California Environmental Protection Agency

Air Resources Board

PROCEDURE FOR THE ANALYSIS OF C3 TO C12 HYDROCARBONS IN AUTOMOTIVE EXHAUST BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY

Standard Operating Procedure No. MLD 120A
Revision 1.0

April 1998

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SOP No. MLD 120A - PROCEDURE FOR THE ANALYSIS OF C3 TO C12 HYDROCARBONS IN AUTOMOBILE EXHAUST SAMPLES BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY

1 Introduction

1.1 This procedure describes a compound identification/compound confirmation analytical method for C3 to C12 hydrocarbons in automotive exhaust samples by gas chromatography/mass spectrometry (GC/MS).

2 Method Summary

2.1 This procedure uses a GC/MS with a GC equipped with a capillary column system, a single-stage quadrupole mass spectrometer and a cryogenic pre-concentration system.

2.2 All sampling, sample transfer from Tedlar bags, cryogenic pre-concentration, analytical column separation, data acquisition and data processing are either manually controlled or data system (DS) controlled.

2.3 A GC/MS data system is used to acquire, store and process data. Data processing includes peak enhancement, background subtraction and compound identification. Reports are prepared and submitted in hard copy and on the Air Resources Board's data communication system or on an appropriate electronic data storage medium.

2.4 Excessive water or carbon dioxide in the sample (as in the case when a large volume of sample is passed through the trap) may block the helium flow in the cryogenic trap or the GC column at sub-ambient temperature. When this happens, Ascarite may be used to remove water and carbon dioxide in the sample prior to cryogenic pre-concentration.

3 Interferences and Limitations

3.1 Compounds which do not elute from the gas chromatograph capillary column system under the described operating conditions will not be detected. Examples include heavy hydrocarbons, some oxygenates, and compounds with acidic and basic functional groups.

3.2 Compounds with molecular weights less than 35 atomic mass units (amu, including methane and C2 hydrocarbons), the starting mass of mass spectrometer scan range, will not be detected.

3.3 When Ascarite is used prior to cryogenic pre-concentration, compounds which are removed by Ascarite will not be detected. Some of these compounds include water, carbon dioxide and compounds with acidic functional groups.

3.4 Co-eluting compounds and compounds with very close GC retention times may not have peak resolution clean enough for positive identification.

3.5 Compound identification is limited to only those compounds listed in the data system's National Institute of Standards and Technology (NIST) Mass Spectral Library. The current Library has about 60,000 mass spectral entries.

3.6 Isomeric compounds (e.g., branched alkanes with the same carbon numbers, cis- and trans- isomers, cycloalkanes and alkenes of the same carbon numbers, cycloalkenes and dienes with the same carbon numbers, stereo-isomers and aromatic isomers) have very similar or identical mass spectra and cannot be identified solely from mass spectral library search data. Other identification techniques such as retention times and comparison with authentic samples are also required.

3.7 Except for 1,3-butadiene (and possibly other dienes too), hydrocarbons have been shown to be stable for at least 24 hours in the Tedlar sampling bags (ARB SOPs No. MLD 102/103), provided the sample bags do not leak and are not exposed to bright light or sunlight or excessive heat. Sunlight may cause reaction of the reactive hydrocarbons.

3.8 This procedure does not provide accurate compound quantitation data. Any quantitation data from this method, if included in the analysis reports, are for information only.

4 Instruments and Apparatus

4.1 Tedlar bags, 2 mil thickness, nominally 5 to 10 liters in capacity and equipped with Swagelok Quick-Connect fittings, are used to store and transport samples from the dyno to the test facility.

4.2 A Finnigan-MAT 7000 SSQ GC/MS/DS with a Varian 3400 GC is used in the analysis and data processing.

4.3 The analytical column is a J&W DB-1 WCOT capillary column, 60 meters x 0.32 millimeters internal diameter with a 1 micron film thickness.

4.4 The preconcentration system is an air actuated multi-valving system designed and installed on the GC by Lotus Consulting. This unit is basically the same as the other cryogenic traps installed on the GCs used with SOPs 102/103. The major difference is that in addition to the built-in 30-mL sample loop, this unit has a mass flow controller (MFC) for other sample volume sizes (volume determined by varying flow rate and flow time).

5 Reagents and Materials

5.1 All gases used in the analysis are of the highest commercial purity available.

5.2 Carrier helium is passed through water, oxygen and hydrocarbons scrubbers before entering the GC system.

5.3 Ascarite is 20-30 mesh and is available from chemical suppliers such as Aldrich Chemical Company.

CAUTION: HANDLE ASCARITE WITH EXTREME CARE! ASCARITE IS CORROSIVE, TOXIC, AND HYGROSCOPIC! DO NOT EXPOSE TO AIR.

5.4 Liquid nitrogen (LN_2) is used to cool the cryogenic trap and GC oven.

CAUTION: HANDLE LN_2 WITH EXTREME CARE! IT CAN CAUSE SEVERE BURN ON SKIN. USE LN_2 ONLY IN WELL VENTILATED AND OPEN AREAS.

5.5 FC43 (perfluorotributylamine, CAS# 00259-70-6), the tuning and calibration compound, is available from chemical suppliers such as Aldrich Chemical Company.

CAUTION: HANDLE FC43 WITH CARE! IT IS AN IRRITANT AND HYGROSCOPIC! DO NOT EXPOSE TO AIR.

6 Procedure

6.1 Typical operating parameters for the GC and the sampling and cryogenic pre-concentration are:

GC:

Carrier helium head pressure	About 17 psi at column temp 60°C
Carrier helium flow rate	About 1.5 mL/min. at ambient temp. and atmospheric pressure
Column temperature	Initial column temp. at -50°C, hold 2 min. *(enter 2 + GC's "time in min. from start to sample injection" to GC's "Initial column temp", see examples in Appendices A and B),* programmed to 180°C at 3°C/min., then to 250°C at 30°C/min., and hold at 250°C until end of run

Total GC run time	With fixed volume sampling loop (loop): 100 min. With mass flow controller (MFC): varies (see Appendix B)

Sampling and cryogenic pre-concentration:

Sample size	With loop: 30 mL With MFC: varies, equals to sampling time multiplied by sample flow rate set on MFC (see Section 6.6.3 and Appendix B)
Sampling time	With loop: 4 min. With MFC: varies
Sample flow rate	With loop: about 40 mL/min. With MFC: varies, normally about 10 mL/min.
Purge helium flow rate	With loop: about 10 mL/min. With MFC: varies, normally about 10 mL/min.
Purge nitrogen flow rate	With MFC only: varies, normally about 10 mL/min.
External valve/sample loop temp.	200^{o}C
Internal valve temperature	200^{o}C
Cryogenic trap temperature	At freeze out: -190^{o}C (LN_2 temp.) At sample injection, temp. is programmed to 250^{o}C at 300^{o}C/min., then hold at 250^{o}C until end of run
Relay settings	With loop: varies, see Appendix A With MFC: varies, see Appendix B

6.2 Typical operating conditions for the mass spectrometer are:

Transfer line temperature	250^{o}C
Ionizer temperature	150^{o}C
Manifold temperature	70^{o}C
Manifold vacuum	10^{-6} range (at 60^{o}C)
Emission current	40 to 400 microampere (µA), normally at 400 µA (see Section 6.6.4 and Appendices A and B)
Electron multiplier voltage	-400 to -1800 volts, normally from -1200 and up (see Section 6.6.4 and Appendices A and B)
Electron energy	70 electron volts (eV)
Scan range	Normally m/z 35 to m/z 250
Scan rate	Normally 1 sec/scan
Total scan time	Normally about 5000 scans (5000 sec.) from GC start (mass spectra from start to sample injection time + 5 min. are not recorded to allow sampling time and air peak to go through; see Appendices A & B)

6.3 GC/MS tuning and calibration procedure

6.3.1 The manufacturer's recommended procedure is followed for routine GC/MS tuning and calibration.

6.3.2 With FC43 (perfluorotributylamine) as the tuning and calibration compound, the GC/MS is tuned and calibrated using the Autotune|Standard Tune and Calibrate command. If the FC43 spectrum obtained with the tune file meets the following two criteria, the tune file will be saved.

(1) Mass assignment accuracy: m/z 69, 219 and 502 peaks must be within $\pm$ 0.25 amu.

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(2) Relative peak areas: with the m/z 69 peak area at 100%, the relative peak area of the m/z 219 peak must be 50-95% and that of the m/z 502 peak must be 2-20%.

6.3.3 At the beginning of the day and prior to sample analysis, the GC/MS tuning and calibration are checked with FC43. If the FC43 spectrum meets the two criteria in 6.3.2, the instrument is ready for analysis.

6.3.4 If these criteria are not met, the instrument will be tuned and/or calibrated again and a new tune file will be acquired. The above steps (6.3.2 and 6.3.3) will be repeated until the criteria are met.

6.4 Sample Preparation

6.4.1 Normally the sample is analyzed as received in a Tedlar bag which is connected to the sampling port via a Quick-Connect.

6.4.2 If the sample contains a large amount of water or carbon dioxide or the sample is very dilute and a large volume of the sample is needed for analysis, the sample can be passed through Ascarite to remove the water and carbon dioxide before passing through the cryogenic trap. The Ascarite tube should be purged with helium for at least 30 minutes before and after use.

6.5 At the same time, the GC/MS is set to ready status.

6.6 Sample Analysis

6.6.1 When ready, the GC and the MS are started simultaneously.

6.6.2 When the 30-mL sample loop is used, sample is drawn into the sample loop to purge and fill the loop. The loop is isolated and the pressure inside the loop is allowed to stabilize. The isolated sample is then purged with helium into the cryogenic trap where the organic components (with water and carbon dioxide) are frozen and trapped while air and methane

are allowed to pass through. To inject sample, the cryogenic trap is heated from LN_2 temperature to 250°C at the rate of 300°C/min. while the sample loop is purged with carrier helium into the GC.

6.6.3 When a different sample volume is pre-concentrated for analysis, the MFC is used. The sample is drawn directly into the cryogenic trap through the MFC. The MFC is set at a certain flow rate (e.g., 10 mL/min.) for an appropriate sampling time (say 9 min.) so that a certain desired sample volume (in this example, 10 mL/min. x 9 min. is 90 mL) is drawn through the trap. The trap is then heated and purged with carrier helium to inject sample as described in 6.6.2.

6.6.4 During the GC sampling time, the filament and the electron multiplier on the MS remain off. At the time of sample injection, the filament and the electron multiplier are turned on but set at the minimum settings, 40 µA and -400 volts respectively (these settings are too low to record any mass spectrum). After the air peak has passed through the column (about 5 min.) the filament and the electron multiplier are reset at their normal settings until the end of the analysis. In doing so, the total ion chromatogram will have retention time (in scans) of 0 scan at sample injection time, but normal mass spectra are recorded only after the air peak has gone through.

6.6.5 During analysis the GC effluent is introduced into the mass spectrometer which scans normally at a rate of 1 second per scan from m/z 35 to m/z 250.

6.6.6 The total MS scan is set at or around 5000 (5000 seconds) when the fixed volume sample loop is used. When the MFC is used, both the GC run time and the MS scan time may need to be adjusted depending on the length of the sampling time (see Appendix B).

6.7 Data Processing

6.7.1 The resulting raw data file, a total ion chromatogram, is stored in the data system for data processing.

6.7.2 The raw data file or its enhanced file is examined peak by peak.

6.7.3 Every GC peak is identified using a combination of mass spectral library search data, relative retention times, comparison with standards, and other programming tools available in the data system.

6.7.4 Unresolved peaks need special processing (e.g., using single ions or peak addition/peak subtraction from selected scans) for proper peak identification.

6.7.5 After peak identification is complete, a report of analysis results is created and submitted on the Air Resources Board's data communication system or on an appropriate electronic data storage medium such as a disk.

6.8 Data files are stored on the data system or on electronic data storage media such as disks or tapes.

6.9 A typical CVS bag 1 exhaust sample may contain as many as 200 or more components.

7 Quality Control

7.1 The GC/MS must be tuned and calibrated according to the procedure described in Section 6.3 with all criteria met. If tuning and calibration do not meet these criteria, the ionizer and the analyzer may need cleaning and/or service.

7.2 At the beginning of the day prior to sample analysis, a system blank is acquired with helium or zero nitrogen.

7.2.1 Peaks appearing in the blanks are considered background peaks or contaminants. Typically there are two or three small peaks from column bleeding in the high temperature region.

7.2.2 If contaminants other than those normal ones appear, the sampling line, the loop and the trap must be purged and the column must be cleaned (conditioned) at an elevated temperature according to the column manufacturer's instruction. A blank is re-run to assure the system is clean and free from contamination.

8 References

8.1 ARB SOP No. MLD 120.

8.2 ARB SOP No. MLD 102A/103B.

Appendix A - Example of Operating Parameters with the 30-mL Sample Loop

The following is an example of the instrument operating parameters when the 30-mL fixed volume sample loop is used. At standby, purge helium purges the loop and the trap continuously. At start, the sample purges and fills the loop at 40 mL/min. for 4 min., and then the sample pressure in the loop is allowed to stabilize for 55 sec. At 5 min., the sample is purged from the loop into the cryogenic trap by purge helium at 10 mL/min. for 9 min. At 14 min. (sample injection time), the trap is heated to 300°C in less than 2 min. with carrier helium transferring the sample into the GC column, and at the same time the filament and the electron multiplier are turned on at their minimum settings. At 16 min., the relays return to standby. At 19 min., the filament and the electron multiplier are reset to their normal settings. The total GC run time is 100 min., and the total number of MS scans is 5000 scans from sample injection.

GC Switches:	Scrubber in Series / Bypass	Bypass	
	Mass Flow Controller / Fixed Loop	Fixed Loop	
	S/S Capillary / Gas Sampling	Gas Sampling	
	IS STD Enabled / IS STD Disabled	IS STD Disabled	
	Valve 1A Delay	D 55 S	
	Scrubber Delay	(Inactive)	
	Purge helium flow rate	10 mL/min.	
	Sample flow rate	40 mL/min.	
GC Method:	Initial column temperature (°C)	-50	
	Initial column hold time (min.)	16	(sample injection time + 2)
	Program 1 final column temp. (°C)	180	
	Program 1 column rate (°C/min.)	3	
	Program 1 column hold time (min.) 0		
	Program 2 final column temp. (°C)	250	
	Program 2 column rate (°C/min.)	30	
	Program 2 column hold time (min.)	5.01	(to make end time 100 min.)
	Initial injector temperature (°C) *(for cryogenic trap)*	-80	(lowest GC setting, actual temp. is at LN_2 temp.)
	Initial injector hold time (min.)	14.05	(sample injection time + 0.05)
	Program 1 final injector temp. (°C)	250	
	Program 1 injector rate (°C/min.)	300	
	Program 1 injector hold time (min.)	84.85	(to make end time 100 min.)
	Initial auxiliary temp. (°C) *(for transfer line)*	250	
	Initial auxiliary hold time (min.)	0	
	Initial relays	-1-2+3-4	
	Program 1 relay time in min.	0.01	(reset)

Program 1 relays	-3
Program 2 relay time in min.	0.03 (purge and fill sample loop with sample)
Program 2 relays	+1
Program 3 relay time in min.	4 (stop filling loop, pressure in loop allowed to stabilize)
Program 3 relays	-1
Program 4 relay time in min.	5 (sample from loop to cryogenic trap, purge trap with helium)
Program 4 relays	+3
Program 5 relay time in min.	14 (sample injection, trap heats to 250°C in about 2 min. with carrier helium transferring sample from trap to GC column)
Program 5 relays	+4
Program 6 relay time in min.	16 (reset)
Program 6 relays	-4
Method complete - end time (min.)	100

MS settings:

At 0 min.	filament off	
electron multiplier off		
At 14 min.	filament on	40 µA
electron multiplier on		400 volts
At 19 min.	filament on	400 µA
electron multiplier on		1100-1800 volts

Appendix B - Example of Operating Parameters with Mass Flow Controller

When the mass flow controller (MFC) is used, the sample volume is flow rate times flow time. Since the flow rate and the flow time can vary, therefore, to coordinate the proper sampling and sample injection timing sequence, the GC initial column hold time, the initial injector hold time, the relay time settings, the end times and the filament and the electron multiplier off and on times should be adjusted accordingly. The following is an example with MFC flow rate set at 10 mL/min. and flow time at 9 min. for a total sample volume of 90 mL. At standby, purge helium purges the trap continuously. At start, the sample purges the sampling line for 1 min. From 1 min. to 10 min., the sample is directed into the cryogenic trap. At 10 min., purge helium replaces the sample flow and purges the trap for 4 min. at 10 mL/min. At 14 min. (sample injection time), the trap is heated to 300 ^{o}C in less than 2 min. with carrier helium transferring the sample into the GC and at the same time, the filament and the electron multiplier are turned on at their minimum settings. At 16 min., the relays return to standby. At 19 min., the filament and the electron multiplier are reset to their normal settings. The total GC run time is 100 min., and the total number of MS scans is 5000 scans from sample injection.

GC Switches:	Scrubber in Series / Bypass		Bypass
	Mass Flow Controller / Fixed Loop		Mass Flow Controller
	S/S Capillary / Gas Sampling		Gas Sampling
	IS STD Enabled / IS STD Disabled		IS STD Disabled
	Valve 1A Delay		D 1 S
	Scrubber Delay		(Inactive)
	Purge helium flow rate		10 mL/min.
	Purge nitrogen flow rate		10 mL/min.
	Sample flow rate (on MFC)		varies (10 mL/min. in this example)
GC Method:	Initial column temperature (^{o}C)		-50
	Initial column hold time (min.)		16 (sample injection time + 2)
	Program 1 final column temp. (^{o}C)		180
	Program 1 column rate (^{o}C/min.)		3
	Program 1 column hold time (min.)		0
	Program 2 final column temp. (^{o}C)		250
	Program 2 column rate (^{o}C/min.)		30
	Program 2 column hold time (min.)	5.01	(to make end time 100 min.)
	Initial injector temperature (^{o}C) *(for cryogenic trap)*		-80 (lowest GC setting, actual temp. is LN_2 temp.)
	Initial injector hold time (min.)		14.05 (sample injection time + 0.05)
	Program 1 final injector temp. (^{o}C)		250
	Program 1 injector rate (^{o}C/min.)		300
	Program 1 injector hold time (min.)	84.85	(to make end time 100 min.)

	Initial auxiliary temp. (^{o}C) *(for transfer line)*	250	
	Initial auxiliary hold time (min.)	0	
	Initial relays	-1-2-3-4	
	Program 1 relay time in min.	0.01	(purge line with sample)
	Program 1 relays	+1	
	Program 2 relay time in min.	1	(begin sample into trap)
	Program 2 relays	+3	
	Program 3 relay time in min. purge trap with helium)	10	(stop sample into trap,
	Program 3 relays	-1-3	
	Program 4 relay time in min. to 250^{o}C in about 2 min.	14	(sample injection, trap heats with carrier helium transferring sample from trap to GC column)
	Program 4 relays	+4	
	Program 5 relay time in min.	16	(reset)
	Program 5 relays	-4	
	Method complete - end time (min.)		100

MS settings:	At 0 min. filament off electron multiplier off	
At 14 min.	filament on	40 µA
	electron multiplier on	400 volts
At 19 min.	filament on	400 µA
	electron multiplier on	1100-1800 volts