mass and DRI photoacoustic instrument for determination of black carbon mass concentrations. The continuous monitors will all sample from a common sampling manifold. The photoacoustic instrument is equipped with pressure, temperature, and relative humidity sensors so that the mass concentration can be adjusted to the desired ambient condition of pressure and temperature. Data from the real-time sensors can also be used to evaluate total particulate emissions by accumulating it over the sample period, and can be compared with data from the filter samplers.

Figure 4-4. Sample Train of DRI Equipment



Procedures for operation of the photoacoustic instrument, QCM, and MPS, as well as daily continuous instrument checklists, can be found in Appendix A.

4.7.2 Collection of Time Integrated PM and Toxics Samples

The vehicles will be tested on the EPA transportable dynamometer using a Unified Driving Cycle that will be composed of three phases. Teflon and quartz samples are collected for each phase and additional samples are integrated over the entire three phases of the UDC. These samples include whole air samples in stainless steel canisters, DNPH cartridges and Teflon-impregnated glass fiber (TIGF) filters with a backup cartridge consisting of XAD-4 resin.

The following substrates are proposed for this program:

- Gelman (Ann Arbor, MI) polymethylpentane ringed, 2.0 mm pore size, 47 mm diameter PTFE Teflon-membrane Teflo filters (#RPJ047) for particle gravimetric mass and elements.
- Pallflex (Putnam, CT) 47 mm diameter pre-fired quartz-fiber filters (#2500 QAT-UP) for water soluble chloride, nitrate and sulfate and for organic and elemental carbon measurements.

- Pallflex (Putnam, CT) TX40HI20-WW 102 mm diameter teflon-impregnated glass fiber filters for the DRI Sequential Fine Particulate/Semi -Volatile Organic Compounds Sampler (PSVOC sampler).
- Polystyrene-divinylbenzene resins, XAD-4 in a cartridges for collection of semi-volatile PAH. The Amberliete XAD-4 resin (20-60 mesh) is purchased from Aldrich Chemical Company, Inc.

Daily checklists pertaining to the time integrated sampler are included in Appendix A.

4.7.2.1 *Teflon and Quartz Filters*

Time-integrated samples for laboratory analysis are collected during each unified cycle test and a 60-minute tunnel blank each day as follows using specially adapted samplers designed and constructed at DRI. Sample air is drawn from the CVS via ½” insulated copper tubing to a small heated stainless steel chamber. The sample air exits via a PM2.5 cyclone contained in the chamber to a heated diffusing chamber approximately 1m tall, containing a thermistor temperature probe. From this chamber, the sample air exits through the two filter cartridges. Flow rates for each filter are set to 56 lpm by adjustable valves to give a combined flow of approximately 113 lpm as required by the inlet cyclone. Single oil-less pump is used to draw air through the sampler.

4.7.2.2 *PUF/XAD/PUF Cartridge and Filter*

A separate sampler for determination of particulate and semi-volatile organic compounds collects samples on 100 mm Teflon-impregnated glass fiber (TIGF) filters followed by glass cartridges containing XAD adsorbent at a flow rate of 112 lpm. The material collected on these media are removed by solvent extraction and analyzed at DRI by gas chromatography and mass spectrometry. A single filter and adsorbent pair were collected for each unified cycle, combining phases 1, 2 and 3. Sampling is suspended during the 10-minute soak period by turning off the pump. Sample air is drawn from the dynamometer CVS via ½” insulated copper tubing to a small heated stainless steel chamber. The sample air exited via a PM2.5 cyclone contained in the chamber to a heated diffusing chamber, containing a thermistor temperature probe, approximately 50cm tall. From this chamber, the sample air exits via the filter followed by the XAD cartridge. Flow rates are approximately 113 lpm as required by the inlet cyclone, and are monitored by an in-line TSI 4000 mass-flow meter. A single oil-less pump is used to draw air through the sampler.

4.7.2.3 *Carbonyl DNPH Cartridges*

Sample air is drawn from heated cyclone chamber via a ¼” diameter Teflon hose and passed through DNPH cartridges using a 6-channel sampler with integrated pump and mass flow controller. Airflow is maintained at 500 cc/min. A single cartridge is exposed for the duration of the 3 phases of the unified cycle and sampling is suspended during the 10-minute soak by switching to an unused channel.

4.7.2.4 Canister Sampling

For motor vehicle exhaust sampling, NO₂ is of concern, since it may react with 1,3 butadiene. Atkinson et al. (1984) described the series of reactions involving NO₂ and dialkenes and the consequence of the presence of NO. The reaction proceeds via initial NO₂ addition to the double bond, followed by rapid addition of O₂ to the peroxy radical. In the absence of NO these peroxy radicals react with NO₂ to yield the thermally unstable peroxy nitrates. Upon addition of NO, however, the peroxy radical will react rapidly with NO leading to a rapid disappearance of the peroxy nitrates. The alkoxy radicals formed from the reaction of the peroxy radical with NO will then decompose, react with O₂, ultimately leading to the formation of HO₂ radical. The reaction of HO₂ radical with NO generates HO radicals, which react with alkenes leading to rapid loss of alkenes. Modeling of this chemical system by Stockwell (2004) shows the following results for a canister samples containing 1,3-butadiene (43 ppbv), NO (10.0 ppm) and NO₂ (1.0 ppm) in various combination, assuming a canister pressure of 1.5 atmospheres and NO emission rate of 2.2 mg/mile. This emission rate was the highest among 57 LDGVs tested during the Gas/Diesel PM Split Study (Fujita et al., 2001; Gabele, 2003). The decay rate of 1,3-butadiene in NO₂ alone was linear with a rate of about 9% loss per 24-hour period. With NO alone, the disappearance of 1,3-butadiene is about 50% in the first 22 hours and over 90% in 65 hours.

Under separate funding by the U.S. Department of Energy's National Renewable Energy Laboratory, DRI is currently evaluating the efficiency of a denuder for removing both nitric oxide (NO) and nitrogen dioxide (NO₂) from the sampling stream prior to collection in stainless steel canisters. This evaluation will consist of the following three parts.

Determine the stability of a 1,3-butadiene standard in two sets of three synthetic canister samples over a period of three weeks. Each set includes a canister containing 1,3-butadiene with purified zero air and canisters with addition of NO and NO₂, respectively. Aliquots are analyzed by gas chromatography within the first hour, after 1 week and after three weeks. NO and NO₂ levels correspond to the highest NO_x emitter in DOE's Gas/Diesel PM Split Study. This task was completed in June, 2004 and decay rates match those predicted by Stockwell (2004).

Evaluate the removal efficiency of a denuder for removing NO_x (NO and NO₂). Saathoff et al. (2003) recently reported the use a denuder containing cobalt oxide coated ceramic granulate to remove NO_x. Varying concentrations of NO_x will be passed through the denuder and the denuded sampling stream will be monitored with a chemiluminescence NO_x analyzer. Three levels of NO_x will be used, which correspond to 2.0, 1.0 and 0.5 times the highest NO_x emitter in DOE's Gas/Diesel PM Split Study.

Exhaust from an in-use high-mileage automobile will be collected in two sets of two canisters, one with an upstream NO_x denuder and one without the denuder. Samples will be collected from a sampling manifold to ensure a well-mixed exhaust sample and NO_x concentrations in the sampling manifold will be monitored with a chemiluminescence analyzer. The three sample sets will be collected over a five-minute period from cold-start, and after a two-hour soak. Aliquots will be analyzed by gas chromatography within the first hour, after 1 week and after three weeks.

The cobalt oxide will replace the triethanolamine (TEA) denuder that was originally proposed to remove NO₂. Sample air is drawn from heated cyclone chamber via a ¼" diameter Teflon hose and passed through a Teflon filter and a denuder coated with the denuder to remove NO_x before being pumped into a Summa polished steel canister. Air flow was controlled by a needle valve to obtain the necessary flow rate to fill the canisters to approximately 15" Hg positive pressure over the duration of the complete unified cycle. Sampling is interrupted during the 10-minute soak by switching to a bypass channel. The sampler draws a total flow of 2 lpm, but only about 300 cc/min of that was pumped into the canisters.

4.8 Laboratory Analytical Methods

Analytical procedures that may be required for the accomplishment of the Statement of Work tasks are listed in Table 4-3. All QC requirements designated in these methods will be met. For required tasks not described in an EPA- or ASTM-approved method, SOPs will be required and archived. These SOPs are stand-alone documents and are not included with this document.

Table 4-3. Summary of Laboratory Related SOPs

DRI SOP No.	Observable/Method	Title
2-102.4	PM Gravimetry	Gravimetric Analysis Procedures
2-106.3	Quartz Fiber Filter Prep	Pre-firing of Quartz Fiber filters for Carbonaceous Material Sampling
2-108.3	Sectioning of Filters	Sectioning of Teflon and Quartz Filter Samples
2-109.4	Ionic Species Filter Extraction	Extraction of Ionic Species from Filter Samples
2-110.4	Filter Pack Processing	Filter Pack Assembling, Disassembling, and Cleaning Procedure
2-111.4	Filter Pack Shipping and Receiving	Sample Shipping, Receiving, and Chain-of-Custody
2-114.1	PM _{2.5} FRM Mass	PM _{2.5} FRM Gravimetric Analysis
2-201.1	Filter Sectioning	Filter Sectioning
2-202.1	Filter Extraction	Filter Extraction
2-203.4	IC Analysis	Analysis of Filter Extracts and Precipitation Samples by Ion Chromatography
2-204.4	TOR Carbon Analysis	Thermal/Optical Reflectance Carbon Analysis of Aerosol Filter Samples
2-205.2	XRF Analysis	X-ray Fluorescence (XRF) Analysis of Aerosol Filter Samples
2-703.1	VOC by GC	Analysis of VOC in Ambient Air by Gas Chromatography with Cryogenic Concentration
2-704.1	VOC by GC/MS	Analysis of VOC in Ambient Air by Gas Chromatography and Mass Spectrometry
2-710.1	Carbonyls by HPLC	Analysis of Carbonyl Compounds by High Pressure Liquid Chromatography
2-750.1	Analysis of SVOC by GC/MS	Analysis of Semi-Volatile Organic Compounds by Gas Chromatography and Mass Spectrometry

The following numbers of samples are to be collected in each of the two test rounds: 903 Teflon, 903 quartz, 349 TIGF/XAD, 337 canisters and 349 DNPH cartridges. Of the total samples

collected, the following numbers of analytical measurements are budgeted: 903 gravimetric mass, 114 XRF (protocol A), 38 ICP/MS, 309 TOR carbon analysis (IMPROVE), 38 ion chromatography, 17 GC/MS analysis of combined TIGF/XAD extracts, 18 GC/MS of TIGF extract, 18 GC/MS of XAD extract, 32 canisters by GC-FID and 38 DNPH cartridges by HPLC-UV. The following specific chemical analysis protocol applies to the Kansas City LDGV emissions characterization study.

- Following gravimetric mass and XRF (protocol A) analysis of the three Teflon filters for the separate phases of the UDC, the three filters will be extracted together and the composite sample analyzed for elements by ICP-MS. We recommend Mn, As, Hg and Pb for elemental analysis by ICP-MS based upon results of the Gas/Diesel PM Split Study and the relative detection limits shown in Table A7-1b for XRF and ICP-MS.
- Each quartz filter will be sectioned into two halves. One half of each quartz filter for the three phases of the UDC will be used for thermal optical reflectance carbon analysis (TOR) using the IMPROVE protocol. Remaining halves of the three quartz filters will be extracted together and analyzed by ion chromatography for chloride, sulfate and nitrate.
- TIGF/XAD samples will be analyzed for PAHs, methylated-PAHs, oxy-PAHs, nitro-PAHs, hopanes, steranes, organic acids, cycloalkanes and alkanes by GC/MS. The TIGF filters and XAD will be extracted and analyzed separately for the 1991 to 1995 and 1996 and newer categories in order to improve the analytical sensitivity of the method by reducing contributions of background contamination. The filter and XAD will be extracted and analyzed together for the two older model year categories.

4.8.1 Protocol for Selection of Samples for Chemical Analysis

Each of the two rounds of vehicle testing will be completed over approximately two months. Because organic samples should be extracted within a month after sample collection, compositing decisions will need to be made before the end of each round of testing. Timely decisions are also required due to the limited number of canisters that will be available to the project. Due to other programmatic needs, DRI can only supply about 120 stainless steel canisters to the Kansas City Study. That number is about a third of the total number of canister samples that are planned for each round. Consequently, about a third of the available canisters must be recycled on a weekly basis. This section describes the rationale and operational procedures for selecting samples for chemical analysis.

Most vehicles newer than ten years and with mileage accumulations less than 100K that were tested in the Gasoline/Diesel PM Split Study yielded mass loadings below the optimum target loadings of 200 ug per sample for carbon analysis and 1 mg per sample for organic speciation. Table 4-4 show the numbers of trucks and cars that will be recruited for the Kansas City Study in each of the four model year groupings (pre-80, 80-90, 91-95 and 96 and newer) and the approximate numbers of vehicles that are expected to be tested within each stratum. PM loadings

will be sufficient for chemical analysis for most vehicles in the two older model year categories and compositing of samples is an option for these strata. In contrast, compositing is a necessity for the two new model year categories in order to obtain adequate analytical sensitivity for organic analysis.

Because the study design calls for testing the vehicles in random order, no media composites will be collected (i.e., sampling multiple vehicles on the same media). Rather an appropriate number of samples will be extracted and analyzed together where analytical methods allow compositing prior to the chemical analysis (e.g., elements by ICP-MS, ions by IC, organic speciation by GC/MS, carbonyl compounds by HPLC-UV, and volatile organics by GC-FID). Table 4-4 shows the numbers of planned chemical analyses and approximate numbers of composite samples by test vehicle category. The total number of composite samples and average number of samples in each composite are shown, along with the corresponding percentages of vehicles in the composites relative to the total number of vehicles tested in each stratum. These percentages are larger for the two newer model year categories because no compositing is assumed for these categories. These numbers are intended to reflect the overall objectives of the project. They are tentative and subject to approval by the sponsor.

We anticipate that about 40 sample sets (including 6 dilution tunnel blanks) will be collected during a week of sampling. If vehicles are tested randomly in portion to the sampling strata, the numbers of vehicles tested in each stratum are listed in Table 4-5. The second number is the average number of samples that would be required to for a composite.

Sufficient numbers of samples would be collected weekly to create composites in all categories except for the 1996 and newer categories. A decision will be needed on a timely basis to either analyze the sample set, hold them for subsequent compositing with other samples, or remove the sample from further consideration by either archiving the sample or, in the case of canisters, to discard the sample and recycle the clean evacuated canister back to the field. We propose to make these decisions on a weekly basis beginning at the conclusion of the second week. The decisions each week will be based on the previous two weeks of sampling. The target mass loadings for each composite is a minimum of 1 mg of organic carbon, which will be estimated by the differences of the continuous mass measurements (either QCM or DataRam or DustTrak) minus the continuous black carbon measurements by PA. Composites will consist of samples with similar OC to PM ratios. Some composite containing high black carbon to PM ratios (i.e., black smokers) will be analyzed as well. The weekly decision will be made by DRI and posted at the end of the day each Monday.

Table 4-4. Number of Planned Chemical Analyses and Approximate Number of Composite Samples by Test Vehicle Category

	No. in Stratum	No. Tested	No in Comp	No. of Comp	% Tested	Teflon filter		quartz filter		TIGF/XAD POC and SVOC	TIGF	XAD	canister	DNPH cartridge
						mass	elements	OC/EC	Ions		POC	SVOC	VOC	Carbonyls
Round 1														
Daily Tunnel Blanks		60	10			60	6	60	6		6	6	6	6
Test Vehicles		250				750								
Truck - Pre 1980	50	26	1	4	15.4%		4	12	4	4			4	4
Truck - 1980 to 1990	100	52	1	4	7.7%		4	12	4	4			4	4
Truck - 1991 to 1995	70	36	3	2	16.5%		2	18	2		2	2	2	2
Truck - 1996 and newer	40	21	5	2	48.0%		2	30	2		2	2	2	2
Car - Pre 1980	40	21	1	5	24.0%		5	15	5	5			5	5
Car - 1980 to 1990	50	26	1	4	15.4%		4	12	4	4			4	4
Car - 1991 to 1995	80	42	3	3	21.6%		3	27	3		3	3	3	3
Car - 1996 and newer	50	26	5	2	38.4%		2	30	2		2	2	2	2
Replicate Vehicle Tests		15				45		45						
Weekly Calibration Vehicle		12				36		36						
Field/Transport Blanks		12				12	6	12	6		3	3		6
						903	38	309	38	17	18	18	32	38
Round 2														
Daily Tunnel Blanks		60	10			60	6	60	6		6	6	6	6
Test Vehicles		230				690								
Repeat Vehicle from Round 1		25				75								
Truck - Pre 1980	50	27	1	4	15.1%		4	12	4	4			4	4
Truck - 1980 to 1990	100	53	1	4	7.5%		4	12	4	4			4	4
Truck - 1991 to 1995	70	37	3	2	16.1%		2	18	2		2	2	2	2
Truck - 1996 and newer	40	21	5	2	47.1%		2	30	2		2	2	2	2
Car - Pre 1980	40	21	1	5	23.5%		5	15	5	5			5	5
Car - 1980 to 1990	50	27	1	4	15.1%		4	12	4	4			4	4
Car - 1991 to 1995	80	43	3	3	21.2%		3	27	3		3	3	3	3
Car - 1996 and newer	50	27	5	2	37.6%		2	30	2		2	2	2	2
Replicate Vehicle Tests		10				30		30						
Weekly Calibration Vehicle		12				36		36						
Field/Transport Blanks		12				12	6	12	6		3	3		6
						903	38	294	38	17	18	18	32	38
Total Round 1 and 2						1806	76	603	76	34	36	36	64	76

Table 4-5. Composite Breakdown

Test Vehicles	Vehicles Tested Weekly	No. in Composite
Truck - Pre 1980	3	1
Truck - 1980 to 1990	6	1
Truck - 1991 to 1995	4	3
Truck - 1996 and newer	3	5
Car - Pre 1980	3	1
Car - 1980 to 1990	3	1
Car - 1991 to 1995	5	3
Car - 1996 and newer	3	5

4.8.2 Mass Gravimetric Analysis

Unexposed and exposed Teflon-membrane filters are equilibrated at a temperature of $20 \pm 5^{\circ}\text{C}$ and a relative humidity of $30 \pm 5\%$ for a minimum of 24 hours prior to weighing. Weighing is performed on a Sartorius SE2 electro microbalance with ± 0.0001 mg sensitivity. The charge on each filter is neutralized by exposure to a polonium source for 30 seconds prior to the filter being placed on the balance pan. The balance is calibrated with a 20 mg Class M weight and the tare is set prior to weighing each batch of filters. After every 10 filters are weighed, the calibration and tare are re-checked. If the results of these performance tests deviate from specifications by more than ± 5 mg, the balance is re-calibrated. If the difference exceeds ± 15 mg, the balance is recalibrated and the previous 10 samples are re-weighed. At least 30% of the weights are checked by an independent technician and samples are re-weighed if these check-weights do not agree with the original weights within ± 0.015 mg. Pre- and post-weights, check weights, and re-weights (if required) are recorded on data sheets as well as being directly entered into a data base via an RS232 connection. All PM_{2.5} and PM₁₀ Teflon filters will be analyzed for mass. All weights are entered by filter number into the DRI aerosol data base.

4.8.3 Elements by XRF

Table A7-1b compares the elements that are quantified by XRF and ICP-MS and the associated minimum detection limits. Neither method will provide data for all specified elements. We recommend a combination of XRF using DRI protocol A for three Teflon filters from each phase of the UDC and ICP-MS for selected elements (e.g., Pb and Hg As, and Mn) Total cost per test would be comparable to the budget estimate in our original proposal.

4.8.4 Elements by ICP-MS

Teflon-membrane filters will be analyzed with a Thermo Elemental X7 Inductively Coupled Plasma Mass Spectrometer with Collision Cell and Xi interface for the following elements: Mn, As, Hg and Pb. A quality control standard and a replicate from a previous batch are analyzed with each set of 14 samples. When a quality control value differs from specifications by more than $\pm 5\%$ or when a replicate concentration differs from the original value (when values exceed 10 times the detection limits) by more than $\pm 10\%$, the samples are re-analyzed. If further tests of

standards show that the system calibration has changed by more than $\pm 2\%$, the instrument is re-calibrated as described above. All ICP-MS results are directly entered into the DRI databases.

4.8.5 Elemental and Organic Carbon

The thermal/optical reflectance (TOR) method measures organic (OC) and elemental (EC) carbon. The TOR method is based on the principle that different types of carbon-containing particles are converted to gases under different temperature and oxidation conditions. The different carbon fractions from TOR are useful for comparison with other methods which are specific to a single definition for organic and elemental carbon. These specific carbon fractions also help distinguish among seven carbon fractions reported by TOR:

- The carbon evolved in a helium atmosphere at temperatures between ambient and 120°C (OC1)
- The carbon evolved in a helium atmosphere at temperatures between 120°C and 250°C (OC2)
- The carbon evolved in a helium atmosphere at temperatures between 250°C and 450°C (OC3)
- The carbon evolved in a helium atmosphere between 450°C and 550°C (OC4)
- The carbon evolved in an oxidizing atmosphere at 550°C (EC1)
- The carbon evolved in an oxidizing atmosphere between 550°C and 700°C (EC2)
- The carbon evolved in an oxidizing atmosphere between 700°C and 800°C (EC3)

The thermal/optical reflectance carbon analyzer consists of a thermal system and an optical system. The thermal system consists of a quartz tube placed inside a coiled heater. Current through the heater is controlled to attain and maintain pre-set temperatures for given time periods. A portion of a quartz filter is placed in the heating zone and heated to different temperatures under non-oxidizing and oxidizing atmospheres. The optical system consists of a He-Ne laser, a fiber optic transmitter and receiver, and a photocell. The filter deposit faces a quartz light tube so that the intensity of the reflected laser beam can be monitored throughout the analysis.

As the temperature increases from ambient ($\sim 25^\circ\text{C}$) to 550°C , organic compounds are volatilized from the filter in a non-oxidizing (He) atmosphere while elemental carbon is not oxidized. When oxygen is added to the helium at temperatures greater than 550°C , the elemental carbon burns and enters the sample stream. The evolved gases pass through an oxidizing bed of heated manganese dioxide where they are oxidized to carbon dioxide, then across a heated nickel catalyst which reduces the carbon dioxide to methane (CH_4). The methane is then quantified with a flame ionization detector (FID).

The reflected laser light is continuously monitored throughout the analysis cycle. The negative change in reflectance is proportional to the degree of pyrolytic conversion from organic to

elemental carbon which takes place during organic carbon analysis. After oxygen is introduced, the reflectance increases rapidly as the light-absorbing carbon is burned off the filter. The carbon measured after the reflectance attains the value it had at the beginning of the analysis cycle is classified as elemental carbon. This adjustment for pyrolysis in the analysis is significant, as high as 25% of organic or elemental carbon, and it cannot be ignored.

The system is calibrated by analyzing samples of known amounts of methane, carbon dioxide, and potassium hydrogen phthalate (KHP). The FID response is ratioed to a reference level of methane injected at the end of each sample analysis. Performance tests of the instrument calibration are conducted at the beginning and end of each day's operation. Intervening samples are re-analyzed when calibration changes of more than $\pm 10\%$ are found.

Known amounts of American Chemical Society (ACS) certified reagent grade crystal sucrose and KHP are committed to TOR as a verification of the organic carbon fractions. Fifteen different standards are used for each calibration. Widely accepted primary standards for elemental and/or organic carbon are still lacking. Results of the TOR analysis of each filter are entered into the DRI database.

4.8.6 Ion Chromatographic Analysis for Chloride, Nitrate, and Sulfate

Water-soluble chloride, nitrate, and sulfate are obtained by extracting the quartz-fiber particle filter in 15 ml of deionized-distilled water (DDW). The extraction vials are capped and sonicated for 60 minutes, shaken for 60 minutes, then aged overnight to assure complete extraction of the deposited material in the solvent. The ultrasonic bath water is monitored to prevent temperature increases from the dissipation of ultrasonic energy in the water. After extraction, these solutions are stored under refrigeration prior to analysis.

Water-soluble chloride (Cl^-), nitrate (NO_3^-), and sulfate ($\text{SO}_4^{=}$) are measured with the Dionex 2020i (Sunnyvale, CA) ion chromatograph (IC). In IC, an ion-exchange column separates the sample ions in time for individual quantification by a conductivity detector. Prior to detection, the column effluent enters a suppressor column where the chemical composition of the component is altered, resulting in a matrix of low conductivity. The ions are identified by their elution/retention times and are quantified by the conductivity peak area. Approximately 2 ml of the filter extract are injected into the ion chromatograph. The resulting peaks are integrated and the peak integrals are converted to concentrations using calibration curves derived from solution standards. The Dionex system for the analysis of Cl^- , NO_3^- , and $\text{SO}_4^{=}$ contains a guard column (AG4a column, Cat. No. #37042) and an anion separator column (AS4a column, Cat. No. #37041) with a strong basic anion exchange resin, and an anion micro membrane suppressor column (250' 6 mm ID) with a strong acid ion exchange resin. The anion eluent consists of sodium carbonate (Na_2CO_3) and sodium bicarbonate (NaHCO_3) prepared in DDW. The DDW is verified to have a conductivity of less than 1.8×10^{-5} ohm/cm prior to preparation of the eluent. For quantitative determinations, the ion chromatograph is operated at a flow rate of 2.0 ml/min.

The primary standard solution containing NaCl , NaNO_3 , and $(\text{Na})_2\text{SO}_4$ are prepared with reagent grade salts which were dried in an oven at 105°C for one hour and then brought to room temperature in a desiccator. These anhydrous salts are weighed to the nearest 0.10 mg on a

routinely calibrated analytical balance under controlled temperature ($\sim 20^{\circ}\text{C}$) and relative humidity ($\pm 30\%$) conditions. These salts are diluted in precise volumes of DDW. Calibration standards are prepared at least once within each month by diluting the primary standard solution to concentrations covering the range of concentrations expected in the filter extracts and stored in a refrigerator. The calibration concentrations prepared are at 0.1, 0.2, 0.5, 1.0, and 2.0 mg/ml for each of the analysis species.

Calibrations curves are performed weekly. Chemical compounds are identified by matching the retention time of each peak in the unknown sample with the retention times of peaks in the chromatograms of the standards. A DDW blank is analyzed after every 20 samples and a calibration standard is analyzed after every 10 samples. These quality control checks verify the baseline and calibration, respectively. Environmental Research Associates (ERA, Arvada, CO) standards are used daily as an independent quality assurance (QA) check. These standards (ERA Wastewater Nutrient and ERA Mineral WW) are traceable to NIST simulated rainwater standards. If the values obtained for these standards do not coincide within a pre-specified uncertainty level (typically three standard deviations of the baseline level or $\pm 5\%$), the samples between that standard and the previous calibration standards are re-analyzed.

After analysis, the printout for each sample in the batch is reviewed for the following: 1) proper operational settings, 2) correct peak shapes and integration windows, 3) peak overlaps, 4) correct background subtraction, and 5) quality control sample comparisons. When values for replicates differ by more than $\pm 10\%$ or values for standards differ by more than $\pm 5\%$, samples before and after these quality control checks are designated for re-analysis in a subsequent batch. Individual samples with unusual peak shapes, background subtractions, or deviations from standard operating parameters are also designated for re-analysis.

4.8.7 Semi-Volatile Organic Compounds

Because no media compositing will be possible, TIGF filters and XAD cartridges be extracted and analyzed separately for the 1991 to 1995 and 1996 and newer categories. TIGF filter have very low background and removing the artifacts from the XAD will improve the detection limits for particulate organic species. Several samples will be composited together based on appropriate sample composite criteria (e.g., emission rate and ratio of photoacoustic black carbon to QCM mass).

Prior to extraction, the following deuterated internal standards are added to each filter-sorbent pair: naphthalene-d₈, acenaphthylene-d₈, phenanthrene-d₁₀, anthracene-d₁₀, chrysene-d₁₂, fluoranthene-d₁₀, pyrene-d₁₀, benz[a]anthracene-d₁₂, benzo[e]pyrene-d₁₂, benzo[a]pyrene-d₁₂, benzo[k]fluoranthene-d₁₂, coronene-d₁₂, and benzo[g,h,i]perylene-d₁₂, high molecular weight aliphatic hydrocarbons ranging from dodecane-d₂₆ to octacosane-d₅₈, cholestane-d₄; and polar organics ranging from benzoic-d₃ acid to cholesterol-d₆. The filter-XAD pairs will be extracted by Dionex ASE with dichloromethane followed by acetone to expand the polarity range of analytes; these extraction solvents have been reported to yield high recovery of PAH (Chuang et al., 1987) and other compounds of interest (Hawthorne et al., 1988, 1989).

The extracts are then combined and concentrated by rotary evaporation at 20°C under gentle vacuum to ~1 mL and filtered through 0.45 mm Acrodiscs (Gelman Scientific), with the sample flask rinsed twice with 1 mL CH₂Cl₂ each time. Approximately 100 µL of acetonitrile is added to the sample and CH₂Cl₂ was evaporated under a gentle stream of nitrogen. The final sample volume is adjusted to 1 mL with acetonitrile. This procedure has been tested by Atkinson et al. (1988). The detailed procedure is described in DRI standard operating procedures.

The extracts are then split into two fractions. The first fraction is analyzed without further alteration for PAH, alkanes, hopanes, and steranes by a GC/MS using an electron impact select ion storage (SIS) method. The second fraction is derivatized using a mixture of bis(trimethylsilyl)trifluoroacetamide (BSTFA), trimethylsilylchlorosilane (TMCS), and silylation grade pyridine to convert the polar compounds into their trimethylsilyl derivatives for analysis of organic acids, cholesterol, sitosterol, and levoglucosan. Samples are then analyzed by GC/MS using isobutane chemical ionization SIS method.

For hopanes and steranes, the samples are precleaned prior to GC/MS analysis using a solid phase extraction (SPE) technique described by Wang et al. (1994a,b). Clean up is conducted on a 6ml Supelco SPE cartridge packed with 0.5g of SiOH. Samples are spiked on to a SPE cartridge along with ten microliters of n_tetacosane-d50 (internal standard) and the PAH internal standard described above. Elution and fractionation is conducted with 1ml of hexane followed by 1.25 ml of benzene/hexane (1:1). Hopanes and steranes are eluted along with n_tetacosane-d50 in the hexane fraction, while the PAH are eluted in the hexane/benzene with the PAH internal standards.

The samples are analyzed either by the EI (electron impact) or isobutane chemical ionization (polar compounds) GC/MS technique. A Varian Star 3800CX GC equipped with an 8200CX Automatic Sampler and interfaced to a Varian Saturn 2000 Ion Trap was used for these analyses. Injections (1 µL) were made in the splitless mode onto a 30 m 5% phenylmethylsilicone fused-silica capillary column (DB-5ms, J&W Scientific). Quantification of the individual compounds is obtained by selective ion storage (SIS) technique, monitoring the molecular ion (or the characteristic ion) of each compound of interest and the corresponding deuterated internal standard, added prior to extraction. Calibration curves for the GC/MS quantification are made for the most abundant and characteristic ion peaks of the hopanes, steranes, PAH and other organic compounds of interest using the deuterated species most closely matched in volatility and retention characteristics as internal standards. Authentic PAH standards (purchased from Aldrich, Inc.) plus National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 1647 (certified PAH) with the addition of deuterated internal standards and of those compounds not present in the SRM (i.e., methoxylated phenols, hopanes, steranes, lactones, cholesterol) are used to make calibration solutions. For quantifying hopanes and steranes the following authentic standards are used: C27 20R-5a,14a,17a-cholestane (purchased from Aldrich), 17b(H),21b (H)-hopane, 17a(H),21b(H)-30-norhopane, and 17a(H),21b(H)-hopane (purchased from Chiron AS, Norway). The remaining hopane and steranes are identified based on their mass spectra and retention time comparison with data available in the literature (Wang and Fingas, 1995; Rogge et al., 1993). For quantification of the hopanes and steranes for which authentic standards are not available, the response factor of standards most closely matched in volatility and retention characteristics are used. A three-level calibration is

performed for each compound of interest and the calibration check (using median calibration standards) is run every ten samples to check for accuracy of analyses. If the relative accuracy of measurement (defined as a percentage difference from the standard value) is less than 30%, the instrument is recalibrated.

Recently, the Organic Analytical Laboratory (OAL) has received Varian 1200 triple quadrupole gas chromatograph – mass spectrometer (GC/MS/MS) system. The tandem MS/MS system allows for structural elucidation of unknown compounds with precursor, product and neutral loss scan. The GC interface allows for sensitive analyses of complex mixtures in electron impact (EI) as well as positive and negative chemical ionization (CI) mode. Negative CI offers a superior sensitivity for the analysis of nitro-PAH (mutagens and/or suspected carcinogens) that could be emitted from combustion sources, including motor vehicle engines. The sensitivity of this instrument in full scan EI/MS mode is approximately 1 pg/ul with 20:1 signal-to-noise ratio (S/N). In EI/MS SIM mode it reaches 50 fg/ul with 10:1 S/N. For negative CI, 10 fg/ul of octafluoronaphthalene gives S/N of 20:1. This superior sensitivity offers the advantage of analyzing small samples collected during a short sampling time.

4.8.8 Gaseous Air Toxics

Gaseous air toxic include canister sampling for VOC (benzene, toluene, ethylbenzene, —& p-,o-xylene, ie. BTEX, styrene, n-hexane, naphthalene, 1,3-butadiene, MTBE), and DNPH-coated Sep Pak cartridges sampling for carbonyl compounds (formaldehyde, acetaldehyde, acrolein). The DRI Organic Analytical Laboratory (OAL) routinely uses these methods and DRI standard operating procedures (SOPs) for sampling and analysis are available upon request.

Canister Samples

Canister samples are analyzed for speciated VOC concentrations promptly upon receipt of samples from the field, using gas chromatography/mass spectrometry method according to guidance provided by the EPA Method TO-15. The GC/MS system includes: Entech 7100 preconcentrator, Varian 3800 gas chromatograph with FID and column switching valve, and Varian Saturn 2000 ion trap mass spectrometer. The Entech preconcentrator consisted of three traps: 50% glass beads/50% Tenax, held at –100°C during sample transfer, 100% Tenax held at –40°C and a final focusing trap (a piece of silico-steel capillary) held at –180°C. The sample is desorbed from the first trap at 10°C, from the second trap at 200°C and from the third one at approximately 70°C to a transfer line heated to 110°C and connected to the head of the first column. The sample is injected at the head of a 60 m x 0.32 mm polymethylsiloxane column (CPSil-5, Varian, Inc.) held at 30°C. This column is connected to the switching valve leading into a 30 m x 0.53 mm GS-GasPro column (J&W Scientific). After approximately 7 min the valve was switched so that the effluent from the first column eluted onto a second 15 m x 0.32 mm polymethylsiloxane column connected to the mass spectrometer. The column switch was timed so that the C2 and C3 compounds eluted on the FID and all C4 and higher compounds eluted on the mass spectrometer. The GC program is as follows: 30°C held for 2 min, then 8°C/min up to 260°C. Calibration of the system is conducted with a mixture that contained the most commonly found hydrocarbons (75 compounds from ethane to n-undecane, purchased from Air Environmental), MTBE, and halocarbons (23 compounds from F12 to the

dichlorobenzenes, purchased from Scott Specialty Gases). The standards are prepared in 6 L Silco-Steel canisters (Restek, Bellefonte, PA) by mixing three different standards through a multi-valve manifold using a Baratron absolute capacitance manometer (MKS Instruments, Andover, MA) to determine the pressure each standard added to the mixture. Prior to mixing, approximately 0.2 ml of ultrapure water is added to the canister to humidify the mixture (for mixture stability). The concentrations in the mixture are in the range of 0.2 to 10 ppbv. Three point external calibrations are run prior to analysis, and one calibration check is run every 24 hours. If the response of individual compounds is more than 10% off, the system is recalibrated.

For canisters the replicate analysis is conducted at least 24 hours after the initial analysis to allow re-equilibration of the compounds within the canister. The replicate analyses are flagged in our database and the programs we have for data processing extract these replicates and determine a replicate precision. Replicate analysis is important because it provides us with a continuous check on all aspects of each analysis, and indicates problems with the analysis before they become significant.

Carbonyl Compounds

Formaldehyde, acetaldehyde and acrolein will be collected with Sep-Pak cartridges that have been impregnated with an acidified 2,4-dinitrophenylhydrazine (DNPH) reagent (Waters, Inc), according to the EPA Method TO-11A. When the exhaust is drawn through the cartridge, carbonyls in the sample are captured by reacting with DNPH to form hydrazones, which are separated and quantified using HPLC in the laboratory (Fung and Grosjean, 1981). After sampling, the cartridges will be eluted with acetonitrile. An aliquot of the eluent will be transferred into a 1-ml septum vial and injected with an autosampler into a high performance liquid chromatograph (Waters Alliance System) for separation and quantitation of the hydrazones (Fung and Grosjean 1981). Since acrolein undergoes isomerization when reacted with DNPH on the silica-gel cartridges forming two products, both peaks will be identified and quantified and the total concentration will be reported.

4.9 Quality Control

Testing Site

Internal QC checks for sampling and sample analysis activities must be determined prior to project start-up. These QC checks may include duplicate samples, matrix spikes, surrogates, and blanks for each type of sample and sample matrix.

PEMS Overview

For each integrated sample, the run number, start and stop time, elapsed time, initial and final flow rate, and any exceptional occurrences are recorded on log sheets which are kept with the media at all times. Bar coded stickers with unique media IDs are attached to all media and their corresponding log sheets for tracking. Immediately after the conclusion of each test cycle the media are repacked with the log sheets and stored in a refrigerator, except for the canisters, which are packed and shipped via 2-day express to DRI each day. All media are packed into

coolers with ice packs and shipped overnight back to DRI where they were logged in and placed in cold storage until analysis.

Continuous data are backed up via the wireless network and processed at the end of each sampling day to determine phase-averaged values. Run number, date, time, and vehicle license plate number were attached to all files to identify the data.

- For those instruments whose measurement depends on accurate flow rate determinations, such as the TEOM and QCM, the indicated flow rate must be checked against the flow rate measured with a Gillibrator bubble flow rate meter.
- The continuous instruments must be checked for leaks in a manner that is appropriate for each instrument. The sample system will be under substantial negative pressure with respect to the ambient pressure.
- Inlet integrity and sample line losses need to be evaluated at the outset by the combination of models from the aerosol spread sheets, and from direct measurement. A line transfer measurement needs to be performed that determines the mass concentration upstream of an instrument inlet, as well as the downstream concentration. These measurements can be performed, for example, with two Dustrak nephelometers. The two Dustraks must first be compared in a side-by-side test with a common inlet to make sure they are responding at the same clip.
- The instruments must be checked for any zero offsets. Filtered air can be introduced to the inlet of the instrument in question, and a measurement of the indicated quantity needs to be performed to quantify, and correct, any zero offsets. This measurement can also be performed when vehicle exhaust enters the sampling chamber, in which case any unexpected sensitivity to exhaust gas can be discovered and quantified.
- Daily plots will be made of the data from the continuous instruments as time series to provide immediate feedback in a raw form for the integrity of the sampling system, and of each instrument. Time-averaged data for each phase of the test will be obtained daily, and compared against filter-sampled data if available.
- Continuous measurements can provide an assessment of the likely loadings that are occurring on filter media. The flow rate used to deliver sample to the filter media can be adjusted accordingly.

The DRI photoacoustic instrument has a built in piezo electric transducer for use in occasionally evaluating the microphone calibration. Results from this measurement must be looked to ensure that the instrument is working properly.

As described earlier in this plan, all PEMS units used in this study will a full a complete warm-up, zero and audit sequence to verify CO, CO₂, NO_x, and THC measurement accuracy. Calibrations will be performed as necessary to bring the PEMS into proper calibration. The concentrations and accuracy of all gasses used for auditing and calibrating will be recorded, and

data files will be generated during all audits to preserve records of system accuracy and calibrations.

All PEMS system flows and pressures will be verified and recorded, and ambient conditions as measured by the PEMS will be recorded and verified with independent measurements. A sample system leak check will be performed to verify sample system integrity, and a FID fuel leak check will also be performed. System temperatures (FID oven and chiller) will also be verified and recorded, and all sample rates and transport delay settings will be verified.

PEMS units will be removed from service if any out “out of range” operating conditions are identified. All pertinent audit, verification, and calibration information will be recorded on data collection sheets, as shown in Appendix A. Also included in Appendix A are detailed usage guidelines to provide the PEMS technician item-specific instructions along with appropriate SEMTECH user manual references.

Laboratory

Prior to the start of the field work, all samplers will be checked for leaks and the in-line flow meters will be cross calibrated using reference flow measurement devices. Leak testing will be performed by capping the inlet lines leading to each sampler and turning on the pumps. If the flow meter readings decrease to less than 10% of the nominal sampling flow rate in a reasonably short time the system will be passed. If not, the source of the leak will be identified and fixed, then the test repeated. With the exception of the Teflon/Quartz filter sampler all units need to achieve near-zero flow rates during the leak test. Due to the friable nature of the pre-fired quartz filters it is not possible to obtain a perfect seal in the filter holders without damaging the media, but the <10% criteria can still be met for each filter individually and for the system as a whole. In addition to the vacuum test, the sum of flows through each of the two filter cartridges will be compared to the total flow entering the inlet and need to agree within 5%.

All flowmeters will be calibrated using either a Gillibrator electronic bubble meter or a rotameter that has been cross-calibrated with a Roots meter at DRI. Calibration flows will be measured at the inlet point of each sampler (or outlet for the canister sampler) with appropriate sampling media installed. The resulting calibrations will be used to determine the desired nominal flow rates, and will be marked on a label on each flowmeter so that the operator can observe any deviations during testing. Variations in nominal flow rate due to sampler problems will be recorded in a logbook.

4.10 Sample Handling and Custody

Testing Site

All samples will follow the chain-of-custody requirements and standard Good Laboratory Practices required for labeling, recording, and tracking all samples from collection through database archival. It will be the responsibility of the laboratory personnel to maintain internal logbooks and records that provide a custody record throughout sample collection.

Identifying labels are attached to each fuel and oil sample container. Label information will include the unique vehicle identifier, date/time of collection, and sampler initials. To protect the label from water and solvent damage, each label will be waterproof. The sample labels permanently identify each sample collected and link each sample to the vehicle from which it was collected.

In addition to the vehicle identification number, each sample container will be numbered consecutively and a sample sheet identifying each sample will be included in the shipping box, if appropriate. These sample sheets are retained by the laboratories as physical evidence of sample receipt and must therefore be signed by the sampler. The sample sheet will contain a summary of the field logbook entries for all the samples collected and will be maintained on electronic format (spreadsheets).

Onsite sampling staff will record sampling events in a formal field logbook. Logbooks will be maintained and archived as a permanent record of all sample collection activities performed.

Laboratory

A sample is considered in custody when received by the laboratory receiving department from an official package courier. At this time, it is logged into the general receiving logbook a representative of the laboratory signs for the package. The samples are bar-coded into the respective Laboratory Information Management System (LIMS), in lieu of updating the chain-of-custody form (if supplied), and the samples are stored properly. Damaged shipping containers, evidence of damage and/or tampering, etc., are brought to the attention of the Laboratory Director and QA Manager. If necessary, a review is initiated to determine whether the damage compromised the integrity and/or quality of the sample. All condensed phase samples and sample extracts are stored in freezers. The rooms are locked when not in use and the building has limited access (i.e., locked from 1730 to 0730 weekdays and 24 hours weekends to ensure access by authorized personnel only).

When a sample is analyzed, its unique identification number is recorded in a written logbook for each instrument (e.g., run list) and/or the LIMS. These unique identification numbers allow the sample to be tracked through LIMS and/or written records during sample preparation, analysis, and data validation. Condensed phase samples and sample extracts are archived for at least one year following the completion of the project.

Several types of laboratory records are routinely maintained. Written records include receiving logbooks, shipping logbooks, chain-of-custody forms, project folders, instrument logbooks, instrument service logbooks, calibration records which include a calibration standard logbook, a canister cleaning logbook, and sampler maintenance and cleaning logbooks. Computerized records include LIMS, method files, calibration files, raw data files, processed data files, and combined data files.

Written records are maintained in the appropriate location in the laboratory. Written records are always maintained in non-erasable ink so that alterations are easily noted. Project folders include sample lists and other information regarding the sample and project. Instrument

logbooks record each sample analyzed and pertinent information regarding the analysis. All calibrations are also recorded. Other calibration records include the calibration logbook that includes information about the standard solutions made in the laboratory. Service logbooks and files show services and/or modifications done to the instruments. The canister cleaning LIMS record includes the unique can and ID number and the project the canister is assigned, date of last cleaning, and QA certification lot number and information. Logbooks are kept on file in the laboratory for a minimum of 5 years.

Computerized records are maintained on a central computer (the LIMS file server). The data collection system includes a history record that maintains lists of files created or modified, and the name of the person creating or modifying the file. An original report is printed after analysis and documents the method and calibration file used including the last modification date of the file. Backups of computerized records, including but not limited to removable media (floppy disks) and tapes, are stored in the LIMS manager's office for off-site storage.

4.11 Inspection/Acceptance of Supplies and Consumables

Staff are authorized to acquire property and supplies from vendors, and are authorized to make appropriate transactions. Accountable property that is acquired and charged to the Work Assignment will be authorized on an individual line item basis and will be authorized by the Project Manager or Acting Project Manager.

Receiving Process

Upon arrival, property will be examined to determine quantity received, condition, and to identify transit related discrepancies. When shortages or damages are identified at time of delivery, the carrier's signature will be obtained. Shipped items will be checked from a copy of the original invoice and the packing slips to document quantities received and condition, and will be moved to a protected area for distribution. Full accountability is established once the invoice has been compared to the purchase order, prices have been adjusted for all items ordered and shipped, and the invoice has been sent to the accounting department for payment. Gas cylinders and all returnable or reusable containers will be accounted for and immediately returned to their appropriate vendors.

Discrepancies in Shipments

If an overage, shortage, or damage upon receipt is discovered, necessary actions will be taken directly with the vendor or supplier.

SECTION 5: DATA MANAGEMENT AND VALIDATION

5.1 Data Acquisition Requirements (Non-Direct Measurements).

Testing Site

Exhaust emissions measurements must be accurately acquired, mathematically manipulated, and logged onto computer storage devices for archival. Quality assurance of each step ensures that transfer errors are eliminated and that data in the database truly represent the data collected during the experimental run.

A primary function of this work area is to provide for the generation of emissions reports with accompanying statistics according to the procedures specified in the Federal Register for determining emission rates of pollutants from mobile sources and in accordance with Federal Testing and Work Assignment requirements and guidelines. The task of this specialized section is multi-functional to accomplish assignment objectives. We will assist as requested in the design and specification of computer systems necessary to acquire, archive, process, and report the vast quantities of physical and analytical data generated during each vehicle test, project, and the overall mobile source program. The proposed staff will be responsible for the installation, operation, preventive maintenance, troubleshooting, and repair of the computer systems and peripherals utilized in this area as requested. Support will be provided in the area of software development, enhancement, and evaluation of software packages. The staff has the responsibility of software maintenance and updating.

Laboratory

The goal of data processing is to provide accurately combined data into a single database for each analysis. Depending on the analysis, the data includes calculations for replicate precision, mean blank values, blank variability, blank-corrected concentrations, and standard errors for each reported value based on combined volume, replicates and blank uncertainties. The standard error is calculated based on the combined volume for carbonyl and semi-volatile compound; replicates for hydrocarbon, SVOC, and carbonyls; and blank uncertainties for carbonyl and SVOC, the minimum detection limits is substituted for hydrocarbon data. The uncertainty analysis allows us to present our data with absolute uncertainties associated with each number in the report.

The primary function of laboratory data management is to store data in a consistent fashion that is both secure and available. To serve this need, file server systems have been established that provide a central storage area for all laboratory and field data. The databases have defined structures that are maintained in one area where all field names are consistent and permit easy merging and comparison of the various databases. Locating all data on a central file server prevents problems associated with having multiple copies of the same data set, and allows the individuals charged with data processing, security, validation, and QA access to the same databases.

5.2 Reporting

Analytical personnel will be responsible for reducing analytical data according to the method used and providing both raw and summary data with a case narrative and along with the completed sample calculations. Records of all weighings, calibrations, system performance checks, blanks, surrogate recoveries, and any other method-required QC data will be provided, along with the raw sample data and notes of problems and corrective action taken. Notes from logbooks made by onsite sampling personnel will be reduced and compiled.

Reports of analysis will be generated for all samples analyzed in support of the Statement of Work. These reports, along with the applicable chain-of-custody documentation (if required), will be provided as required in accordance with the schedule within the Work Plan. These reports of analysis will be provided in both a written and a computerized format. The computerized reports will be on CD-ROMs in either Microsoft Excel 5.0, Lotus for Windows, or ASCII format, as directed by ERG and the EPA Work Assignment Manager.

5.3 BKI Data Review, Verification, and Validation

Data will be examined for compliance with all QC requirements for the method used for analysis. Notations will be made concerning any deviations from these criteria. Outliers will be tested according to ASTM E-178-80 or other applicable standard, and appropriate notations will be made in the summary report concerning the rejection of any data as outliers.

5.4 DRI Verification and Validation Methods

Data validation will be performed by DRI personnel according to SOPs. This validation will begin with examination of the raw data, summary data, and field and laboratory validation codes. We will ensure that all the required data are included, sample calculations are complete, and that the summary data accurately represent the raw data. The validation data will be assembled with the reduced laboratory notation and data validation notations, and a report will be prepared.

Mueller (1980), Mueller et al., (1983), and Watson et al. (1983, 1989, 1995) define a three-level data validation process for an environmental measurement study. Data records are designated as having passed these levels by entries in the column of each data file. These levels, and the validation codes that designate them, are defined as follows:

Level 0 (ZERO): These data are obtained directly from the data loggers that acquire the data in the field. Averaging times represent the minimum intervals recorded by the data logger, which do not necessarily correspond to the averaging periods specified for the database files. Level 0 data have not been edited for instrument downtime, nor have procedural adjustments for baseline and span changes been applied. Level 0 data are not contained in the database; although they are consulted on a regular basis to ascertain instrument functionality and to identify potential episodes prior to receipt of Level 1A data.

Level 1A (1A): These data have passed several validation tests applied by the measurement investigator prior to data submission. The general features of Level 1A are: 1) no removal of data values and use of flagging data when monitoring instruments did not function within procedural

tolerances; 2) flagging measurements when significant deviations from measurement assumptions have occurred; 3) verifying computer file entries against data sheets; 4) replacement of data from a backup data acquisition system in the event of failure of the primary system; 5) adjustment of measurement values for quantifiable baseline and span or interference biases; and 6) identification, investigation, and flagging of data that are beyond reasonable bounds or that are unrepresentative of the variable being measured.

Level 2 (2): Level 2 data validation takes place after data from various measurement methods have been assembled in the master database. Level 2 validation is the first step in data analysis. Level 2A tests involve the testing of measurement assumptions (e.g. internal nephelometer temperatures do not significantly exceed ambient temperatures), comparisons of collocated measurements, and internal consistency tests (e.g. the sum of measured aerosol species does not exceed measured mass concentrations). Level 2 tests also involve the testing of measurement assumptions, comparisons of collocated measurements, and internal consistency tests.

Level 3 (3): Level 3 is applied during the model reconciliation process, when the results from different modeling and data analysis approaches are compared with each other and with measurements. The first assumption upon finding a measurement, which is inconsistent with physical expectations, is that the unusual value is due to a measurement error. If, upon tracing the path of the measurement, nothing unusual is found, the value can be assumed to be a valid result of an environmental cause. The Level 3 designation is applied only to those variables that have undergone this reexamination after the completion of data analysis and modeling. Level 3 validations continue for as long as the database is maintained.

A higher validation level assigned to a data record indicates that those data have gone through, and passed a greater level of scrutiny than data at a lower level. All data supplied to the Kansas City LDGV emission characterization study database will have undergone data validation through Level 1A.

5.5 Verification and Validation for the PEMS

All PEMS testing and audit data will be collected and transferred to a main repository on a daily basis. Each file name, as well as fields within each data file, will be used to indicate the associated BKI dynamometer run number (if applicable), vehicle license plate digits, and type of file (audit, preconditioning run, dyne test, or drive-away). Independent tracking logs will also be maintained for all PEMS test files.

After the PEMS files are transferred to the main repository, they will be processed and reviewed. PEMS audit records will be reviewed to ensure all testing is performed within allowable accuracy limits. PEMS emission measurements taken during dynamometer testing will be calculated and compared with those measured by the dynamometer sampling system (both overall and phase-specific emissions). In addition, application of appropriate correction factors and transport delays will be verified for each sampling system.

5.6 QC Calculations

Measurement precision will be assessed by calculating the relative standard deviation of the results of replicate measurements. The equation used is:

$$s = \sqrt{\sum \frac{(x_i - \bar{x})^2}{(n-1)}}$$

where s is the standard deviation, x_i is an individual measurement, \bar{x} is the mean of the measurements, and n is the number of measurements compared.

Acceptance criteria will be based on the relative standard deviation:

$$RSD = \frac{s}{\bar{x}} * 100\%$$

where RSD is the relative standard deviation, s is the standard deviation, and \bar{x} is the mean.

Accuracy will be assessed by measuring the agreement between the accepted value for a QC material versus the determined value:

$$\%R = 100\% * \frac{C_m}{C_a}$$

where R is recovery, C_m is the measured concentration of the QC material, and C_a is the accepted value for the QC material.

Completeness of data will be calculated in the following way:

$$\%C = 100\% * \frac{v}{n}$$

where C is completeness, v is the number of valid measurements, and n is the number of measurements necessary to achieve a specified statistical level of confidence.

For QA purposes, substantial comparisons among measurements will be made to determine their predictability, comparability, and equivalence. Although the different observables measured are quite diverse, it is possible that they may be highly correlated owing to their quantification of related particle properties or to large fluctuations caused by emissions and meteorology. Relationships between variables will depend on the composition of the aerosol as well as meteorological conditions. Measures of predictability, comparability, and equivalence are applied to data sets stratified by aerosol composition and season. Predictability requires a consistent and reliable relationship between measurements, even if they are of different quantities. Comparability can be established between monitors that ostensibly measure the same

observable, but with different principles. PM2.5 mass acquired from the DataRam nephelometer, QCM and gravimetric mass are expected to be comparable.

5.7 MSOD Data Management

In accordance with the requirements set forth in the original Scope of Work, data procured over the course of the project will be processed and delivered in the EPA's MSOD format. Field data collection procedures have been designed with MSOD data collection requirements in mind.

After collecting the vehicle testing information, datasets to be imported into the EPA MSOD will be prepared. Data integrity and accuracy are of the utmost importance, and in order to ensure that the data prepared for the MSOD accurately represents the data that was originally received, the following four step approach for electronic data handling and manipulation has been developed, described below:

- Import raw data into SAS dataset(s);
- Clean up and Convert data to match MSOD format and export to text files;
- Import text files into the MSOD load files; and
- Verify the validity of the output database and files.

This approach separates raw import and data cleanup issues from project-specific issues of data format conversion and validation. In the first three stages, emphasis is placed on automation. Scripts and programs will be used as much as possible, to provide repeatable steps for the verification stage and documentation. In the first import stage, the raw input data will be loaded into SAS datasets. The data will be imported into datasets that mimic, to the extent possible, the design of the original files. In this way, each raw input file will map to one or more specific SAS datasets, with close agreement in table content and layout. While some data cleanup may be needed for a successful data import, no data manipulation (such as unit conversions or factor manipulation) will be performed at this stage. Minor data cleanup may be required because of conflicts between file types, such as end-of-record or end-of-data discrepancies, differences in character sets, conflicting numeric formats, or data types that do not convert directly. Once the data is imported, the raw import data will be considered "read only" and no updates will be made unless the import process is modified and repeated. After the data is loaded into the raw datasets, it will be reviewed for data integrity and completeness.

Once the data review and clean up is complete, the raw import datasets will remapped and all required conversions and data manipulation will be performed in SAS, moving and converting data from raw and intermediate datasets into final text files. These text files will then be imported directly into MSOD load tables (in DBF format) supplied by EPA. The final step in the process will involve running EPA's EPAVAL program against each of the DBF import tables. This program will quality assure each of the tables and log all errors encountered. Each of the errors will then be reviewed and addressed accordingly. Once the import tables for each dataset are complete they will be delivered to EPA for further verification and loading into the MSOD.

SECTION 6: ASSESSMENT AND OVERSIGHT

6.1 Assessment and Response Actions

Corrective action will be initiated as a result of internal QC checks that reveal instruments or systems operating outside the range required for acceptable data, or in the event of any system failure. For example, corrective action will be performed for the following conditions: analytical system shown “out of control” according to method acceptance criteria, analytical precision outside DQOs, and analytical accuracy outside acceptability range as defined by DQOs.

The system used for corrective action is the “closed loop” system, including the following elements.

- Problem definition;
- Assignment of responsibility for investigation of the problem;
- Problem investigation;
- Determination of appropriate corrective action;
- Implementation of corrective action;
- Verification of problem correction; and
- Implementation/dissemination of procedural changes, if any.

To enhance the timeliness of corrective action and minimize the generation of unacceptable data, problems identified by internal QC checks will be resolved at the lowest possible management level. Staff will correct the out-of-control conditions (indicated by their QC data) by using the corrective action information contained in the SOPs referenced in this QAAP and then will report the problem and corrective action taken to the Project Manager.

Problems involving any change in scheduling, the sample work plan, or performance of analytical tasks will be handled in a manner agreed upon by the Project Manager and the EPA WAM.

Performance audits typically include the submission of blind samples such as NIST Standard Reference Materials in an appropriate matrix to the analytical laboratory, and comparison of their results with the certified values. Systems audits typically include examination of sampling and packaging procedures, as well as examination of records from calibration and maintenance of both field and analytical equipment and evaluating the training of field and laboratory personnel.

Monthly internal audits/checks for sampling and sample analysis activities will be performed according to guidelines established by 48 CFR PART 46 - QUALITY ASSURANCE FAC 97-14, November 23, 1999 and the EPA Interim final EPA QA/R-5 November 1999, Interim guidelines and Specifications for Preparing Quality Management Plans, or as otherwise directed by the EPA Project Officer through ERG. These QC checks will include duplicate samples,

matrix spikes, surrogates, and blanks for each type of sample and sample matrix independent of the quarterly audits for the regulated emissions bench.

The Project Manager will perform monthly spot checks of such project activities, evaluation of response to EPA and ERG communications, completion of QC data by laboratory personnel, and recording and archiving of data. In addition, a monthly summary will be prepared and submitted as part of the Monthly Progress Report to document the overall QA program activities and findings for project activities.

The most frequently used audit by onsite staff is the Technical System Audit (TSA), which is a qualitative on-site evaluation of an entire measurement system. These audits will be performed by a QA representative that is independent of the data collection activity. The TSA examines the entire operation: all equipment, facilities, personnel, record keeping, data validation, calibration procedures, reporting requirements, and QC procedures. TSAs will be scheduled and performed during the beginning of data collection activities and annually thereafter, or can be initiated any time by the Project Manager or QA Manager, or by the EPA Project Officer or QA Manager. TSAs can also be initiated when a new employee is hired in order to ensure that the staff is following the proper procedures described in SOPs. Most TSAs are based on project progress reports or the results of performance evaluation (PE) studies. Frequently, problems revealed in a PE audit will trigger a TSA to determine the cause. The two main purposes of a TSA are to determine that project personnel and equipment are functioning properly and that all procedures are being implemented as prescribed in the Quality Management Plan and other project planning documents. This objective evidence is gathered by interviewing personnel, examining records, and observing project activities. Checklists are used to guide the TSA. The checklists are prepared based on performance criteria, such as Data Quality Objectives (DQOs), that are listed in the project's Quality Management Plan and other planning documents.

Data Quality Audits (DQAs) will be used to evaluate documentation associated with data quality indicators to verify that the data are of known quality. Its primary purpose is to verify the existence of quantitative and qualitative indicators of data quality. The following activities will be evaluated against the QA project plan and any other relevant documentation on a quarterly basis and reported in the quarterly QA report.

- Recording, and transferring raw data;
- Calculations, including equations used;
- Documentation of data-handling methods; and
- Selection and discussion of data quality indicators.

QA representatives will implement the DQA which entails tracing data through their processing steps and duplicating intermediate calculations in the beginning of each project and quarterly thereafter. A representative set of the data will be used from raw data and instrument readouts through data manipulation and through data reduction to summary data, data calculations, and final reported data. The focus is on identifying a clear, logical connection between the steps. Particular attention is paid to the use of QC data in evaluating and reporting the data set. DQAs

will be conducted throughout the project, or afterwards as required. They may be prescheduled or performed at the request of our Project Manager, QA Manager or by ERG and EPA staff if problems are discovered.

6.2 Reports to Management

To provide essential feedback to management on the progress of the QA Program, a quarterly report will be prepared for the Program Director by the Project Manager. In addition, a summary of QC activities will be made in the monthly progress report prepared for the EPA. Both of these reports will address the following.

- Status of any major QA activities;
- Corrective actions taken during the period;
- Summaries of measures of precision and accuracy for the materials prepared during the period;
- Performance and system audit results; and
- Significant changes in facilities, personnel, major analytical or support equipment, procedures, data processing, or reporting.

In addition to these quarterly outputs, QA-specific deliverable outputs will be provided for all of the compositional parameters according to the schedule given in Table 6-1.

Table 6-1. Schedule for QC Deliverable Outputs.

Output	Time Period
THC Analysis	Monthly
CO Analysis	Monthly
NO _x Analysis	Monthly
CO ₂ Analysis	Monthly
CVS Verification	Monthly
HC Blind Audit Results	Quarterly
CO Blind Audit Results	Quarterly
NO _x Blind Audit Results	Quarterly
CO ₂ Blind Audit Results	Quarterly
QC Notebook (PC/AT)	Quarterly

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Appendix A

Study Modifications made between Rounds 1 and 2

A1. Changes from Round 1

Round 2 test procedures, equipment, and testing conditions differed somewhat from those during Round 1. The most notable differences are discussed in an Appendix to the updated QAPP, and are presented below:

Onsite PEMS repair support

Onsite PEMS repair support was available throughout the Round 2, and greatly reduced equipment downtime and shortages. Most PEMS problems were minor issues such as stuck solenoids, loose or dirty contacts and fittings, water in the system, or blown relays, and were able to be repaired quickly. Most larger repairs, such as system module and CPU board replacements, could also be accomplished onsite (after receipt of necessary repair materials).

Temperatures and ambient conditions

Round 2 testing was conducted during the winter, as opposed to the Round 1 summer study. Since this portion of the study was to be conducted at ambient temperatures, an enclosed and heated structure was erected in which to conduct PEMS installation activities. This prevented operation of the units sub-freezing temperatures (beyond their specified operating temperature range). Operation of the PEMS units below freezing temperatures was occasionally necessary, and resulted in various operational problems, such as water freezing in the FID exhaust drain lines and internal filters, and freezing in the flowmeter pressure-differential measurement tubes and exhaust sample lines. The signal transducer boxes used with the new pressure-differential flowmeters occasionally would not warm up to operating temperature (as indicated by the “warm-up” indicator LED), and some emissions measurement drift was seen during some conditioning runs (as evidenced by pre-test and post-test audits). This drift may be due to auditing the PEMS in the heated installation bay and then performing the conditioning test in a vehicle’s trunk or bed at ambient temperatures.

Flowmeter changes

Hot-wire anemometer-style flowmeters were used throughout the Round 1 summer portion of the study. These were replaced with pressure-differential style flowmeters for Round 2 of the study. These new flowmeters transmitted pressure signals through flexible tubes to a signal transducer box which converted the pressure-differential signal and exhaust temperature measurement into an exhaust mass flow rate determination.

Flowmeter mounting changes

License plate brackets and suction cup clamp assemblies were primarily used to install the flowmeters used during Round 1 of the study. This posed concerns associated participants or pedestrians burning themselves (particularly on driveway testing) or the assemblies falling off. Occasionally, flowmeters were hung underneath the rear of the vehicle, which was generally laborious and exposed the flowmeter to water and possible dragging damage. The new pressure-differential flowmeters were significantly larger and heavier, so common bicycle racks were used for flowmeter installations during Round 2. Wire meshes were secured to these racks to allow mounting of license plates and to protect against burns.

Software changes

Several PEMS software changes were implemented prior to or during Round 2. This new software allowed use of the new pressure-differential flowmeters, and it also allowed activation of auto-zero and automatic FID heater shut-down after a period of time (auto-zeros were performed only on drive-away testing). Another software update involved adding a “session manager” which “bundled” all the audits and second by second test information into one file. The following software changes were implemented throughout the study (including both Rounds 1 and 2):

- Rollout beginning July 12, 2004: Software Version 9.03
- Rollout beginning August 17, 2004: Software Version 9.03 SP1
- Rollout beginning November 23, 2004: Software Version 9.04
- Rollout beginning December 6, 2004: Software Version 9.05 SP1
- Rollout beginning December 16, 2004: Software Version 9.05 SP2

Testing was continued with Software Version 9.05 SP2 through the end of Round 2.

A.2 Procedural changes between Rounds 1 and 2

The equipment downtime experienced during Round 1 was greatly reduced during Round 2 through the addition of an on-site PEMS repair and support person. Most repairs were minor, such as stuck solenoids, loose or dirty contacts and fittings, water in the system, or blown relays, and were able to be repaired quickly. Most larger repairs, such as system module and CPU board replacements, were also accomplished onsite (after necessary repair items were received onsite). This increase in equipment up-time allowed significantly more driveaways to be conducted in Round 2 than were possible during Round 1 of the study.

As mentioned in Section 2.4.1, the hot-wire anemometer-style flowmeters used throughout the Round 1 summer portion of the study were replaced with pressure-differential style flowmeters for Round 2 of the study. Measurements from the original hot-wire anemometer flowmeters were adversely affected by heat radiation effects at low vehicle speeds and idle. Since convective cooling minimized these effects when vehicles were in motion, low-speed and idle flow measurements were biased low. This bias was eliminated with the use of pressure-differential style flowmeters provided for Round 2 of the study. These flowmeters relied on a bank of differential pressure sensors (as opposed to a hot-wire anemometer) in order to determine corrected mass exhaust flowrates. However, the orifices in the differential pressure sensors used in these new flowmeters were susceptible to particulate matter clogging and moisture freezing. This condition was minimized as much as possible by thoroughly purging all orifices with high-pressure dry compressed nitrogen prior to each use, and by maintaining the flowmeters and tubing assemblies in above-freezing conditions.

Earlier in the study, problems were encountered with preventing moisture and exhaust fumes from entering vehicles during testing. The new flowmeters required additional tubing to be routed out of the trunk (generally requiring the trunk to be propped open wider). Standard household pipe insulation purchased at a hardware store was found to fairly effectively seal trunks. Carbon monoxide detectors were used to ensure vehicle exhaust was not entering the passenger compartment.

As mentioned in Section 2.4.1, Round 2 testing was conducted during the winter, as opposed to the Round 1 summer study. Operation of the PEMS units below freezing temperatures was occasionally necessary, and proved to be problematic because of water freezing in system components and measurement drift. Battery life seemed greatly reduced during Round 2 testing, perhaps due to battery cycle fatigue (these were the original batteries used since the start of the study) and also possibly due to operation in the cold temperatures.

In order to prevent trunks from inadvertently popping open, as would occasionally happen with the original vice-grip-devised trunk latches, heavy-duty zip-ties were used (with metal rings installed in the trunk latch assembly) to secure trunks. These zip ties, which are typically used for securing building ventilation and may be found at a typical hardware store, also prevented motorists from tampering with the PEMS units installed in trunks during driveaway tests.

Experience gained during Round 1 of the study helped streamline Round 2 testing. For example, installation procedures and sequences were modified in order to minimize lost time in the event of equipment malfunctions. Certain “tricks” and procedures for equipment software helped expedite installations and minimize system resets. The incorporation of a session manager into the host software also allowed consolidation of audit and test information into one test file, thereby expediting equipment setup and reducing time needed for test processing and analysis.