



Standard Test Method for Determination of Total Hydrocarbon Contribution by Gas Distribution System Components¹

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INTRODUCTION

Semiconductor clean rooms are serviced by high-purity gas distribution systems. This test method presents a procedure that may be applied for the evaluation of one or more components considered for use in such systems.

1. Scope

1.1 This test method covers the testing of components for total hydrocarbons (THC) contribution to a gas distribution system at ambient temperature. In addition, this test method allows testing of the component at elevated ambient temperatures as high as 70°C.

1.2 This test method applies to in-line components containing electronics grade materials in the gaseous form, such as those used in semiconductor gas distribution systems.

1.3 Limitations:

1.3.1 This test method is limited by the sensitivity of current instrumentation, as well as by the response time of the instrumentation. This test method is not intended to be used for components larger than 12.7-mm (½-in.) outside diameter nominal size. This test method could be applied to larger components; however, the stated volumetric flow rate may not provide adequate mixing to ensure a representative sample. Higher flow rates may improve the mixing but excessively dilute the sample.

1.3.2 Different instrumental methods (such as flame ionization detector (FID), mass spectrometer (MS)) will yield total hydrocarbon (THC) levels that are not comparable due to different sensitivities to different molecular species. Hydrocarbon contaminants of high-purity gas distribution systems can be subdivided into two general categories: (1) noncondensable hydrocarbons ($<C_4$), that are present due to difficulty of removal and relative atmospheric abundance, and (2) condensable hydrocarbons, that are often left behind on component surfaces as residues. Condensable hydrocarbons include pump oils, degreasing agents, and polishing compound vehicles.

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1.3.3 Because of the tremendous disparity of hydrocarbon species, it is suggested that direct comparisons be made only among data gathered using the same detection method.

1.3.4 This test method is intended for use by operators who understand the use of the apparatus at a level equivalent to six months of experience.

1.4 The values stated in SI units are to be regarded as the standard. The inch-pound units given in parentheses are for information only.

1.5 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use. Specific hazard statements are given in Section 5.*

2. Terminology

2.1 Definitions:

2.1.1 *baseline*—the instrument response under steady state conditions.

2.1.2 *glove bag*—an enclosure that contains a controlled atmosphere. A glove box could also be used for this test method.

2.1.3 *heat trace*—heating of component, spool piece, or test stand by a uniform and complete wrapping of the item with resistant heat tape.

2.1.4 *methane (CH_4) equivalent*—that concentration of CH_4 that causes the same instrument response as the sample.

2.1.4.1 *Discussion*—The calibration gas contains a known concentration of methane (CH_4). Instrument response to zero gas and span gas defines the calibration curve for the analyzer. Instrument response to the sample is the summation of the response for each hydrocarbon reaching the detector. The concentration reported is the methane concentration, from the calibration curve that corresponds to the instrument response to

the sample. The sample's concentration is equivalent to the methane concentration that would produce the same instrument response.

2.1.5 *minimum detection limit (MDL) of the instrument*—the lowest instrument response above zero detectable that is readable by the instrument and at least two times the amplitude of the noise.

2.1.6 *response time*—the time required for the system to reach steady state after a measurable change in concentration.

2.1.7 *spool piece*—a null component, consisting of a straight piece of electropolished tubing and appropriate fittings, used in place of the test component to establish the baseline.

2.1.8 *standard conditions*—101.3 kPa, 0.0°C (14.73 psia, 32°F).

2.1.9 *test component*—any device being tested, such as a valve, regulator, or filter.

2.1.10 *test stand*—the physical test system used to measure impurity levels.

2.1.11 *zero gas*—a gas that has a THC concentration below the MDL of the analytical instrument. This purified gas is used for both instrument calibration and component testing.

2.2 Abbreviations:

2.2.1 *FID*—flame ionization detector.

2.2.2 *MFC*—mass flow controller.

2.2.3 *MS*—mass spectrometer.

2.2.4 *ppbv*—parts per billion by volume assuming ideal gas behavior, equivalent to nmole/mole (such as nL/L).

2.2.4.1 *Discussion*—The same as molar parts per billion (ppb).

2.2.5 *ppbw*—parts per billion by weight (such as ng/g).

2.2.6 *ppmv*—parts per million by volume assuming ideal gas behavior, equivalent to $\mu\text{mole/mole}$ (such as $\mu\text{L/L}$).

2.2.6.1 *Discussion*—The same as molar parts per million (ppm).

2.2.7 *ppmw*—parts per million by weight (such as $\mu\text{g/g}$).

2.2.8 *slpm*—standard liters per minute. The gas volumetric flow rate measured in liters per minute at 0.0°C (32°F) and 101.3 kPa (1 atm).

2.2.9 *THC*—total hydrocarbon.

2.3 Symbols:

2.3.1 P_1 —the inlet pressure measured upstream of the purifier and filter in the test apparatus.

2.3.2 P_2 —the outlet measured downstream of the analyzer in the test apparatus.

2.3.3 Q_1 = the bypass sample flow not going through the analytical system.

2.3.4 Q_2 = the total sample flow through the analytical system.

2.3.5 Q_s = the flow through the spool piece or component.

2.3.6 T_a = the temperature of the air discharged by the analyzer's cooling exhaust.

2.3.7 T_s = the temperature of the spool piece or component.

2.3.7.1 *Discussion*—The thermocouple must be located in contact with the outside wall of the component or spool piece.

2.3.8 $V-1$, $V-2$ = inlet and outlet valves of bypass loop, respectively.

2.3.9 $V-3$, $V-4$ = inlet and outlet valves of test loop, respectively.

3. Significance and Use

3.1 The purpose of this test method is to define a procedure for testing components being considered for installation into a high-purity gas distribution system. Application of this test method is expected to yield comparable data among components tested for purposes of qualification for this installation.

4. Apparatus

4.1 Materials:

4.1.1 *Test Gas*, purified nitrogen or argon with a maximum THC concentration not exceeding the manufacturer's stated minimum detection limit of the instrument (MDL). Particulate filtration of the test gas to 0.02 μm or finer is required, using a typical electronics grade filter. The filter must be compatible with the 94°C (200°F) bake-out.

4.1.2 *Spool Piece*, that can be installed in place of the test component is required. This piece is to be a straight section of 316L electropolished stainless steel tubing with no restrictions. The length of the spool piece shall be 200 mm. The spool piece shall have the same end connections as the test component.

4.1.2.1 *Components with Stub Ends*—Use compression fittings with nylon or teflon ferrules to connect the spool piece and test component to the test loop. Keep the purged glove bag around each component for the duration of the test. In the case of long pieces of electropolished tubing, use two glove bags, one at each end.

4.1.3 *Tubing*, used downstream of the purifier shall be 316L electropolished stainless steel seamless tubing. The diameter of the sample line to the analyzer shall not be larger than 6.4 mm ($\frac{1}{4}$ in.). The length of the sample line from the tee (installed upstream of the pressure gage P_2) to the analyzer shall not be more than 600 mm to minimize the effect (adsorption/desorption) of the sample line on the result. The sample line shall have no more than two mechanical joints.

4.1.4 *Valves*, diaphragm or bellows type and must be capable of unimpaired operation at 94°C (200°F). The use of all-welded, all-metal valves is preferred.

4.2 Instrumentation:

4.2.1 *THC Analyzer*—The THC analyzer is to be placed downstream of the test component. Accurate baseline readings must be obtained prior to and subsequent to each of the tests. The baseline must return to levels <100 ppbv, before and after the tests. Deviations greater than this require that all results be rejected and a new test component be tested. The analyzer must be capable of accurately recording changes in THC concentrations on a real-time basis, within the constraints of the data acquisition system.

4.2.2 *THC analyzer calibration*—Two-point calibration, zero and span, is to be performed regularly. Zero gas is defined as below the manufacturer's stated MDL of the instrument, supplied by purified gas, with the purifier in close proximity to the analyzer. Span gas is analyzed at the lowest possible detection range, which may not be at the lowest detection range

of the instrument. Span gas is 5–10 ppmv methane, $\pm 20\%$ for FID. Calibration is based on traceable methane concentration in the base gas (nitrogen or argon).

4.2.3 *Flame Ionization Detector (FID)*—The FID detects hydrocarbon species by ionizing the organic material in a flame. Ions produced in the hydrogen flame yield a measurable current, directly related to the quantity of hydrocarbons introduced to the flame. Burner gases, hydrogen, and air are not to contain measurable amounts of THC. Purifiers are available for this purpose (especially to remove methane). Burner gases must be maintained at a temperature between 18 and 26°C (64 and 78°F).

4.2.3.1 The THC data are referred to as ppmv quantity of CH₄ equivalents, corresponding to the sum of the number of equivalent carbons. Simple, low molecular weight hydrocarbons are readily detected and quantified as total THC. Higher molecular weight hydrocarbons and more substituted hydrocarbons may not be detected well. The FID is, therefore, a specific group detector that yields quantification of total hydrocarbons for a specific detectable group.

4.3 *Pressure and Flow Control*—Upstream pressure is to be controlled with a regulator upstream of the test component. Flow is to be controlled at a point downstream of the sampling port and monitored at that point. A mass flow controller is preferred for maintaining the flow as described in 8.3. However, a variable area flowmeter plus a back pressure regulator may be used instead. Sampling is to be performed via a tee in the line, with a run of straight tubing before the mass flow controller. All lines must conform to 4.1.3. Inlet pressure is monitored by P_1 . Test flow is the sum of Q_1 and Q_2 . Q_1 is directly controlled, and Q_2 is the total flow through the analyzer (refer to Fig. 1).

4.4 *Bypass Loop*—The design of the bypass loop is not restricted to any one design. It could be, for example, a 3.2-mm (1/8-in.) 316L stainless steel coil or a flexible tube section. This allows the flexibility necessary to install test components of different lengths.

5. Hazards

5.1 Precautions:

5.1.1 It is required that the user have a working knowledge of the respective instrumentation and that the user practice proper handling of test components for trace organic analysis. Good laboratory practices must also be understood.

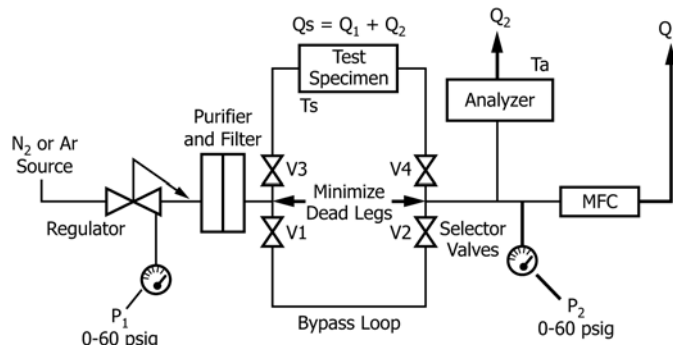


FIG. 1 Test Schematic

5.1.2 It is required that the user be familiar with proper component installation and that the test components be installed on the test stand in accordance with manufacturer's instructions.

5.1.3 Do not exceed ratings (such as pressure, temperature, and flow) of the component.

5.1.4 Gloves are to be worn for all steps.

5.1.5 Limit exposure of the instrument and test component to atmospheric and hydrocarbon contamination before and during the test.

5.1.6 Precautions must be taken to insure that the temperature measured by the thermocouple is as close as possible to that of the spool piece or the test component. Use appropriate insulation and conductive shield to achieve as uniform a temperature as possible.

5.1.7 Ensure that adequate mixing of the test gas is attained.

6. Preparation of Apparatus

6.1 A schematic drawing of a recommended test apparatus located inside a clean laboratory is shown in Fig. 1. Deviations from this design are acceptable as long as baseline levels consistent with 4.2.1 can be maintained. Nitrogen or argon gas is purified to remove water and hydrocarbons. The base gas is then filtered by an electronics grade, high purity, point of use gas filter (pore size rating $\leq 0.02\ \mu\text{m}$) before it is delivered to the test component.

6.2 A bypass loop may be used to divert gas flow through the test stand and the analyzer whenever the spool piece or a test component is installed or removed from the test stand. This prevents the ambient air from contaminating the test apparatus and the hydrocarbon analyzer; thus, the analyzer baseline remains the same. A glove bag is used to enclose test component lines of the test apparatus during the installation and removal of the spool piece and the test piece.

6.3 A total hydrocarbon analyzer capable of detecting hydrocarbon concentration levels down to <50 ppb is connected to the test stand to sample the gas flowing through the test piece. The THC analyzer uses hydrogen fuel for the generation of the flame required for the FID in the instrument. The purified and filtered base gas from the test stand containing <10 ppb THC is used as the zero gas source for the analyzer. Since the analyzer is sensitive to the sample flow rate, the metering valves within the analyzer should be adjusted to yield the flow rates required by the specification for an inlet pressure of 30 psig. The gas flow rate Q_s is set to 1 L/min.

6.4 Inlet gas pressure is controlled by a pressure regulator and measured immediately upstream of the purified by an electronic grade pressure gage. Flow measurement is carried out by a MFC located downstream of the analyzer. The outlet pressure of the gas is measured immediately downstream of the analyzer by another electronic grade pressure gage. The MFC along with its digital readout should be calibrated before use to control and display the gas flow rate Q_1 .

6.5 The temperature of the spool piece, test specimen, analyzer cell compartment, and the THC concentration measured by the analyzer can either be recorded continuously by a data logger or collected and stored in a computer using a data acquisition program.

7. Calibration

7.1 Calibrate instruments regularly in accordance with manufacturer’s instructions.

7.2 *THC Analyzer Calibration*—Perform two-point calibration, zero and span, regularly. Zero gas is defined as below the manufacturer’s stated MDL of the instrument, supplied by purified gas, with the purifier in close proximity to the analyzer. Analyze span gas at the lowest possible detection range, that may not be at the lowest detection range of the instrument. Span gas is 5 to 10 ppmv methane, ±20 % for FID. Base calibration on traceable methane concentration in the base gas (nitrogen or argon).

8. Conditioning

8.1 *Pressure*—The test component is to be tested at 200 kPa gage (30 psig), as measured by P_2 .

8.2 *Temperature*— T_s is to be in the ambient temperature range of 18 to 26°C (64 to 78°F) and in the higher mean temperature range of 69 to 71°C (156 to 160°F). T_a must not deviate more than ±1°C (2°F) from the time of calibration to the termination of the test. T_a must either be within the range of 18 to 26°C (64 to 78°F) or be consistent with the analytical systems manufacturer’s specifications, whichever is more stringent.

8.3 The flow rate Q_s for components is 1 standard L/min with ±2 % tolerance.

8.4 Gas quality must be maintained at flow specified in 8.3.

9. Procedure (see Fig. 2)

9.1 This test procedure applies to the use of an FID (see Fig. 2).

9.2 *Bake-out*—With the spool piece and Valves V-1, V-2, V-3, and V-4 open, bake out the system (downstream of purifier to upstream of analyzer, exclusive of the exhaust leg) at 94°C (200°F) until outlet THC concentration is stable below 50 ppbv. Flow of the gas is specified in 8.3. Cool to lower T_s . Close Valves V-1 and V-2.

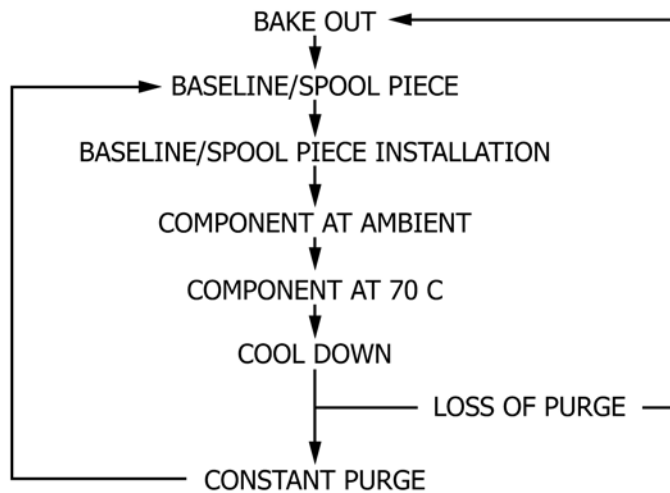


FIG. 2 Test Procedure Sequence

9.3 *Baseline*—Flow gas through the test stand with the spool piece installed on the test stand. Use the flow rate as defined in 8.3. Flow for 30 min after the THC concentration has attained a level of <510 ppbv. Utilizing heat tape, heat the spool piece and upstream tubing to within 80 mm of the upstream valve. Turn on the current and monitor the THC of the outlet and the T_s , as specified in 8.2. The time required to reach the higher T_s must be less than or equal to 10 min. Continue testing for 30 min after a stable baseline is reestablished (<100 ppbv). Cool until the lower T_s is reached.

9.4 Place the spool piece, test component (in original bagging), and fittings into a glove bag or nitrogen tent without disconnecting. Purge the glove bag with approximately five glove bag volumes of inert gas. Disconnect the spool piece while maintaining the flow through the system. Maintain the spool piece in the proximity of the positive flow. Reinstall the spool piece on the test stand. The entire disconnection and reinstallation must be performed within 2 min. Flow through the analyzer must be maintained during disconnection and installation via the bypass loop, using Valves V-1, V-2, V-3, and V-4 (if V-1 and V-2 are open, then V-3 and V-4 will be closed). During disconnection, open Valves V-1 and V-2 first, then close V-3 and V-4. After connection, reverse the order.

9.5 Initiate flow in accordance with 8.3. Monitor T_s and T_a in accordance with 8.2. Monitor THC until a stable baseline is reestablished in accordance with 9.3 (<50 ppbv). Utilizing heat tape, heat the spool piece and upstream tubing to within 80 min of the upstream valve. Turn on current and monitor the THC of the outlet and the T_s , as specified in 8.2. The time required to reach the higher T_s must be less than or equal to 10 min. Continue testing until a stable baseline is reestablished (<50 ppbv). Cool until the lower T_s is reached.

9.6 Without disconnecting the spool piece, place the test component and the fittings in a glove bag or nitrogen tent flushed with clean, dry nitrogen. Open Valves V-1 and V-2 first, then close V-3 and V-4. Disconnect the spool piece while maintaining flow and recap. Maintain flow through the analyzer continuously with Valves V-1 and V-2 during disconnection and installation. Remove the test component caps and install the test component. Open V-3 and V-4 first, then close V-1 and V-2. The time from disconnection of the spool piece to installation of the test component must be less than 2 min.

NOTE 1—The installation conditions of the test component, as well as glove bag conditions, must be the same as the installation conditions for the spool piece as outlined in 9.4 including time required to disconnect and connect. The spool piece must not be removed from the glove bag for the duration of the test.

9.6.1 *Valves, MFCs, and Regulators*—With Valves V-3 and V-4 closed and all gas flowing through the bypass, connect the test component to the test stand. The component will be installed in the “as received” condition (either open or closed). After installation, place the component in the fully open condition.

9.7 Initiate flow in accordance with 8.3. Monitor T_s and T_a in accordance with 8.2 for ambient temperature. Monitor THC until a stable baseline in accordance with 9.3 is re-established (<100 ppbv). Terminate the test after 3 h if a stable baseline is not achieved.

9.8 Utilizing heat tape, heat the test component and upstream tubing to within 80 mm of the upstream valve. Turn on the current and monitor the THC of the outlet and the T_s , as specified in 8.2. The time required to reach the higher T_s must be less than or equal to 10 min. Continue testing until a stable baseline is reestablished (<50 ppbv). Terminate the test in 3 h if a stable baseline is not achieved. Cool until the lower T_s is reached.

9.9 Without disconnecting the test component, place the spool piece in a glove bag or nitrogen tent purged with clean, dry nitrogen. Open V-1 and V-2 first, then close V-3 and V-4. Disconnect the test component while maintaining flow and cap. Remove the spool piece caps and install the spool piece. Open Valves V-3 and V-4. The time from disconnection of the test component to installation of the spool piece must be less than 2 min. The 2-min limit reduces the exposure of the test piece to the glove bag environment. Maintain flow through the analyzer via Valves V-1 and V-2 during disconnection and installation.

9.10 With Valves V-1, V-2, V-3, and V-4 open, maintain a purge through the system with a purified gas. Q_f may be reduced to a minimum of 0.5 standard L/min, or 10 % of the mass flow controller range. Start the next test run in accordance with 9.3 (establishment of stable baseline). If the gas flow is not maintained, the system must be baked out, in accordance with 9.1, prior to further testing.

9.11 *Sampling Frequency*—Perform and record sampling continuously (or at a maximum of 1-min intervals for digitally acquired data) during the specified time period.

10. Report

10.1 *Data Analysis*—Refer to X2.1 for a numerical example.

10.2 Report the following information:

10.2.1 *Data Collection*—Present a plot of THC concentration versus time for (1) the respective spool piece baseline and (2) the test component. Plot the elevated temperature data as a continuation of the ambient temperature data. Use a dual y-axis to plot T_s versus time on the same plot (refer to Fig. 3).

10.2.2 *Data Handling*—To determine THC contribution of the test component, compute the difference between the spool piece plot and the component plot derived in 10.1 and graph the results. Use a dual y-axis (concentration ppbv and T_s) (refer to Fig. 4).

10.2.3 Complete the table given in Figs. 5-7.

11. Precision and Bias

11.1 The precision and bias for this test method are being determined.

12. Keywords

12.1 components; contamination; gas distribution; hydrocarbon analyzer; hydrocarbon contribution; hydrocarbon outgassing; semiconductor processing

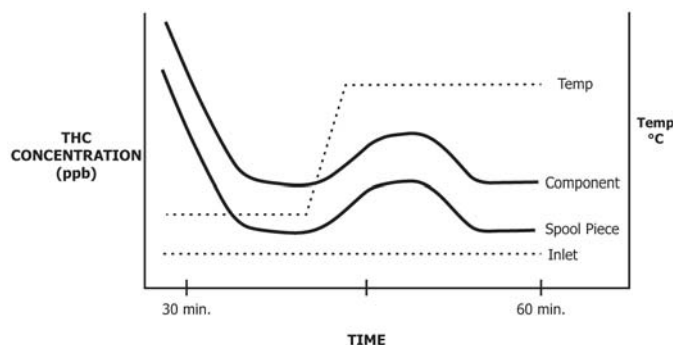


FIG. 3 Component THC Contribution

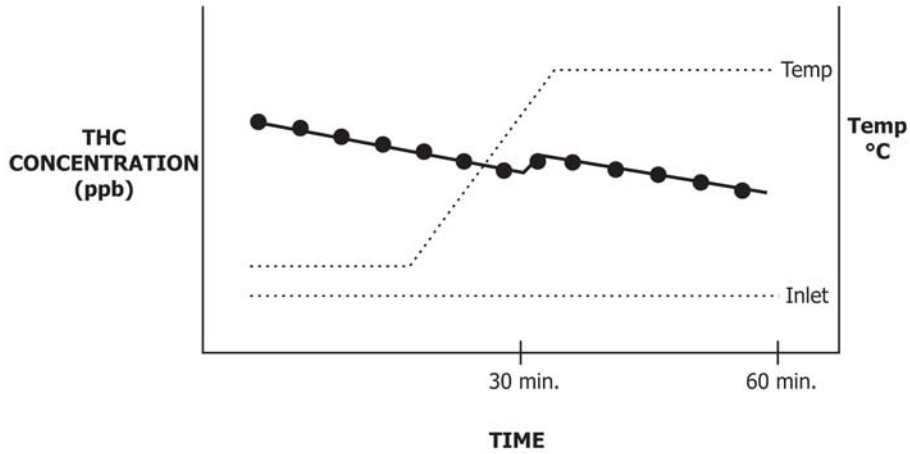


FIG. 4 Net Component THC Contribution

Date: _____ Operator: _____
 Test Location: _____ Spool Piece: _____
 Test Component: _____
 Model Number: _____ Serial Number: _____
 Analyzer: _____
 Model Number: _____ Serial Number: _____
 Last Calibration Date: _____
 Base Gas: _____
 Flow Meter: _____ Model Number: _____
 Calibration Date: _____ Cal Temperature: _____ °C
 Cal Pressure: _____ Cal Gas: _____
 MFC: _____ Model Number: _____
 Calibration Date: _____ Cal Temperature: _____ °C
 Cal Pressure: _____ Cal Gas: _____

I. Bake-out (if warranted)
 T_a : _____ °C Q_1 : _____ standard L/min $Q_5(Q_1+Q_2)$: _____ standard L/min
 T_s : _____ °C Q_2 : _____ standard L/min P_2 : _____ mm Hg
 Barometric Pressure: _____ mm Hg
 Ambient Temperature: _____ °C
 Data Acquisition Rate: _____
 Data File Name: _____
 Attach data presentation in graphical form.

II. Spool Piece Baseline
 A. Low Temperature
 T_a : _____ °C Q_1 : _____ standard L/min $Q_5(Q_1+Q_2)$: _____ standard L/min
 T_s : _____ °C Q_2 : _____ standard L/min
 Barometric Pressure: _____ mm Hg
 Ambient Temperature: _____ °C
 Data Acquisition Rate: _____
 Data File Name: _____
 Attach data presentation in graphical form.

Note-Archive all acquired data. Note file name on test data, if applicable.

FIG. 5 Hydrocarbon Contribution Data Table

B: High Temperature

T_a : _____ °C Q_1 : _____ standard L/min $Q_s(Q_1+Q_2)$: _____ standard L/min
 T_s : _____ °C Q_2 : _____ standard L/min
 Barometric Pressure: _____ mm Hg
 Ambient Temperature: _____ °C
 Data Acquisition Rate: _____
 Data File Name: _____

Attach data presentation in graphical form.

III. Spool Piece

A. Low Temperature

T_a : _____ °C Q_1 : _____ standard L/min $Q_s(Q_1+Q_2)$: _____ standard L/min
 T_s : _____ °C Q_2 : _____ standard L/min
 Barometric Pressure: _____ mm Hg
 Data Acquisition Rate: _____
 Data File Name: _____
 Ambient Temperature: _____ °C

Total time for disconnection/installation: _____
 Attach data presentation in graphical form.

B. High Temperature

T_a : _____ °C Q_1 : _____ standard L/min $Q_s(Q_1+Q_2)$: _____ standard L/min
 T_s : _____ °C Q_2 : _____ standard L/min
 Barometric Pressure: _____ mm Hg
 Ambient Temperature: _____ °C
 Data Acquisition Rate: _____
 Data File Name: _____

Attach data presentation in graphical form.

FIG. 6 Hydrocarbon Contribution Data Table (Continued)

IV. Test Component

A. Low Temperature

T_a : _____ °C Q_1 : _____ standard $Q_s(Q_1+Q_2)$: _____ standard L/min
 T_s : _____ °C Q_2 : _____ standard L/min
 Barometric Pressure: _____ mm Hg
 Data Acquisition Rate: _____
 Data File Name: _____
 Ambient Temperature: _____ °C

Total time for disconnection/installation: _____
 Attach data presentation in graphical form.

B. High Temperature

T_a : _____ °C Q_1 : _____ standard L/min $Q_s(Q_1+Q_2)$: _____ standard L/min
 T_s : _____ °C Q_2 : _____ standard L/min
 Barometric Pressure: _____ mm Hg
 Ambient Temperature: _____ °C
 Data Acquisition Rate: _____
 Data File Name: _____

Attach data presentation in graphical form.

FIG. 7 Hydrocarbon Contribution Data Table (Continued)

APPENDIXES
(Nonmandatory Information)
X1. ALTERNATIVE TESTS

X1.1 Atmospheric Pressure Ionization Mass Spectrometer (APIMS)—This test method may be conducted using an atmospheric pressure ionization mass spectrometer. APIMS is a complex technique that will ultimately yield better sensitivities (possibly parts per trillion (pL/L)) than vacuum MS techniques.

X1.2 Mass Spectrometer (MS)—Since many complex hydrocarbons are poorly detected by a flame ionization detector (FID), an alternative method to detect species outside of the above described “THC group” is mass spectrometry. For example, the quadrupole mass spectrometer accurately detects hydrocarbon species by ionizing organic moieties in a vacuum (APIMS, however, ionizes at atmospheric pressure). The ionized fragments are detected semi-quantitatively, but individually. In other words, the presence of individual components rather than total THC is reported. The mass spectrometer (MS) will detect the presence of hydrocarbons not readily detected by FID.

X1.2.1 This test method is semi-quantitative. In the case of MS, data collection is equivalent, except that individual species must be tabulated uniquely.

X1.3 Nondispersive Infrared Spectroscopy (NDIR)—This detection technique is based on the selective absorption of infrared radiation due to specific molecular vibrational mode of hydrocarbon impurities.

X1.4 Cryogenic Concentration—The cryogenic concentration technique involves passing between 10 and 100 L of sample gas through a glass tube immersed in a cryogenic liquid (preferably liquid argon). The concentrator contains glass beads to increase the available surface area for condensation. To obtain sufficient flow through the concentrator, use a sampling duration between 20 min and 1 h, with a flow rate of 5 to 10 standard L/min. Theoretically, all of the higher boiling components in the gas stream will condense within the glass tube. The sample must be kept immersed in the same cryogenic liquid until it is connected to the analyzer. Only then is the sample allowed to warm up.

X1.4.1 The analytical instrument used for analysis of the concentration samples must be a gas chromatograph/mass spectrometer (GC/MS), that is sensitive to sample concentrations in the nanogram range. Using the cryogenic concentration technique, the detection limit can be extended down to the low parts per trillion (ppt; for example, pL/L) or below.

X2. APPLICATION NOTES

X2.1 Mass Contribution Calculation—This appendix demonstrates the determination of total mass of methane equivalent contributed by the component under test from the concentration versus time curve shown in Fig. 3. The following symbols apply in the deviation:

- m_B = mass of base gas,
- m_I = mass of measured methane equivalent,
- MW_B = molecular weight of base gas,
- MW_I = molecular weight of methane,
- n_B = number of moles of base gas,
- n_I = number of moles of methane,
- p_B = pressure of base gas,
- p_I = pressure of methane equivalent,
- p_T = total system pressure,
- P_R = pressure at which MFC was calibrated,
- $Q_{s,m}$ = total mass flow through test component,
- $Q_{s,v}$ = total volume flow through test component,
- ρ_R = density of base gas at T_R and P_R ,
- R = universal gas constant,
- T = system temperature,
- t = time,
- T_R = temperature at which MFC was calibrated,
- V_B = volume occupied by base gas, and

V_I = volume occupied by methane equivalent.

X2.2 Most commercial instruments report the measured methane equivalent concentration in units of ppmv. The concentration axis is first converted to ppmw. The relationship between them may be derived as follows:

X2.2.1 Recognizing that at low methane equivalent concentrations:

$$V_B \gg \gg V_I \quad \text{and} \quad m_B \gg \gg m_I, \quad (\text{X2.1})$$

The equations defining ppmv and ppmw may be simplified to:

$$\text{ppmv} \sim (V_I/V_B) \times 10^6 \quad (\text{X2.2})$$

$$\text{ppmw} \sim (m_I/m_B) \times 10^6 \quad (\text{X2.3})$$

X2.2.2 At low pressures, assume both gases obey the ideal gas law:

$$p_I V_I = n_I RT \quad (\text{X2.4})$$

$$p_B V_B = n_B RT \quad (\text{X2.5})$$

Dividing Eq X2.4 by Eq X2.5:

$$p_I V_I / p_B V_B = n_I / n_B \quad (\text{X2.6})$$

Using Amagat's law of partial volumes: $p_I = p_B = p_T$,
Eq X2.6 becomes:

$$V_I/V_B = n_I/n_B \quad (X2.7)$$

with:

$$n_I = m_I/MW_I \quad (X2.8)$$

$$n_B = m_B/MW_B \quad (X2.9)$$

X2.2.3 Substituting Eq X2.8 and Eq X2.9 into Eq X2.7 and multiplying by 10^6 :

$$(V_I/V_B) \times 10^6 = (m_I/m_B) \times (MW_B/MW_I) \times 10^6 \quad (X2.10)$$

X2.2.4 Substituting the simplified definitions of ppmv and ppmw into Eq X2.10:

$$\text{ppmv} = \text{ppmw} \times MW_B/MW_I \quad (X2.11)$$

$$\text{ppmw} = \text{ppmv} \times MW_I/MW_B \quad (X2.12)$$

X2.2.5 Eq X2.12 is the required relationship for converting instrument response in ppmv to ppmw.

X2.3 The time axis in Fig. 3 must be converted from units of time to units of mass of base gas. This conversion will be demonstrated for the case where a mass flow controller is on the downstream bypass of the component under test measuring Q_I . (See Fig. 1.)

X2.3.1 Most MFCs report and control based on a set point, that is given in units of volume flow at P_R and T_R (the calibration temperature and pressure of the MFC). The MFC is a device that will maintain a given volume flow rate despite small changes in upstream or downstream pressure or fluctuations in temperature. To convert to a mass flow ρ_R , the base gas density at P_R and T_R is needed, and:

$$Q_{1,m} = Q_{1,v} \times \rho_R \quad (X2.13)$$

X2.3.2 Any flow diverted to the analyzer(s) ($Q_{2,m}$) must also be included in the calculation of total mass flow:

$$Q_{s,m} = Q_{1,m} + Q_{2,m} \quad (X2.14)$$

X2.3.3 If a rotameter is used to calculate $Q_{2,m}$, a separate measurement of room temperature and barometric pressure will be necessary. Once $Q_{s,m}$ is established, the total amount of base gas moving through the component is given by:

$$m_B = Q_{s,m} \times t \quad (X2.15)$$

X2.3.4 The ppmv versus time curve given in Fig. 3 can now be converted into a ppmw versus mass of base gas curve (refer to Fig. X2.1). A unit area under such a curve is given by:

$$(m_I/m_B) \times m_B = m_I \quad (X2.16)$$

X2.3.5 The total mass of methane equivalent measured ($m_{I,T}$) is given by the area under the ppmw versus m_B curve:

$$m_{I,T} = \int_0^{m_{RT}} \text{ppmw} dm_B \quad (X2.17)$$

X2.3.6 Integration may be carried out numerically by the trapezoid, Simpson's, or by any of the other quadrature methods (refer to Fig. X2.2). Alternatively, the data may be fit to a function that can be integrated in closed form and evaluated. The quadrature methods are easily applicable to digitized data and do not require knowledge of the underlying

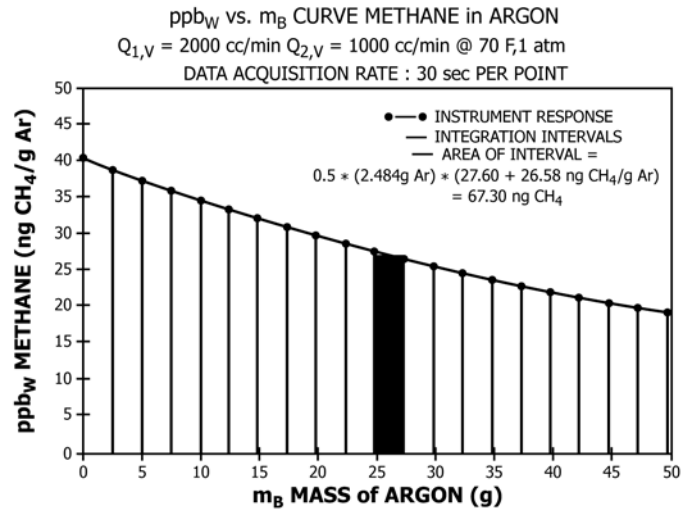


FIG. X2.1 Example Calculation Graph

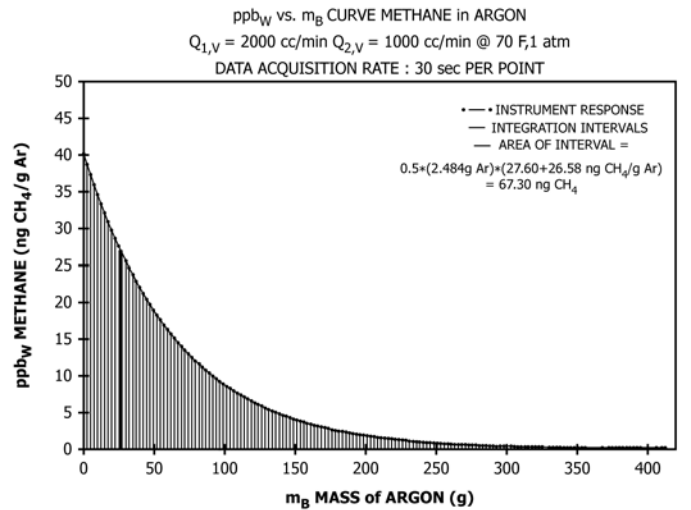


FIG. X2.2 Example Calculation Graph

functional form of the data. As a final example, the total mass of hydrocarbons from a component will be evaluated using the trapezoid rule for the data in the following example (data acquisition rate is 1 point every 30 s):

$$Q_{I,V} = 1000 \text{ cm}^3/\text{min} \text{ at } 101.3 \text{ kPa, } 21^\circ\text{C} (14.73 \text{ psia, } 70^\circ\text{F})$$

$$Q_{2,V} = 2000 \text{ cm}^3/\text{min} \text{ at } 101.3 \text{ kPa, } 21^\circ\text{C} (14.73 \text{ psia, } 70^\circ\text{F})$$

$$\rho_R = 0.001656 \text{ g/cm}^3 \text{ at } 101.3 \text{ kPa, } 21^\circ\text{C} (14.73 \text{ psia, } 70^\circ\text{F})$$

$$MW \text{ methane} = 16.043 \quad (X2.18)$$

$$MW \text{ argon} = 39.948 \quad (X2.19)$$

$$\text{ppbw} = 0.4016 \times \text{ppbv} \quad (X2.20)$$

$$Q_{s,m} = 50 \text{ cm}^3/\text{s} \times 0.001656 \text{ g/cm}^3 = 0.0828 \text{ g/s Ar} \quad (X2.21)$$

$$m_B = 0.0828 \text{ g Ar/s} \times t \quad (X2.22)$$

X2.3.7 The results of the test are given in Table X2.1. The first column is the time into the run. The second column is the ppbv of methane measured at a given time. Column 3 is the mass of argon that has passed through the component, calculated from Eq X2.14. Column 4 is the ppbw of methane

TABLE X2.1 Data for Sample Calculation

Analyzer Exhaust 2000 cc/s: Bypass 1000 cc/s at 70°F, 1 atm Data Acquisition Rate 1 Point Every 30 s						
Time, s	ppbv	mB, g Ar	ppbw, ng H ₂ O/g Ar	Area of Segment, ng H ₂ O	Total Area, ng H ₂ O	
30	96.3194	2.484	43.4401	109.9668	109.967	
60	92.7744	4.968	41.8412	105.9194	215.886	
90	89.3597	7.452	40.3012	102.0210	317.907	
120	86.0708	9.936	38.8179	98.2660	416.173	
150	82.9029	12.420	37.3892	94.6493	510.822	
180	79.8516	14.904	36.0131	91.1657	601.988	
210	76.9126	17.388	34.6876	87.8103	689.798	
240	74.0818	19.872	33.4109	84.5783	774.377	
270	71.3552	22.356	32.1812	81.4654	855.842	
300	68.7289	24.840	30.9967	78.4670	934.309	
330	66.1993	27.324	29.8559	75.5790	1009.888	
360	63.7628	29.808	28.7570	72.7973	1082.685	
390	61.4160	32.292	27.6986	70.1179	1152.803	
420	59.1555	34.776	26.6792	67.5372	1220.340	
450	56.9783	37.260	25.6972	65.0514	1285.392	
480	54.8812	39.744	24.7514	62.6572	1348.049	
510	52.8612	42.228	23.8404	60.3510	1408.400	
540	50.9156	44.712	22.9630	58.1298	1466.530	
570	49.0417	47.196	22.1178	55.9903	1522.520	
600	47.2367	49.680	21.3037	53.9295	1576.450	
630	45.4981	52.164	20.5196	51.9446	1628.394	
660	43.8235	54.648	19.7644	50.0328	1678.427	
690	42.2106	57.132	19.0370	48.1913	1726.618	
720	40.6570	59.616	18.3363	46.4176	1773.036	
750	39.1606	62.100	17.6614	44.7092	1817.745	
780	37.7192	64.584	17.0114	43.0636	1860.809	
810	36.3310	67.068	16.3853	41.4786	1902.287	
840	34.9938	69.552	15.7822	39.9520	1942.239	
870	33.7058	72.036	15.2013	38.4815	1980.721	
900	32.4652	74.520	14.6418	37.0652	2017.786	
930	31.2703	77.004	14.1029	35.7010	2053.487	
960	30.1194	79.488	13.5839	34.3870	2087.874	
990	29.0109	81.972	13.0839	33.1214	2120.995	
1020	27.9431	84.456	12.6023	31.9023	2152.898	
1050	26.9146	86.940	12.1385	30.7281	2183.626	
1080	25.9240	89.424	11.6917	29.5972	2213.223	
1110	24.9699	91.908	11.2614	28.5078	2241.731	
1140	24.0509	94.392	10.8469	27.4586	2269.189	
1170	23.1656	96.876	10.4477	26.4479	2295.637	
1200	22.3130	99.360	10.0632	25.4745	2321.112	
1230	21.4918	101.844	9.6928	24.5369	2345.649	
1260	20.7008	104.328	9.3360	23.6338	2369.282	
1290	19.9389	106.812	8.9924	22.7640	2392.046	
7920	0.0050	655.776	0.0023	0.0057	2987.625	
7950	0.0048	658.260	0.0022	0.0055	2987.630	
7980	0.0047	660.744	0.0021	0.0053	2987.636	

equivalent calculated from Eq X2.13. Column 5 is the area of the trapezoid for each interval. Finally, Column 6 is the total area up to and including the current interval. The graphs of these results are shown in Fig. X2.1 and Fig. X2.2.

X2.3.8 The final result for this test is 2660.388 ng methane, or 2.66 µg.

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