Methane Measurement Using Gas Chromatography—SAE J1151a

SAE Recommended Practice
Editorial Change July 1979

THIS IS A PREPRINT WHICH IS SUBJECT TO REVISIONS AND CORRECTIONS. THE FINAL VERSION WILL APPEAR IN THE 1980 EDITION OF THE SAE HANDBOOK.

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LAND SEA AIR SPACE

PREPRINT

METHANE MEASUREMENT USING GAS CHROMATOGRAPHY—SAE J1151a

SAE Recommended Practice

Report of Automotive Emissions Committee approved August 1976 and completely revised June 1979. Editorial change July 1979.

1. Purpose—This SAE Recommended Practice provides a means for a batch measurement of the methane concentration in light-duty vehicle exhaust samples. Nonmethane hydrocarbon concentration can be obtained by subtracting the methane concentration from the total hydrocarbon concentration obtained by a separate measurement made in accordance with accepted practices such as SAE J1094a (November, 1978), J254 (June, 1971), or a current Federal Test Procedure.[1]

2. Scope—This SAE Recommended Practice describes instrumentation for determining the amount of methane in air and exhaust gas.

3. Sections—The remainder of this practice is divided into the following sections:

4. Definitions of Terms and Abbreviations.
5. Equipment.
6. Principle of Operation.
7. Instrument Operating Procedure.
8. Instrument Performance Specifications.
9. Maintenance.

4. Definitions of Terms and Abbreviations

4.1 Terms Used

4.1.1 Flame Ionization Detector (FID)—A hydrogen-air diffusion flame detector that produces a signal proportional to the mass flow rate of hydrocarbons entering the flame per unit time.

4.1.2 Parts Per Million Carbon (ppm C)—The mole fraction times 10^6 of hydrocarbon measured on a methane equivalence basis.

4.1.3 Calibrating Gas—Gas of known methane concentration used to establish the instrument response curve.

4.1.4 Span Gas—Gas of known methane concentration routinely used to set the instrument output level.

4.1.5 Gas Chromatogram—The recorder output plot of the FID signal against time which shows a peak corresponding to the elution of methane.

4.2 Abbreviations and Symbols

°C	—degree(s) Celsius
CH_4	—methane
CO	—carbon monoxide
CO_2	—carbon dioxide
cm	—centimeter(s)
CVS	—constant volume sampler
FID	—flame ionization detector
Fig.	—figure
g	—gram
GC	—gas chromatograph(ic)
h	—hour(s)
HC	—hydrocarbon(s)
ID	—inside diameter
in	—inch
kPa	—kilopascal
NMHC	—nonmethane hydrocarbon(s)
min	—minute(s)
m	—meter
mm	—millimeter(s)
µm	—micrometer(s)
O_2	—oxygen
OD	—outside diameter
ppm	—parts per million
ppm C	—parts per million carbon
psig	—pound(s) per square inch, gage
s	—second(s)
scfh	—standard cubic foot per hour
SAE	—Society of Automotive Engineers, Inc.
SS	—stainless steel
%	—percent

5. Equipment

5.1 Safety Precautions—Flammable FID fuel (containing hydrogen) and potentially toxic 2% CO in exhaust gas are vented from this instrument at low flow rates of approximately 80 cm^3/min (0.2 scfh). At these low flow rates, there should not normally be a hazard from these gases, but precautions should be observed to insure dilution of these potentially hazardous vented gas streams.

The instrument uses flammable fuel and the precautions specified by the manufacturer should be observed.

The sample bypass line in the instrument has a flow of about 2000 cm^3/min (4 scfh) of automotive exhaust gas. This flow should be discharged outside of the building or into an adequately ventilated area.

5.2 Instrument—A gas chromatograph is used to separate the methane from the other constituents of an exhaust gas sample. The concentration of methane is determined with a FID. A typical suitable gas chromatograph is described in this section. (An example of a similar commercially available instrument is the Bendix Model 8205 Methane Analyzer.)

5.3 Component Description—The schematic diagram in Fig. 1 shows a typical gas chromatograph assembled to routinely determine methane. The following components are typically used.

5.3.1 Valve, V1—Sample injection and switching valve, should be low dead volume, gas tight, and heatable to at least 150°C.

5.3.2 Valve, V2—Used to provide supplementary fuel to the FID burner.

5.3.3 Valve, V3—Used to select span gas, sample, or no flow.

5.3.4 Valve, V4—Used as a restrictor to match the flow resistance of the Porapak N column.

5.3.5 Valve, V5—Used as a restrictor to match the flow resistance of the Molecular Sieve column. This valve allows equalizing backflush and foreflush flow rates through the Porapak column.

5.3.6 Valve, V6—Used as a restrictor for controlling the rate of sample flow to fill the sample loop.

5.3.7 Pressure Regulator, PR1, and Pressure Gage, G1—To control flow rate of the fuel which is also the carrier gas.

5.3.8 Pressure Regulator, PR2, and Pressure Gage, G2—Back-pressure regulator for controlling the rate of sample flow to the sample loop in conjunction with valve V6. Should be adjusted in the pressure range from 7 to 34 kPa (1 to 5 psig).

5.3.9 GC Column—Porapak N, 180/300 µm (equivalent to 50/80 mesh), 610 mm (2 ft) length x 2.16 mm (0.085 in) ID x 3.18 mm (1/8 in) OD SS, to separate air, CH_4, and CO from the other sample constituents. The column is conditioned 12 h or more at 150°C with carrier gas flowing prior to initial use. Valve V1 should be in the fill/backflush position during the conditioning.

5.3.10 GC Column—Molecular Sieve Type 13X, 250/350 µm (equivalent to 45/60 mesh), 1220 mm (4 ft) length x 2.16 mm (0.085 in) ID, 3.18 mm (1/8 in) OD SS, to separate methane from oxygen, nitrogen, and CO. The column is conditioned 12 h or more at 150°C with carrier gas flow prior to initial use. Valve V1 should be in the fill/backflush position during the conditioning.

5.3.11 Sample Loop—A sufficient length of SS tubing to obtain 1 cm^3 volume.

5.3.12 Oven—To maintain columns and valves at a stable temperature for analyzer operation, and to condition columns at 150°C.

5.3.13 Valve Actuator—To actuate sample injection and switching valve.

5.3.14 Valve Programmer—Timing unit to control valve actuator.

5.3.15 Dryer—To remove water and other contaminants which might be present in the carrier gas, a filter dryer containing Molecular Sieve is used (for example, Disposa-Purge, Applied Science Laboratories, Inc.). If it is a visual indicating type, the dryer is replaced when the need is indicated. Otherwise, it is replaced or reconditioned monthly. If the dryer has a metal body, it can be reconditioned after removing it from the instrument by flowing approximately 50 cm^3/min of dry nitrogen through the dryer while it is heated to 150°C in an oven for 12 h.

5.3.16 Restrictor, R3—For controlling the rate of air flow to FID.

5.3.17 Pressure Regulator, PR3—Used with pressure gage, G3, and restrictor, R3, to control air flow to FID.

5.3.18 Filters F1, F3, F4—Sintered metal filters to prevent grit from entering the instrument.

5.3.19 Filters F2, F5—Sintered metal filters in the sample stream to prevent grit from entering the pump or instrument. Should be of sufficiently large area to have a pressure drop of less than 15 kPa (2 psi) at the bypass flow rate used of approximately 2000 cm^3/min (4 scfh).

5.3.20 Pump—Used to bring sample to gas chromatograph.

5.3.21 Valve, V7—Used with flowmeter, FM1, to regulate bypass sample flow rate. The bypass sample flow rate should be fast enough to flush out

[1] See Code of Federal Regulations, Title 40 Protection of Environment, Page 86, Subpart B, Emission Regulations for 1977 and Later Model Year New Light-Duty Vehicles and New Light-Duty Trucks; Test Procedure (40 CFR 86.101 et seq) (as amended by the Federal Register, for example, Federal Register, Vol. 42, No. 124, pp. 32954–33004 (June 28, 1977).

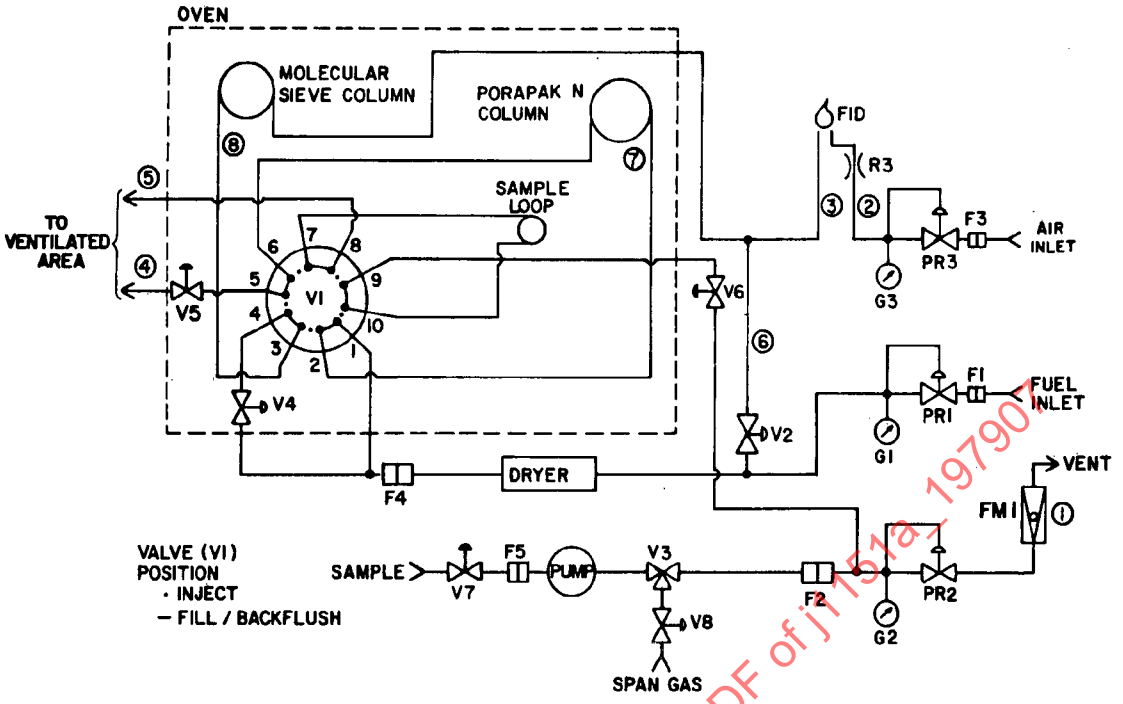

FIG. 1–INSTRUMENT TO MEASURE METHANE

the entire sample line in a time less than the GC analysis time so that while an analysis is being made, the sample loop is filled with the next sample and is ready for the next analysis cycle. A typical bypass flow rate would be 2000 cm^3/min (4 scfh).

5.3.22 Valve, V8–Used with flowmeter, FM1, to equalize bypass flow rates of span gas and sample.

5.3.23 Recorder–The recorder or other readout device should have an input compatible with the FID analyzer output, an accuracy (including the effects of deadband and linearity) of ± 0.25% of full scale or better, a span step response time of 0.4 s or less, and a chart speed of approximately 25 mm/min (1 in/min).

5.3.24 FID–The flame ionization detector generates an electrical current proportional to the flow rate of methane through the burner. The associated electrometer amplifier acts as a current to voltage converter and should have an electronic time constant of less than 0.20 s.

6. Principle of Operation–The instrument (Fig. 1) measures the methane concentration in a sample swept from a fixed volume sample loop by a carrier gas stream when the valve (V1) is in the inject position. The carrier gas can be blended FID fuel. The stream enters the Porapak N gas chromatographic column which temporarily retains NMHC, CO_2, and water, and passes air, methane, and CO to the Molecular Sieve column. As soon as all of the methane elutes from the Porapak N column and has passed through valve V1 toward the Molecular Sieve column, the Porapak N column is backflushed to waste by switching the valve (V1) to the fill/backflush position. Switching V1 also starts filling the sample loop with the next sample. The Molecular Sieve column separates the air (oxygen and nitrogen) and CO from the methane and passes these constituents to the FID which produces a signal peak proportional to CH_4. As soon as the methane peak passes through the FID, valve V1 can be switched back to the inject position to inject the next sample. A complete cycle, from injection of one sample to injection of a second, can be made in 30 s. Automation of injection and backflush switching assures reproducible peak times and shapes and is easily accomplished.

7. Instrument Operating Procedure

7.1 In general, the manufacturer's instructions for operation of the instrument or gas chromatograph should be followed.

7.2 **Component Assembly**–The assembly of the components for the instrument is shown in Fig. 1. The sample and switching valve V1, restrictor valves V4 and V5, sample loop, and the two GC columns are installed in the oven. The outlet of valve V5 and the outlet from valve V1, port 8 must discharge directly into an open area at atmospheric pressure where there can be no effluent build-up. The other components are connected outside the oven with all connecting tubing of minimum length. After all of the connections have been made, as indicated in Fig. 1, leak check the fittings and the instrument is ready for adjustment of operating parameters.

TABLE 1–TYPICAL FLOW RATES

Location (Fig. 1)	Valve V1 Position	
	Inject	Fill/Backflush
	Flow Rate–cm^3/min (room pressure and temperature)	
1. Sample Bypass Vent	2000	2000
2. Burner Air	400	400
3. Total Burner Fuel	100	100
4. Backflush	60	60
5. Sample	95	90
6. Makeup Fuel	30	30
7. Porapak N Column	70[a]	60
8. Molecular Sieve Column	70[a]	70[a]

[a]These flow rates were measured at location 3 with valve V2 closed.

7.3 **Initial Adjustment of Operating Parameters**–The timing sequence is determined by the flow rates of the carrier gas, the gas holdup volume of the system, and the column temperature. Typical flow rates at several instrument locations identified by the encircled numerals in Fig. 1 are given in Table 1. The following procedure would typically be followed to determine satisfactory flow rates of the assembled system and the switching times of the valves.

7.3.1 Set the initial operating parameters. Record oven temperature, gas pressures, and flow rates for later reference.

7.3.1.1 Sample–Adjust the flow of span gas or sample with V8 or V7 so that the flow discharged to the vent is about 2000 cm^3/min (4 scfh). Adjust backpressure regulator PR2 so that gage G2 reads from 7 to 34 kPa (1 to 5 psig). Readjust span gas or sample bypass flow to 2000 cm^3/min. With valve V1 in the fill/backflush position, adjust valve V6 so that the flow from port 8 of valve V1 is 80–100 cm^3/min.

7.3.1.2 Carrier (Hydrogen/Helium Mixture–40%/60%, or the mixture specified in SAE J254 (June, 1971), is recommended. The mixture should

contain less than 1 ppm (C HC). With sampling and switching valve (V1) in the inject position and valve V2 closed, adjust pressure regulator PR1 so that the carrier flow rate through the columns into the FID burner is about 70 cm^3/min. Typically, the pressure regulator PR1 will be set at approximately 140 kPa (20 psig). The flow is readily measured with a soap bubble flowmeter. The elapsed time from sample injection to the appearance of the oxygen peak (Fig. 2) is primarily a function of the carrier flow rate. Turn valve V1 to the fill/backflush position. Adjust valve V4 so that the

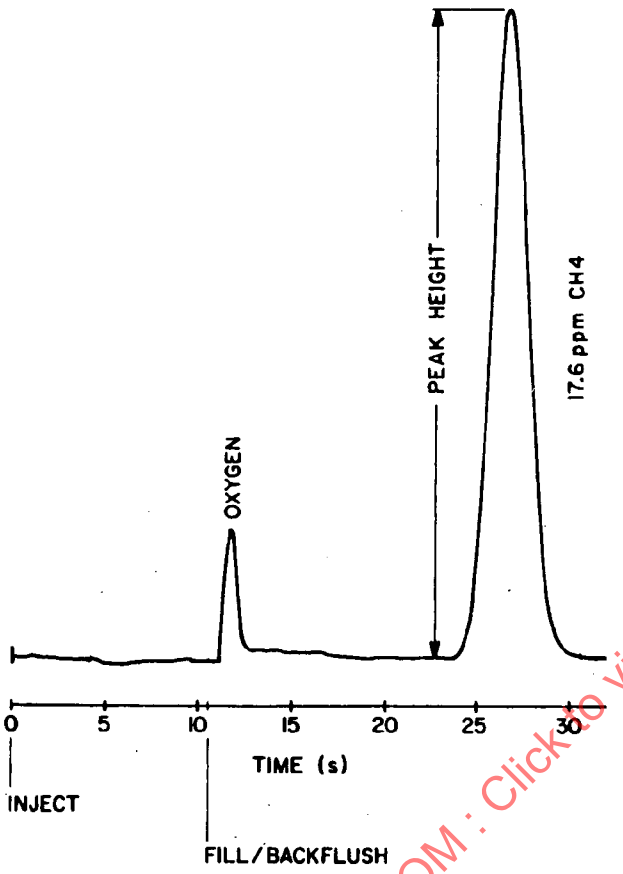

FIG. 2–TYPICAL GAS CHROMATOGRAM

carrier flow rate through the Molecular Sieve column and into the FID burner is the same (within 2%) as when valve V1 is in the inject position. Check the backflush flow rate through valve V5 to confirm that it is approximately equal (within 30%) to the flow rate through the columns into the FID burner.

7.3.1.3 Column Conditioning—With valve V1 in fill/backflush position and carrier gas flowing, adjust oven temperature to 150°C and condition columns for a minimum of 12 h. After conditioning, adjust oven temperature to about 55°C. Open valve V2 to provide a total mixed-fuel flow to the FID burner of about 100 cm^3/min.

7.3.1.4 Air (Should Contain Less Than 1 ppm C HC)—Set the pressure regulator PR3 so that the air flow to the FID burner is in the range of 250–450 cm^3/min. Since all FID units are unique, these settings of fuel and air can be adjusted with the valve V2 and pressure regulator PR3 respectively, to obtain the maximum instrument response using a methane calibration gas. This procedure is described in paragraph 7.3.3.

7.3.1.5 Column Oven Temperature—The column oven should be maintained at a constant temperature. A temperature of about 55°C will allow an analysis time of 30 s. The temperature can be adjusted between 35 and 75°C in order to give a desired analysis time. Allow time for oven temperature to stabilize before making measurements. The temperature control setting that maintains 150°C for use in conditioning the GC columns should be ascertained before column installation.

7.3.2 Timing Sequence—The analysis starts with valve V1 in the fill/backflush position. In this position, the sample loop is flushed and filled with sample (flow rate 80–100 cm^3/min). With a typical instrument, it was found that if the sample select valve, V3, selected the next sample at least 6 s before sample injection, the sample loop was fully flushed and hence a longer flush and fill time gave the same analytical results. The sample is injected by switching valve V1 into the inject position. The sample passes into the Porapak N column from which air elutes first and then methane. Carbon dioxide, higher hydrocarbons, and water vapor are retained longer in the Porapak N column. It is necessary to leave valve V1 in the inject position only long enough for all the methane to elute from the Porapak N column. If valve V1 is in the inject position too long, CO_2 will also elute from the Porapak N column, pass onto the Molecular Sieve column, be absorbed by and gradually deactivate the Molecular Sieve column. The optimum time for switching is found by determining the minimum time required for maximum methane response to be obtained. With a typical instrument at a column flow rate of 73 cm^3/min, it was found that if valve V1 was manually switched from inject to fill/backflush 6 s after injection, the methane peak height was 53% of its ultimate height measured with a later valve switching. If valve V1 was switched 7 s after injection, the methane peak height was 95% of its ultimate height, and if valve V1 was switched 8 s after injection, the ultimate peak height was reached. For this instrument, valve V1 was programmed to stay in the inject position for 9 s. The gases in order of elution from the Molecular Sieve column into the FID analyzer are oxygen, which gives a small peak; nitrogen; methane, which gives the peak that is measured; and CO, which elutes well before the next methane peak. The FID does not respond to the nitrogen and CO peaks. Fig. 2 shows a gas chromatogram obtained with this system. (In normal use a slower chart speed is used.) With valve V1 in the fill/backflush position, the Porapak N column is backflushed to waste clean it out for the next sample. Also during this time, the sample loop is flushed and filled with the next sample to be analyzed. After most of the methane peak has eluted into the FID analyzer, valve V1 can be switched to inject the next sample. The last traces of methane can finish eluting while the next sample is being injected. In a typical instrument, the cycle time was 30 s.

7.3.3 Detector Optimization—The detector response is maximized by the following procedure. Run repeated samples of span gas with the instrument automatically cycling. Adjust the bypass fuel valve V2 until maximum methane peak height above the baseline is obtained. Note that the baseline will shift with changes in fuel flow rate. Adjust the air pressure regulator PR3 to the point where maximum methane peak height is obtained. If the change in methane peak height with air pressure is very small, then a pressure setting should be selected that results in an air flow of 3.2 to 4.5 times the fuel flow rate to the burner. Finally, reoptimize the fuel flow rate by readjusting valve V2 slightly to obtain maximum methane peak height. Detector optimization should be performed when burner maintenance has occurred or at yearly intervals, whichever occurs first.

7.4 Calibration—Each six-bag test series of the Federal Test Procedure is calibrated with a span gas of methane in air. Typically, an analyzer requires only a one-point calibration since response is generally linear with methane content of sample. However, this should be verified for each analyzer because some instruments at certain conditions may be nonlinear and require a calibration curve. A series of calibration gases, containing methane of known concentration in air, covering the range of concentrations within which sample gases may be expected to fall, should be used for calibration. Optionally, a flow blender may be used to blend a single calibration gas with zero grade air to provide a series of intermediate calibration gases. The methane impurity of the zero grade air should be determined and be considered in the calculation of the methane concentration of the intermediate gases. Plot CH_4 peak height (or, if used, CH_4 peak area) against ppm CH_4 of the calibration gas. If a linear response with zero intercept is obtained, linearity is confirmed. The calibration curve should be redetermined after the FID burner is serviced and at monthly intervals.

7.5 Emission Measurement Procedure—A span gas should be measured before and after the sample series. Six methane analyses can be made in 4 min. All these samples may be handled automatically. The instrument should be located near the CVS in order to minimize the length of tubing. Samples are pumped directly from the bag via a Teflon or stainless steel tube to the sample inlet.

7.6 Data Analysis—The methane peak height is used as a measure of the amount of methane. Peak height is the distance from the peak maximum to the peak baseline. The peak baseline is defined as the plateau immediately preceding the peak. (Alternatively, the methane peak area, as determined with an integrator, can be used as a measure of the amount of methane.) Methane concentrations are measured directly, NMGC con-