California Environmental Protection Agency

Air Resources Board

PROCEDURE FOR THE DETERMINATION OF C_2 TO C_{12} HYDROCARBONS IN AUTOMOTIVE EXHAUST SAMPLES BY GAS CHROMATOGRAPHY

Standard Operating Procedure No. MLD 102 / 103
Version 2.2

Author: Christine Maddox
Approved by: Paul Rieger
Effective Date: March 15, 2007

Organic Analysis Section
Southern Laboratory Branch
Monitoring & Laboratory Division
9528 Telstar Avenue
El Monte, CA 91731

SOP No. 102/103 - PROCEDURE FOR THE DETERMINATION OF C_2 TO C_{12} HYDROCARBONS IN AUTOMOBILE EXHAUST SAMPLES BY GAS CHROMATOGRAPHY

1 Introduction

1.1   This document describes a method of analyzing C_2 to C_{12} hydrocarbons by gas chromatography (GC) for samples collected from automotive sources in the approximate concentration range of 1 to 25,000 parts per billion carbon (ppbC).

1.2   This procedure is derived from the Air Resources Board Methods 1002 and 1003 (Ref. 10.1 and 10.2), contained in the California NMOG Test Procedures. These test procedures are incorporated by reference into Title 13 of the California Code of Regulations (Ref. 10.3). This procedure complies with all requirements of Methods 1001 and 1002.

1.3   The target compounds currently analyzed and reported by this method are listed in Table A (light-end analysis) and Table B (mid-range analysis).

1.3   This method does not encompass sample collection procedures.

2 Method Summary

2.1   Automotive exhaust samples are generally collected in Tedlar bags according to the Federal Test Procedure (Ref. 10.4) and/or ARB procedures, using a dynamometer (dyno) and constant volume sampler (CVS) to dilute the exhaust as it is sampled. Other driving cycles and sampling procedures can be used.

2.2   Samples are also received from Sealed Housing Evaporative Determination testing (Ref. 10.4) or other miscellaneous sources.

2.3   Samples received by the laboratory in other containers, such as stainless steel canisters, are transferred to Tedlar bags by laboratory personnel.

   2.3.1   Sample transfer protocol is not addressed in this document.

2.4   The analytical procedure uses two gas chromatographs (GCs), one for analyzing the light-end (C_2 to C_5) hydrocarbons and the other for analyzing the mid-range (C_6 to C_{12}) hydrocarbons. It is possible to extend each analysis to include additional hydrocarbon species.

   2.5   The sample is simultaneously injected into each of two fixed volume loops associated with the GCs using an automated, gas phase sampling valve system. Each GC is equipped with its own cryogenic pre-concentration system (cryotrap). Separation of the sample hydrocarbon mixture into its components takes place in the temperature-programmed chromatographic columns. The flame ionization detectors (FID) are used for hydrocarbon detection and quantification.

2.6   The instrument is calibrated using standards prepared by the National Institute of Standards and Technology (NIST) or by standards traceable to NIST standards.

2.7   The analyst uses a computerized GC data acquisition system that integrates each chromatographic peak and identifies the hydrocarbon associated with it by retention time (Ref. 10.5 and 10.6).

2.8   The hydrocarbon concentrations are determined by dividing the integrated peak areas by the response factors determined from instrument calibrations using propane.

3   Interferences and Limitations

3.1   Any component not part of the exhaust sample (e.g. Tedlar bag contaminants) having a retention time similar to that of any hydrocarbon being measured is an interferent. Therefore, proof of chemical identity requires confirmation by other methods and instrumentation, e.g., gas chromatography/mass spectrometry (MLD Standard Operating Procedure No. 120A, Ref. 10.7).

3.2   Sample bags should not leak or be exposed to sunlight or excessive heat.

3.3   Cold-transient exhaust bag samples must be analyzed by the light-end GC within 8 hours of the completion of the dyno test and by the mid-range GC within 24 hours of completion of the test. Exhaust samples from the cold-stabilized and hot-transient test phases as well as background samples must be analyzed within 24 hours for both light-end and mid-range, although analysis within 8 hours is recommended.

3.4   Propane is used to calibrate the responses of the FIDs on the light-end and mid-range GCs. These response factors are used to determine the concentrations of all the hydrocarbons listed in Tables A and B. Optionally, other compounds that can be detected effectively by the FID but do not have a similar response factor to propane can be measured using this method. However, these compounds must be calibrated separately with a standard containing the compound, or apply a relative response factor to the propane-calibrated measurement.

    3.4.1   A response factor relative to propane must be established by a separate multipoint calibration like that detailed in Section 8.5 for the particular compound. Then the relative response factor is applied to the daily propane calibration to determine the concentration of the corresponding compound.

4   Instrumentation and Apparatus

4.1   Tedlar, 2 mils (0.002 inches) in thickness, is used to make small sample bags, typically 5 to 6 liters in volume, which are used to collect the vehicle emission samples. Each bag is fitted with a stainless steel Swagelok QuikConnect fitting and attached with a custom-machined Teflon nut with O-ring. Sample bags are produced by the Mobile Source Operations and Mobile Source Control Divisions using a specific protocol (Ref. 10.8).

4.2   Two gas chromatographs, Varian 3400, 3600, 3800 or equivalent, are used for the analyses. One GC analyzes for the light-end hydrocarbons and the other GC for the mid-range. Each GC is equipped with a gas sampling loop, cryogenic pre-concentrator and FID detector. The mid-range GC is further equipped with a multi-port, gas sampling valve system (Ref. 10.5 and 10.6) to feed the sample loops of both GCs.

  4.2.1   Operation manuals for these instruments are on file in the laboratory.

4.3   The light-end GC uses a Varian Al$_2$O$_3$/KCl porous layer open tubular (PLOT) analytical column [50 m x 0.32 mm inner diameter (ID)] or equivalent. To prevent water damage to the PLOT column, a Varian Carbowax wall coated open tubular (WCOT) precolumn (25 m x 0.53 mm ID), or equivalent, is used to separate the light-end hydrocarbons from water as well as oxygenated and heavier hydrocarbons. In this manner, only light-end hydrocarbons are injected on the analytical column.

4.4   The mid-range GC uses a Varian DB-1 analytical column (60 m x 0.32 mm ID, 1 um film thickness] or equivalent.

4.5   The light-end and mid-range instrument configurations are shown in Figure 1.

4.6   A low-volume cryotrap of nickel tubing (generally 0.040" ID x 10") wound around an aluminum mandrel for temperature control is used to concentrate the sample at a temperature of about -180° C).

4.7   A source of vacuum, capable of creating a nominal sample flow rate of 100-200 cc/min, is used to draw sample from the TEDLAR bags into the sample loops of the gas chromatographs. Both the LE-GC and the MR-GC are simultaneously sampled.

4.8   The pair of GCs is controlled by a single data system (Varian Star™ version 6.41 or equivalent).

  4.8.1   The software controls sample introduction as well as sample analysis.

5   Reagents and Materials

5.1   Gases used to support the GC analysis shall have the following specifications:

    5.1.1   Helium shall have a minimum purity of 99.9999% and pass through a molecular sieve trap to ensure purity before entering the GC system.

    5.1.2   Hydrogen shall have a minimum purity of 99.995%.

    5.1.3   Zero nitrogen shall have a minimum purity of 99.998%.

    5.1.4   Zero air shall have less than 1 part per million carbon (ppmC) hydrocarbon.

5.2   The working calibration standard contains propane at a concentration level between 0.25 and 1 ppm (molar). This propane standard must be a NIST-certified or a secondary NIST-traceable standard. The composition of the current working calibration standard is shown in Table C and the light-end and mid-range chromatograms of the standard are shown in Figure 2.

    5.2.1   Additional compounds may be included in the calibration standard for response factor comparisons, retention time confirmations, etc, if desired.

    5.2.2   Methyl tertiary butyl ether (MTBE), when present, is quantified using a relative response factor, as described in Section 3.4. This factor is applied to the measured MTBE concentration, calibrated with propane, when the GC data is post-processed.

5.3   The quality control standard (Matheson or equivalent) contains at least the following gases at concentrations between 0.2 and 3 ppmC: ethene, propane, n-butane, and 2-methylpropene for the light-end analysis and n-hexane, n-octane, n-decane, benzene, toluene, and m- or p-xylene for the mid-range analysis. The composition of the current QC standard is shown in Table C and the light-end and mid-range chromatograms of the standard are shown in Figure 3.

    5.3.1   Additional compounds may be included in the control standard for response factor comparisons, retention time verifications, etc., if desired.

5.4   A high concentration standard (greater than the calibration standard) containing the target hydrocarbons listed in Section 5.3 is used for linearity determinations. This standard must have its assay verified by comparison with a NIST-traceable propane standard.

5.5   A low concentration standard containing the target hydrocarbons listed in
        Section 5.3 is used for determining the limit of detection (LOD) for each
        compound. This standard must be within five times the estimated LODs and
        have its assay verified by comparison with a NIST-traceable propane standard.

        5.5.1   In lieu of a low concentration standard, a higher concentration standard
        may be diluted.

5.5   Liquid nitrogen is used to cool the cryogenic traps and column ovens.

6   Safety Requirements

6.1   All employees shall be familiar with the following documents:

        6.1.1   Emergency Plan for 9528 Telstar Avenue (HSL, Ref. 10.9).

        6.1.2   Illness and Injury Prevention Program Guide (Ref. 10.10).

        6.1.3   Material Safety Data Sheets (MSDSs) for all chemicals used in the
        laboratory shall be retained on file in the laboratory.
            6.1.3.1 This file shall be located in an area that is easily accessed in the
        event of an emergency.

        6.1.4   This method has no specific safety requirements beyond the guidelines
        provided in the documents referenced in Sections 6.1.1 through 6.1.4.

7   Procedure

7.1   The suggested operating conditions for the GCs are given in Table D. Each GC
        pair may have some deviation of these conditions to optimize the operation.

7.2   Samples in Tedlar bags are attached to the gas phase auto-sampling valve
        system and simultaneously drawn through a fixed-volume sample loop in the
        light-end GC and through another fixed sample loop in the mid-range GC, with a
        vacuum pump [variable, usually at about 300 mL/min for 2 minutes]. The volume
        of the sample loop may vary for each GC, depending on its intended use. For
        the light-end GC it is usually 10 mL, nominal, and for the mid-range GC it is
        usually 30 mL, nominal.

7.3   For the light-end GC the sample is eluted through the pre-column and loaded
        into the cryotrap; for the mid-range GC the sample is loaded directly into the
        cryotrap.

7.4   After all the light-end hydrocarbons are eluted through the pre-column, the light-end GC pre-column is back flushed to prevent the heavy hydrocarbons and water from eluting onto the analytical column. Helium is flushed backward through the pre-column out to vent.

7.5   After loading, the traps are isolated and then heated for a specific time to maximize the efficiency of the chromatography for the lower boiling point hydrocarbons. Then the isolation valve is opened and the samples are injected into the analytical columns of each GC.

7.6   After running a highly concentrated sample, the analyst may run a blank or flush the sampling system with zero nitrogen before proceeding to the next sample to prevent sample carry-over.

   7.6.1   This procedure is performed at the analysts' discretion, based on knowledge of his specific GC and its current performance.

7.7   For compounds having concentrations above the documented range of instrument linearity (as determined by initial or annual multipoint calibration), a smaller aliquot must be taken (for manual systems, a smaller syringe or smaller loop; for automated systems, a smaller loop) or the sample must be diluted.

   7.7.1   The sample dilution process depends on the equipment used and is not addressed in this document.

7.8   The instrument software controls instrument conditions, sample introduction, sample analysis and data reporting.

7.9   Staff performing this analysis shall be responsible for documenting deviations from this procedure.

8   Data Analysis

8.1   The data system generates separate light-end and mid-range reports, each containing the chromatograms, peak identifications, and corresponding concentrations based on the daily calibration value.

8.2   The target hydrocarbon concentrations, in ppbC, are calculated by the data system using propane as an external standard.

$$Concentration\left(ppbC\right) = \frac{Peak\ Area}{Response\ Factor}$$

The response factor (RF) is calculated from the daily calibration by the following equation:

$$RF = \frac{Area \ of \ Standard \ Propane \ Peak}{Concentration \ of \ Propane \ (ppbC)}$$

8.3   The peak identifications and peak concentrations determined by the data system are reviewed and, if necessary, corrected using the following procedure and criteria:

    8.3.1   The primary peak identification is determined by the data system, using the retention times based on reference calibration runs.

    8.3.2   The relative peak heights of the sample run ("fingerprint") are matched with the typical fingerprint seen in past sample runs. Typical light-end and mid-range chromatograms for an automotive exhaust sample are shown in Figure 4.

    8.3.3   The relative retention indices from GC/MS analyses may be used to help confirm peak identification. GC/MS can be used to:
        8.3.3.1 Develop profiles for new fuel types.
        8.3.3.2 Periodically check current profiles.
        8.3.3.3 Investigate anomalous results of individual samples.

    8.3.4   Any peak with reasonable doubt as to its identity is labeled 'Unidentified'.

    8.3.5   The peak integrations are corrected as necessary in the data system by the analyst.
.
8.4   All peaks identified as target compounds at or above the reporting limit, as defined in Section 9.6.6, are reported. Peaks associated with additional compounds (not in Table A or B and with concentrations $\geq$ the reporting limit) may be reported if special consideration has been given to identify and quantify the particular species.

    8.4.1   Target compounds (in Tables A or B) which co-elute are reported as the major component as determined by the analysis of several samples by GC/MS or other confirmational methods.
        8.4.1.1   The exception to this is the co-elution of m- and p-xylene.
        8.4.1.2   The combined peak is reported as the sum "m- & p-xylene" in the GC report.
        8.4.1.3   GC/MS data and fuel profiles were used to determine that two-thirds of the typical coeluting peak is m-xylene and one-third is due to p-xylene.
        8.4.1.4   The GC data is post-processed to account for this 2:1 ratio.

8.5   Additional calculations may be performed at the clients' request. These calculations typically follow Section G of the California NMOG Test Procedures (Ref. 10.11).

8.6   Details of calculations performed at the clients' request are not addressed in this document.

8.7   Data processing, review, approval and reporting to clients is addressed in MLD Standard Operating Procedure No. 127, "Procedure for Motor Vehicle Emissions Data Management" (Ref. 10.12).

9   Quality Control

9.1   Blank Run: A blank (pure nitrogen or helium) is run once per analysis day. All target hydrocarbon concentrations from the blank analysis must be below the LOD before the analysis may proceed. As an alternative to a daily blank run, a daily partial blank check in tandem with a weekly blank run may be used. A partial blank check is defined as a check of the calibration standard run for interferants over all but the propane region of the chromatogram. The calibration standard must consist of only propane and make-up gas with the concentration of all organic compounds except methane and propane below 2% of the propane standard concentration.

9.1.1   If the blank shows a peak greater than the limit of detection (LOD) in the region of interest, the source of contamination must be investigated and remedied.

9.2   Calibration Run: A single-point calibration is performed for each analysis day. The sample load frequently requires continuous instrument operation into the next calendar day. In these instances, the calibration factor of the previous calendar day is used for all of the samples of such a sample load.

9.2.1   A running chart containing the measured area of the propane peak is established by entering the results of daily calibration standard analyses. Figure 5 demonstrates a typical calibration standard QC chart.

9.2.2   A running mean area and standard deviation for propane is calculated and used to establish the criteria for the latest response factor check.

9.2.3   After twenty successful calibrations have been completed, control limits of $\pm$ 3 standard deviations (3s) or $\pm$ 5% from the current mean area, whichever is greater, are established. A measured area outside of this

limit is considered to fail the quality control requirement with respect to calibration. The analysis in this situation is referred to as a "QC failure."

9.2.4   Similarly, warning limits of $\pm$ 2s or $\pm$ 5% from the current mean area, whichever is greater, are established. A measured area outside of this limit is considered a "warning". When warnings occur on two consecutive analysis day, the second day is considered a QC failure.

9.2.5   A QC failure requires that the instrument and the conditions of analysis be investigated before running samples.

   9.2.5.1   If major problems are discovered or the cause of the failure is unknown, samples should not be analyzed by the GC.
   9.2.6.1   Instrument maintenance and repairs can affect the instrument response. If the response changes sufficiently that the subsequent calibration fails the control limits, a new QC chart should be started.

9.2.6   In the event that twenty successful calibration analyses have not been performed before the need for running samples, the calibration is considered valid if the control standard run (Section 8.3) passes.

9.3   <u>Control Standard Run</u>: The quality control standard is analyzed each analysis day and the concentrations of 10 target compounds (specified in Section 5.3) are checked to see if the day-to-day variability meets specified criteria. The procedure for this quality control check is described below:

9.3.1   A running control chart containing the measured concentrations of the 10 target compounds is established by entering the results of daily control standard analyses. Figure 6 demonstrates a typical set of control standard QC charts.

9.3.2   A running mean concentration and standard deviation for the monitored hydrocarbons is calculated and used to establish the criteria for the latest control standard check.

9.3.3   After twenty successful analyses have been completed, control limits of $\pm$3 standard deviations (3s) or $\pm$ 5% from the current mean concentration, whichever is greater, are established. A measured concentration outside of this limit is considered a QC failure.

9.3.4   Similarly, warning limits of $\pm$ 2s or $\pm$ 5% from the current mean concentration, whichever is greater, are established. A measured concentration outside of this limit is considered a QC warning. When

warnings occur on two consecutive analysis day, the second day is considered a QC failure.

9.3.5 In the event that twenty successful control standard analyses have not been performed before the need for running samples, an alternative QC criterion will be used. In this case, a measured concentration greater than 10% from the certified concentration of the standard is considered a QC failure. If the control standard is not NIST-certified, the cylinder should be certified by the laboratory against a NIST standard (secondary NIST-traceable standard).

9.3.6 A QC failure requires that the instrument and the conditions of analysis be investigated before running samples. If major problems are discovered or the cause of the failure is unknown, samples should not be analyzed by the GC. In the event that samples had been analyzed following a QC failure, those samples are considered invalid.

9.4 Replicate Run: A replicate analysis of one sample bag is performed once per analysis day. The relative percent difference (RPD) in concentration between the pair of analyses is calculated for each of the ten target compounds monitored in the control standard (Section 5.3) and inputted to a replicate chart. A sample replicate chart is shown in Figure 7.

9.4.1 The RPD is calculated as follows:

$$RPD = \frac{|\text{Sample Conc.} - \text{Replicate Conc.}|}{\text{Average Conc. of Both Analyses}} \times 100$$

9.4.2 A limit on the allowable RPD is established based on the average concentration of the replicate runs, as shown in the following table:

Average Measurement for Replicate Runs	Allowable RPD (%)
1 to 10 times LOD	100
10 to 20 times LOD	30
20 to 50 times LOD	20
Greater than 50 times LOD	15

9.4.3 If the measured RPD of any of the ten target compounds is greater than the allowable limit, the sample should be analyzed again. If reanalysis is not feasible or if the RPD criteria are still not met on reanalysis, all of the sample results for that analysis day from the instrument are considered invalid.

9.5   <u>Linearity Determination</u>: A multipoint calibration of each of the ten target hydrocarbons monitored in the control standard (Section 5.3) is performed to confirm instrument linearity. This is done for new instruments, after making instrument modifications which can affect linearity, and at least once per year. An example of a linearity determination is shown in Figure 8.

       9.5.1   The multipoint calibration consists of analyses of at least five concentration levels of NIST-traceable standards distributed over the range of expected sample concentration (generally 10 ppbC to 10,000 ppbC). Each concentration level is measured at least twice. A linear regression analysis based on the 'least squares' method is performed using concentration as the independent variable and peak area as the dependent variable to determine a correlation coefficient (r). The r must be greater than 0.995 for the method to be considered sufficiently linear to ensure the validity of using a single-point calibration for daily analysis.

9.6   <u>LOD Determination</u>: A limit of detection (LOD) determination for each of the ten target hydrocarbons monitored in the control standard (Section 5.3) is performed for new instruments, after making modifications which can affect the sensitivity of an instrument, and at least once per year. Figure 8 shows a typical LOD determination.

       9.6.1   LOD determination consists of analyses of at least four "low" concentration levels of NIST-traceable standards, each above the LOD, with at least five replicate determinations of the lowest concentration standard.

             9.6.1.1   The LOD determination can be performed concurrently with the linearity determination (Section 8.5) if at least five replicate measurements of the lowest concentration level standard are performed.

             9.6.1.2   The concentration of the lowest standard must be greater than the calculated laboratory LOD, and not more than five times the estimated LOD.

       9.6.2   A linear regression analysis is performed on this data set to identify slopes, m_i, for each of the ith target compounds of the control standard (Section 5.3).

       9.6.3   For each of the ith target compounds, the standard deviations, s_i, in units of peak area are determined using the five (or more) replicate measurements of the lowest concentration standard. These are then

converted to units of concentration using the slopes determined in
Section 8.6.1.

$$s_i^{conc} = \frac{s_i^{area}}{m_i}$$

The LOD for each of the ith target compounds can now be calculated
using the following equation:

$$LOD_i = t * s_i^{conc}$$

where t is the Student's t value associated with a 98% confidence interval.

9.6.4   The Student's t value is dependent upon the degrees of freedom
associated with the analysis. The degrees of freedom of the analysis is
equal to the number of replicate measurements, n, of the lowest
concentration standard minus one. An abbreviated table of values of t
associated with a 98% confidence interval is shown below (Ref. 10.13):

Degrees of Freedom (n-1)	t-value
4	3.7
5	3.4
6	3.1
7	3.0

9.6.5   The maximum allowable LOD for each compound is 5 ppbC. The
calculated laboratory LOD must be equal to or lower than the maximum
allowable LOD for sample analyses to be considered valid.

9.6.6   For sample analysis, all peaks identified as target compounds that are
equal to or greater than the maximum allowable LOD must be reported. If
the calculated laboratory LOD is less than the maximum allowable LOD,
SLB may set its reporting limit at the maximum allowable LOD, the
calculated laboratory LOD, or any level in between.

9.6.7   For the purpose of calculating the total mass of all species, the
concentrations of all compounds below the LOD are considered to be
zero.

9.7.1   Crossover Check: Crossover compounds are those that are measured by
both the light-end and mid-range analyses. A crossover check is
performed on each sample by comparing the measurements of these

compounds from the light-end and mid-range chromatograms of each sample.

The crossover guidelines are:

Average Concentration (ppbC)	Relative Percent Difference (RPD)
< 100	up to 150 ppbC
100 to 1000	up to 50%
100 to 5000	up to 25%
> 5000	up to 15%

9.7.3 These guidelines are useful for troubleshooting instrument problems and are considered when evaluating the overall quality of the test results.

9.8 The analyst shall be familiar with the OAS Quality Control Manual (Ref. 10.14).

9.9 Staff performing this analysis shall be responsible for documenting QC failures and corrective actions taken.

9.10 Documentation shall be kept according to the requirements of the Data Management SOP (Ref. 10.12).

10 **References**

10.1 "Method No. 1002: Determination of C$_2$ to C$_5$ hydrocarbons in Automotive Source Samples by Gas Chromatography", Part D of California Non-methane Organic Gas Test Procedures, *California Air Resources Board*, Amended July 30, **2002**.

10.2 "Method No. 1003: Determination of C$_6$ to C$_{12}$ hydrocarbons in Automotive Source Samples by Gas Chromatography", Part E of California Non-methane Organic Gas Test Procedures, *California Air Resources Board*, Amended July 30, **2002**.

10.3 California Code of Regulations (CCR), Title 13, Division 3, Chapter 1.

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

10.5 Bramston-Cook, Randall, "Quantitation of Hydrocarbons in Vehicle Exhaust and Ambient Air", *Lotus Consulting Monograph*, **1996**.

10.6   Bramston-Cook, Randall, "Speciation of Hydrocarbons in Vehicle Exhaust and Ambient Air", *Lotus Consulting Monograph*, **1996**.

10.7   "Procedure for the Analysis of C$_3$ to C$_{12}$ Hydrocarbons in Automotive Exhaust by Gas Chromatography/Mass Spectrometry", *California Air Resources Board, Monitoring and Laboratory Division Standard Operating Procedure No. 120A*, Revision 1.0, **1998.**

10.8   Peterson, David, "CVS & GC Sample Bag Construction and Pre-conditioning – Cell 1", *California Air Resources Board, Mobile Source Control Division Doc. I.D. TP019-LS*, **1996**.

10.9   Emergency Plan for 9528 Telstar Avenue (HSL), *California Air Resources Board* **2005.**

10.10   Illness and Injury Prevention Program Guide, *California Air Resources Board,* **2003**.

10.11   "Determination of NMOG Mass Emissions", Part G of California Non-methane Organic Gas Test Procedures, *California Air Resources Board*, Amended July 30, **2002**.

10.12   "Procedure for Motor Vehicle Emissions Data Management", *California Air Resources Board, Monitoring and Laboratory Division Standard Operating Procedure No. 127*, Revision 2.0, **2003.**

10.13   Harris, Daniel C., "Quantitative Chemical Analysis", *W.H. Freeman & Co.*, 4th ed., **1995.**

10.14   *"Quality Control Manual for the Analysis of Motor Vehicle Exhaust, California Air Resources Board, Monitoring and Laboratory Division*, Fifth Edition, **2001.**

10   Revision History

11.1   Combined light-end/mid-range method:

S.O.P No. MLD 102/103, Revision 2.2, effective March 15, 2007
▪ Revised format
S.O.P No. MLD 102/103, Revision 2.1, effective September 10, 2004
▪ Revised LOD equation to be consistent with latest amendment to Methods 1002 and Methods 1003
▪ Made minor revisions to format

S.O.P No. MLD 102/103, Revision 2.0, effective September 1, 1996
- Combined SOP No. MLD 102 and SOP No. MLD 103 into one document
- Changed scope of method from a range of 20 to 10,000 ppbC to a range of 1 to 25,000 ppbC
- Added target compound list directly to method, rather than just referencing Methods 1002 and Methods 1003
- Changed mid-range calibration gas from a choice of propane or benzene to propane
- Made minor revisions to format

11.2   Light-end method:

S.O.P No. MLD 102, Revision 1.2, effective November 1, 1989

11.3   Mid-range method:

S.O.P. No. MLD 103A, Revision 1.3, effective September 26, 1991

S.O.P No. MLD 103A, Revision 1.2, effective June 5, 1990

S.O.P. No. MLD 103, Revision 1.0, effective November 1, 1989

Figure 1
Light-end and Mid-range Instrument Configurations
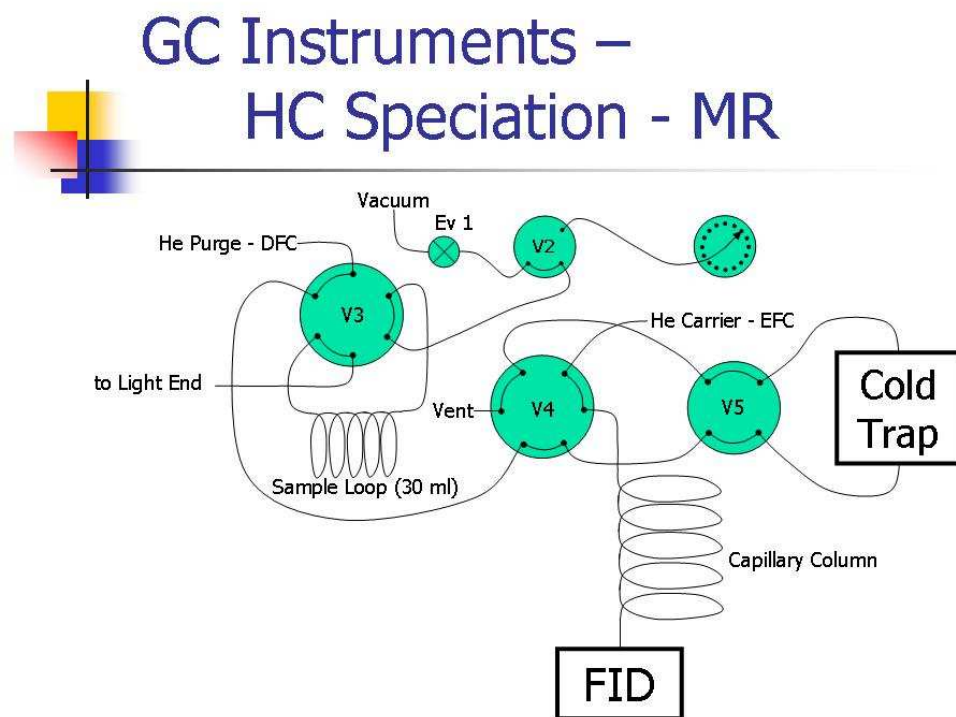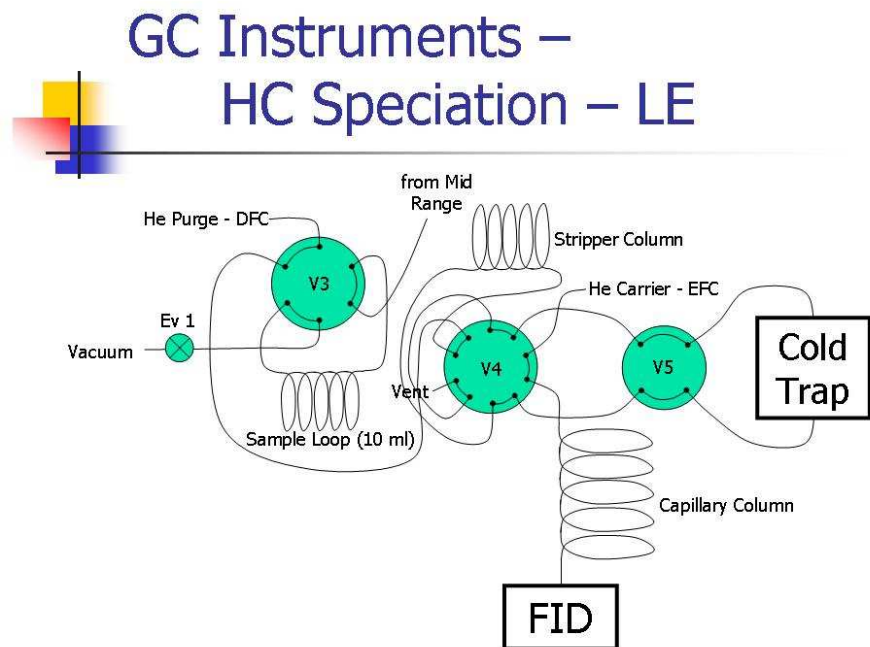
Figure 2
Light End Chromatogram: Calibration Standard (NIST Propane)
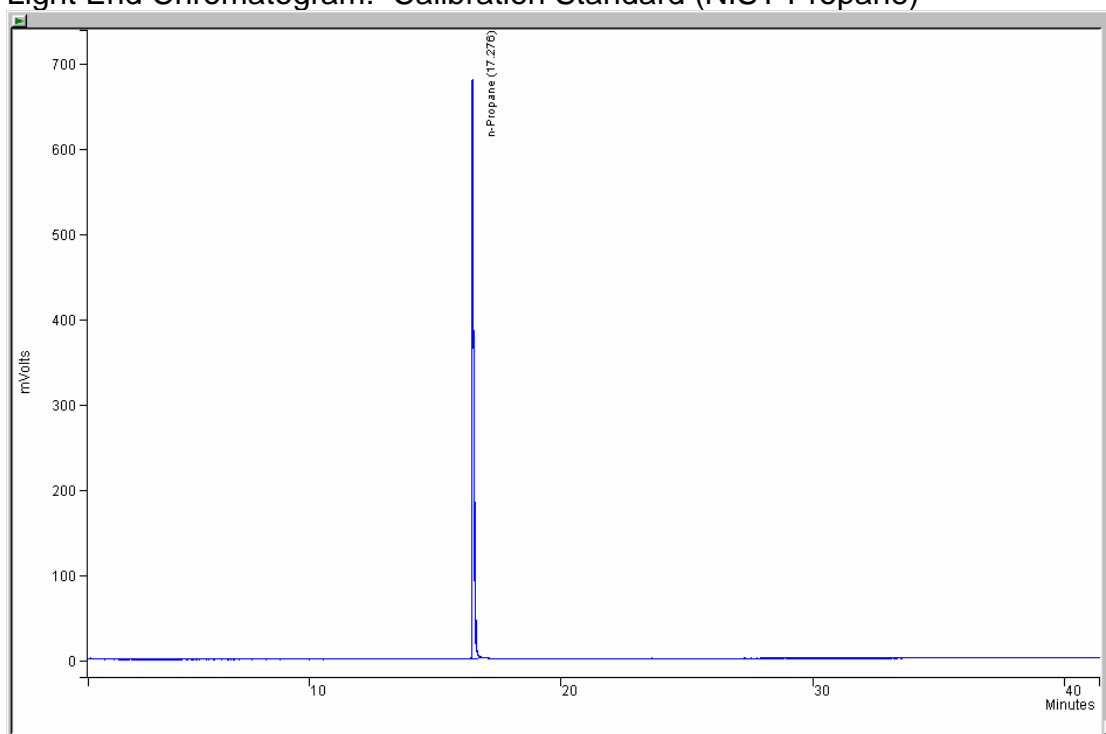
Mid Range Chromatogram: Calibration Standard (NIST Propane)
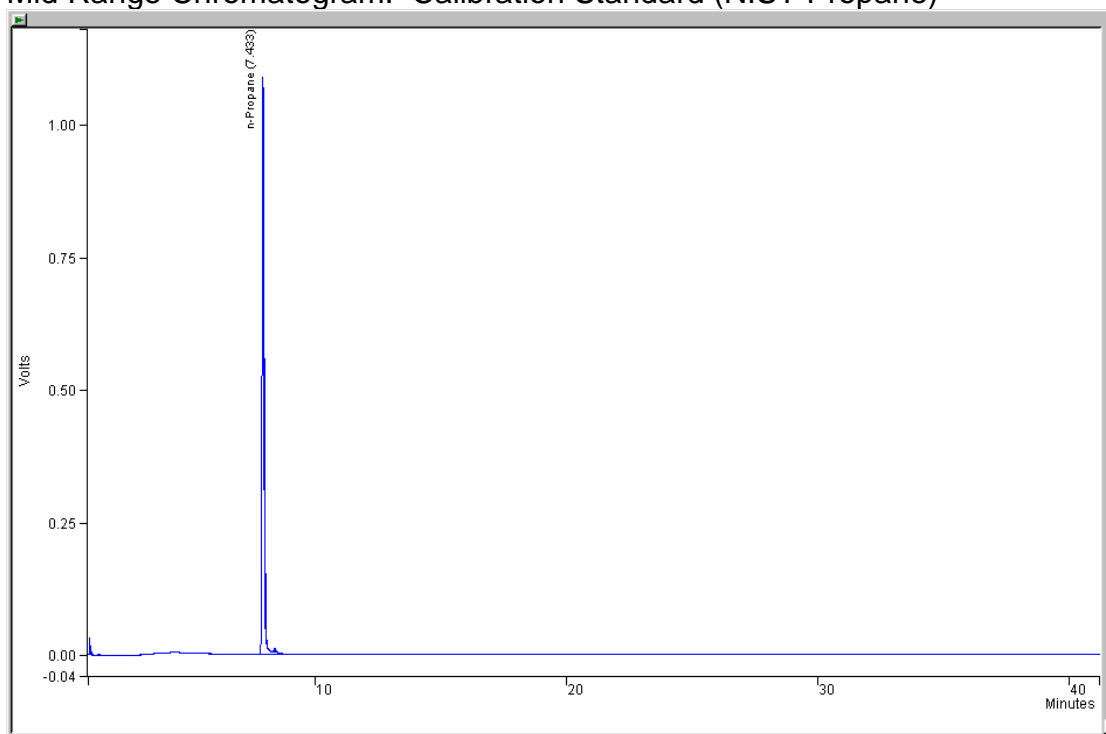
Figure 3
Light End Chromatogram: Control Standard (Matheson "MTGK")
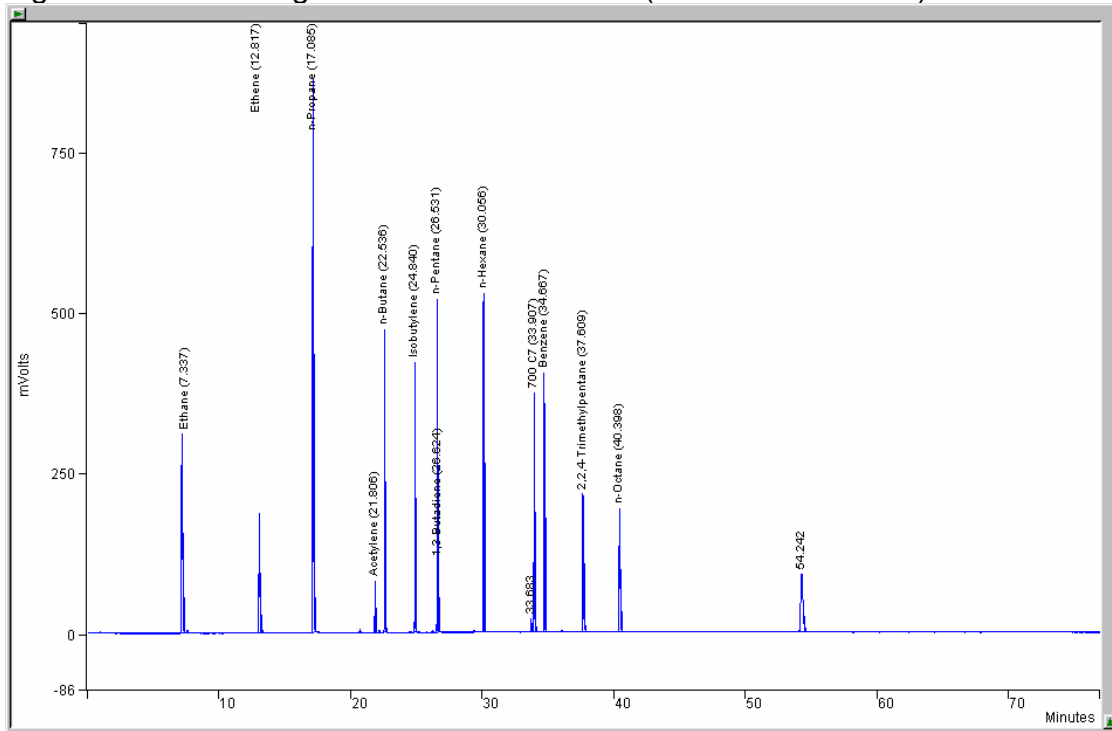
Mid Range Chromatogram: Control Standard (Matheson "MTGK")
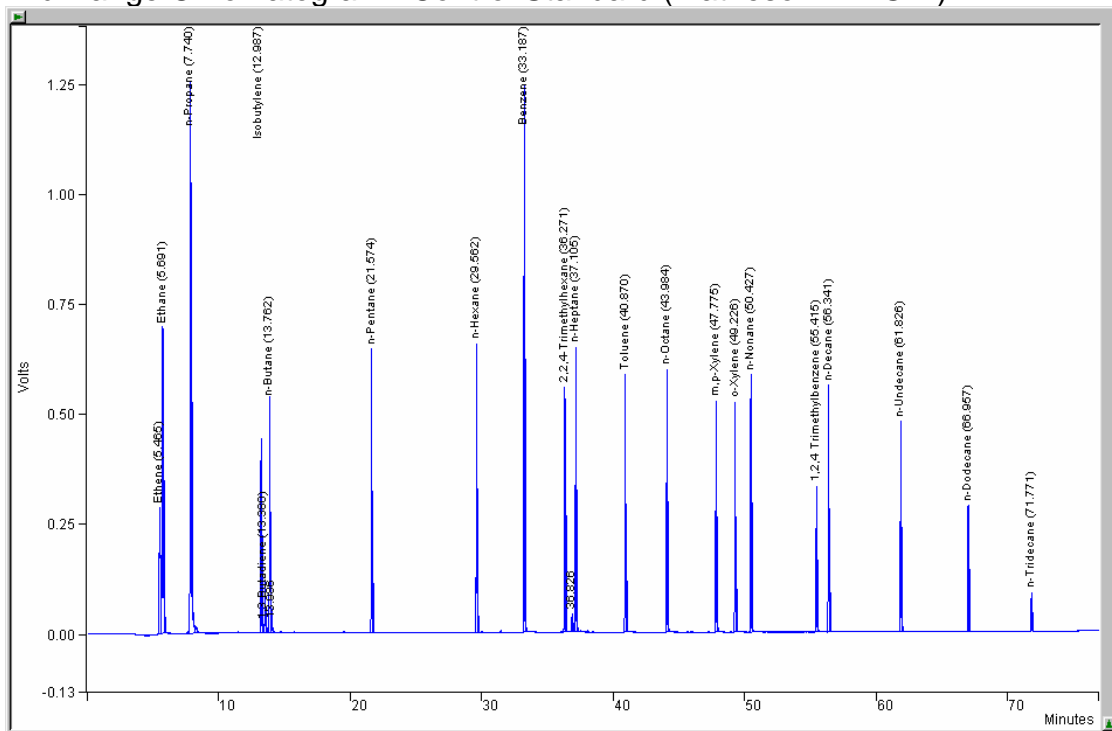
Figure 4

Light End Chromatogram: Typical Automotive Exhaust Sample
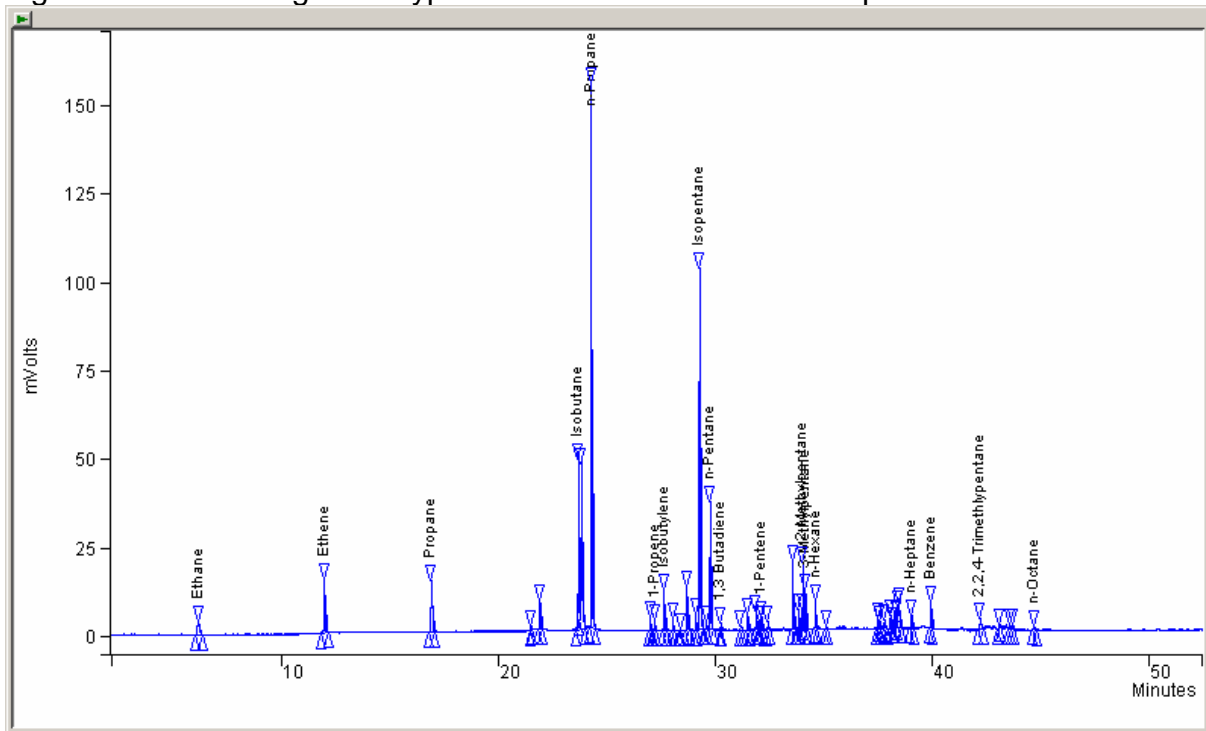
Mid Range Chromatogram: Typical Automotive Exhaust Sample
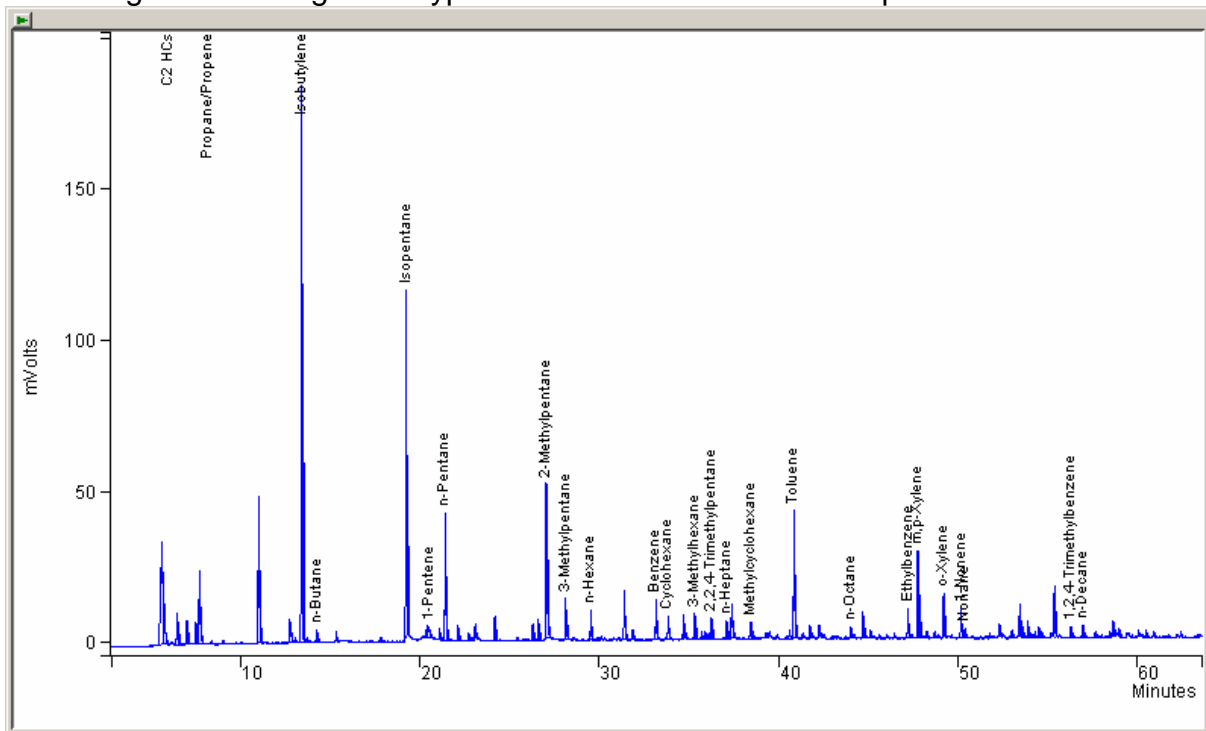
Figure 5

GC7 QC Calibration Charts Second Quarter 2003
NIST Cylinder Number: C3 AAL12007

Label Value, ppbC	3003	3003
Final Mean	295703	623526
Final σ	17104	33475
Final %RSD	5.78	5.37
+5%	310488	654702
+3σ	347015	723951
−3σ	244390	523101
−5%	280917	592350

Number of Data	Date	Light-End Propane			Mid-Range Propane		
		Area Count	Calibration Factor	Status	Area Count	Calibration Factor	Status
1	10/04/2002 11:35	282281			636545		
2	10/07/2002 14:21	266147			606825		
3	10/08/2002 11:25	256255			588932		
4	10/25/2002 14:33	277598			618099		
5	11/01/2002 13:02	291584			608401		
6	11/05/2002 10:31	275820			588372		
7	11/05/2002 12:03	274735			586300		
8	11/18/2002 10:22	269481			564814		
9	11/20/2002 08:45	274640			559640		
10	11/21/2002 08:42	273462			554876		
11	11/26/2002 10:26	271595			550366		
12	02/07/2003 14:49	317811			664876		
13	02/11/2003 16:05	313537			673143		
14	02/13/2003 15:29	313576			666485		
15	02/14/2003 13:16	313195			665357		
16	02/18/2003 15:11	316026			664975		
17	02/19/2003 14:48	301441			620780		
18	02/20/2003 14:31	300767			621506		
19	03/21/2003 11:15	308573			632127		
20	03/27/2003 15:04	296452			627888		
21	04/01/2003 13:00	293705	97.80	OK	627010	208.79	OK
22	04/08/2003 11:16	308530	102.74	OK	648443	215.93	OK
23	04/09/2003 09:07	296447	98.72	OK	617255	205.55	OK
24	04/24/2003 13:53	312749	104.15	OK	663576	220.97	OK
25	04/29/2003 10:55	310597	103.43	OK	659935	219.76	OK
26	05/08/2003 10:45	308663	102.78	OK	644216	214.52	OK
27	05/09/2003 11:27	314076	104.59	OK	643340	214.23	OK
28	05/14/2003 10:35	307741	102.48	OK	645880	215.08	OK
29	05/14/2003 12:08	304274	101.32	OK	631893	210.42	OK
30	05/15/2003 12:16	304329	101.34	OK	624492	207.96	OK
31	05/20/2003 13:00	302851	100.85	OK	628875	209.42	OK
32	05/21/2003 11:31	302548	100.75	OK	630210	209.86	OK
33	06/05/2003 12:17	298361	99.35	OK	625119	208.16	OK
34	06/05/2003 22:29	294041	97.92	OK	609333	202.91	OK
35	06/17/2003 10:23	318491	106.06	OK	651683	217.01	OK

Figure 6

DAILY QC RUN - SECOND QUARTER 2003
LIGHT-END GC7 - 18500
Cylinder Number: MTGK SX23379

		Ethene		Propane		Butane		2-Methylpropene	
Label Value, ppbC		860		3010		1000		510	
Final Mean, ppbC		812		2829		978		814	
Final σ,ppbC		15		52		22		17	
Final %RSD		1.86		1.85		2.24		2.10	
%Diff from Label Value		-5.53		-6.01		-2.17		59.70	
+5%		853		2971		1027		855	
+3σ		858		2986		1044		866	
+2σ		843		2934		1022		849	
−2σ		782		2724		934		780	
−3σ		767		2672		913		763	
-5%		772		2688		929		774	
Date	Time	ppbC	Status	ppbC	Status	ppbC	Status	ppbC	Status
1	09/03/2002	09:57	821		2861		989		824	
2	09/04/2002	16:23	804		2739		960		801	
3	09/05/2002	09:27	827		2860		997		834	
4	10/02/2002	16:18	824		2870		1008		836	
5	10/04/2002	13:08	839		2897		1008		836	
6	11/01/2002	13:33	824		2823		992		823	
7	11/05/2002	13:32	831		2906		1020		836	
8	11/18/2002	11:55	823		2855		1007		828	
9	11/20/2002	10:18	826		2826		989		815	
10	11/21/2002	10:15	827		2822		990		818	
11	11/26/2002	11:59	816		2772		978		810	
12	02/07/2003	16:23	815		2761		956		804	
13	02/11/2003	17:40	800		2854		971		804	
14	02/13/2003	17:03	801		2750		945		786	
15	02/14/2003	14:49	779		2847		990		821	
16	02/18/2003	16:44	799		2796		955		797	
17	02/19/2003	16:21	805		2833		961		800	
18	02/20/2003	16:04	783		2778		972		814	
19	03/21/2003	12:49	784		2764		929		772	
20	03/27/2003	16:37	813		2836		972		812	
21	04/01/2003	14:33	806	OK	2833	OK	978	OK	817	OK
22	04/08/2003	12:49	784	OK	2700	OK	936	OK	782	OK
23	04/09/2003	10:40	813	OK	2811	OK	974	OK	815	OK
24	04/24/2003	15:26	805	OK	2788	OK	958	OK	798	OK
25	04/29/2003	12:28	813	OK	2847	OK	968	OK	808	OK
26	05/08/2003	12:18	824	OK	2876	OK	975	OK	814	OK
27	05/09/2003	13:00	809	OK	2861	OK	977	OK	816	OK
28	05/14/2003	13:42	816	OK	2880	OK	982	OK	820	OK
29	05/15/2003	13:50	818	OK	2859	OK	970	OK	806	OK
30	05/20/2003	14:34	806	OK	2788	OK	969	OK	812	OK
31	05/21/2003	13:05	814	OK	2844	OK	991	OK	830	OK
32	06/04/2003	13:50	829	OK	2902	OK	998	OK	834	OK
33	06/06/2003	00:02	833	OK	2920	OK	1019	OK	853	OK
34	06/17/2003	14:16	799	OK	2808	OK	978	OK	821	OK

DAILY QC RUN - SECOND QUARTER 2003
MID-RANGE GC7 - 18498
Cylinder Number: MTGK SX23379

		Hexane		Benzene		Toluene		Octane		m-Xylene		Decane	
	Label Value, ppbC	1140		1950		1040		1030		960		1100	
	Final Mean, ppbC	1078		2025		982		1004		913		1004	
	Final σ,ppbC	13		25		13		11		12		16	
	Final %RSD	1.16		1.22		1.29		1.11		1.32		1.60	
	%Diff from Label Value	-5.43		3.82		-5.55		-2.49		-4.89		-8.68	
	+5%	1132		2126		1031		1055		959		1055	
	+3σ	1116		2099		1020		1038		949		1053	
	+2σ	1103		2074		1008		1027		937		1037	
	-2σ	1053		1975		957		982		889		972	
	-3σ	1041		1950		944		971		877		956	
	-5%	1024		1923		933		954		867		954	
	Date	Time	ppbC	Status	ppbC	Status	ppbC	Status	ppbC	Status	ppbC	Status	ppbC	Status
1	09/03/2002	09:57	1061		1999		977		987		911		1001	
2	09/04/2002	16:23	1069		2018		985		995		917		1008	
3	09/05/2002	09:27	1091		2059		1006		1015		935		1032	
4	10/02/2002	16:18	1086		2043		996		1009		924		1022	
5	10/04/2002	13:08	1106		2080		1017		1031		947		1044	
6	11/01/2002	13:33	1092		2062		1002		1025		924		1031	
7	11/05/2002	13:32	1095		2039		994		1016		923		1027	
8	11/18/2002	11:55	1067		1982		975		999		909		987	
9	11/20/2002	10:18	1080		2021		991		1008		923		1011	
10	11/21/2002	10:15	1084		2023		993		1012		927		1014	
11	11/26/2002	11:59	1076		2000		981		1007		915		991	
12	02/07/2003	16:23	1077		2013		984		1006		915		981	
13	02/11/2003	17:40	1077		2017		983		1003		914		1010	
14	02/13/2003	17:03	1075		2020		981		1008		920		1009	
15	02/14/2003	14:49	1075		2026		982		1009		921		1011	
16	02/18/2003	16:44	1073		2017		978		1005		914		1007	
17	02/19/2003	16:21	1070		2012		973		1000		907		1003	
18	02/20/2003	16:04	1070		2012		976		1002		912		1000	
19	03/21/2003	12:49	1064		2007		968		990		901		984	
20	03/27/2003	16:37	1073		2012		976		996		910		999	
21	04/01/2003	14:33	1075	OK	2013	OK	976	OK	999	OK	908	OK	1000	OK
22	04/08/2003	12:49	1044	OK	1958	OK	950	OK	973	OK	886	OK	967	OK
23	04/09/2003	10:40	1078	OK	2034	OK	983	OK	1006	OK	918	OK	1009	OK
24	04/24/2003	15:26	1078	OK	2028	OK	979	OK	1003	OK	910	OK	1001	OK
25	04/29/2003	12:28	1080	OK	2028	OK	980	OK	1006	OK	911	OK	1003	OK
26	05/08/2003	12:18	1084	OK	2034	OK	981	OK	1003	OK	907	OK	998	OK
27	05/09/2003	13:00	1064	OK	2001	OK	958	OK	992	OK	884	OK	977	OK
28	05/14/2003	13:42	1096	OK	2050	OK	990	OK	1019	OK	916	OK	1014	OK
29	05/15/2003	13:50	1089	OK	2049	OK	983	OK	1006	OK	908	OK	1007	OK
30	05/20/2003	14:34	1074	OK	2023	OK	975	OK	995	OK	903	OK	996	OK
31	05/21/2003	13:05	1069	OK	2020	OK	971	OK	996	OK	899	OK	988	OK
32	06/04/2003	13:50	1086	OK	2038	OK	982	OK	1004	OK	907	OK	1004	OK
33	06/06/2003	00:02	1101	OK	2073	OK	988	OK	1018	OK	907	OK	1009	OK
34	06/17/2003	14:16	1050	OK	1980	OK	954	OK	980	OK	884	OK	983	OK

Figure 7

GC7 Replicate Analysis
SECOND QUARTER 2003
LIGHT-END GC7 - 18500

	TEST DATE	TEST	ETHENE LOD= 7					PROPANE LOD= 7				
			RUN 1	RUN 2	%RPD	MAX. %RPD	STATUS	RUN 1	RUN 2	%RPD	MAX. %RPD	STATUS
1	04/09/2003	#1 bmd sample bag 1	<LOD	<LOD	<LOD	<LOD	Pass	<LOD	<LOD	<LOD	<LOD	Pass
2	04/10/2003	#8 bmd sample bag 3	<LOD	<LOD	<LOD	<LOD	Pass	<LOD	<LOD	<LOD	<LOD	Pass
3	04/24/2003	nist srm 1800	<LOD	<LOD	<LOD	<LOD	Pass	14	15	8	100	Pass
4	05/08/2003	freon 1 ppm cc60400	<LOD	<LOD	<LOD	<LOD	Pass	<LOD	<LOD	<LOD	<LOD	Pass
5	05/09/2003	f 25 in 5-8 v21 s1	<LOD	<LOD	<LOD	<LOD	Pass	<LOD	<LOD	<LOD	<LOD	Pass
6	05/14/2003	bag fitting sam s1	<LOD	<LOD	<LOD	<LOD	Pass	<LOD	<LOD	<LOD	<LOD	Pass
7	05/20/2003	bag fitting sam s2	<LOD	<LOD	<LOD	<LOD	Pass	<LOD	<LOD	<LOD	<LOD	Pass
8	06/06/2003	bag fitting sam s4	<LOD	<LOD	<LOD	<LOD	Pass	<LOD	<LOD	<LOD	<LOD	Pass
9	06/17/2003	bag fitting sam s6	<LOD	<LOD	<LOD	<LOD	Pass	<LOD	<LOD	<LOD	<LOD	Pass

GC7 Replicate Analysis
SECOND QUARTER 2003
LIGHT-END GC7 - 18500

	TEST DATE	TEST	BUTANE LOD= 7					2-METHYLPROPENE LOD= 7				
			RUN 1	RUN 2	%RPD	MAX. %RPD	STATUS	RUN 1	RUN 2	%RPD	MAX. %RPD	STATUS
1	04/09/2003	#1 bmd sample bag 1	<LOD	<LOD	<LOD	<LOD	Pass	<LOD	<LOD	<LOD	<LOD	Pass
2	04/10/2003	#8 bmd sample bag 3	<LOD	<LOD	<LOD	<LOD	Pass	<LOD	<LOD	<LOD	<LOD	Pass
3	04/24/2003	nist srm 1800	20	20	1	100	Pass	20	20	4	100	Pass
4	05/08/2003	freon 1 ppm cc60400	<LOD	<LOD	<LOD	<LOD	Pass	<LOD	<LOD	<LOD	<LOD	Pass
5	05/09/2003	f 25 in 5-8 v21 s1	32	33	1	100	Pass	70	74	5	30	Pass
6	05/14/2003	bag fitting sam s1	<LOD	<LOD	<LOD	<LOD	Pass	<LOD	<LOD	<LOD	<LOD	Pass
7	05/20/2003	bag fitting sam s2	<LOD	<LOD	<LOD	<LOD	Pass	<LOD	<LOD	<LOD	<LOD	Pass
8	06/06/2003	bag fitting sam s4	<LOD	<LOD	<LOD	<LOD	Pass	<LOD	<LOD	<LOD	<LOD	Pass
9	06/17/2003	bag fitting sam s6	<LOD	<LOD	<LOD	<LOD	Pass	<LOD	<LOD	<LOD	<LOD	Pass

SOP No. 102/103 - PROCEDURE FOR THE DETERMINATION OF C_2 TO C_{12} HYDROCARBONS IN AUTOMOBILE EXHAUST SAMPLES BY GAS CHROMATOGRAPHY

Figure 8

Linearity/LOD Determination for GC 7
February 20-24, 2001

Ethene Assay (ppbC)	Light End Peak Area	Propane Assay (ppbC)	Light End Peak Area	n-Butane Assay (ppbC)	Light End Peak Area	Isopentane* Assay (ppbC)	Light End Peak Area	Rep. #	Standard (Dilution)
5.2	467	5.25	521	6.4	648	5.2	522	1	NIST D (5%)
5.2	445	5.25	524	6.4	652	5.2	556	2	NIST D (5%)
5.2	470	5.25	537	6.4	651	5.2	477	3	NIST D (5%)
5.2	479	5.25	552	6.4	652	5.2	503	4	NIST D (5%)
5.2	460	5.25	570	6.4	649	5.2	485	5	NIST D (5%)
10.4	928	10.5	1061	12.8	1280	10.4	1035	1	NIST D (10%)
10.4	945	10.5	1074	12.8	1257	10.4	1062	2	NIST D (10%)
52	4663	52.5	5275	64	6290	52	5034	1	NIST D (50%)
52	4602	52.5	5238	64	6386	52	5117	2	NIST D (50%)
104	9301	105	10443	128	12522	104	10013	1	NIST D
104	9399	105	10375	128	12552	104	9926	2	NIST D
2580	249885	2751	256295	3152	299900	2640	246325	1	NIST E
2580	249503	2751	254961	3152	295858	2640	243700	2	NIST E
9920	1022063	9000	713458	10640	950506	9950	929245	1	NIST WW
9920	1015907	9000	755477	10640	958711	9950	931477	2	NIST WW

* = Isopentane substituted for Isobutylene because of standards availability

Slope (Area/ppbC)	102.34	Slope (Area/ppbC)	82.58	Slope (Area/ppbC)	90.11	Slope (Area/ppbC)	93.46
R value	0.99987	R value	0.99858	R value	0.99985	R value	1.00000
T factor	3.7	T factor	3.7	T factor	3.7	T factor	3.7
std deviaton	12.7	std deviaton	20.4	std deviaton	1.8	std deviaton	31.7
LOD (ppbC)	0.46	LOD (ppbC)	0.91	LOD (ppbC)	0.07	LOD (ppbC)	1.25

Hexane Assay (ppbC)	Mid Range Peak Area	Benzene Assay (ppbC)	Mid Range Peak Area	Toluene Assay (ppbC)	Mid Range Peak Area	Octane Assay (ppbC)	Mid Range Peak Area	p-Xylene Assay (ppbC)	Mid Range Peak Area
5.2	1133	5.15	1156	5.2	1156	5.1	1172	5.2	749
5.2	1169	5.15	1166	5.2	1068	5.1	1067	5.2	864
5.2	1130	5.15	1128	5.2	1157	5.1	1164	5.2	898
5.2	1103	5.15	1099	5.2	1102	5.1	1035	5.2	887
5.2	1102	5.15	1146	5.2	1149	5.1	1097	5.2	829
10.4	2259	10.3	2284	10.4	2380	10.2	2310	10.4	2205
10.4	2218	10.3	2325	10.4	2369	10.2	2400	10.4	2095
52	11027	51.5	10948	52	11468	51	11256	52	10664
52	11057	51.5	10867	52	11270	51	11155	52	10579
104	22147	103	21709	104	21729	102	22026	104	18766
104	21788	103	21425	104	21542	102	21879	104	18801
2550	563197	2526	551922	2569	556168	2504	557799	2264	485629
2550	561483	2526	550686	2569	556685	2504	556547	2264	483105
8880	2219655	10020	2256642	10080	2245456	10000	2268698	9920	2163655
8880	2202299	10020	2238686	10080	2220416	10000	2256235	9920	2147615

Slope (Area/ppbC)	246.81	Slope (Area/ppbC)	223.95	Slope (Area/ppbC)	221.22	Slope (Area/ppbC)	226.03	Slope (Area/ppbC)	217.13
R value	0.99940	R value	0.99996	R value	0.99996	R value	0.99999	R value	0.99998
T factor	3.7	T factor	3.7	T factor	3.7	T factor	3.7	T factor	3.7
std deviaton	27.4	std deviaton	26.4	std deviaton	39.8	std deviaton	59.9	std deviaton	60.0
LOD (ppbC)	0.41	LOD (ppbC)	0.44	LOD (ppbC)	0.67	LOD (ppbC)	0.98	LOD (ppbC)	1.02

LOD = (t * std deviation)/slope

SOP No. 102/103 - PROCEDURE FOR THE DETERMINATION OF C$_2$ TO C$_{12}$ HYDROCARBONS IN AUTOMOBILE EXHAUST SAMPLES BY GAS CHROMATOGRAPHY

Table A Light End Hydrocarbons

Compound Name	GC Peak #	GC Peak Name	CAS Number
Ethane	200	C2	00074-84-0
Ethene	250	C2=	00074-85-1
Propane	300	C3	00074-98-6
1-Propene	350	C3=	00115-07-1
2-Methylpropane	390	2MC3	00075-28-5
Ethyne (acetylene)	395	C2yne	00074-86-2
n-Butane	400	C4	00106-97-8
1,2-Propadiene	410	12C3==	00463-49-0
trans-2-Butene	450	t2C4=	00624-64-6
1-Butene	455	1C4=	00106-98-9
2-Methylpropene	460	2MC3=	00115-11-7
cis-2-Butene	465	c2C4=	00590-18-1
2,2-Dimethylpropane	470	22MC3	00463-82-1
Cyclopentane*	485	CY5	00287-92-3
2-Methylbutane	490	2MC4	00078-78-4
1,2-Butadiene	495	12C4==	00590-19-2
1-Propyne	498	1C3yne	00074-99-7
n-Pentane*	500	C5	00109-66-0
1,3-Butadiene	510	13C4==	00106-99-0
3-Methyl-1-butene*	525	3M1C4=	00563-45-1
Cyclopentene	530	CY5=	00142-29-0
trans-2-Pentene	535	t2C5=	00646-04-8
2-Methyl-2-butene	540	2M2C4=	00513-35-9
1-Pentene	545	1C5=	00109-67-1
2-Methyl-1-butene	550	2M1C4=	00563-46-2
cis-2-Pentene	555	c2C5=	00627-20-3
1-Butene-3-yne	565	1C4=3yne	00689-97-4
2-Butyne	560	2C4yne	00503-17-3
2,2-Dimethylbutane*	570	22MC4	00075-83-2
Methylcyclopentane*	575	MCY5	00096-37-7
1-Butyne	580	1C4yne	00107-00-6
2,3-Dimethylbutane*	585	23MC4	00079-29-8
2-Methylpentane*	590	2MC5	00107-83-5
3-Methylpentane*	595	3MC5	00096-14-0
2-Methyl-1,3-butadiene*	598	2M13C4==	00078-79-5
1,3-Cyclopentadiene*	610	13CY5==	00542-92-7
3,3-Dimethyl-1-butene*		33M1C4=	00558-37-2
4-Methyl-1-pentene*		4M1C5=	00691-37-2
n-Hexane*	600	C6	00110-54-3

*   Measured and reported for record as part of mid-range analysis

Table B Mid Range Hydrocarbons

Compound Name	GC Peak #	GC Peak Name	CAS #
1,2-Propadiene*	320	12C3=	00463-49-0
Propyne*	325	C3yne	00074-99-7
2-Methylpropane*	360	2MC3	00075-28-5
2-Methylpropene*	390	2MC3	00115-11-7
1,3 Butadiene*	395	13C4==	00106-99-0
n-Butane*	400	C4	00106-97-8
1,3-Butadiyne	440	13C4yne	00460-12-8
3-Methyl-1-butene	460	3M1C4=	00563-45-1
2-Methylbutane*	475	2MC4	00078-78-4
n-Pentane	500	C5	00109-66-0
2-methyl-1,3-butadiene	505	2M13C4==	00078-79-5
3,3-Dimethyl-1-butene	513	33M1C4=	00558-37-2
trans-1,3-Pentadiene	525	t13C5==	02004-70-8
2,2-Dimethylbutane	535	22MC4	00075-83-2
Cyclopentene	550	CY5=	00142-29-0
4-Methyl-1-pentene	555	4M1C5=	00691-37-2
3-Methyl-1-pentene	557	3M1C5=	00760-20-3
Cyclopentane	560	CY5	00287-92-3
2,3-Dimethylbutane	565	23MC4	00079-29-8
2,3-Dimethyl-1-butene	567	23M1C4=	00563-78-0
Methyl-tert-butyl-ether	568	MTBE	01634-04-4
4-Methyl-cis-2-pentene	569	4Mc2C5=	00691-38-3
2-Methylpentane	570	2MC5	00107-83-5
4-Methyl-trans-2-pentene	572	4Mt2C5=	00674-76-0
3-Methylpentane	585	3MC5	00096-14-0
1-Hexene	590	1C6=	00592-41-6
2-Methyl-1-pentene	588	2M1C5=	00763-29-1
n-Hexane	600	C6	00110-54-3
trans-3-Hexene	603	t3C6=	13269-52-8
cis-3-Hexene	604	c2C6=	07642-09-3
trans-2-Hexene	606	t2C6=	04050-45-7
2-Methyl-2-pentene	608	2M2C5=	00625-27-4
3-Methyl-trans-2-pentene	610	3Mt2C5=	00616-12-6
3-Methylcyclopentene	612	3MCY5=	01120-62-3
cis-2-Hexene	615	c2C6=	07688-21-3
2-Methyl-cis-2-pentene	620	2Mc2C5=	00922-62-3
1-Ethyl-tert-butyl-ether	622	ETBE	00637-92-3
2,2-Dimethylpentane	626	22MC5	00590-35-2
Methylcyclopentane	629	MCY5	00096-37-7
2,4-Dimethylpentane	630	24MC5	00108-08-7
2,2,3-Trimethylbutane	632	223MC4	00464-06-2
3,4-Dimethyl-1-pentene	635	34M1C5=	07385-78-6
2,4-Dimethyl-1-pentene	640	24M1C5=	02213-32-3

*   Measured and reported for record as part of light-end analysis

Compound Name	GC Peak #	GC Peak Name	CAS #
1-Methylcyclopentene	648	1MCY5=	00693-89-0
Benzene	650	Benzene	00071-43-2
3-Methyl-1-hexene	651	3M1C6=	03404-61-3
3,3,-Dimethylpentane	653	33MC5	00562-49-2
2,4-Dimethyl-2-pentene	654	24M2C5=	00625-65-0
Cyclohexane	655	CY6	00110-82-7
2-Methyl-trans-3-hexene	657	2Mt3C6=	00692-24-0
4-Methyl-trans-2-hexene	664	4Mt2C6=	03683-22-5
2-Methylhexane	667	2MC6	00591-76-4
2,3-Dimethylpentane	668	23MC5	00565-59-3
Cyclohexene	670	CY6=	00110-83-8
3-Methylhexane	675	3MC6	00589-34-4
trans-1,3-Dimethylcyclopentane	680	t13MCY5	01759-58-6
cis-1,3-Dimethylcyclopentane	683	c13MCY5	02532-58-3
3-Ethylpentane	685	3EC5	00617-78-7
trans-1,2-Dimethylcyclopentane	688	t12MCY5	00822-50-4
2,2,4-Trimethylpentane	690	224MC5	00540-84-1
1-Heptene	692	1C7=	00592-76-7
3-Methyl-trans-3-hexene	694	3Mt3C6=	03899-36-3
trans-3-Heptene	699	t3C7=	14686-14-7
n-Heptane	700	C7	00142-82-5
2,4,4-Trimethyl-1-pentene	701	244M1C5=	00107-39-1
2-Methyl-2-hexene	703	2M2C6=	02738-19-4
trans-2-Heptene	706	t2C7=	14686-13-6
3-Ethyl-2-pentene	707	3E2C5=	00816-79-5
3-Methyl-cis-2-hexene	708	3Mc2C6=	10574-36-4
2,3-Dimethyl-2-pentene	710	23M2C5=	10574-37-5
cis-2-Heptene	713	c2C7=	06443-92-1
Methylcyclohexane	718	MCY6	00108-87-2
2,2-Dimethylhexane	722	22MC6	00590-73-8
2,4,4-Trimethyl-2-pentene	728	244M2C5=	00107-40-4
Ethylcyclopentane	730	ECY5	01640-89-7
2,5-Dimethylhexane	733	25MC6	00592-13-2
2,4-Dimethylhexane	735	24MC6	00589-43-5
1,2,4-Trimethylcyclopentane	740	124MCY5	02815-58-9
3,3-Dimethylhexane	742	33MC6	00563-16-6
1a,2a,3b-Trimethylcyclopentane	745	123MCY5	15890-40-1
2,3,4-Trimethylpentane	748	234MC5	00565-75-3
Toluene	750	Toluene	00108-88-3
2,3,3-Trimethylpentane	755	233MC5	00560-21-4
2,3-Dimethylhexane	760	23MC6	00584-94-1
2-Methylheptane	765	2MC7	00592-27-8
4-Methylheptane	770	4MC7	00589-53-7
3,4-Dimethylhexane	772	34MC6	00583-48-2
3-Methylheptane	775	3MC7	00589-81-1
cis-1,3-Dimethylcyclohexane	776	c13MCY6	**00638-04-0**

Compound Name	GC Peak #	GC Peak Name	CAS #
trans-1,4-Dimethylcyclohexane	777	t14MCY6	02207-04-7
2,2,5-Trimethylhexane	785	225MC6	03522-94-9
trans-1-Methyl-3-ethylcyclopentane	787	t1M3ECY5	02613-65-2
cis-1-Methyl-3-ethylcyclopentane	788	c1M3ECY5	16747-50-5
1-Octene	790	1C8=	00111-66-0
2,2,4-Trimethylhexane	792	224MC6	16747-26-5
trans-4-Octene	796	t4C8=	14850-23-8
n-Octane	800	C8	00111-65-9
trans-2-Octene	805	t2C8=	13389-42-9
trans-1,3-Dimethylcyclohexane	810	t13MCY6	02207-03-6
2,4,4-Trimethylhexane	815	244MC6	16747-30-1
cis-2-Octene	820	c2C8=	07642-04-8
2,3,5-Trimethylhexane	825	235MC6	01069-53-0
2,4-Dimethylheptane	827	24MC7	02213-23-2
cis-1,2-Dimethylcyclohexane	830	c12MCY6	02207-01-4
2,6-Dimethylheptane	835	26MC7	01072-05-5
Ethylcyclohexane	836	ECY6	01678-91-7
3,5-Dimethylheptane	840	35MC7	00926-82-9
Ethylbenzene	850	Ebe	00100-41-4
1,3,5-Trimethylcyclohexane	853	135MCY6	01839-63-0
2,3-Dimethylheptane	857	23MC7	03074-71-3
m- & p-Xylene	860	m- & p-Xylene	00108-38-3 00106-42-3
4-Methyloctane	865	4MC8	02216-34-4
2-Methyloctane	866	2MC8	03221-61-2
3-Methyloctane	870	3MC8	02216-33-3
Styrene	875	Styrene	00100-42-5
o-Xylene	880	o-Xylene	00095-47-6
2,2,4-Trimethylheptane	882	224MC7	14720-74-2
1-methyl-4-Ethylcyclohexane	885	1M4ECY6	06236-88-0
2,2,5-Trimethylheptane	890	225MC7	02091-95-6
1-Nonene	892	1C9=	00124-11-8
n-Nonane	900	C9	00111-84-2
3,3-Dimethyloctane	905	33MC8	04110-44-5
(1-Methylethyl)benzene	910	iPBe	00098-82-8
2,3-Dimethyloctane	918	23MC8	07146-60-3
2,2-Dimethyloctane	920	22MC8	15869-87-1
2,5-Dimethyloctane	925	25MC8	15869-89-3
2,4-Dimethyloctane	930	24MC8	04032-94-4
2,6-Dimethyloctane	935	26MC8	02051-30-1
n-Propylbenzene	940	nPBe	00103-65-1
1-Methyl-3-ethylbenzene	950	1M3EBe	00620-14-4
1-Methyl-4-ethylbenzene	955	1M4EBe	00622-96-8
1,3,5-Trimethylbenzene	960	135MBe	00108-67-8
2-Methylnonane	965	2MC9	00871-83-0
1-Methyl-2-ethylbenzene	970	1M2EBe	**00611-14-3**
1,2,4-Trimethylbenzene	980	124MBe	**00095-63-6**

SOP No. 102/103 - PROCEDURE FOR THE DETERMINATION OF C_2 TO C_{12} HYDROCARBONS IN AUTOMOBILE EXHAUST SAMPLES BY GAS CHROMATOGRAPHY

Compound Name	GC Peak #	GC Peak Name	CAS #
(2-Methylpropyl)benzene	995	iBBe	00538-93-2
(1-Methylpropyl)benzene	998	sBBe	00135-98-8
n-Decane	1000	C10	00124-18-5
1-Methyl-3-(1-methylethyl)benzene	1005	1M3iPBe	00535-77-3
1,2,3-Trimethylbenzene	1010	123MBe	00526-73-8
1-Methyl-4-(1-methylethyl)benzene	1015	1M4iPBe	00099-87-6
2,3-Dihydroindene (indan)	1020	INDAN	00496-11-7
1-Methyl-2-(1methylethyl)benzene	1030	1M2iPBe	00527-84-4
1,3-Diethylbenzene	1035	13EBe	00141-93-5
1-Methyl-3-n-propylbenzene	1040	1M3nPBe	01074-43-7
1,4-Diethylbenzene	1045	14EBe	00105-05-5
1-Methyl-4-n-propylbenzene	1046	1M4nPBe	01074-55-1
1,3-Dimethyl-5-ethylbenzene	1047	13M5EBe	00934-74-7
1,2-Diethylbenzene	1050	12EBe	00135-01-3
1-Methyl-2-n-propylbenzene	1060	1M2nPBe	01074-17-5
1,4-Dimethyl-2-ethylbenzene	1065	14M2EBe	01758-88-9
1,3-Dimethyl-4-ethylbenzene	1070	13M4EBe	00874-41-9
1,2-Dimethyl-4-ethylbenzene	1075	12M4EBe	00934-80-5
1,3-Dimethyl-2-ethylbenzene	1080	13M2EBe	02870-04-4
n-Undecane	1100	C11	01120-21-4
1,2-Dimethyl-3-ethylbenzene	1095	12M3EBe	00933-98-2
1,2,4,5-Tetramethylbenzene	1105	1245MBe	00095-93-2
1,2,3,5-Tetramethylbenzene	1110	1235MBe	00527-53-7
1-(Dimethylethyl)-2-methylbenzene	1120	1M2tertBBe	01074-92-6
5-Methylindan	1130	5MINDAN	00874-35-1
4-Methylindan	1132	4MINDAN	00824-22-6
1-Ethyl-2-n-propylbenzene	1135	1E2nPBe	16021-20-8
2-Methylindan	1140	2MINDAN	00824-63-5
1,2,3,4-Tetramethylbenzene	1145	1234MBe	00488-23-3
n-Pentylbenzene	1150	nPenBe	00538-68-1
1-Methyl-2-n-butylbenzene	1160	1M2nBBe	01595-11-5
Naphthalene	1170	NAPTHALENE	00091-20-3
1-(Dimethylethyl)-3,5-dimethylbenzene	1175	13M5tBBe	00098-19-1
1,3-di-n-Propylbenzene	1190	13nPBe	17171-72-1
n-Dodecane	1200	C12	00112-40-3

Table C. Working Standards Assays

DESCRIPTION	DAILY CALIBRATION	DAILY CONTROL	ALTERNATE NIST CONTROL (Section 8.3.5)
Cylinder Name	"NIST Propane"	"MTGK"	NIST "E"
Vendor	NIST	Matheson	NIST
Cylinder Number	AAL12007	SX23379	CC127168

Compounds	Cylinder Label Value (ppbC)		
Methane		1040	
Ethane		2000	
Ethene		860	2546
Propane	3003	3010	2815
Acetylene		180	
n-Butane		1000	2688
2-Methylpropene		510	2522
n-Pentane		1040	
1,3-Butadiene		360	
2-Methylbutane			2505
n-Hexane		1140	2470
Benzene		1950	2481
n-Heptane		1080	
Toluene		1040	2509
n-Octane		1030	2502
m-Xylene		960	
p-Xylene			2479
o-Xylene		1020	
2,2,4-Trimethylpentene		1020	
n-Nonane		1100	
1,2,4-Trimethylbenzene		810	
n-Decane		1100	2447
n-Undecane		1170	
n-Dodecane		1250	
n-Tridecane		1190	

Table D. Typical GC Operating Conditions

GC Parameter	Light-end GC	Mid-range GC
Column type	Alumina/KCl PLOT	DB-1 WCOT
Column size	0.32 mm ID, 50 m	0.32 mm ID, 60m
Helium carrier velocity	2 mL/min at 200°C	2 mL/min at 200°C
Hydrogen gas flow (for FID)	25 mL/min	25mL/min
Zero Air gas flow (for FID)	300 mL/min	300 mL/min
Nitrogen make-up flow (for FID)	30 mL/min	30 mL/min
Auxiliary sample valve	150°C	150°C
Precolumn temperature	40°C	N/A
Column temperature	0°C (hold 7 min)	-50°C, (hold 2 min)
	5°C/min to 50°C	3°C/min to 170°C
	10°C/min to 200°C	47°C/min to 200°C
	hold 15 min	30°C/min to 250°C
Cryotrap/Injector Program	-180°C	-180°C
	250°/min to 200°C	250°C/min to 200°C
	hold for remainder	hold for remainder
Detector Temperature	250°C	300°C
Detector Attenuation	8	8
Detector range	12	12
Total analysis time	60 min	90 min