# California Environmental Protection Agency

# Air Resources Board

**PROCEDURE FOR MOTOR VEHICLE EMISSIONS DATA MANAGEMENT**

**Standard Operating Procedure No. MLD 127**
**Revision 1.0**

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# SOP No. MLD 127 - PROCEDURE FOR MOTOR VEHICLE EMISSIONS DATA MANAGEMENT

## 1 Introduction

1.1 Motor vehicle exhaust reports consist of data from up to seven different sources of analysis. These are:

1.1.1 Light-end hydrocarbons [collected in Tedlar bags, analyzed by gas chromatography (GC), SOP 102/103]

1.1.2 Mid-range hydrocarbons (collected in Tedlar bags, analyzed by GC, Sop 102/103), including ethers (e.g., MTBE).

1.1.3 Carbonyls [collected on cartridges, analyzed by high performance liquid chromatography (HPLC), SOP 104]

1.1.4 Methane and non-methane hydrocarbons [Pre-concentration, Direct Injection Flame Ionization Detector (PDFID, SOP 119)]

1.1.5 Alcohols (collected in impingers, analyzed by GC, SOP 101)

1.1.6 Dynamometer (dyno) instruments [Federal Test Procedure (FTP), Ref. 1] operated by Mobile Source Division (MSD)

1.1.7 GC/mass spectroscopy (GC/MS, SOP 120)

1.2 The alcohol analysis is required only for alcohol-based fuels. Additional tests are analyzed for alcohol at MSD's request.

1.3 Analyses by PDFID and GC/MS are confirmatory tests.

1.3.1 PDFID is not required; however, it is performed on most tests.

1.3.2 Periodic GC/MS confirmation analyses are required; normally, one sample per week is analyzed.

1.4 Each analysis generates hard copies and electronic files, which are converted to appropriate reporting formats, and then stored.

1.5 The data from the light-end, mid-range, carbonyl, PDFID, alcohol and dyno are merged to form the "Motor Vehicle Emissions Report".

1.6 GC/MS results are compared to light-end and mid-range results in a separate report.

1.7 This document describes the generation and storage of this data.

## 2 Individual Analyses

2.1 Sample Login

2.1.1 Samples are received from MSD (or other source).

2.1.2 A chemist logs them in on an SLB program ("Login Samples").

2.1.3 The program assigns a sample number and data file number to each bag.

2.2 Light-end and Mid-range Hydrocarbon Analysis

2.2.1 Raw data files ("SAMPLE.RUN") are generated by a Varian Star data system.

2.2.2 These files are converted to ASCII files ("SAMPLE.RPA" for light-end; "SAMPLE.RPB" for mid-range) by the Varian software.

2.2.3 Hard copies of the chromatograms and peak tables are printed out by the chemist.

2.2.4 The chemist evaluates the peak identifications assigned by the data system and notes any corrections on the hard copy.

2.2.5 The "SAMPLE.RPA" (.RPB) files are converted to a specific format ("SAMPLE.RP2"), using a Southern Laboratory Branch (SLB) program called "Light-end Report" (or "Mid-range Report").

2.1.5.1 In this program, the "SAMPLE.RPA (or .RPB)", the sample number and the data file number are typed in manually.

2.2.6 The "SAMPLE.RP2" files are then edited in WordStar, as necessary.

2.2.7 Using an SLB program called "Merge Light-end" (or "Merge Mid-range"), each set of "SAMPLE.RP2" files (usually corresponding to the three modes, plus background, of an FTP test) is merged.

2.2.8 The merged light-end product is saved into an "LTEST.MDD" file [MDD corresponds to the month (M) and date (DD)].

2.2.9 The merged mid-range product is saved into an "MTEST.MDD" file.

2.3 Carbonyl Analysis

2.3.1 For a regular FTP test, eight samples are received.

2.3.1.1 one primary sample and one background from each of the three modes

2.3.1.2 one backup cartridge for phase 1 sample

2.3.1.3 one blank cartridge

2.3.2 Raw data files ("SAMPLE.ARS") are generated by the HPLC.

2.3.2 These sample files are then merged by SLB programs "SEND ALD" and "GO ALD" to generate a delimited ASCII file ("TTEST.MDD") for each dyno test.

2.4 Alcohol Analysis

2.4.1 Nine samples are received for each normal FTP test:
- 2.4.1.1 primary and backup samples for each of the three modes
- 2.4.1.2 primary and backup impingers for the background sample
- 2.4.1.3 one traveling blank impinger

2.4.2 The GC data system produces "SAMPLE.RUN" files for each sample.

2.4.3 These GC results and sample volume are entered into a LOTUS spreadsheet, "ALC#" (each new spreadsheet is named sequentially).

2.4.4 The spreadsheet converts the concentrations from micrograms/milliliter (µg/mL) to parts per billion carbon (ppbC). The primary and backup concentrations are summed.

2.4.5 SLB program "ALCNEW" converts the results into a single delimited ASCII file ("ATEST.MDD") for each dyno test.

2.5 PDFID Analysis

2.5.1 Each of the dyno sample bags is analyzed and raw data files ("SAMPLE.RUN") created for each bag.

2.5.2 The results of methane and total non-methane hydrocarbons (NMHC) are manually entered into a LOTUS spreadsheet.

2.5.3 The methane results are corrected for the decreased oxygen content of the exhaust samples, compared with ambient air. The correction assumes a 10:1 dilution ratio for each test phase (background sample needs no correction).

2.5.4 SLB program "PDFID" generates one delimited ASCII file ("PTEST.MDD") for each dyno test.

2.6 GC/MS Analysis

2.6.1 An exhaust sample, normally bag 1, is analyzed.

2.6.2 A raw data file (a total ion chromatogram) is generated and stored on the GC/MS data system. These files are numbered sequentially, "####" (e.g., "2014").

2.6.3 The raw data file is enhanced for data processing and an enhanced file created. This data is stored in a file with the raw data file number with the suffix "E", "####E" (e.g., 2014E)

2.6.3 Using the enhanced ion chromatogram, each peak is examined and identified.

2.6.4 A GC/MS Analysis Report listing all compounds, CAS numbers, retention times and relative peak sizes is typed manually on PESII.

2.7 Dyno Analyses

2.7.1 Analyses performed by the dyno instrumentation are:
2.6.1.1 Carbon Monoxide (CO)
2.6.1.2 Carbon Dioxide (CO2)
2.6.1.3 Oxides of nitrogen (NOx)
2.6.1.4 Methane
2.6.1.5 Total hydrocarbons (THC)

2.7.2 Dyno data is collected and processed by the Motor Vehicle Data Acquisition System (MVDAS).

2.7.3 SLB program “DYNOCUT” converts the results into a single delimited ASCII file (YTEST.MDD) for each dyno test.

## 3 Merging Data from Individual Analyses

3.1 A LOTUS spreadsheet template is provided by MSD.

3.1.1 This spreadsheet contains all of the formulas necessary to generate test results.

3.1.2 The spreadsheet template also contains QuickBasic macros to import data.

3.2 Corresponding light-end, mid-range, carbonyl, alcohol, PDFID and dyno data are imported into preassigned cell ranges (loading areas) in the template.

3.3 The data is imported in ppbC [or parts per million Carbon (ppmC)] units.

3.4 The resulting file is saved as "TEST.MDD".

3.4.1 This file contains raw data, formulae, constants, reference data, and calculated results.

3.4.2 The spreadsheet formulae perform calculations and make corrections (e.g., methane response factors, converting ppmC to ppbC, Ref 9.2) to the raw data, yielding final ppbC results, which may be printed out (Section 4.3).

3.4.3 The spreadsheet then subtracts the background concentration(s) from sample concentrations to yield net ppbC results.

3.4.4 The net ppbC data is then converted to mg/mile, using molecular weights and other constants (contained in the spreadsheet template), dilution factor and distance driven (from the imported MVDAS data).

3.4.5 The mg/mile data for each phase is weighted according to duration of the phase (see Ref. 9.2) to yield composite mg/mile results.

3.4.6 The spreadsheet also utilizes speciated GC, alcohol, and aldehyde results to calculate non-methane organic gas (NMOG), and the individual reactivities of these compounds to calculate the reactivity (ozone/mile) and specific reactivity (ozone/NMOG).

## 4 Report Generation

4.1 Selected information from the "TEST.MDD" file is converted to a PESII report by an SLB program, "PRTN2".

4.2 Selected information from the "TEST.MDD" file is printed out using SLB macros contained in a LOTUS file called "NEW7.WK4". This file is updated periodically, as necessary, to provide additional information or change response factors. The file is then saved under the next sequential number (e.g., "NEW8.WK4").

4.2.1 The "A" macro calls up the "TEST.MDD" file.

4.2.2 The "B" macro produces the "Motor Vehicle Emissions Report" report in ppbC units.

4.2.3 The "C" macro produces the Motor Vehicle Report in milligram/mile (mg/mile) units.

4.2.4 The "T" macro produces a file to be uploaded into the SLB ACCESS database. The macro also saves this file with a "T" appendix to the test name, e.g., "TESTT.DAT".

4.3 A separate SLB program compares GC/MS results with light-end and mid-range results and generates a comparison file on PES.

4.3.1 The "TEST.MDD" spreadsheets are converted to ASCII files using SLB program "Convert4".

4.3.2 The GC/MS Analysis Reports on PES are converted to ASCII files and downloaded.

4.3.3 SLB program "Exhaust3" combines each GC/MS Analysis Report with the corresponding light-end and mid-range data contained in "TEST.MDD" and generates a comparison report in ASCII format. This is an intermediate file named "FID####" (e.g., "FID2014").

4.3.4 This intermediate file is uploaded to PES and annotated, as necessary.

4.3.5 Due to the replacement of PES, this program must be modified to another format.

## 5 Evaluation

5.1 Motor Vehicle Emissions Reports

5.1.1 Several quality control (QC) checks are automatically generated by the "NEW7.WK4" program.

5.1.1.1 NMHC Comparison

5.1.1.1.1 Results from GC, dyno, and PDFID are compared.

5.1.1.1.2 Results that vary by more than 20% or 4 ppmC fail this test.

5.1.1.1.3 Since PDFID is a confirmatory test, GC results must pass either the dyno or PDFID comparison; they may also pass the other comparison, but it is not required.

5.1.1.2 Elapsed time between sample collection and analysis is compared with SOP sample holding time requirements:

| | | | |
|---|---|---|---|
| 5.1.1.2.1 | Light-ends: | bag 1 | 8 hours |
| | | other bags | 24 hours |
| 5.1.1.2.2 | Mid-range: | all bags | 24 hours |
| 5.1.1.2.3 | Alcohols: | all samples | 6 days |
| 5.1.1.2.4 | Carbonyls: | all samples | 30 days |
| 5.1.1.2.5 | PDFID: | bag 1 | 8 hours |
| | | other bags | 24 hours |

5.1.1.2.6 Any sample that exceeds any of the maximum allowable holding times fails this test.

5.1.1.3 Crossover compound comparisons

5.1.1.3.1 Compounds that are measured by both the light-end and mid-range analyses are compared.

5.1.1.3.2 The pass/fail criteria are:

| **Average Concentration (ppbC)** | **Maximum Allowable Relative Percent Difference (RPD)** |
|---|---|
| < 100 | 150 ppbC |
| 100 to 1000 | 50% |
| 100 to 5000 | 25% |
| > 5000 | 15% |

5.1.1.3.3 Any compound that exceeds these tolerances fails this test.

5.1.1.4 Relative Bag Concentration Test: for normal FTP tests, the relative bag concentrations are:

bag 1 > bag 3 > bag 2 > background

Each compound and phase total is assigned a number from 0 to 4:
0 = all concentrations in order
1 = 1 concentration out of order
2 = 2 concentrations out of order
3 = 3 concentrations out of order
4 = 4 concentrations out of order

5.1.2 Of these tests (5.1.1), two must be passed to report results as "Data for Record":
- 5.1.2.1 GC/DYNO FID/PDFID comparisons must pass the requirement(s) in Section 5.1.1.1.
- 5.1.2.2 Elapsed times must pass the requirements in Section 5.1.1.2.
- 5.1.2.3 For a test with all six analyses, this corresponds to 33 QC requirements, with an additional four tests passed if GC results match both dyno and PDFID results.
- 5.1.2.4 Any test that fails the NMHC and/or elapsed times tests is reported as "FYI" or is aborted, depending on the overall data quality.

5.1.3 The other automatic QC tests are considered when evaluating the overall quality of the test results.

5.1.4 Manual QC Checks
- 5.1.4.1 The presence or absence or MTBE should be consistent with fuel type.
- 5.1.4.2 The light-end to mid-range ratios should be appropriate for fuel type.
- 5.1.4.3 GC/DYNO FID/PDFID results are checked for gross differences; for example, GC results may be consistent with PDFID, but grossly different from dyno FID. The automatic check does not flag this situation.
- 5.1.4.4 Elapsed times are double-checked.
- 5.1.4.4 Crossover compound comparisons are visually checked for overall trends.
- 5.1.4.5 Specific reactivity should be appropriate for fuel type.
- 5.1.4.6 Duplicate tests of the same vehicle/fuel are checked (as time allows) for:
  - 5.1.6.6.1 Consistency of peak identifications
  - 5.1.6.6.2 Consistency of NMHC totals
  - 5.1.6.6.3 Consistency of specific reactivity

5.1.5 The hard copy reports are approved and signed by the OAS manager and/or QC coordinator.

5.2 GC/MS Comparison Reports

5.2.1 The GC/MS Comparison Reports list GC/MS and GC/FID compound comparison information.

5.2.2 This information includes CAS numbers, compound names and corresponding FID concentrations and MS peak sizes.

5.2.3 The comparison is evaluated by the chemist, and any anomalies are checked and reported.

## 6 Reporting Results to MSD

6.1 The electronic file, "TEST.MDD", is copied onto a floppy.

6.2 The floppy and hard copies of ppbC and mg/mile reports are submitted to MSD.

6.3 The report log is signed by MSD staff to document that the reports have been received.

6.4 The release of exhaust data to anyone outside MSD must be approved by MSD management.

## 7 DATA STORAGE

7.1 Hard Copies

7.1.1 Light-end and Mid-range Data
- 7.1.1.1 Sample chromatograms and merged reports corresponding to each dyno test are filed in one light-end folder and one mid-range folder for each dyno test.
- 7.1.1.2 These folders are filed by date/test number in the laboratory.

7.1.2 Carbonyl Data
- 7.1.2.1 Chromatograms are filed by test date in file folders stored in the laboratory
- 7.1.2.2 Reports for each dyno test are filed in binders and stored in the laboratory.

7.1.3 Alcohol Data
- 7.1.3.1 Chromatograms and reports are filed by date in file folders in the laboratory.

7.1.4 PDFID Data
- 7.1.4.1 Chromatograms and corresponding data reports are filed by date (in file folders) and stored in the laboratory.

7.1.5 GC/MS data
- 7.1.4.1 Hard copies of raw data, GC/MS Analysis Reports and GC/FID-GC/MS Comparison Reports are filed by file number and stored in the laboratory.

7.1.6 Dyno Data
- 7.1.6.1 Dyno data storage is the responsibility of MSD.

7.1.7 Motor Vehicle Emissions Reports
- 7.1.7.1 Hard copies are filed in binders by year/project/vehicle/test date

7.2 Electronic Files

7.2.1 Light-end and Mid-range Data
- 7.2.1.1 "SAMPLE.RUN"
  - 7.2.1.1.1 Stored on hard drive
  - 7.2.1.1.2 Backed up onto optical disk
- 7.2.1.2 "SAMPLE.RPA"/"SAMPLE.RPB"
  - 7.2.1.2.1 Stored on hard drive
  - 7.2.1.2.2 Backed up onto optical disk
- 7.2.1.3 "LTEST.MDD"/ "MTEST.MDD"
  - 7.2.1.3.1 Stored on hard drive
  - 7.2.1.3.2 Backed up onto optical disk

7.2.2 Carbonyl Data
- 7.2.2.1 "SAMPLE.ARS"
  - 7.2.2.1.1 Stored on hard drive
  - 7.2.2.1.2 Backed up onto optical disk
- 7.2.2.2 "TTEST.MDD"
  - 7.2.2.2.1 Stored on hard drive
  - 7.2.2.2.2 Backed up onto optical disk

7.2.3 Alcohol Data
- 7.2.3.1 "SAMPLE.RUN"
  - 7.2.3.1.1 stored on hard drive
  - 7.2.3.1.2 backed up onto optical disk
- 7.2.3.2 "ATEST.RPA"
  - 7.2.3.2.1 stored on hard drive
  - 7.2.3.2.2 backed up onto optical disk

7.2.4 PDFID Data
- 7.2.4.1 "SAMPLE.RUN"
  - 7.2.4.1.1 stored on hard drive
  - 7.2.4.1.2 backed up onto optical disk
- 7.2.4.2 "PTEST.MDD"
  - 7.2.4.2.1 stored on hard drive
  - 7.2.4.2.2 backed up onto optical drive

7.2.5 GC/MS Data
- 7.2.5.1 "####"
  - 7.2.5.1.1 stored on hard drive
  - 7.2.5.1.2 backed up onto tape

7.2.5.2 "####E"
7.2.5.2.1 stored on hard drive
7.2.5.2.2 backed up onto tape
7.2.5.3 GC/MS Analysis Reports
7.2.5.3.1 Stored on PES
7.2.5.4 GC/FID-GC/MS Comparison Reports
7.2.5.3.2 Stored on PES

7.2.6 Dyno Data
7.2.6.1 Stored on MVDAS
7.2.6.2 Record maintenance is the responsibility of MSD

7.2.7 Motor Vehicle Emissions Reports
7.2.7.1 One copy of "TEST.MDD" is backed up onto optical disk
7.2.7.2 One copy is transferred onto a 3.5 inch floppy disk (one file per disk) for easy retrieval.
7.2.7.3 Floppies are filed by test date and stored in the laboratory.

## 8 Access Database

8.1 ACCESS 2.0 Database software is used to store final motor vehicle exhaust data. Maintenance of the database is the responsibility of the Environmental Studies and Operations Support Section. The database contains:

8.1.1 Carbonyl cartridge data (µg/mL)

8.1.2 Alcohol impinger data (µg/mL)

8.1.3 Light-end hydrocarbon data (ppbC and mg/mile)

8.1.4 Mid-range hydrocarbon data (ppbC and mg/mile)

8.1.5 Carbonyl ppbC and mg/mile data

8.1.6 Alcohol ppbC and mg/mile data

8.1.7 PDFID ppbC and mg/mile data for methane and NMHC

8.1.8 Dyno FID ppbC and mg/mile data for methane and NMHC

8.1.9 Reactivity and specific reactivity, based on speciation results.

8.1.10 Dyno data for CO, CO2 and NOx in ppbC (ppb for NOx) and mg/mile

8.2 For each FTP test, eight records are generated in the database:

8.2.1 Background (ppbC only)

8.2.2 Phase 1 ppbC results

8.2.3 Phase 2 ppbC results

8.2.4 Phase 3 ppbC results

8.2.5 Phase 1 mg/mile results

8.2.6 Phase 2 mg/mile results

8.2.7 Phase 3 mg/mile results

8.2.8 Composite mg/mile results

8.3 Each record consist of three linked tables.

8.3.1 The first six fields of each record contain:
- 8.3.1.1 test number
- 8.3.1.2 project number
- 8.3.1.3 units
- 8.3.1.4 test phase
- 8.3.1.5 regular/duplicate test designation
- 8.3.1.6 test date

8.3.2 These six fields are common to each of the three linked tables.

8.4 The ACCESS database file name consists of nine characters:

8.4.1 The first character is "E", for exhaust test.

8.4.2 The second through fourth characters indicate the month and year of the earliest data (e.g., April 1993 is designated "493").

8.4.3 The fifth through seventh characters indicate the month and year of the latest data (e.g., December 1995 is designated as "C95").

8.4.4 The eighth and ninth characters indicate the version number (e.g., version #1 is "V1").

8.4.5 The complete file name for the example given is "E493C95V1".

8.5 File maintenance: new data may be added to an existing (or empty) database using the

following procedures:

8.5.1 The "TESTT.DAT" file (see Section 4.2.4) is retrieved into an empty LOTUS 4 worksheet.

8.5.2 The file is saved as a LOTUS3 file on a 3.5 inch floppy disk. The file name will be "TESTT.WK3." Up to 14 database files can be placed on one disk.

8.5.3 Care must be taken that duplicate test numbers (usually conducted on different days, thereby having different file extensions) are not processed onto the same floppy disk. Since the new file extension is .WK3, rather than the date, the second file would overwrite the first.

8.5.4 The custom ACCESS macro "load" is used to input the set of disks prepared in the previous steps.

8.5.5 "Redo"s (corrected data) may also be processed, using the same procedure, if the database needs to be corrected.

8.5.6 The database is backed up on at least two different PCs.

8.6 Tests aborted by either MSD ("dyno abort") or MLD ("GC abort") are not added to the ACCESS database. GC aborts are maintained in a separate database.

8.7 Database distribution

8.7.1 The release of exhaust data to anyone outside MSD must be approved by MSD management.

8.7.2 The database is periodically transmitted via modem or through the INTERNET to interested clients.

8.7.3 Files transmitted through the INTERNET are password-protected.

## 9 References

9.1 Code of Federal Regulations, Title 40, Part 86.

9.2 Air Resources Board, "California Non-methane Organic Gas Test Procedures", Part G.

9.3 MLD SOP No. 101.

9.4 MLD SOP No. 102.

9.5 MLD SOP No. 103.

9.6 MLD SOP No. 104.

9.7 MLD SOP No. 119.

9.8 MLD SOP No. 120.