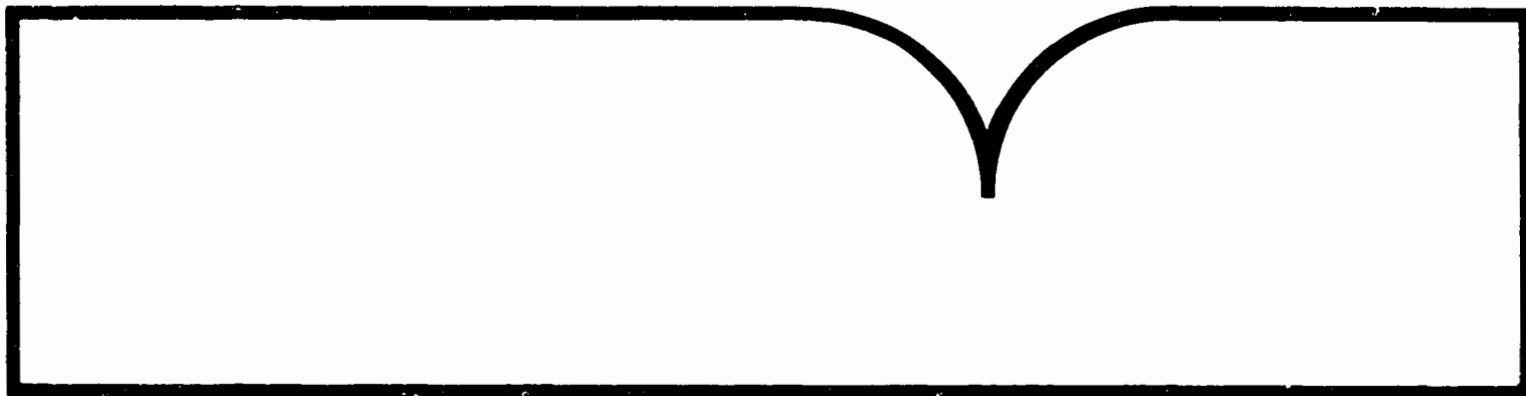


Emissions and Fuel Economy of DOE Flex-Fuel Vehicles

(U.S.) Environmental Protection Agency, Research Triangle Park, NC

1992



U.S. Department of Commerce
National Technical Information Service

NTIS

TECHNICAL REPORT DATA

1. REPORT NO. EPA/600/A-92/042	2.	3. PB92-153055
4. TITLE AND SUBTITLE EMISSIONS AND FUEL ECONOMY OF DOE FLEX-FUEL VEHICLES		5. REPORT DATE
7. AUTHOR(S) F.M. Black, USEPA T. Kleindienst, ManTech		6. PERFORMING ORGANIZATION CODE
9. PERFORMING ORGANIZATION NAME AND ADDRESS Atmospheric Research and Exposure Assessment Laboratory Office of Research and Development U.S. Environmental Protection Agency Research Triangle Park, N.C. 27711		8. PERFORMING ORGANIZATION REPORT NO.
12. SPONSORING AGENCY NAME AND ADDRESS Atmospheric Research and Exposure Assessment Lab - RTP Office of Research and Development U.S. Environmental Protection Agency Research Triangle Park, N.C. 27711		10. PROGRAM ELEMENT NO.
15. SUPPLEMENTARY NOTES		11. CONTRACT/GRANT NO.
16. ABSTRACT <p>The U.S. Department of Energy and the U.S. Environmental Protection Agency have established, through a Memorandum of Understanding, a coordinated framework for collaborative research examining the impact of alternative motor vehicle fuels on air quality and risk to public health and welfare. A cooperative effort to examine the emissions and fuel economy of DOE flex-fuel vehicles, capable of operating on a variety of liquid fuels, and the atmospheric chemistry of the emissions, will begin in January, 1992. During the first year, emissions will be characterized for 6 vehicles, 2 conventional fuel baseline vehicles and 4 flex-fuel vehicles, using up to 9 fuels. Additionally, a dual-chamber irradiation facility will be constructed to support future study of the atmospheric chemistry of the emissions. These studies will examine the formation of ozone and toxic compounds. A detailed description of the experimental procedures to be used is provided.</p>		13. TYPE OF REPORT AND PERIOD COVERED <i>Conf. Proceeding</i>
17. KEY WORDS AND DOCUMENT ANALYSIS		14. SPONSORING AGENCY CODE EPA/600/09
a. DESCRIPTORS	b. IDENTIFIERS/ OPEN ENDED TERMS	c. COSATI
18. DISTRIBUTION STATEMENT <u>RELEASE TO PUBLIC</u>	19. SECURITY CLASS <u>(This Report)</u> UNCLASSIFIED	21. NO. OF PAGES 15
	20. SECURITY CLASS <u>(This Page)</u> UNCLASSIFIED	22. PRICE

Emissions and Fuel Economy of DOE Flex-Fuel Vehicles

Frank Black

Mobile Source Emissions Research Branch
U.S. Environmental Protection Agency
Research Triangle Park, N.C.

Taduesz Kleindienst

ManTech Environmental Technology, Inc.
Research Triangle Park, N.C.

ABSTRACT

The U.S. Department of Energy and the U.S. Environmental Protection Agency have established, through a Memorandum of Understanding, a coordinated framework for collaborative research examining the impact of alternative motor vehicle fuels on air quality and risk to public health and welfare. A cooperative effort to examine the emissions and fuel economy of DOE flex-fuel vehicles using a variety of potential fuels, and the atmospheric chemistry of the emissions, will begin in January, 1992. During the first year, emissions will be characterized for 6 vehicles, 2 conventional fuel baseline vehicles and 4 flex-fuel vehicles, using up to 9 fuels. Additionally, a dual-chamber irradiation facility will be constructed to support future study of the atmospheric chemistry of the emissions. These studies will examine the formation of ozone and toxic compounds. A detailed description of the experimental procedures to be used is provided.

THE ALTERNATIVE MOTOR FUELS ACT OF 1988 requires the Secretary of the Department of Energy (DOE) to ensure that Federal Government motor vehicle fleets include the maximum number practical of vehicles compatible with alternative fuels such as methanol, ethanol, and compressed natural gas. The Act further requires the Secretary, in cooperation with the Environmental Protection Agency (EPA) and the National Highway Traffic Safety Administration (NHTSA), to conduct a study examining the safety, fuel economy, and emissions of such vehicles. DOE and EPA have established a Memorandum of Understanding agreeing to a framework for collaborative research examining the characteristics of emissions from motor vehicles using alternative fuels, and the atmospheric chemistry of the emissions. This paper describes experimental protocols for planned 1992 activities.

Initial program efforts will include characterization of tailpipe and evaporative emissions from 6 motor vehicles with up to 9 fuels. Laboratory simulations of roadway driving conditions will be used to produce

samples representative of automotive evaporative and tailpipe emissions. Emissions characterization will include measurements of total hydrocarbon (THC), carbon monoxide (CO), carbon dioxide (CO₂), nitrogen oxides (NO_x), methanol (MeOH), ethanol (EtOH), methyltertiarybutyl ether (MTBE), aldehydes (RCHO), and over 200 individual hydrocarbon compounds. Vehicle fuel economy will also be characterized. Additionally, irradiation chamber facilities suitable for studying the atmospheric chemistry of the emissions will be designed, constructed, and characterized.

TECHNICAL APPROACH - EMISSIONS CHARACTERIZATION

Emission tests will be conducted at the EPA Mobile Source Emissions Research Branch (MSERB) laboratory located at Research Triangle Park, N.C. In addition to all of the equipment required for measuring regulated emissions (THC, CO, NO_x, CO₂) from automobiles, this laboratory is equipped with a temperature controlled chassis dynamometer enclosure permitting variation of driving simulation ambient temperature, and all of the equipment and instrumentation required for measuring aldehyde, alcohol, ether, and detailed HC emission rates. Although both exhaust and evaporative tests will be conducted according to the Federal Test Procedure (FTP), the fuels and ambient test temperatures may be varied outside the parameters prescribed for emissions certification (1). *

TEST VEHICLES AND FUELS--Six 1991 motor vehicles will be studied including a conventional gasoline and 2 alcohol flex-fuel Ford Taurus automobiles, and a conventional fuel and 2 alcohol flex-fuel Chevrolet Lumina automobiles. Nine fuels with specifications

* Numbers in Parentheses indicate references at end of the paper.

provided in Table 1 will be used during the 1992 program. The 4 reformulated gasolines will be provided from a set of fuels examined in the Auto/Oil Air Quality Improvement Research Program (2). A total of 40 emissions tests will be completed as indicated in Table 2. Table 3 provides an overview of the activities of a typical test week.

Table 1. Program Test Fuels.

1. Indolene (EPA emissions certification fuel)
2. CAAA Summer Baseline Unleaded Gasoline
8.7 psi RVP, 87.3 (R + M)/2 octane, 339 ppm sulfur, 1.53% benzene, 32.0% aromatic, 9.2% olefin, 58.8% paraffin
3. M85 (85% methanol, 15% unleaded gasoline)
4. E10 (10% ethanol, 90% unleaded gasoline)
5. E85 (85% ethanol, 15% unleaded gasoline)
6. Reformulated gasoline 1 (Auto/Oil code C)
8.7 psi RVP, 288 F T90, 15.4% MTBE, 43.8% aromatic, 3.3% olefin, 37.5% paraffin
7. Reformulated Gasoline 2 (Auto/Oil code J)
8.6 psi RVP, 356 F T90, 14.9% MTBE, 21.4% aromatic, 4.0% olefin, 59.7% paraffin
8. Reformulated Gasoline 3 (Auto/Oil code N)
8.8 psi RVP, 292 F T90, 13.9% MTBE, 21.4% aromatic, 5.7% olefin, 59.0% paraffin
9. Reformulated Gasoline 4 (Auto/Oil code M)
8.7 psi RVP, 356 F T90, 14.5% MTBE, 18.0% aromatic, 21.8% olefin, 45.7% paraffin

VEHICLE PREPARATION--A major goal of this program is assessment of the impact of varied fuel formulations on motor vehicle emissions. Each vehicle will be tested with multiple fuels. To assure that fuel memory effects are minimized, each vehicle will be preconditioned with each test fuel prior to emissions evaluation using the following sequence:

1. Remove the evaporative canister from the vehicle

Table 2. Year 1 Test Matrix.

Vehicles	Fuels	No. of Tests
Conv. Baseline - 1,2	Indolene, Reform. Gas. 3	4
FFV - 3,4,5,6	Indolene, Summer Base., Reform. Gas. 1,2,3,4 M85, E10, E85	36

Table 3. Typical Test Week.

Day 1 - quality assurance
Day 2 - vehicle conditioning with fuel 1
Day 3 - emission tests with fuel 1
Day 4 - vehicle conditioning with fuel 2
Day 5 - emission tests with fuel 2
Week 2 would involve a similar sequence with fuels 3 and 4, and so on.

and purge with 300°F nitrogen at 20 l/min until the incremental weight loss is less than 1 g in 30 min (typically takes 3-4 hrs and removes 100 to 120 g of adsorbed gasoline vapors).

2. Drain the vehicle fuel tank of the previous test fuel, add 5 gal of the following test fuel, and complete an Urban Dynamometer Driving Schedule (UDDS) (initial 1372 sec of the FTP driving schedule to be described later) (1). Drain and refuel to 40% of capacity with the test fuel. Return the "purged" canister to the vehicle. Heat the vehicle fuel tank from 72°F to 120°F using a 2-hr linear temperature ramp. Repeat as necessary (with refueling between each heat build) until the canister reaches a "break-through" load. "Break-through" is defined by monitoring the evaporative emission rate as a function of time, and noting when the slope of emissions versus time changes abruptly. Figure 1 provides a typical "break-through" trace.

3. Drain the vehicle fuel tank and refuel to 40% of capacity. Complete a UDDS driving sequence followed

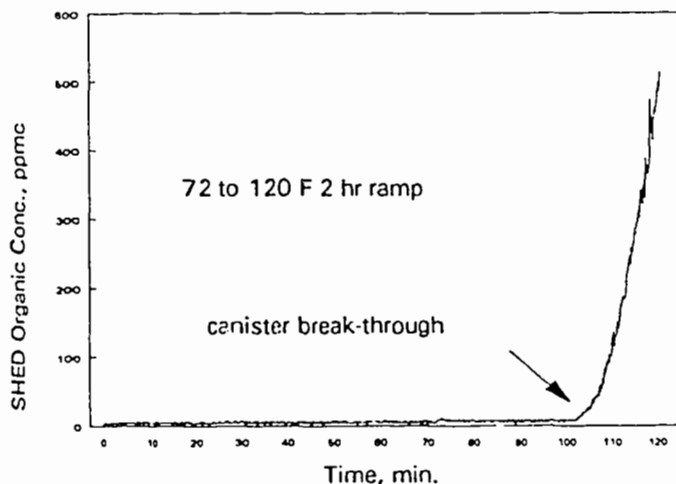


Figure 1. Evaporative Canister "Break-through" Trace.

by overnight soak in preparation for the FTP emissions tests described in the following discussion.

EMISSIONS CHARACTERIZATION--Tailpipe and evaporative emissions will be examined using procedures defined for Federal light-duty motor vehicle emissions certification (1). Figure 2 provides a flow diagram of the test sequence. After an overnight soak at the test temperature, a diurnal (Di) evaporative emissions test is completed, followed by a urban transient driving tailpipe emissions test, followed by a hot soak (HS) evaporative emissions test. Figure 3 provides a schematic of the chassis dynamometer test cell, and a speed versus time trace for the FTP transient driving schedule used to simulate urban driving conditions. The FTP driving schedule includes a cold engine start (after an overnight soak, see Fig. 2), 21.3 mi/h average speed, 2.4 stops/mi, 19% idle operation, 11.1 mi traveled, and 31.3 min duration (plus 10 min engine off soak period). The first 505 sec of the FTP driving schedule is commonly referred to as test phase 1, the next 867 sec as test phase 2, and the final 505 sec as test phase 3.

Evaporative Emissions Determination--Motor vehicle evaporative emissions are measured using a Sealed Housing for Evaporative Determination (SHED). The vehicle is sealed within the SHED enclosure and the Di and HS emissions determined in accordance with the FTP (1). At the conclusion of each evaporative test, samples are taken from the SHED into a 60L Tedlar bag for gas chromatographic (GC) analysis of methanol,

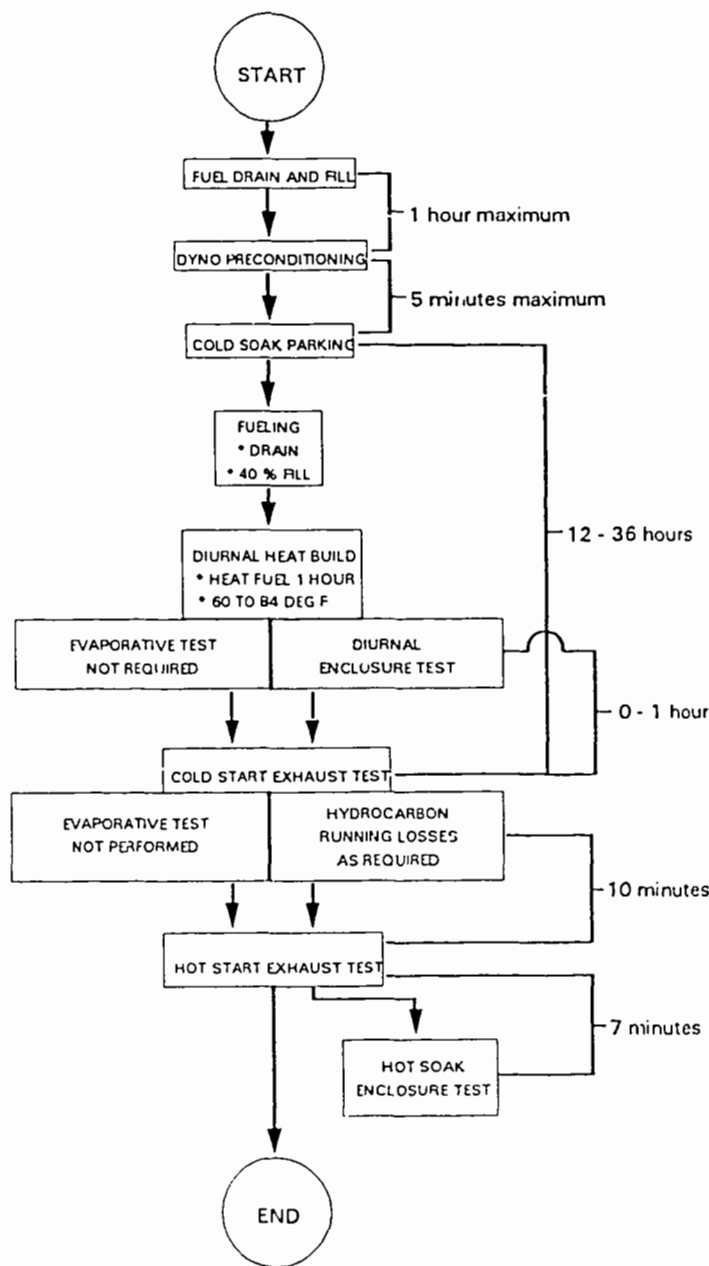


Figure 2. Emissions Test Sequence.

ethanol, MTBE, and detailed HCs, as appropriate. Samples for THC analysis are taken directly from the SHED to a heated ($235 \pm 15^{\circ}\text{F}$) FID (HFID). Evaporative THC emissions are reported as non-oxygenated THC by correcting the THC value for HFID response to methanol (or other oxygenates). The organic emission rates may also be reported as Organic Material Hydrocarbon Equivalent (OMHCE) according to equation 1 for methanol fuels (1):

$$OMHCE_{evap} = HC_{Di} \text{ mass} + \frac{14.3594}{32.042} CH_3OH_{Di} \text{ mass} + HC_{HS} \text{ mass} + \frac{14.2284}{32.042} CH_3OH_{HS} \text{ mass} \quad (1)$$

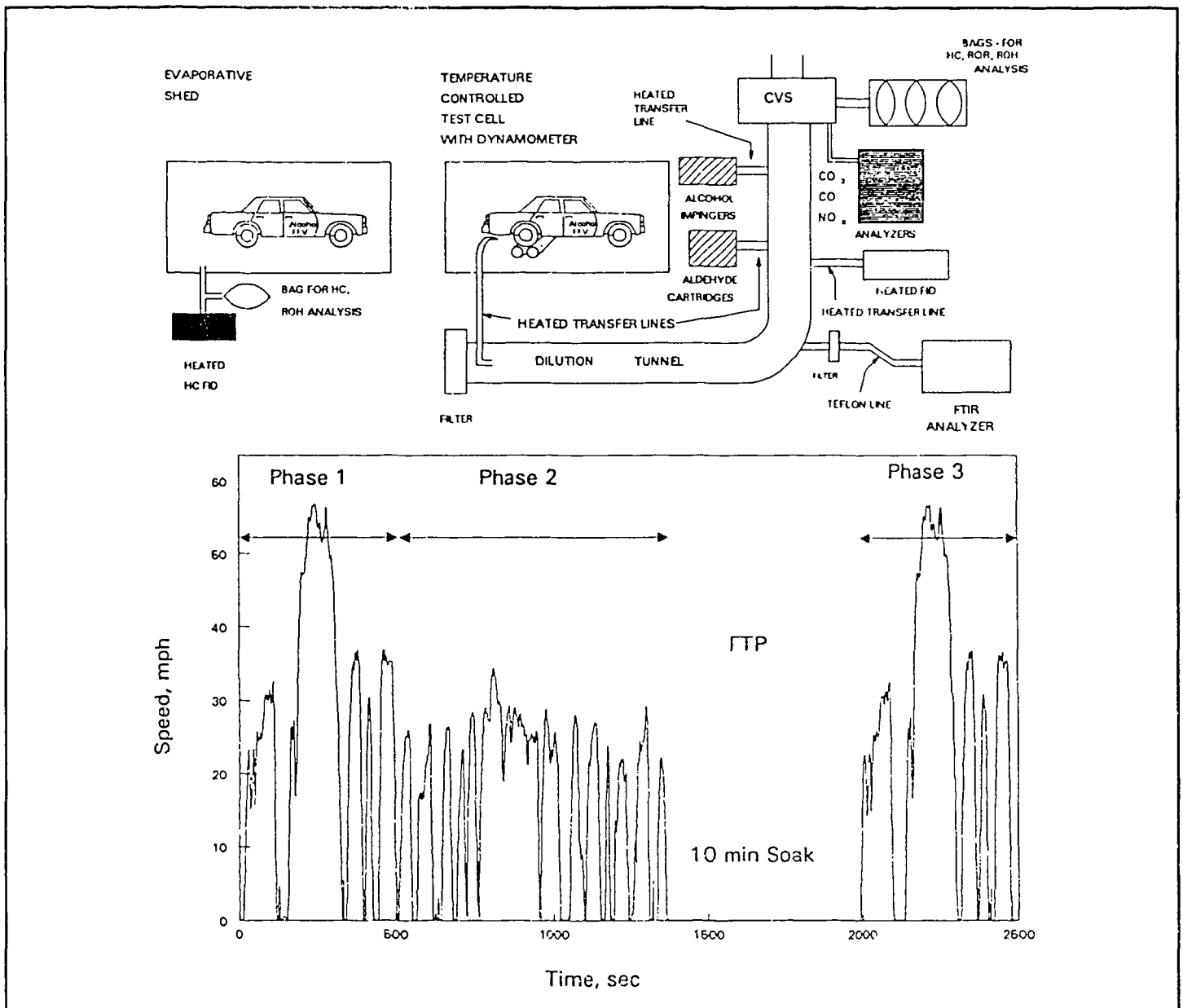


Figure 3. Test Cell Configuration and Driving Cycle.

where:

$HC_{Di\ mass}$ and $HC_{HS\ mass}$ = Di and HS emissions hydrocarbon mass in grams, respectively, and

$CH_3OH_{Di\ mass}$ and $CH_3OH_{HS\ mass}$ = Di and HS emissions methanol mass in grams, respectively;

which assume that the evaporative Di emissions hydrogen to carbon ratio is 2.33 and HS emissions hydrogen to carbon ratio is 2.2 (conforming with conventional gasoline standards). Similar calculations can be completed for ethanol fuels using appropriate coefficients for ethanol.

Di and HS evaporative emissions tests are conducted in conjunction with the FTP, as shown in Figure 2. Following an overnight soak in the Temperature Controlled Test Chamber (TCTC) at the test temperature, the vehicle is pushed into the SHED for the Di test. During the Di test, tank fuel temperature is elevated using a 24°F/hr ramp, e.g., 40 to 64°F for a 40°F test, 60 to 84°F for a 70°F test, and 72 to 96°F for a 90°F test. The initial 1992 program matrix (see Table 2) will examine Di evaporative emissions from 60 to 84°F, with tailpipe emissions examined at 70°F (as in Federal emissions certification). Following the Di test, the vehicle is pushed back into the TCTC and allowed to equilibrate at the test temperature. After temperature equilibrium is reached, the UDDS is run, followed immediately by the HS evaporative test. The SHED is not

equipped to be operated at reduced ambient temperatures; therefore, a subambient (e.g. 40°F) evaporative emission test would be conducted at laboratory temperatures near 70°F. This should have little effect on Di tests which are conducted with engine and fuel cold. HS tests, which begin with engine and fuel warm, should be somewhat affected in that the engine and fuel will not cool as rapidly as they would in a cooler environment. For a high temperature evaporative emissions test (e.g. 90°F), an appropriate Di temperature ramp (e.g. 72°F to 96°F) would be used and the SHED temperature for HS maintained at the elevated test temperature (e.g. 90°F). The Di and HS evaporative emission rates are combined according to equation 2 to permit comparisons with tailpipe exhaust rates.

$$Evap. Emissions, g/mi = \frac{(3.05 \text{ trips/day} \times \text{hot soak emissions, g/trip}) + \text{diurnal emissions, g/day}}{31.1 \text{ mi/day}} \quad (2)$$

$$OMHCE_{tailpipe} = HC_{mass} + \frac{13.8756}{32.042} (CH_3OH_{mass}) + \frac{13.8756}{30.0262} (HCHO_{mass}) \quad (3)$$

Exhaust Emissions Determinations -- Vehicle exhaust emission tests will be conducted using an electric chassis dynamometer (Horiba Instruments, Inc.) to simulate vehicle road load. The dynamometer rolls are enclosed within a TCTC permitting vehicle soak and operation at temperatures from 20°F to 110°F as illustrated in Figure 3.

Exhaust gases are sampled using a constant volume sampling (CVS) technique commonly used for vehicle emissions certification tests (1). A heated transfer tube is used within the TCTC to direct vehicle raw exhaust to a "dilution tunnel" where the exhaust is cooled and diluted prior to sampling for analysis. Exhaust gas is thoroughly mixed in the dilution tunnel with 70°F dilution air. Total flow through the dilution tunnel is held constant (e.g. 750 CFM). Aliquots of the diluted exhaust are collected directly from the dilution tunnel at a constant flow rate over the duration of the test, permitting determination of pollutant mass emission rates (g/mi) from sample concentration, total diluted exhaust volume, and distance traveled. The sampling system has previously been qualified for quantitative transfer of methanol, formaldehyde, and other compounds of interest at varied ambient temperatures from the motor vehicle tailpipe to the analytical instrumentation (3,4).

Regulated emissions (THC, CO, NO_x, CO₂) are sampled and analyzed using standard Federal certification procedures (1). THC emissions are reported as

non-oxygenated HC by using a procedure to correct the THC value for FID response to alcohols (5). Tailpipe organic emissions rates may also be reported as OMHCE wherein total organic carbon mass is calculated according to equation 3 for methanol fuels which assumes that the hydrogen to carbon ratio of all tailpipe organic emissions is 1.85 (permits conformity with conventional gasoline emission standards) (1). Similar calculations can be completed for ethanol fuels using appropriate coefficients for ethanol and acetaldehyde.

The FTP driving schedule includes three test phases: a cold start transient phase (505 sec.), a stabilized phase (867 sec.), and a hot start transient phase (505 sec.). There is a 10 minute engine-off soak period between phases two and three. Emissions from

each phase are analyzed separately and then combined to calculate a "weighted" emission rate according to equation 4:

$$Y_{wm} = 0.43 \frac{Y_{ct} + Y_s}{D_{ct} + D_s} + 0.57 \frac{Y_{ht} + Y_s}{D_{ht} + D_s} \quad (4)$$

where:

Y_{wm} = weighted mass emissions of each pollutant, i.e. HC, CO, NO_x, CO₂, MeOH, etc. in grams per vehicle mile,

Y_{ct} = mass emissions calculated from the transient phase of the cold start test, in grams per test phase,

Y_s = mass emissions calculated from the stabilized phase of the cold start test, in grams per test phase,

Y_{ht} = mass emissions calculated from the transient phase of the hot start test, in grams per test phase,

D_{ct} = the measured driving distance during the transient phase of the cold start test, in miles,

D_s = the measured driving distance during the stabilized phase of the cold start test, in miles, and

Dht = the measured driving distance during the transient phase of the hot start test, in miles.

Fuel Economy--Fuel economy is evaluated both in terms of miles traveled per gallon of fuel consumed (mi/gal) and in terms of BTUs of energy consumed per mile traveled (BTU/mi). Mi/gal fuel economy is determined using classical carbon balance equations with appropriate carbon weight fraction for the varied fuels. Equations are presented in Figure 4. Energy based fuel economy is calculated using appropriate energy densities for the varied fuels. Equations are presented in Figure 5.

Because of the lower energy densities of the alcohol fuels, reduced mi/gal fuel economies are expected, depending on the fraction of the fuel that is alcohol. However, improved energy efficiencies are possible with alcohol fuels, off-setting somewhat, the reduced fuel energy densities. Table 4 provides examples of fuel economies observed with FFVs using gasoline and M85 (85% methanol, 15% gasoline) fuels.

Analytical Chemistry--As previously discussed, THC, CO, NO_x, and CO₂ are sampled and analyzed using standard Federal emissions certification procedures (1). Samples for exhaust detailed HC measurements are collected by pumping a constant aliquot of the diluted exhaust from the CVS into Tedlar bags for subsequent analysis by gas chromatography. Gas chromatographs equipped with flame ionization detectors (FIDs) are used for the detailed HC analysis (6). Each instrument uses three analytical columns -two packed columns that resolve C₁ and C₂ HCs, and a capillary column that resolves C₃-C₁₂ HCs. The method provides quantitation of over 200 HC compounds. Figure 6 provides a schematic of the chromatographic system for detailed HC analysis.

Aldehyde compounds, sampled from the dilution tunnel through a heated (235 ± 15^oF) sample line (at 1 LPM), are collected on dinitrophenyl- hydrazine (DNPH)-coated silica gel cartridges. Individual aldehydes, which are collected on the cartridge as DNPH aldehyde derivatives, are subsequently analyzed by high performance liquid chromatography. This sampling technique and analytical method permits quantitative determination of 15 individual aldehydes (7). Figure 7 provides a schematic of the chromatographic system for aldehyde analysis.

Alcohols are sampled using water impingers and analyzed using a previously described GC method (8). Ethers are sampled into Tedlar bags, similar to the detailed HC practice, for subsequent GC analysis using previously described GC procedures (9,10). Figures 8

$$\text{mi/gal} = \frac{\text{g Carbon / gal fuel}}{\text{g Carbon in exhaust / mi}}$$

$$\text{mi/gal} = \frac{K1 (\text{fuel g / gal})}{K1 (\text{g OM / mi}) + K2 (\text{g CO / mi}) + K3 (\text{g CO}_2 / \text{mi})}$$

K1 = Fuel carbon weight fraction
= 0.866 (gasoline), 0.375 (MeOH), 0.449 (M85)

K2 = CO carbon weight fraction = 0.429

K3 = CO₂ carbon weight fraction = 0.273

Figure 4. Carbon-Balance Fuel Economy.

$$\text{BTU/mi} = \frac{8.34 * \text{heating value, BTU/lb} * \text{fuel density, g/ml}}{\text{fuel economy, mi/gal}}$$

where:

	Heating Value, BTU/lb	Density, g/ml
MeOH	8,600	0.79
Gasoline	18,700	0.74
M85	10,115	0.78

Figure 5. Energy-Based Fuel Economy.

Table 4. Example FFV Fuel Economies.

Fuel	mi/gal	BTU/mi
M0	21.8	5,305.0
M85	13.3	4,996.8

and 9 provide schematics of the chromatographic systems used for alcohol and ether analyses, respectively.

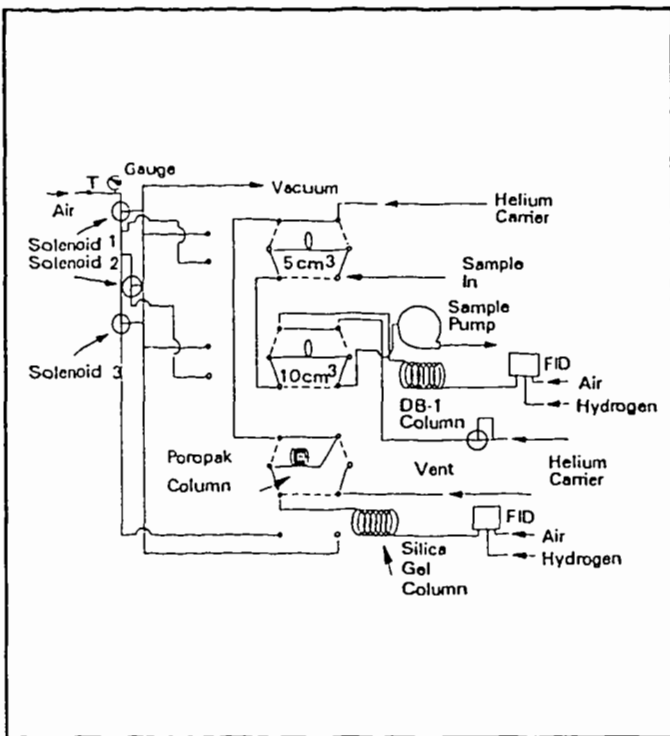


Figure 6. C₁ to C₁₂ Hydrocarbon Chromatography.

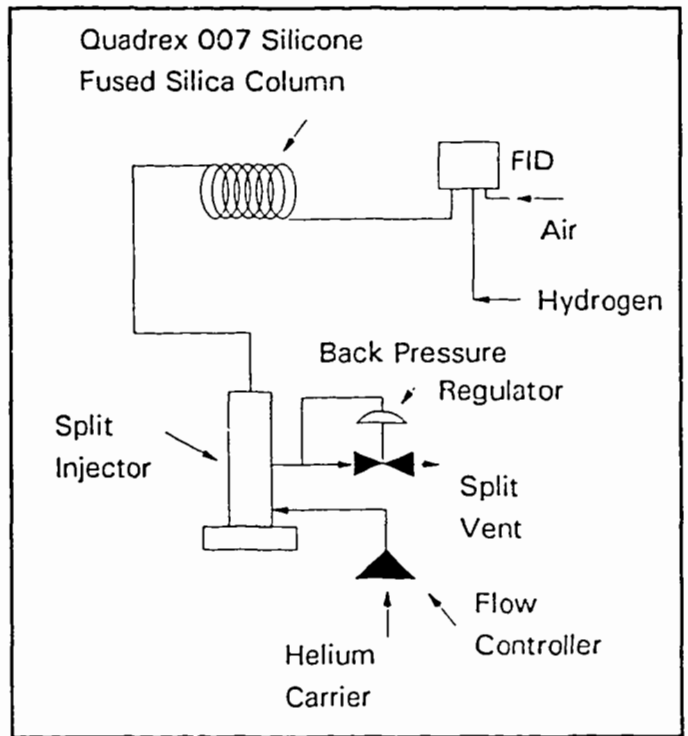


Figure 8. Alcohol Chromatography.

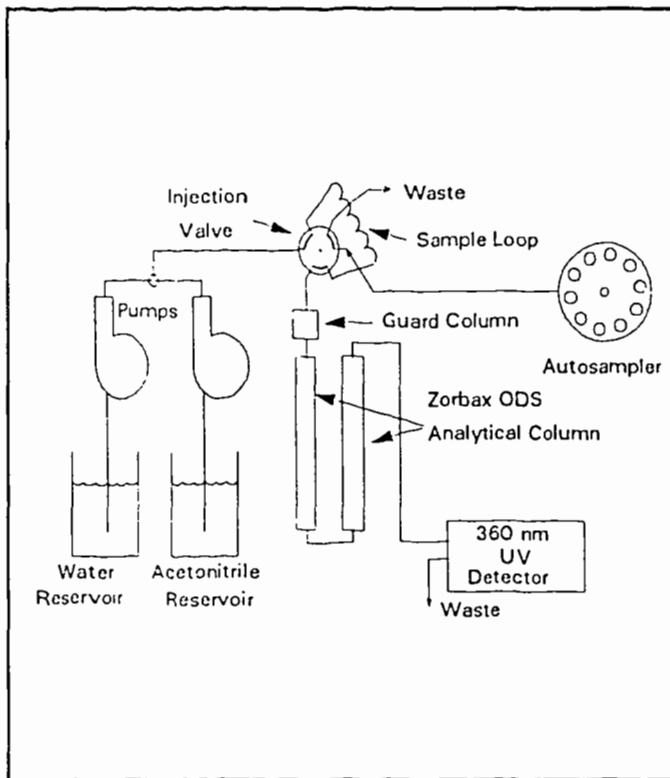


Figure 7. Aldehyde Chromatography.

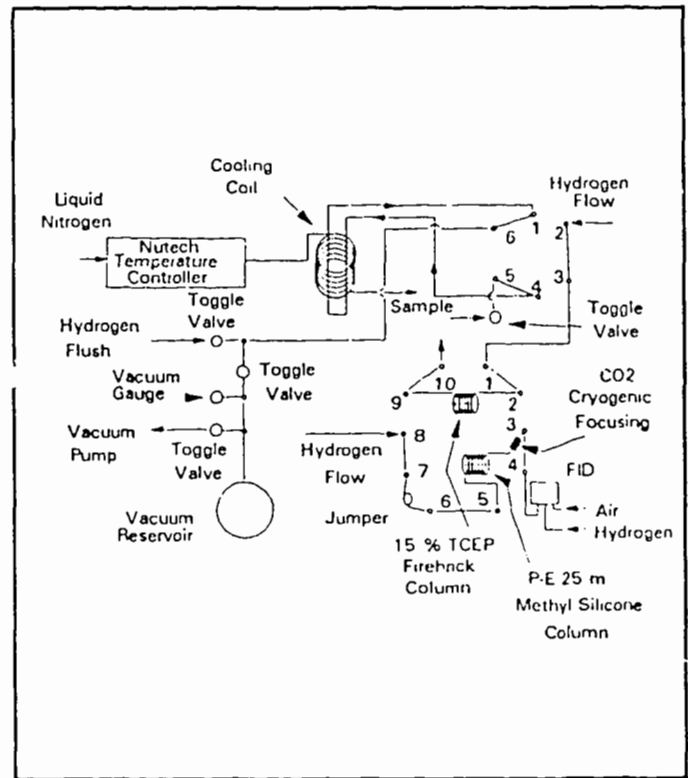


Figure 9. Ether Chromatography.

QUALITY ASSURANCE--The Quality Assurance/Quality Control (QA/QC) Plan and Procedures include *Organization and Responsibility*, assigning QC responsibilities to program staff, *Objectives for*

Measurements and Performance establishing accuracy and precision goals for all program measurement systems, *Outputs* providing both the outputs which are necessary to assure that equipment is properly main-

tained, and outputs needed to assess and monitor QC, *Statistical Methods* describing how outputs, such as accuracy and precision, are to be calculated, *Reports* identifying all QC reporting requirements and milestones, and *Audits* describing system audit procedures.

Organization and Responsibility--The EPA technical program at Research Triangle Park, N.C. is supported by an onsite contract with ManTech Environmental Technology, Inc. QC/QA organization for this program provides overall project QA responsibility to the EPA Project Officer. All QC reports or outputs related to measurements performed by ManTech personnel are the responsibility of the ManTech Technical Supervisor.

QC Objectives for Measurement and Performance--The quality assurance objectives for accuracy and precision are presented in Table 5. If at any time it is noted that deviations in measured values exceed the objectives, testing is stopped, equipment is examined, and testing is resumed after the problem has been corrected.

Table 5. Quality Assurance Objectives.

PARAMETER	ACCURACY, %	PRECISION, %
THC Analysis	10	2
CO Analysis	10	2
NO _x Analysis	10	2
CO ₂ Analysis	10	2
Alcohol Analysis	10	5
Ether Analysis	10	5
Aldehyde Analysis	10	5
Detailed HC Analysis	10	5
Dyno Speed	5	5
Dyno Torque	5	5
Reid Vapor Pressure	10	5
PDP Counter	10	5
SHED Volume	2	2
SHED Leak Rate	10	5

Gravimetric Balance	5	1
Gravimetric Weights	1	1
SHED Temperature	5	5
Dyno Cell Temperature	5	5
Veh. Coolant Temperature	5	5
Fuel Temperature	5	5
Catalyst Temperature	10	10
CVS Temperature	5	5
Dyno Cell Pressure	5	2
CVS Pressure	5	2

QC Procedures and Outputs--The QC outputs required for this program are given in Tables 6 and 7. All outputs should be completed within the specified periods for the duration of the program. Outputs given in Table 6 are "nondeliverable" which means that the QC work, when completed, is signed off in the QC Notebook with no other report required. The Project Officer reviews all QC Notebooks monthly insuring that all equipment is being properly maintained and quality controlled. Outputs given in Table 7 are reported directly to the Project Officer since these indicate the status of compliance with the data specifications stated in the previous section.

Table 6. QC Nondeliverable Outputs.

OUTPUTS ¹	TIME PERIOD
Calibrate THC Analyzer (86.121-82,90)	Daily
Adjust THC FID for optimum HC response (86.121-82)	Annually
THC Analyzer linearity checks (86.121-82,90)	Monthly
THC Analyzer MeOH response (86.121-90)	Monthly

Calibrate CO Analyzer (86.122-78)	Daily
CO Analyzer H ₂ O interference check (86.122-78)	Annually
CO Analyzer linearity check (86.122-78)	Monthly
Calibrate NO _x Analyzer (86.123-78)	Daily
NO _x Analyzer converter efficiency check (86.123-78)	Weekly
NO _x Analyzer linearity check (86.123-78)	Monthly
Calibrate CO ₂ Analyzer (86.124-78)	Daily
CO ₂ Analyzer linearity check	Monthly
Calibrate CVS (86.119-78,90)	Semi-annually
Calibrate temperature transducers (ASTM E220-80)	Monthly
Calibrate pressure transducers (CVS Protocol)	Monthly
Calibrate dry test meters (86.120-82)	Monthly
Verify currency of NBS cylinder certificates	Monthly
Calibrate dyno speed signal (EPA 650/4-75-024d, TP 202)	Monthly
Calibrate dyno load cell (86.118-78 & manuf. recommendations)	Monthly
Calibrate weights (ASTM E617-81)	Quarterly
Calibrate RVP (80.Appendix D, ASTM D323-89)	Monthly
Calibrate GCs (GC RPM)	Daily

Calibrate HPLC (Aldehyde RPM)	Daily
Calibrate SHED (86.117-78,90)	Annually
Characterize SHED leak rate (86.117-78,90)	Monthly
Perform dyno preventative maintenance	As Scheduled
Perform SHED preventative maintenance	As Scheduled
Oxygenate methods cross-checks	Monthly
Detailed HC methods cross-checks	Monthly
Calibrate Ether analyzer (80-Appendix F)	Daily

¹ numbers in parenthesis are Federal Register references unless otherwise indicated

Table 7. QC Deliverable Outputs.

OUTPUTS ¹	TIME PERIODS
THC Analysis	Monthly
CO Analysis	Monthly
NO _x Analysis	Monthly
CO ₂ Analysis	Monthly
Methanol Analysis	Monthly
Aldehyde Analysis	Monthly
Detailed HC Analysis	Monthly
Ether Analysis	Monthly
Dyno Speed	Monthly
Dyno Torque	Monthly
SHED Temperature	Monthly
Cell Temperature	Monthly
Coolant Temperature	Monthly
Fuel Temperature	Monthly
Catalyst Temperature	Monthly
CVS Temperature	Monthly
SHED Pressure	Monthly
Cell Pressure	Monthly

CVS Pressure	Monthly
SHED Volume (and integrity)	Monthly
Balance	Monthly
Reid Vapor Pressure	Monthly
PDP Counter	Monthly
HC Blind Audit Results	Quarterly
CO Blind Audit Results	Quarterly
NO _x Blind Audit Results	Quarterly
CO ₂ Blind Audit Results	Quarterly
Gravimetric Weights	Annually
QC Notebook	Monthly

¹ measures of precision and accuracy unless otherwise indicated

Accuracy and precision for most of the parameters listed in Table 5 are determined using "blind" samples which have been referenced to the National Institute of Standards and Technology (NIST). Because NIST standards are not available for detailed HC and aldehyde measurements, research protocol methods (RPMs) are used to assure the accuracy and precision of these measurements.

Any parameter which fails to achieve its specified accuracy or precision goal shall be corrected before testing can proceed. Data whose integrity has been compromised due to the malfunctioning of any instrument or system during its collection shall be discarded and the tests rerun. For this reason, the Project Officer reviews all data being generated daily and ceases testing when trends reveal the likelihood of some component malfunction or other system irregularity.

QC Statistical Methods--All accuracy determinations (except for SHED Volume) are made by comparing the mean measured value from three separate measurements of the reference material with the actual value of the reference material according to equation 5:

$$\% \text{ Accuracy} = \frac{MV - RV}{RV} \times 100 \quad (5)$$

where MV - RV = absolute magnitude of mean value minus reference value.

The reference material is presented to the analyzer operator as an "unknown"; span gases are not used for

determining accuracy and precision. All reference materials are NIST, directly referenced to NIST, or prepared in accordance with an accepted Standard Operating Procedure (SOP) when NIST standards are not available. Measures of accuracy and precision involve pollutant concentrations, temperatures, and pressures near the median values experienced in the empirical program. Accuracy of the SHED volume is assured in accordance with standard practice (1).

Precision is calculated by taking the standard deviation (SD) of ten measurements for emissions analyzers and three for all other devices, and dividing it by the mean value (MV) according to equation 6:

$$\% \text{ Precision} = \frac{SD}{MV} \times 100 \quad (6)$$

Reports--Routine "deliverable" outputs (Table 7) are reported to the Project Officer in accordance with the QC procedures and outputs section; and other outputs entered in a QC Notebook which is presented monthly to the Project Officer as a "deliverable" output. The Project Officer makes a QC Evaluation Report quarterly and within the Final Report. The Evaluation Report is a brief summary of QA/QC within the project and is meant to highlight problem areas, their resolution or nonresolution, and recommended action to be taken in the event of unresolved issues.

Audits--An annual systems audit of the project is conducted by the MSERB QA Officer and/or the Branch Chief. The systems audit focuses on the project's adherence to required procedures. For example, instrument logs or notebooks are checked to see if the equipment is being properly maintained and calibrated, procedures for determining accuracy and precision are discussed with personnel who actually perform these measures, and QA equipment, such as calibration gases and meters, are examined for documented certification. Instrument operators are questioned about the daily or routine procedures they follow when running a test. Particular attention is directed to insuring that SOPs and RPMs are being followed. As deficiencies are noted, the person responsible is instructed to insure that immediate corrective action is taken.

TECHNICAL APPROACH - ATMOSPHERIC CHEMISTRY

Comprehensive evaluation of the impact of alternative fuels on risk to public health and welfare must include examination of the atmospheric chemistry of the emissions. The formation of photochemical oxi-

dants in urban environments including ozone, results from chain reactions involving hydrocarbons and oxides of nitrogen (NO_x) in the presence of sunlight. These reactions produce many organic compounds, including aldehydes and ketones, peroxyacetyl nitrate (PAN), organic nitrates and peroxides, and others. Some of the products have different genotoxic (i.e., mutagenic or possibly carcinogenic) properties than the reactant compounds, that is, the original emissions.

ManTech Environmental Technology has developed experimental protocols permitting the direct study of the atmospheric chemistry of motor vehicle emissions, including the formation of ozone, and toxic and mutagenic compounds (11). The protocols involve irradiation of mixtures of motor vehicle tailpipe exhaust (generated by prescribed driving cycles) and surrogates of evaporative emissions or background urban air organic compound mixtures. The surrogate addition is necessary to achieve HC/NO_x ratios typical of urban air mixtures. Automobile emissions typically have HC/NO_x ratios of about 1 to 3, whereas urban atmospheres have ratios in the 7 to 12 range. The formation of ozone and other toxic chemicals is sensitive to this ratio. At the lower ratios (i.e., 1 - 3), atmospheric chemistry proceeds extremely slowly.

In these studies, continuous measurements are made of the major inorganic chemical species present in the chamber, which include NO, NO_x, O₃, and CO. The total hydrocarbon signal is also measured continuously. Hydrocarbons in the mixture are speciated by gas chromatography using two columns (DB1 and Carbowax) in series. This GC is also capable of measuring numerous reaction products following irradiation including organic nitrates and nitro compounds. PAN and other peroxyacyl nitrates are measured using a dedicated GC having a packed carbowax column and electron capture detection. Carbonyl compounds are sampled by impinger collection through DNPH derivatizing agent and quantified by HPLC. Nitric acid can also be formed through photochemical reactions and is measured by collection on nylon filters and analysis by ion chromatography. These measurements are made before irradiation and periodically during the progress of the photochemical reaction.

During 1992, ManTech will construct and characterize an irradiation chamber facility interfaced with a motor vehicle similar to that illustrated in Figure 10. In the experiments for this study, the chamber design will be portable permitting both indoor irradiations with UV-A and UV-B blacklights, and outdoor irradiations with actual sunlight. The design uses two identical 8,000 L chambers permitting contrasts between the reaction products of the motor vehicle exhaust mixtures and reference mixtures. The initially conceived design

allows the chamber to be operated with or without dilution, depending on the objectives of individual experiments. The chamber will be characterized by irradiating mixtures of single hydrocarbons and NO_x, which have well-studied profiles of reactant disappearance and product formation.

Following construction and characterization of the chamber facility, an extensive three-phase testing program will be initiated examining the atmospheric chemistry of emissions from the previously described vehicles and fuels. In most experiments, direct comparisons will be made of the oxidant and/or toxic compound(s) formation, by comparison of the irradiated reference and the test mixtures. The major two phases include: oxidant formation studies and detailed chemical characterization of the photooxidation products. In an optional third phase, characterization of the mutagenicity of the reactants and products can be made using Ames bioassays by procedures already developed.

REFERENCES

1. Code of Federal Regulations, Title 40, Part 86, Control of Air Pollution from New Motor Vehicle and New Motor Vehicle Engines: Certification and Test Procedures, Office of the Federal Register National Archives and Records Administration, Washington, D.C., July, 1990.
2. Burns, V.R., Bensen, J.D., "Description of Auto/Oil Air Quality Improvement Research Program," SAE 912320, International Fuels and Lubs Meeting, Toronto, Canada, October, 1991.
3. Baugh, J., Ray, W., Black, F., Snow, R., "Motor Vehicle Emissions Under Reduced Temperature Idle Conditions", Atmos. Env., Vol. 21(10), pp 2077-2082 (1987).
4. Sigsby, J.E., McArver, A., Snow, R., "Evaluation of a FTIR Mobile Source Measurement System," EPA/600/S3-89/036, U.S. Environmental Protection Agency, Research Triangle Park, NC, August, 1989.
5. Gabele, P.A., Baugh, J.O., Black, F.M., Snow, R., "Characterization of Emissions Using Methanol-Gasoline Blended Fuels," JAPCA, Vol. 35, pp. 1168-1175 (1985).
6. Sigsby, J.E., Duncan, J., Crews, W., Burton, C., "Research Protocol Method for Analysis of Detailed Hydrocarbons Emitted from Automobiles by Gas Chromatography," EPA/600/S3-89/036, U.S. Environmental Protection Agency, Research Triangle Park, NC, August, 1989.

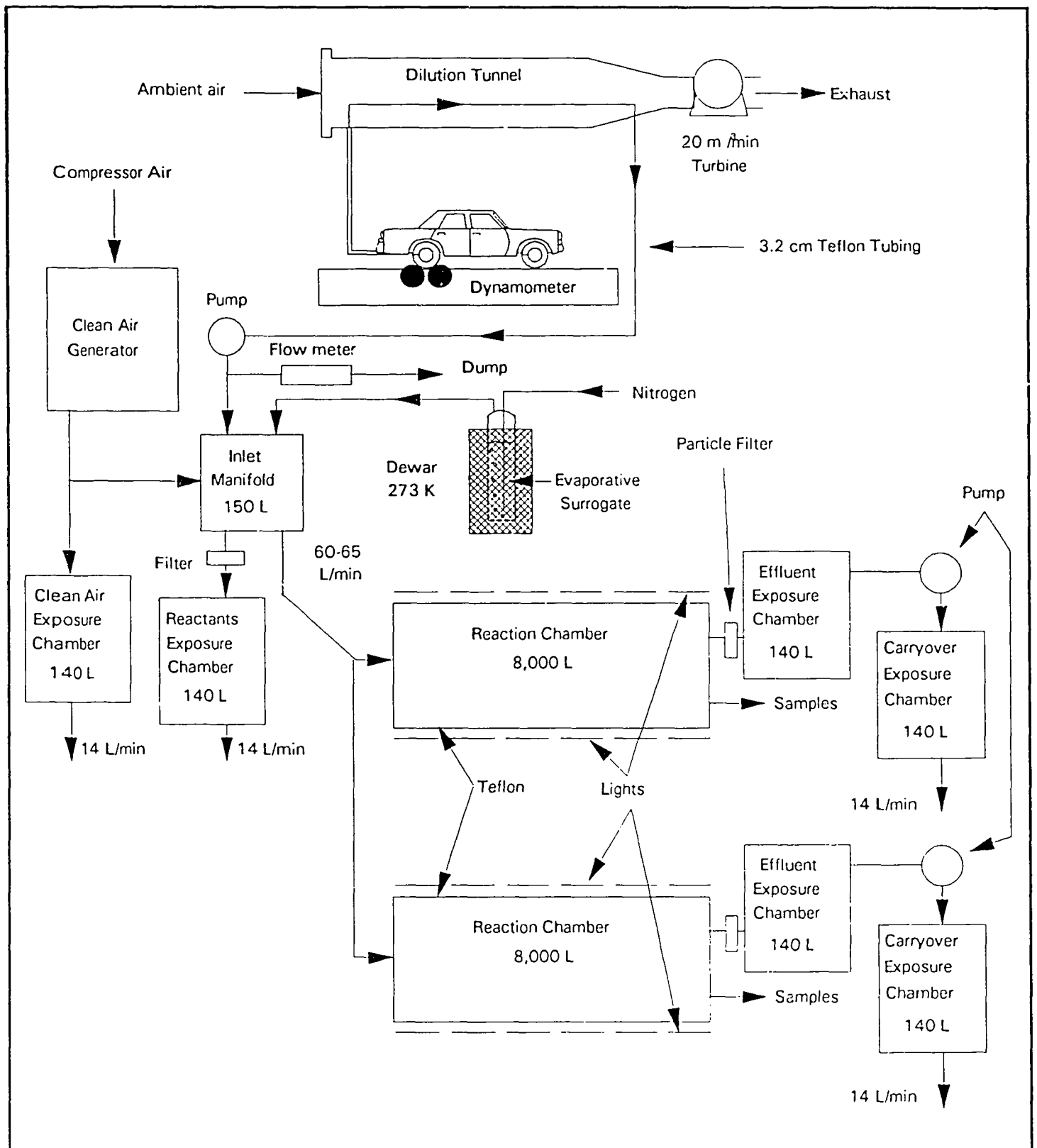


Figure 10. Schematic of Test Apparatus for Examining the Photochemical Oxidant and Toxic Compound Products from Irradiated Automobile Exhaust Mixtures.

matography," U.S. Environmental Protection Agency, Research Triangle Park, NC, June 1989.

7. Tejada, S.B., "Evaluation of Silica Gel Cartridges Coated In Situ with Acidified 2,4-Dinitrophenylhydrazine for Sampling Aldehydes and Ketones in Air", Intern. J. Environmental Anal. Chem., Vol. 26, pp 167-185 (1986).

8. U.S.EPA, "Calculation of Emissions and Fuel Economy When Using Alternative Fuels - Appendix A-5: Measurement of Methanol," EPA 460/3-83-009, Office of Mobile Sources, Ann Arbor, MI, March, 1983

9. Federal Register, "Test Method for Determination of C1 to C4 Alcohols and MTBE in Gasoline by Gas Chromatography," Vol. 54(54), pp 11904-11910, March 22, 1989.

10. Duncan, J.W., Burton, C.D., Crews, W.S., "A Method for Measurement of Methanol, Ethanol, and Methyltertiarybutyl Ether Emissions from Motor Vehicles," Northrop Services, Inc., Research Triangle Park, NC, 1988.

11. Kleindienst, T.E., Smith, D.F., Hudgens, E.E., Snow, R.F., Perry, E., Bufalini, J.J., Claxton, L.D., Black, F.M., Cupitt, L.T., "The photooxidation of automobile emissions: measurements of the transformation products and their mutagenic activity," In Review, Atmos. Environ., (1991).

The information presented in this document has in part been funded by the United States Environmental Protection Agency. It has been subjected to the Agency's peer and administrative review, and has been approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.