California Environmental Protection Agency

⊖▤ Air Resources Board

PROCEDURE FOR THE DIRECT DETERMINATION OF TOTAL NON-METHANE HYDROCARBONS AND METHANE IN MOTOR VEHICLE EXHAUST USING CRYOGENIC PRECONCENTRATION AND FLAME IONIZATION DETECTION

Standard Operating Procedure No. MLD 119
Revision 2.1

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Organic Analysis Section
Southern Laboratory Branch
Monitoring and Laboratory Division
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**SOP No. MLD 119 - PROCEDURE FOR THE DIRECT DETERMINATION
OF TOTAL NON-METHANE HYDROCARBONS AND METHANE
IN MOTOR VEHICLE EXHAUST USING CRYOGENIC PRECONCENTRATION
AND FLAME IONIZATION DETECTION**

1   Introduction

1.1   This procedure describes a direct method for measuring the total non-methane hydrocarbon (NMHC) and methane emissions in samples from motor vehicle exhaust testing. This preconcentrated direct flame ionization method, termed PDFID, is based on a similar method developed for ambient air measurements. The PDFID method has been modified and extended for application to higher level vehicle emissions samples and the additional measurement of methane (from the same sample). This gas chromatographic (GC) method separates NHMC from methane cryogenically and measures methane by both cryogenic and mole sieve separation. This method can be extended to other source hydrocarbon emissions of similar or higher concentration range.

1.2   The method is used as a confirmation tool for the determination of non-methane hydrocarbons calculated from dynamometer (dyno) results and also by summing the individual hydrocarbon species found from hydrocarbon speciation testing of the same sample (SOP 102/103). The run-to-run time is under seven minutes to accommodate the need for routine testing.

1.3   The procedure described herein may involve the use of hazardous materials and practices. This procedure does not address the safety and health factors associated with their use. It is the responsibility of the user of this SOP to establish safe laboratory operating practices.

2   Method Summary

2.1   This procedure describes a method for separating and measuring both the methane and total non-methane hydrocarbons found in vehicle exhaust samples. The method provides two separate, parallel analyses from a single sample injection:

2.1.1 The cryogenic method uses a pre-concentrator (liquid nitrogen cooled) to separate the methane from the non-methane hydrocarbons contained in the vehicle exhaust sample. Both methane and total non-methane hydrocarbon components are measured using a standard flame ionization detector (FID).

2.1.2 The mole sieve separation method measures methane directly, without pre-concentration, by separating it from the NMHC with a molecular sieve (MS) column and measuring it with a second FID.

2.2   For routine motor vehicle exhaust testing, the vehicle is tested according to the Federal Test Procedure (FTP, Ref. 9.1), using a dynamometer (dyno) and constant volume sampler (CVS) to dilute the exhaust for sampling.

2.3   Samples are also received from CVS testing using non-FTP driving cycles, Sealed Housing Evaporative Determinations (SHEDs, Ref. 9.1), gas standard cylinders or canisters, and hydrocarbon-containing samples from other miscellaneous sources.

2.4   The instrument is calibrated with external standards (containing both methane and propane in zero air) which are diluted with ultra-pure air to establish the respective FID responses over the desired concentration range.

2.5   A PC-based data system is used to acquire data and integrate the peak areas to determine concentrations of methane and total non-methane hydrocarbons.

3   Interferences and Limitations

3.1.1   An interference in the methane fraction is caused by any compound in the sample which coelutes with methane and either:

        (1) has a non-zero instrument response or
        (2) alters the FID response to methane (e.g., oxygen)

3.1.2   An interference in the non-methane hydrocarbon fraction is any non-hydrocarbon present in a sample which coelutes with the non-methane hydrocarbon peak and has a non-zero instrument response (e.g., methanol, ethanol).

3.2   Oxygen coelutes with methane during the cryogenic separation and effects the FID response to methane. Vehicle emission samples have reduced oxygen levels compared to normal air, due to the combustion of air in the engine. CVS sample oxygen concentrations less than that of normal air (20.95%) will cause a lowering of the methane FID response using this method. This response lowering is approximately proportional to the lowering of oxygen level in the sample.

3.2.1   Assuming the test vehicle engine combustion process is stoichiometric or near stoichiometric, the CVS dilution will yield an oxygen concentration of about 19%, or 90% of normal. Methane measurements on bag 1, bag 2, and bag 3 samples are affected by any oxygen deficit present in the diluted combustion samples. A correction to the PDFID methane measurement must be made to account for the oxygen deficit. Methane measurements on the background dilution air sample need no oxygen deficit correction.

3.2.2   Zero methane concentration measurements are affected by the oxygen gas contained in the sample. Use of linear calibration techniques with a nonzero

intercept near the zero concentration limit for methane are used to correct for this effect.

3.2.3   Ultra-pure air with a normal oxygen concentration of 20.95% is the standard dilution gas for methane calibration mixtures and provides the reference oxygen concentration needed for determining the correct methane FID response. Highly purified zero air should be used as the dilution gas for all methane (and propane) standards. Reconstituted zero air should not be used as the diluent, since the normal error in oxygen concentration ($\pm$ 1%) can affect the methane calibration.

3.2.4   The FID response for the mole sieve methane measurement is not affected by the change in oxygen concentration; therefore, no oxygen correction is required.

3.2.5   The cryogenic NMHC measurement also unaffected by changes in the sample oxygen concentration.

3.3   The FID detector calibration response may have a slight dependence upon the cryotrap temperature.

3.4   To maximize sample integrity, sample bags should not leak or be exposed to bright light or excessive heat. Sample bags should be shielded from direct sunlight to avoid accelerated hydrocarbon composition changes in the sample as a result of chemical reactions with compounds in the exhaust mixture. The compound 1,3- butadiene, most of which is contained in the transient phase of the cold- start test sample (FTP bag 1), is unstable. Therefore, all cold-start CVS bag 1 samples should be analyzed within 8 hours, although analysis within 2 hours is recommended. Samples from the stabilized phase of the cold start test (FTP bag 2), the stabilized phase of the hot- start test (FTP bag 3), and the background dilution air (FTP background) will contain lesser amounts of this compound. The CVS bag 2 sample, the CVS bag 3 sample, and the CVS background sample should be analyzed within 24 hours, although analysis within 6 hours is recommended. Sample storage for extended time periods, beyond 24 hours, is not recommended because of the likelihood of sample degradation or the occasional loss of sample due to sample bag leaks.

3.5   The limit of detection (LOD) is determined using propane and methane as the analytes and ultra-pure air as the diluent. LOD measurements on actual exhaust hydrocarbon samples will yield higher LODs for NMHC than for methane, due to the wider integration peak caused by the broader range of the hydrocarbon boiling point distribution of the exhaust hydrocarbons.

3.6   The typical NMHC concentration range observed in background dilution air is 0.8 to 2.0 ppmC. The typical methane concentration range observed in background

dilution air is 1.9 to 2.5 ppmC. These levels represent the lower concentrations that must be adequately measured for good quantitation.

4   Instrumentation and Apparatus

4.1   Samples are contained in Tedlar bags or stainless steel canisters, equipped with quick-connectors for direct connection to the instrument.

4.2   A preconcentrator with a cryogenically controlled trap (Nutech Model 3500 or equivalent) is used to separate the methane from the non-methane hydrocarbons. The preconcentrator temperature is in the range of -177ºC to 182ºC, with the exact temperature determined empirically as explained in Section 6.1. It must be capable of cooling to its operating temperature within 2 minutes and maintain a stable temperature within $\pm$ 1ºC for the methane analysis period. The preconcentrator trap must be capable of being heated to 200ºC within 2 minutes to complete the run within 7 minutes.

4.2.1   The molecular sieve column is maintained at 200ºC during the whole operation of the apparatus.

4.3   A gas chromatograph (Varian Model 3400 or equivalent) provides a temperature controlled transfer oven and flame ionization detector (FID) with associated electrometer for signal measurement.

4.3   The instrumentation (either preconcentrator or gas chromatograph) must contain associated valving and controls to effect a complete analysis. A PC-controlled data acquisition system, Varian Star version 5.5 or equivalent, is required to determine sample concentrations based on peak areas. Linear curve fitting with both zero (for non-methane hydrocarbons) and nonzero (for methane) intercept capabilities are required.

4.4   Refer to Figure 1 for a schematic/description of the apparatus.

4.5   Refer to Figure 2 for a typical chromatogram from the data system.

5   Reagents and Materials

5.1   Helium carrier gas shall have a minimum purity of 99.9999 percent. It is desirable to further filter the helium with a molecular sieve trap and/or a liquid nitrogen condensation trap to ensure gas purity before entering the system.

5.2   Hydrogen for the operation of the FID shall have a minimum purity of 99.995 percent.

5.3   Air for the operation of the FID shall be zero grade, containing less than 1 ppm hydrocarbon impurity (measured as methane).

5.4   Liquid nitrogen (LN$_2$, -196ºC) is the cryogen used to control the temperature of the preconcentrator which separates the methane from the remaining non-methane hydrocarbons.

5.5   Ultra-pure air used as a dilution gas shall have a minimum purity of less than 0.1 ppm hydrocarbon (measured as methane). The nominal oxygen concentration of the natural air is 20.95%.

5.6   Standards

5.6.1   National Institute of Standards and Technology (NIST) standard reference materials (SRMs) and/or NIST-traceable standards shall constitute the calibration standards.

5.6.2   For quality control standards, it is recommended to use NIST and/or NIST-traceable standards; however, gravimetric standards may also be used.

5.6.3   All gas standards shall be prepared in ultra-pure air containing oxygen at a nominal concentration of 20.95%. It is recommended that highly purified natural air, rather than reconstituted air, be used as the diluent gas to maintain the proper proportion of oxygen at 20.95%.

5.6.4   Table 1 shows the NIST SRMs that are currently available which have organic hydrocarbon concentrations in an appropriate range for evaluating the performance of a direct non-methane hydrocarbon analyzer.

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Table 1. Currently Available NIST Standard Reference Materials

SRM Identification	Composition	Concentration
SRM 1665b	Propane in Air	2.89 ppmC
SRM 2760	Methane in Air	50 ppm
SRM 2764	Propane in Air	0.75 ppmC
SRM 2764	Propane in Air	0.729 ppmC
SRM 2764	Propane in Air	0.735 ppmC
SRM 1800	C2-C10 hydrocarbons	0.4 ppmC

5.6.6   The suggested compositions of calibration gases are shown in Table 2.

Table 2. Suggested Calibration Gases

Level	Gas 1	Nominal Concentration	Gas 2	Nominal Concentration	Testing Frequency
L1	methane	0.0 ppmC	propane	0.0 ppmC	daily
L2	methane	100 ppmC	propane	300 ppmC	daily

5.6.7   The suggested compositions of quality control gases are shown in Table 3.

Table 3. Suggested Control Standard Gases

GAS	Nominal Concentration	Testing Frequency
Methane/Propane (QC1, low level)	10/10 ppmC	daily
Methane/Propane (QC2, moderate level)	30/30 ppmC	daily
Wide-range Standard (C1-C13)	25 ppmC	as needed
Ethane (low level)	2-40 ppmC	as needed
NIST SRM 1660a-Methane/Propane	4/3 ppmC	as needed

6   Analytical Procedure

6.1   The sample is transferred directly from the Tedlar bag into a heated (150^EC), 10 cubic centimeters (cc) fixed sample loop, using a vacuum pump. Next, the sample is injected into a temperature-controlled preconcentrator, cooled with liquid nitrogen, to trap all non-methane hydrocarbons in the sample. The methane, along with the coseparating oxygen gas, passes through the preconcentrator and is measured with the FID. The preconcentrator is then heated (nominally to 200^0C) and the trapped non-methane hydrocarbons are measured as a group, with the FID detector, as they boil off the trap. The preconcentrator temperature is set at a nominal -180°C to trap all non-methane hydrocarbons without trapping methane. The actual temperature is determined empirically as the minimum temperature that traps 100% of an ethane sample.

6.2   A source of error for this technique is the temperature control of the cryogenic trap during the measurement of the methane signal and collection of the non-methane hydrocarbons. A high trap temperature will prevent the condensation of light hydrocarbons, such as ethane and ethene, with the non-methane fraction and these light hydrocarbons would then be measured with methane signal. A low trap temperature may result in some methane being trapped and subsequently measured with the non-methane hydrocarbons as a composite signal. These effects are minimized by precise temperature control.

6.3   Typical instrument operating parameters are as follows:

Preconcentrator	Nutech Model 3500
Injector oven temperature	150℃
Valve oven temperature	150℃
Transfer line temperature	150℃
Gas Chromatograph	Varian Model 3400
Oven temperature	150℃
FID temperature	250℃ or higher

6.4   Gas flow rates to the flame ionization detector (FID) shall be within the following tolerances:

    Helium carrier gas   30 + 1.0 cc/min
    FID hydrogen   30 + 1.0 cc/min
    FID air   300 + 5.0 cc/min

    Tthe FID burner gas flow rates are adjusted, if necessary. A log of these measurements shall be maintained.

6.5   The cryotrap is pre-cooled and the daily calibration testing performed.

6.5.1   The zero level (ultra-pure air) is measured.

6.5.2   The level methane and propane calibration standard(s) is measured.

6.5.3   The high level methane and propane calibration standard(s) is measured.

6.5.4   The detector response factor is adjusted as noted below.

6.6   Control standards are measured.

6.6.1   The low level methane and propane standard(s) is measured.

6.6.2   The high level methane and propane standard(s) is measured.

6.6.3   The wide-range hydrocarbon mixture control standard is measured.
6.6.4   The concentrations are verified as correct.

6.7   A Tedlar bag containing the sample is connected to the sample port of the PDFID.

6.8   Test aliquots are collected in two heated sample loops (10 cc each) using the vacuum pump.

6.8.1   One sample aliquot is injected into the pre-cooled preconcentrator. Methane is measured first at the FID detector. After the methane has passed through the preconcentrator, the helium flow is reversed, the trap is rapidly heated to 200°C, and the non-methane hydrocarbons from the same sample aliquot are measured with the FID detector.

6.8.2   The second aliquot passes through a Poropack Colum prior to entering the molecular sieve column.

6.8.3   Both columns are maintained at 200°C.

6.9   The sample identification, peak areas, total methane (using 20.95% sample oxygen content as reference) and total non-methane hydrocarbon concentrations are provided by PC-based data system.

6.10   The total analysis time is under five minutes. The run-to-run time is seven to nine minutes.

6.11   Instrumentation from other manufacturers, similar configurations, or design improvements may require different operating parameters. Any changes to these operating conditions must be documented.

7   Calculations

7.1   The concentration of methane and non-methane hydrocarbons in air, in units of ppmC, is calculated by the PC-based data system using an external standard method.

        Measured Concentration = (Peak Area) x (Response Factor)

        This basic equation is modified as indicated below.

7.2   Calibration tests involving measurements of standard gases are used to determine calibration factors by the following equation.

        Response Factor (RF)   =   Concentration of Standard (ppmC)
                                              Area Counts generated by Standard

7.3   Propane calibration gases, methane calibration gases and ultrapure air are used to determine the standard calibration curve, described under 7.4, for the FID response. An average of the peak areas from at least seven repeat analyses of the standard gases are used to specify the initial calibration curve for each gas.

7.4   Standard calibration curve

7.4.1   The standard calibration curve for non-methane hydrocarbons is linear with a zero intercept. The calibration curve is derived from two calibration gases and ultrapure air. The standard calibration curve for non-methane hydrocarbons is not dependent on the sample oxygen concentration. Peak area counts and cylinder hydrocarbon concentrations are used to define this line.

7.4.2   The standard calibration curve for methane, based on two calibration gases and ultrapure air, is linear with nonzero intercept. The methane response (both zero offset and response factor) is dependent on the oxygen concentration in the sample. A reference oxygen concentration of 20.95% is used to define the standard calibration curve for methane. Peak area counts and cylinder hydrocarbon concentrations are used to define this line.

7.5   Daily Calibration Update

7.5.1   Two calibration tests using NIST or NIST-traceable standards are performed each day for propane and methane. These tests are used to verify the calibration accuracy and correct for small changes in the daily operating conditions. High and low level standards, containing both propane and methane gases, are used in these tests. The uncorrected concentrations for methane and propane of the standards are calculated as follows:

Measurement (Std 1) = (Peak Area 1) x (Response Factor)

Measurement (Std 2) = (Peak Area 2) x (Response Factor)

7.5.2   A Calibration Correction Factor (CCF) or ratio based on the propane calibration gases is determined from the calibration runs (7.5.1) and the standard equation for concentration (7.1). The Calibration Correction Factor is calculated from the following equation.

CCF = ½ * [(Conc Std 1)/(Meas Std 1) + (Conc Std 2)/Meas Std 2)]

The individual response factors [(conc. std.)/(meas. std.)] from the measurements for the two gases must be within 2% of each other.

7.5.3   The measurement accuracy of the methane calibration gases is verified using the CCF and the methane calibration curve. The methane accuracy should be within +2% for these gases.

7.5.4   The Calibration Correction Factor (CCF) is entered into the data system software as a multiplier. This factor takes into account small daily fluctuations in the overall NMHC calibration. The new software multiplier is calculated from the previous software multiplier used to determine the CCF by the following equation.

(New Multiplier) = (Previous Multiplier) x (CCF)

The value of the multiplier is nominally 1.0.

7.6   The equation in section (7.1) becomes:

Measured Concentration = (Peak Area) x (Response Factor) x (CCF)

modified for calculating sample non-methane hydrocarbon and observed methane concentrations.

7.7   Methane correction for sample oxygen

7.7.1   The measured concentration of methane is referenced to the standard oxygen concentration of 20.95% used for the calibration standards.

7.7.2   For CVS samples, the sample oxygen concentration will fall in the range 18 to 21%, resulting in differing methane FID responses. The oxygen concentration or an estimate of this value may be used to correct the measured methane concentration.

7.7.3   The methane reading obtained directly from the analysis is the observed reading referenced to a sample oxygen level of 20.95%. This value is directly reported by the analyst, and can be corrected by one of the methods below (7.7.4 through 7.7.6).

7.7.4   The equation for direct determination of the actual methane concentration requires a simultaneous experimental measurement of the sample oxygen level (in %) to obtain the proper FID response constants.

7.7.5   A detailed equation for calculating the methane concentration based on CVS dilution terms is the following.

Detailed Methane = (Measured Methane) x [1/(1-1/DF)] x (Factor 1) x (Factor 2)

where:

DF   = the dilution factor determined for the CVS sample;
Factor 1 = the effect of excess oxygen contained in the engine-out or raw
             exhaust, normally 1.00; and
Factor 2 = represents the effect of the vehicle emissions control system on the
             excess oxygen level, normally 1.00.

7.7.6 Any changes to these equations shall be documented.

8   Quality Control

8.1   A blank analysis (consisting of ultrapure air) is performed daily to verify that contamination and/or sample carryover are not present. The total non-methane hydrocarbon reading must be below the limit of detection. This test is also used to verify the zero level methane area counts found from burning the coseparating oxygen and methane in the FID.

8.2   Daily Calibration

8.2.1 Two tests with known standard gases are performed daily.

8.2.2 Determination of the Calibration Factor Correction (CCF), based on two runs with standard gases, is a part of the day's analysis.

8.2.3 The two individual calibration factors for propane and for methane should be within 2%.

8.2.4 The area counts for the reference compounds should be plotted on a control chart (Section 8.3) to verify that these are within three standard deviations of the average values.

8.3   Daily Quality Control

8.3.1 Control standards contain specified amounts of the hydrocarbons of interest and are analyzed daily to asses both the accuracy and precision of the instrument. A series of quality control standards are analyzed daily and the results plotted in control chart (Section 8.4).

8.4   Quality Control Charts

8.4.2   Instrument responses to the control standards are monitored daily to determine the precision based on at least 20 daily control sample results.

8.4.2   Instrument responses are charted to verify the stability of both the instrument and the standard.

8.4.3   Quality control charts are maintained for both calibration standards and control standards and files are updated weekly.

8.4.4   A quality control chart is maintained for each compound in the control standard (calibration standard). The control charts, used on a daily basis, establish that the method is "in-control". The following describes how a typical control chart is constructed:
   (1)   Obtain at least 20 daily control standard results;
   (2)   Calculate the control standard mean concentration (area counts or response factors for calibration standard) and standard deviation for the monitored compound; and
   (3)   Create a control chart for the monitored compound by placing the dates on the x-axis and the concentrations (area counts, response factors) on the y-axis. Establish an upper and lower warning limit at two standard deviations (2s) or 5%, whichever is greater, above and below the average concentration. Establish an upper and lower control limit at three standard deviations (3s) or 5%, whichever is greater, above and below the average concentration.

8.4.5   Measurements of all compounds contained in the control (or calibration) standard must be within the control limits ("in-control") before sample analysis may proceed. Values which exceed three standard deviations above or below the mean are considered to be "out of control". If all measurements on two consecutive days exceed two standard deviations above or below the mean, they second day's analysis is also considered to be out of control. If one or more compounds are out of control, it may be necessary to inspect and repair the GC, and rerun the calibration and/or control standards until the control standard criteria are met; when the QC criteria are met, sample analysis can continue. Figure 3 demonstrates a typical QC chart.

8.5   Duplicate tests and repeatability

8.5.1   At least one duplicate analysis is performed daily. The results from the duplicate analysis must meet the criteria for allowable repeatability as expressed by the relative percent difference (RPD %) as defined below. If the criteria are not met, the sample must be reanalyzed; if the criteria are still not met, all results for the day from this instrument must be aborted unless the reason for the deviation can be specified. Normally, a bag 1 vehicle test sample is selected for the duplicate

test; however, a bag 2 sample, a bag 3 sample or a background air sample may also be used.

8.5.2   Equation for relative percent difference (RPD):

RPD (%) = (Difference between original and duplicate measurements) x 100
               (Average of original and duplicate measurements)

8.5.3   Criteria for repeatability:

Average Measurement of Duplicate Runs	Allowable RPD (%)
0.5 to 1.0 ppmC	20
1.0 to 3.0 ppmC	10
greater than 3.0 ppmC	5

These repeatability criteria are applicable when the analysis times of the replicate samples are less that 8 hours apart.

8.6   Multipoint Calibration

8.6.1   A multipoint linearity check is performed for propane and methane at least every six months. The multipoint consists of a minimum of seven concentrations, each above the LOD. These concentrations are evenly (approximately) distributed over the range of expected sample concentration. Each concentration is measured at least three times.

8.6.2   A linear regression analysis is performed on the data using concentration and average area counts to determine the regression correlation coefficient (r). The r-value must be greater than 0.995 to be considered sufficiently linear.

8.6.3   The linearity is verified for the following compounds/mixtures on a yearly basis.

Control Compounds	Nominal Linear Range
methane	0 - 500 ppmC
propane	0 - 300 ppmC

8.7   Limit of Detection

8.7.1   The LOD is the lowest concentration that can be determined to be statistically different from a blank.

8.7.2   LODs for methane and propane must be determined for new instruments, after making modifications which can affect linearity and/or sensitivity and at least semi-annually. To make the calculations, it is necessary to perform a multipoint

calibration consisting of at least seven "low" concentration levels, each above the expected LOD.

The LOD is calculated using the following equation:

$$\text{LOD (ppbC)} = \frac{|b| + (t \times s)}{m}$$

where

|b| = the absolute value of the y-intercept, area counts

m = the slope of the linear regression, area counts/ppbC

s = the standard deviation of at least ten measurements of the lowest concentration standard, area counts

t = the t-factor for 99 percent confidence for a one-sided normal (Gaussian) distribution, dimentionless

The number of degrees of freedom is equal to the number of runs (n) of the lowest concentration standard, minus one. An abbreviated t-table is (Ref.9.1):

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

8.7.1   The concentration of the lowest standard must be greater than the calculated laboratory LOD, and not more than five times the estimated LOD. The maximum allowable LOD is .10 ppmC measured as propane. The calculated laboratory LOD must be equal to or lower than the maximum allowable LOD.

8.7.2   All peaks identified as target compounds that are equal to or exceed the maximum allowable LOD must be reported.

8.7.3   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.

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

8.7.5   The relative responses of the PDFID instrument to different hydrocarbon gases have been determined (based on propane = 1.00) and are given in Table 4.

Table 4. PDFID Response Relative to Propane

Test Gas	Cylinder No.	Concentration	Relative Response
Benzene	SRM 1806	9.78*6=58.68 ppmC	0.96
Ethane	A6820	2.16 ppmC	1.05
Ethane	SA5901	40 ppmC	0.99
Methane	SA4304	25.05 ppmC	1.00
Methane	28246	9.16 ppmC	1.01
Methane	CC26424	17.0 ppmC	1.02
Propane	ALM008362	2.99 ppmC	0.99
Propane	54316	297 ppmC	0.98
Propane	SA5906	295.60 ppmC	1.00
Propane	SA3224	89.20 ppmC	1.00
1,3-Butadiene	CC105065	2.00 ppmC, unanalyzed	1.00
Wide-range HC (C2-C10 Mixture)	CC6390	1.09 ppmC	0.97
Methanol	AAL7203	289.6 ppmC	0.69
Methanol	AAL14449	476.3 ppmC	0.70
MTBE	ALM027114	4.93 ppmC	0.84

9   References

9.1   COMPENDIUM METHOD TO-12, "Method for the Determination of Non-methane Organic Compounds (NMOC) in Ambient Air Using Cryogenic Preconcentration and Direct Flame Ionization Detection (PDFID)," Quality Assurance Division, Environmental Monitoring Systems Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711, May, 1988.

9.2   Zafonte, L., Yeung, T.S., and Daymon, D., "The Measurement of Non-methane Organic Compounds in Automobile Exhaust Using the PDFID Technique," Proceedings of the 1991 Joint EPA/AWMA International Symposium on Measurements of Toxic and Related Air Pollutants, Document VIP-21, Air and Waste Management Association, 1991.

9.3   "Injury and Illness Prevention Plan," California Environmental Protection Agency, Air Resources Board, Monitoring and Laboratory Division, Southern Laboratory Branch; document dated April, 1993, or latest revision.

9.4   "Quality Control Manual," California Environmental Protection Agency, Air Resources Board, Monitoring and Laboratory Division, Southern Laboratory Branch; document dated September, 1996 or latest revision.

A Mole Sieve (MS) Foreflush
B Restrictor
C Flameout Restrictor
D MS Back Flush
E MS Back Flush Restrictor
F Vent
G Molecular Sieve Column
H Methane Sampling Loop
I Cap
J Auto Sampler
K Vent
L Methane Sampling Loop
M Purge to Trap
N Flameout Restrictor
O Flow Restrictor
P Trap to FID
Q Cryotrap
R Flow Indicator
S Vacuum Pump

Figure 1. Flow Diagram

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Title        : Direct NonMethane Hydrocarbons
Run File     : C:\Star5.0\qa22020.run
Method File  : c:\star5.0\pd2.mth
Sample ID    : QA2

Injection Date: 04/01/1999 10:38      Calculation Date: 04/01/1999 10:42

Operator    : PBD                      Detector Type: ADCB (10 Volts)
Workstation: AXTAF31ABA                Bus Address  : 20
Instrument : PDFID                     Sample Rate  : 20.00 Hz
Channel    : A = DNMHC FID             Run Time     : 4.002 min

** Star Chromatography Workstation Version 5.2 ** 00299-1f08-d91-23e9 **

Chart Speed =    4.95 cm/min   Attenuation = 50            Zero Offset = 10%
Start Time  =    0.000   min      End Time  = 4.000   min   Min / Tick  = 0.50
```
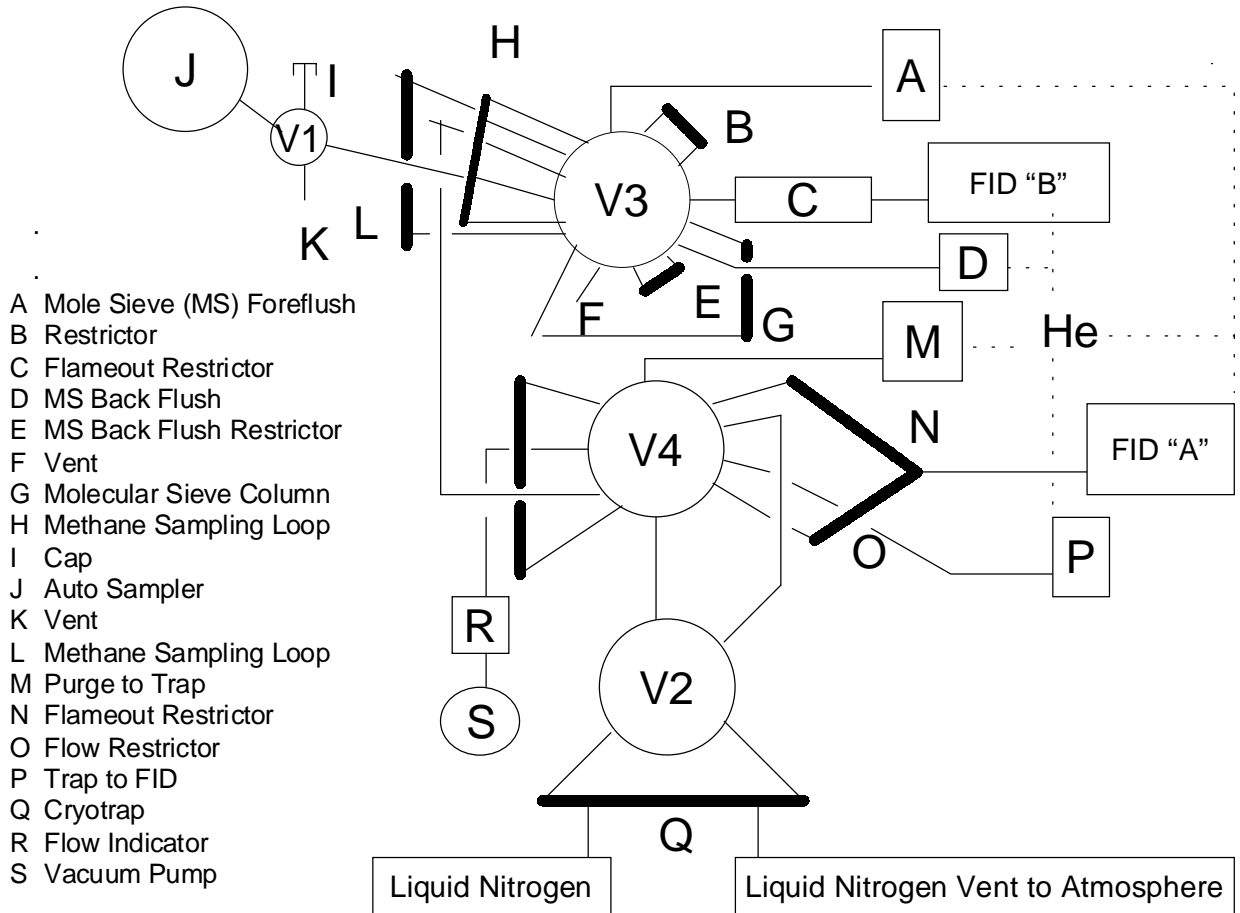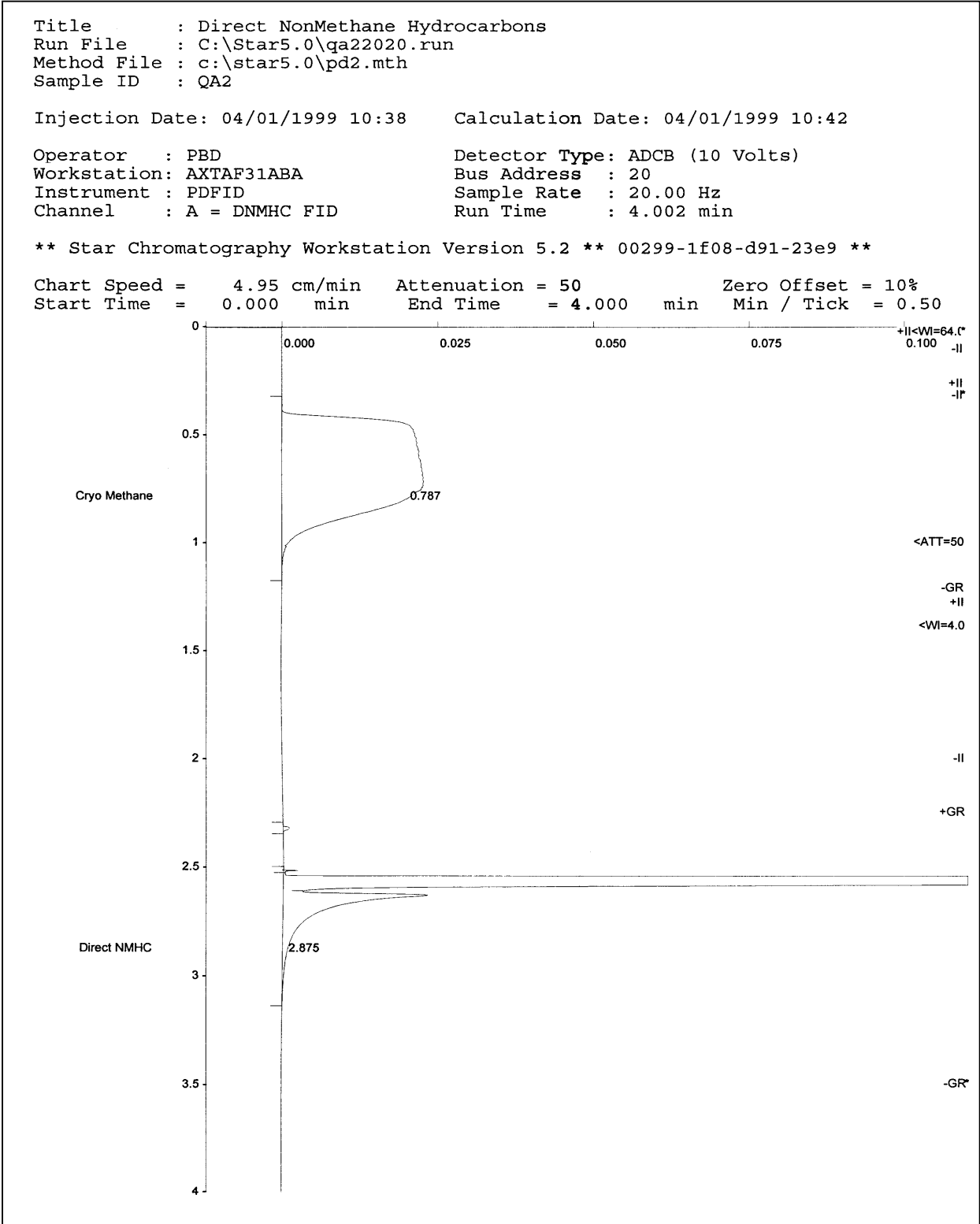

Figure 2. Typical Chromatogram

PDFID Quality Control Chart for Propane using 4.677 ppmC Propane

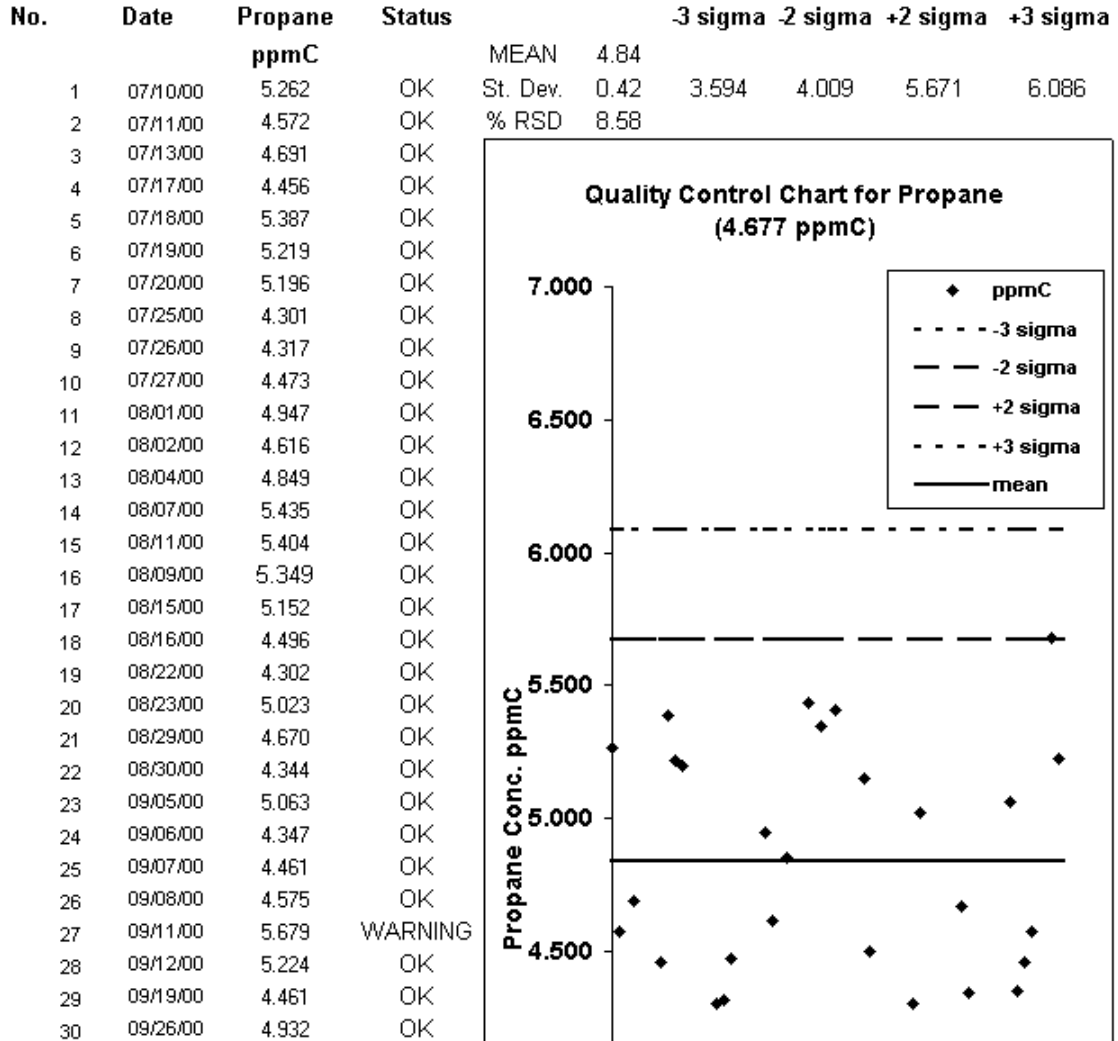| No.	Date	Propane ppmC	Status			-3 sigma	-2 sigma	+2 sigma	+3 sigma
				MEAN	4.84				
1	07/10/00	5.262	OK	St. Dev.	0.42	3.594	4.009	5.671	6.086
2	07/11/00	4.572	OK	% RSD	8.58				
3	07/13/00	4.691	OK						
4	07/17/00	4.456	OK						
5	07/18/00	5.387	OK						
6	07/19/00	5.219	OK						
7	07/20/00	5.196	OK						
8	07/25/00	4.301	OK						
9	07/26/00	4.317	OK						
10	07/27/00	4.473	OK						
11	08/01/00	4.947	OK						
12	08/02/00	4.616	OK						
13	08/04/00	4.849	OK						
14	08/07/00	5.435	OK						
15	08/11/00	5.404	OK						
16	08/09/00	5.349	OK						
17	08/15/00	5.152	OK						
18	08/16/00	4.496	OK						
19	08/22/00	4.302	OK						
20	08/23/00	5.023	OK						
21	08/29/00	4.670	OK						
22	08/30/00	4.344	OK						
23	09/05/00	5.063	OK						
24	09/06/00	4.347	OK						
25	09/07/00	4.461	OK						
26	09/08/00	4.575	OK						
27	09/11/00	5.679	WARNING						
28	09/12/00	5.224	OK						
29	09/19/00	4.461	OK						
30	09/26/00	4.932	OK						

Figure 3. Typical Control Chart