California Environmental Protection Agency

Air Resources Board

PROCEDURE FOR THE ANALYSIS OF C3 TO C12 HYDROCARBONS IN AUTOMOTIVE EXHAUST BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY WITH PRE-CONCENTRATION SYSTEM

Standard Operating Procedure No. MLD 148
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SOP No. 148 - PROCEDURE FOR THE ANALYSIS OF C3 TO C12 HYDROCARBONS IN AUTOMOTIVE EXHAUST BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY WITH PRE-CONCENTRATION SYSTEM

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1 Introduction

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) with a pre-concentration system. This SOP is the replacement of MLD SOP 146.

2 Method Summary

2.1 This procedure uses a GC equipped with a capillary column system, an single-stage quadrupole mass spectrometer, a gas pre-concentration system and a cryogenic focusing system. The exhaust sampling method is not part of this SOP. A typical, but not exclusive, method of sampling gases is detailed in the CARB Quality Assurance Manual, Volume II, Appendix Q.

2.2 The gas sample, contained in the Tedlar bag, is drawn into the pre-concentration system. Then, the concentrated sample is transferred into a cryogenic focusing system and a gas chromatograph capillary column system. Finally, compounds in the sample are determined by a quadrupole mass spectrometer. The operations are either manually controlled or software program controlled.

2.3 The pre-concentration system is designed to concentrate C3-C12 hydrocarbons and exclude diatomic gases, carbon monoxide, and significant quantities of water and carbon dioxide. The gas sample in the Tedlar bag, is drawn into a fixed volume sample loop that has been previously evacuated using a vacuum pump. Once the sample loop is filled to ambient pressure, the sample is flushed through a pre-concentrating adsorbent trap using helium. After the sample has been loaded on the adsorbent trap, the trap is heated to desorb the trapped compounds which are then flushed through a cryogenic focusing trap.

2.4 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 copies, on the Air Resources Board's data communication system or on an appropriate electronic data storage medium.

3 Interferences and Limitations

3.1 Compounds which do not elute from the gas chromatograph capillary column system or from the pre-trap of pre-concentration 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 Co-eluting compounds and compounds with very close GC retention times may not have peak resolution clean enough for positive identification.

3.3 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 170,000 mass spectral entries.

3.4 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.

3.5 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, sunlight or excessive heat. Sunlight may cause reactions of the reactive hydrocarbons.

3.6 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 Instrument and Apparatus

The system consists of three major parts: an automated sampling and concentration system, a gas chromatograph, and a quadrupole mass spectrometer. All three parts are inter-connected but are operated by two separate software systems that run concurrently.

4.1 The automated sampling and pre-concentrator is a Varian 3800 gas chromatograph modified by Lotus Consulting (See Figure 1). An automated stream selector valve (SSV) with multiple heated lines terminating in Swagelok Quick-Connect fittings is used to obtain gas samples from Tedlar bags. The sample 'loop' is a glass cylinder. The pre-trap is a nickel tubing coil packed with a series of adsorbents (Table 1), affixed to a temperature controlled mandrel. A low-volume nickel tubing (generally 0.040" ID x 10") wound around an aluminum mandrel for temperature control is used as a cryogenic focusing trap (cryo-trap).

A multi-port gas sampling valve system (Ref. 8.5) is used to feed sample in the system.

4.2 The gas chromatograph containing the analytical column is a Thermo Trace GC modified by Lotus Consulting to receive a gas phase sample from the concentration system. The analytical column is a 60 meter, 0.25 mm i.d. DB-1 with a 1.0 um film thickness or equivalent.

4.3 The mass spectrometer is a Thermo DSQ II single stage quadrupole mass spectrometer with a transfer line connecting it to the Trace GC. The transfer line is connected to the analytical column with a Swagelok connection and it is set at a temperature comparable to the highest temperature that the column oven reaches during the temperature program.

4.4 A computer is used to control the whole system, Figure 1. Varian software (currently Star 6.4) is used to control the pre-concentration device and to give the Thermo GC a start signal. Thermo Xcalibur software (1.4) is used to operate the Trace GC and the mass spectrometer, store and analyze data. These two softwares are concurrently run.

Alternative instruments of similar capabilities are acceptable. If alternative instruments are used, different parameters and reagents, etc. may be used.

5 Reagents and Materials

5.1 Helium is used to support the pre-concentration system and GC analysis shall have the following specifications. It should have a minimum purity of 99.9999% and pass through scrubbers to ensure purity by further removing water, oxygen and hydrocarbons before entering the GC system.

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

5.3 The quality control standard contains at least the following gases at concentrations between 5 and 100 ppbC: propane, n-butane, 2-methylpropene, n-hexane, n-octane, n-decane, benzene, toluene, and xylene for the analysis. The composition of the current QC standard (NIST SRM-1800) is shown in Table 2.

Additional compounds may be included in the control standard for retention time verifications, etc.

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

6 Procedure

6.1 A schematic of the instrument is shown in Figure 1. Typical operating conditions for the pre-concentrator are given in Table 1 and typical operating conditions for the GC/MS are listed in Table 3.

6.2 Tedlar bags with gas samples are attached to the gas phase auto-sampling valve system and are drawn into a fixed volume sample 'loop' using a vacuum pump. The pump is then shut off and the loop is allowed to fill with the sample to ambient pressure. The volume of the sample loop may vary, depending on its intended use. This method currently uses a 200 mL loop.

6.3 Gas inside the sample loop is transferred to the pre-trap by flushing with a stream of helium through the sample loop and the pre-trap which is vented to atmosphere. The pre-trap can be heated to 300 ℃ or cooled to liquid nitrogen temperature (-196 °C). For optimum retention of hydrocarbons with minimum retention of carbon dioxide, water, and other unwanted gases, the pre-trap is typically set to adsorb hydrocarbons at 50 ℃ and desorb them at 270 ℃. The sample loop is flushed for 20 minutes at a flow rate of about 90 mL/min. After sample is loaded on the column, the sample loop is cleaned by vacuuming and flushing three times.

6.4 After the pre-trap has been loaded, it is heated to 270 ℃ and the desorbed analyte is flushed through a cryogenic focusing trap held at about -190 ℃ for three minutes. Then, the cryo-trap is isolated and heated. The contents of the heated cryo-trap are then injected onto the GC column. The heating time of the isolated trap is chosen to maximize the efficiency of the resolution of lower boiling point hydrocarbons, such as propene and propane. For this method, 30 seconds is sufficient.

6.4.1 The low (adsorbing) temperature of the cryo-trap is chosen to maximize the retention of lower boiling point hydrocarbon from the sample and to minimize the retention of impurities from the helium transfer gas. For this method, -190 ℃ is recommended.

6.4.2 The high (desorbing) temperature of the cryo-trap is chosen to maximize the desorption of C3-C12 hydrocarbon and minimize any potential high temperature reactions within the trap. For this method, 270 ℃ is used.

6.5 A column temperature program is used for the C3-C12 hydrocarbon analysis. A typical one is an initial temperature of -45 °C held for 1 minutes followed by a 2.5 °C /min. ramp to 150 °C, then a 10 °C /min. ramp to 225 °C and hold for one minute.

6.6 The single-stage quadrupole MS detector is used to identify hydrocarbon compounds.

6.6.1 A typical condition for the MS detector is listed in Table 3.

6.6.2 During the GC sampling time, the filament and the electron multiplier are off. At the time of sample injection, the filament and the electron multiplier are turned on 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.

6.7 Daily Operation

6.7.1 At the beginning of the sample analysis day, make sure that there is enough helium gas for the operation and Star and Xcalibur are started without any error.

6.7.2 Instrument calibration test must be conducted according to the procedure described in QC Section 7.1.

6.7.3 A blank and quality control standard are analyzed before sample analysis. Blank and quality control should meet QC requirements, listed in Section 7.2 and 7.3.

6.8 Data Processing

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

6.8.2 The raw data file is examined peak by peak.

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

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

6.8.5 After peak identification is completed, 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.

7 Quality Control

7.1 The GC/MS needs an instrument calibration test every operation day and must meet all criteria. A maintenance tune is conducted with FC-43 (Perfluourtributylamine). All key ions: m/z 69, 131, 219, 414, and 502 values must be within 0.2 amu of their theoretical values. If any error is indicated, immediate actions should be taken to fix such problems. Ion intensities should be at least 1,000,000 counts or greater for ion 69. Multiplier will gradually deteriorate over time and the voltage set at will gradually increase to compensate for this. When it exceeds 2000 V a new multiplier should be ordered. If leak check fails, the air leak needs to be located and corrected before proceeding. Note that a minor air leak is not considered to be a failure, but a warning flag should be addressed ASAP. Relative peak areas: with the m/e 69 usually with peak area at 100%, the relative peak area of the m/e 219 peak must be 40-90%, and that of the m/e 502 peak must be 1-30%. When the maintenance tune doesn't match above criteria, a full automatic tune will be performed and a new tune file will be created. If tuning still does not meet these criteria, the ionizer and the analyzer may need cleaning and/or service.

7.2 Prior to sample analysis every day, a system blank is acquired with helium.

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

7.2.2 If there are contaminants other than those normal ones, 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.

7.3 The quality control standard is analyzed each analysis day and the retention times of 9 target compounds (specified in Section 5.3) are checked to see if the day-to-day variability meets the following criteria: Retention time change of each compound in the standard must be within ±0.2 minutes. Compound retention times are re-established if such retention times are significantly changed after service or maintenance.

8 References

8.1 ARB SOP No. MLD 120a.

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

8.3 ARB SOP No. MLD 137.

8.4 CARB Quality Assurance Manual, Volume II, Appendix Q.

8.5 Bramston-Cook, Randall, “Speciation of Hydrocarbons in Vehicle Exhaust and Ambient Air”, Lotus Consulting Monograph, 1996.

Table 1 Typical Concentration System Operating Conditions

Heated Sample Lines (Varian Rear Oven)	Isothermal 80° C
Sample Loop Valving Oven (Varian Front Oven)	Isothermal 180° C
Cryo Trap Valving Oven (Varian Middle Oven)	Isothermal 180° C
Pre-trap Standby Temperature	270° C
Cryo-trap Standby Temperature	270° C
Sample Loop transfer He flow	90 mL/min.
Pre-trap transfer He flow	8 mL/min.
Pre-trap Composition:	0.196 g Glass Beads
	0.095 g Carbopack C
	0.077 g Carbopack B
	0.153 g Carbopack 1003

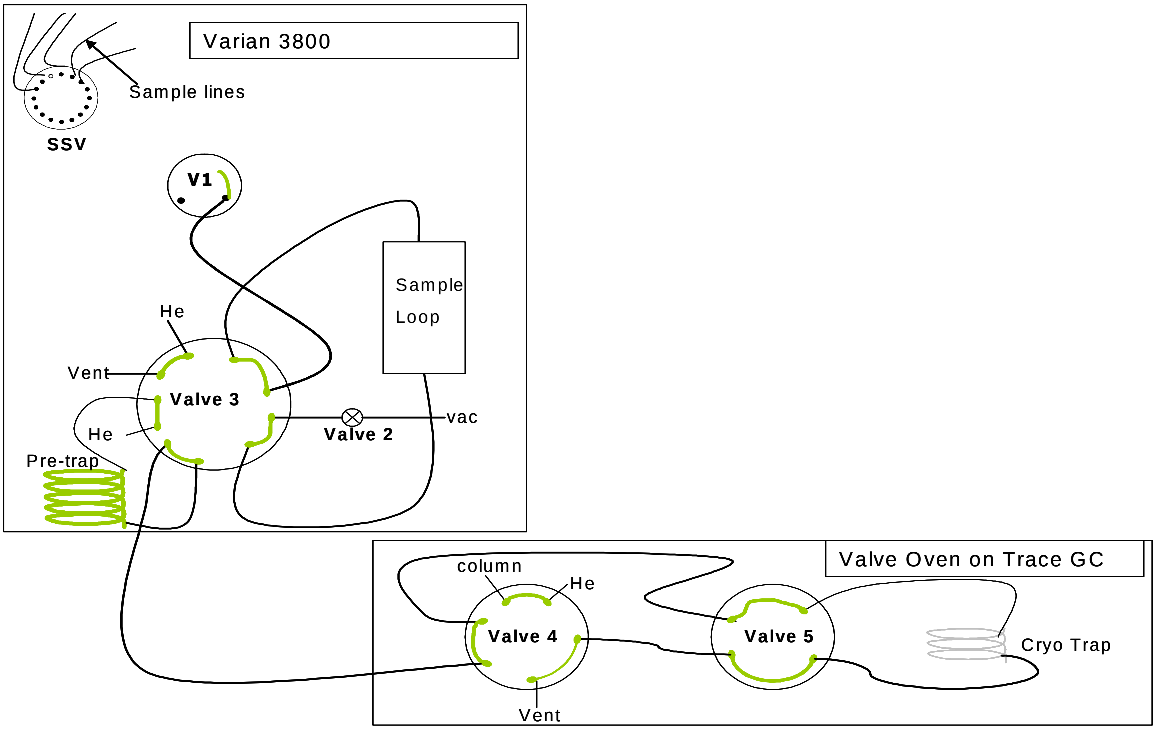
Table 2 Compounds in Quality Control Standard*

Compound	Cylinder Label Value (ppbC)
Ethane	10.2±0.4
Propene	15.6±0.6
Propane	16.2±0.6
Isobutane	22.0±0.8
Isobutene	22.0±0.8
n-Butane	21.20±0.8
2-Methylpropene	25.5±1.0
2-Methylbutane	29.0±1.0
n-Hexane	31.8±1.2
Benzene	31.2±1.2
Toluene	36.4±1.4
n-Octane	40.8±1.6
o-Xylene	40.8±1.6
n-Decane	51.0±2.0

*NIST standard(SRM-1800)

Table 3 Typical GC/MS Operating Conditions

Column Oven Standby Temperature	150° C
Column Helium Flow	1.5 mL/min.
MS Transfer Line Temperature	225° C
Ion Source Temperature	220° C
Ion Gauge Pressure	10^{-6} torr
Emission Current	100 µA
Electron Multiplier Voltage	1300 volts
Electron Energy	70 Electron volts (eV)
Scan Range	Normally m/e 33 to m/e 225
Scan rate (amu/sec)	1500
Time of Sample Injection	35 Minutes after run start



Sample Delivery and Concentrator System

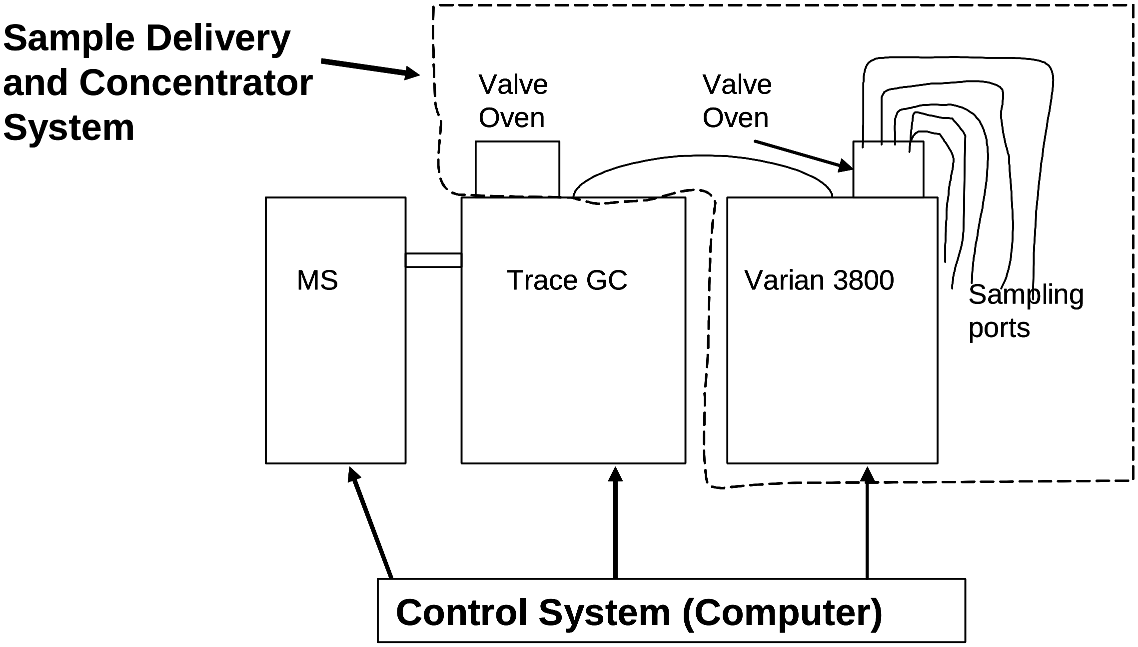


Figure 1. GC/MS Schematic/Valve Diagram