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Appendix 7

Vehicle Emission Testing and Gasoline Headspace Analysis Protocol

Vehicle Emission Testing

An ARB study is underway to clarify the effects of using ethanol in gasoline as an oxygenate additive. PTSD is the lead division in the study and requires vehicle exhaust emission comparisons, using three fuels with ten vehicles. One fuel will be a regular, unleaded, non-oxygenated fuel. The second will be a regular gasoline blended with about two percent oxygen (from ethanol) by weight. MTBE content in this fuel should be below one percent by weight. The third fuel will be a California commercial Phase 2 summer grade fuel with about 11% of MTBE. Complete speciation analyses for hydrocarbons, carbonyls, and alcohols will be required for all emission test samples in this program.

Project Engineer

Paul Allen in PTSD will be the project engineer. Any changes to this test plan must be approved by the project engineer before they are implemented. Jerry Ho in MSOD will be the on-site project engineer to coordinate with Paul to manage the project. Dennis Calgaro will be the test engineer for this project.

Test Vehicles

One or two vehicles will be selected per week from July 19 through September 15 (10 vehicles total). The desired source of vehicles is the Vehicle Surveillance Program. State vehicles with E-plates may be selected for this project when surveillance vehicles are not available. Vehicles will be selected based on the baseline FTP emission levels for hot running Bag 2 total hydrocarbon (THC). At least half of the vehicles in this project must have Bag 2 THC emissions in the range of 0.5 to 4 grams/mile. Other than this emission criterion vehicles should be randomly selected from the Surveillance Program.

Fuels

MSOD will obtain commercially available compliant non-MTBE gasolines in drums from fuel distributors (Chevron and Tosco in the San Francisco Bay Area). Gasolines must meet specifications required in California except for oxygen content. The ARB underground tank California Phase 2 summer grade fuel with MTBE will be used as the third fuel. A fuel sample will be obtained from each drum delivered and analyzed (complete organic gas speciation and all specifications for Phase 2 fuel) by MLD Southern Laboratory Branch. The test sequence for the two non-MTBE fuels will be based on Table 1 to avoid potential bias.

Test Cyles

Each vehicle will undergo one cold start Unified Cycle (UC) for each fuel. Regular Bag samples will be collected and analyzed at the end of the test. An extra bag will be sampled at the end of the first 100 seconds of the cold start UC test Bag 1. A modified

aldehyde sample cart will be used to collect the first 100 seconds bag. Second-by-second modal data, bag results, and speciated HC bag analyses are required for all sample bags including the first 100 seconds bag. One composite background bag is acceptable for the regular 3 bag speciation analyses and the first 100 seconds sample analyses. The first 100 second sample will be labeled and reported as sample #4. Modal analyses from the dyno only provide the HC readings for the first 100 seconds; the methane readings for the first 100 seconds sample can only be based on the Pre-concentrated Direct Flame Ionization Detector (PDFID) instrument readings by MLD. The non-methane hydrocarbon (NMHC) readings for the first 100 second sample and the dilution ratio will be calculated and delivered to MLD daily by the on site project engineer.

Vehicle Preconditioning

Test vehicles will be first classified into two groups, one group with adaptive learning and another group without adaptive learning capability. Adaptive learning is defined as vehicles with closed-loop fuel control. Cars equipped with oxygen sensors in the early 80's were the first group of vehicles with adaptive learning.

Each acceptable test vehicle **with adaptive learning** shall be subjected to the following preconditioning schedule:

- Drain the tank fuel
- Add 5 gallons of the correct test fuel
- Run the vehicle on the road for 50 miles (include key on/key off)
- Drain the tank fuel
- Add 3 gallons test fuel
- Start engine - one min. idle
- Drain fuel tank
- Add enough fuel to fill the tank to 40 percent
- Run one dummy CVS-72
- Engine off - five min. soak.
- Start engine - one min. idle
- Engine off - five min. soak
- Start engine - one min. idle
- Engine off - five min. soak
- Run one dummy CVS-72
- Cold soak the vehicle at least 12 hours, but not more than 36 hours prior to a UC or truncated UC

Each acceptable test vehicle **without adaptive learning** shall be subjected to the following preconditioning schedule:

- Drain the tank fuel
- Add 5 gallons of the correct test fuel
- Run the vehicle on the road for 25 miles
- Drain the tank fuel
- Add enough fuel to fill the tank 40 percent

- Run one dummy CVS-72
- Cold soak the vehicle at least 12 hours, but not more than 36 hours prior to a UC or truncated UC

Evaporative Test

One evaporative sample of headspace vapors shall be obtained from a 40 ml glass vial with 10 ml of gasoline heated to 100 degrees F for 2 hours in a SHED cell. The headspace sample is needed to obtain an estimate of diurnal evaporative speciation and to gauge the performance of a mathematical evaporative model developed at U.C. Berkeley. One fuel sample for each drum of gasoline used in this project should be obtained and prepared for headspace evaporative test.

Data Reporting and Quality Control

The test engineer will verify the test results including modal data right after each UC test. Driving violations are acceptable in this test program unless there are too many stalls (>3) that will obviously impact the results. The on-site project engineer will coordinate with MLD to obtain the preliminary GC/DYNO QC results within 2 days. Since a discrepancy exists between the modal data and composite data, the current MLD GC/DYNO QC criteria (based on composite data) may have to be adjusted to account for the difference between the modal and composite data. If the test vehicle successfully completes all three UC tests and passes the MLD QC, the test engineer will release this vehicle back to the Surveillance program. The final speciation test data will be delivered to PTSD (Paul Allen) when MLD completes the full speciation analyses and assigns a "Data for Record" for that test.

Gasoline Headspace Analysis

The Organic Analysis Section of the Monitoring and Laboratory Division (MLD) developed a method to sample and analyze gasoline headspace samples. The following is a brief description of the method.

Gasoline samples are received in 1-liter metal containers and are stored in a refrigerator at approximately $0^{o}C$. One 60-ml portion of each gasoline is transferred to a 60-ml amber glass bottle and the bottles are refrigerated. Using pipettes, 10-ml of each gasoline sample is transferred from its 60-ml bottle to a 40-ml glass vial. The glass vials have plastic screw caps fitted with a Teflon lined septum. The bottles are capped immediately after introduction of the samples.

The Mobile Source Operations Division, according to their standard procedure, makes sample bags (6-liter capacity) with Tedlar material. The bags are fitted with a QuickConnect connector and a port with a Teflon lined septum. The bags are filled with zero nitrogen to their full capacity and evacuated. This process is repeated once. Each bag is then filled with one liter of zero nitrogen.

All sample vials and sample bags are placed inside a variable volume SHED (sealed housing for evaporative determination) maintained at $100^{o}F$ for two hours. At the end of the two hours, using a gas-tight syringe, 0.3 ml of the headspace vapor is extracted from the vial and injected into the sample bag through the septum port. The bag is filled with 50-ml zero nitrogen through this port and another four liters of zero nitrogen through the QuickConnect. The bags are kept at room temperature for two hours before gas chromatography analysis.

A gas chromatograph equipped with a flame ionization detector using standard operating procedures MLD 102 for the light-end hydrocarbons and MLD 103 for the mid-range hydrocarbons is used to analyze the samples. Both these methods are currently available on the ARB's web site under the mobile source programs, Low Emission Vehicle II, non-methane organic gas test procedures, attachment M to the recent regulatory action as procedures 1002 and 1003.

The above procedures are also used to analyze motor vehicle exhaust and evaporative emissions along with the alcohol and carbonyl test methods, numbers 1001 and 1004 respectively. Copies of the methods can also be obtained by contacting MLD in El Monte at (626) 575-6815.