SAE RECOMMENDED PRACTICE J1151

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Methane Measurement Using Gas Chromatography – SAE J1151 JUN83

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METHANE MEASUREMENT USING GAS ϕ CHROMATOGRAPHY—SAE J1151 JUN83

SAE Recommended Practice

Report of the Automotive Emissions Committee, approved August 1976, completely revised June 1983.

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 Vehicle emission terms are defined in SAE J1145, "Emission Terminology and Nomenclature."

4.1.2 CARRIER GAS—A gas that acts as a passive vehicle to transport the sample through a gas chromatograph column.

4.1.3 GAS CHROMATOGRAPHY—A separation technique in which a sample in the gaseous state is carried by a flowing gas (carrier gas) through a tube (column) containing stationary material. The stationary material performs the separation by means of its differential affinity for the components of the sample.

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

[1] See Code of Federal Regulations, Title 40 Protection of Environment, Part 86, Subpart B, Emission Regulations for 1977 and Later Model Year New Light-Duty Vehicles and New Light-Duty Trucks; Test Procedures (40 CFR 86.101 et seq) (as possibly amended by the Federal Register).

The ϕ symbol is for the convenience of the user in locating areas where technical revisions have been made to the previous issue of the report. If the symbol is next to the report title, it indicates a complete revision of the report.

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 cm³/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 cm³/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.

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 × 2.16 mm (0.085 in) ID × 3.18 mm (⅛ 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 × 2.16 mm (0.085 in) ID, 3.18 mm (⅛ 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 approximately 1 cm³ 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. 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 cm³/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

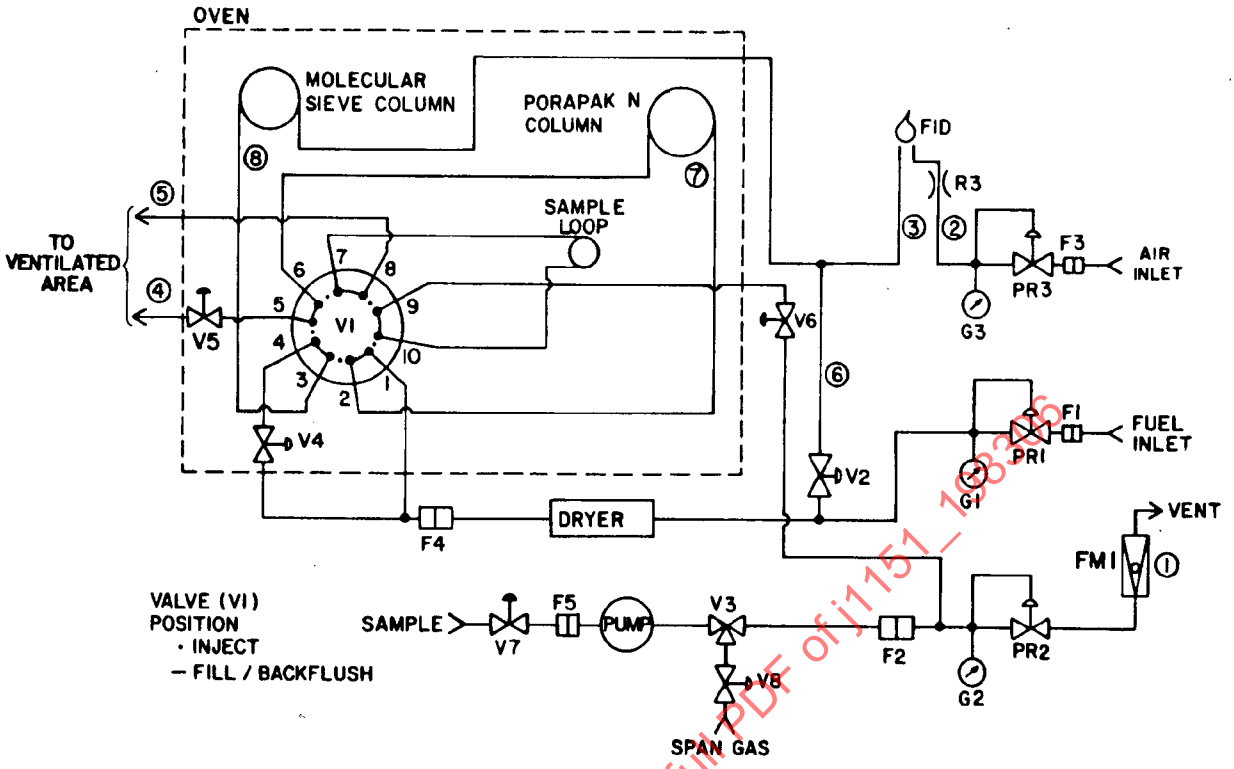

FIG. 1—INSTRUMENT TO MEASURE METHANE

the bypass flow rate used of approximately 2000 cm³/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 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 cm³/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 methane from the air and CO before passing it to the FID. The FID produces a signal peak proportional to the methane concentration in the sample. 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—cm³/min (room pressure and temperature)	
1. Sample Bypass Vent	2000	2000
2. Burner Air	400	400
3. Total Burner Fuel[a]	100	100
4. Backflush	60	60
5. Sample	95	90
6. Makeup Fuel[a]	30	30
7. Porapak N Column[a]	70[b]	60
8. Molecular Sieve Column[a]	70[b]	70[b]

[a] Fuel: 40% H_2/60% He.
[b] 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 cm³/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 cm³/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 cm³/min.

7.3.1.2 *Carrier Gas*—Mixed fuel is recommended to minimize the number of gases required for vehicle exhaust measurements since mixed fuel is also used for total hydrocarbon measurements (see SAE J1094). Mixtures from 38 to 55% hydrogen with the diluent being helium or nitrogen have been found to be acceptable. The carrier gas mixture should contain less than 0.5 ppm C HC. (The oxygen peak height (see Fig. 2) is not a direct response to oxygen, but is caused by a synergistic effect of O_2 on the HC impurity in the mixed fuel, therefore it is an approximate indicator of the hydrocarbon concentration in the fuel.)

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 cm³/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 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.

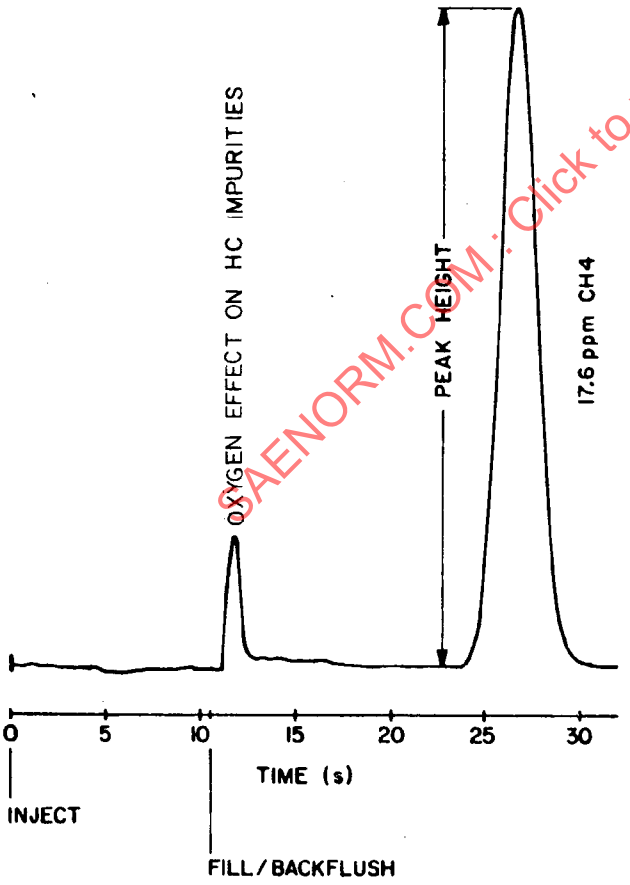

FIG. 2—TYPICAL GAS CHROMATOGRAM

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.

7.3.1.4 *Additional Fuel*—Open valve V2 to provide a total hydrogen flow to the FID burner of about 40 cm³/min (e.g., 100 cm³/min of 40% H_2/60% He fuel).

7.3.1.5 *Air (Should Contain Less Than 0.5 ppm C HC)*—Set the pressure regulator PR3 so that the air flow to the FID burner is approximately ten times the hydrogen flow.

7.3.1.6 *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 cm³/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 cm³/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 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 carbon monoxide. 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 to 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, 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.

7.4 Calibration—Typically, analyzer response is linear (not necessarily passing through the origin) with the methane content of the sample. However, this should be verified for each analyzer prior to its introduction into service and at monthly intervals thereafter. The linearity should also be verified whenever the FID burner is serviced and whenever the fuel carrier gas supply is changed. A series of four or more 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 considered in the calculation of the methane concentration of the intermediate gases. Obtain the least-squares straight line regression of the methane concentration in the calibration gas as a function of methane peak height (or, if used, peak area). It is recommended that the datum point obtained with zero grade air should not be included in the regression. The reason is that if the methane concentration in the zero grade air is lower than the methane concentration in the carrier gas, the sample of zero grade air will produce a negative methane peak. Many peak height or peak area measuring schemes cannot correctly determine the height or area of the negative peak. For each range calibrated, if the deviation of the calibration points from the regres-