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Methane Measurement Using Gas Chromatography—SAE J1151

SAE Recommended Practice
Approved August 1976

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METHANE MEASUREMENT USING GAS CHROMATOGRAPHY—SAE J1151

SAE Recommended Practice

Report of Automotive Emissions Committee approved August 1976.

1. Purpose—This SAE Recommended Practice provides a means for a batch measurement of the methane concentration in light duty vehicle exhaust samples. Non-methane hydrocarbon concentration can be obtained by subtracting the measurement of the methane concentration from a separate measurement of the total hydrocarbon concentration obtained in accordance with accepted practices such as SAE J1094, J254, or a current Federal test procedure.¹

2. Scope—This Recommended Practice incorporates methane analysis instrumentation only.

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

4. Definition of Terms and Abbreviations
5. Equipment
6. Principle of Operation
7. Instrument Operating Procedures
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)—A unit of hydrocarbon concentration equal to the mole fraction of methane multiplied by 10^6 .

4.1.3 PARTS PER MILLION PROPANE (ppm C₃)—A unit of hydrocarbon concentration equal to the hypothetical mole fraction of propane having equal carbon concentration multiplied by 10^6 .

4.1.4 CALIBRATING GAS—Gas of known methane concentration used to establish the instrument methane response curve.

4.1.5 SPAN GAS—Gas of known methane concentration used routinely to set the instrument output level.

4.1.6 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	—centimetre(s)
CVS	—constant volume sampler
FID	—flame ionization detector
fig.	—figure
g	—gram
GC	—gas chromatographic
HC	—hydrocarbon(s)
ID	—inside diameter
kPa	—kilopascal
NMHC	—nonmethane hydrocarbon(s)
min	—minute(s)
mm	—millimetre(s)
µm	—oxygen
O ₂	—oxygen
OD	—outside diameter
ppm	—parts per million
ppm C	—parts per million carbon
ppm C ₃	—parts per million propane equivalent
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 60 cm³/min (0.1 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 FID HC analyzer uses flammable fuel and the precautions specified by the FID HC analyzer manufacturer should be observed.

The sample bypass line in the FID HC analyzer has a flow of about 2000 cm³/min (4 scfh) of automotive exhaust gas. This flow should be discharged outside the building or into an adequately ventilated area.

5.2 Instruments

5.2.1 FID ANALYZER—Any FID hydrocarbon analyzer which is compatible with exhaust hydrocarbon measurements and which has an electronic time constant less than 0.23 s (for example, Beckman Model 400 hydrocarbon analyzer, or equivalent).

5.2.2 RECORDER—The recorder or other readout device should have an input compatible with the FID analyzer output, should have an accuracy (including the effects of deadband and linearity) of $\pm 0.25\%$ of full scale or better, should have a span step response time of 0.4 s or less, and should have a chart speed of approximately 2 cm/min (1 in./min).

5.3 Component Description—The following components are used to modify one of the several commercially available FID hydrocarbon analyzers to measure methane concentrations. The schematic in Fig. 1 shows a typical commercial FID HC analyzer modified to measure methane.

5.3.1 VALVE—V1, should be low dead volume, gas tight, and heatable to at least 150°C (for example, Carle Micro Volume Sampling and Switching Valve, Catalog No. 2040, or equivalent).

5.3.2 VALVE—V2, should be sized to permit a good regulation of fuel flow in the range of 30 to 60 cm³/min with a pressure drop of about 140 kPa (20 psi).

5.3.3 VALVE—V3, used to select span gas, or sample, or no flow.

5.3.4 VALVE—V4, used as a restrictor to match the flow resistance of the Porapak N column (for example, Hoke 1335G2Y with metal handle, or equivalent).

5.3.5 PRESSURE REGULATOR—PR1, and pressure gage, G1, to control fuel flow; provided on commercial FID instruments.

5.3.6 PRESSURE REGULATOR—PR2, and pressure gage, G2, for controlling the rate of sample flow to the sample loop; provided on commercial FID instruments.

5.3.7 GC COLUMN—Porapak N, 180/300 µm (50/80 mesh), 610 mm (2 ft) length \times 2.16 mm (0.085 in) ID \times 3.175 mm (1/8 in) OD SS, to separate air, CH₄, and CO from the other sample constituents. Column is conditioned 12 h at 150°C with carrier flow prior to use and at bimonthly intervals.

5.3.8 GC COLUMN—Molecular Sieve Type 13X, 250/350 µm (45/60 mesh), 1520 mm (5 ft) length \times 2.16 mm (0.085 in) ID, 3.175 mm (1/8 in) OD SS, to separate methane from oxygen, nitrogen, and CO. Column is conditioned 12 h at 150°C with carrier gas flow prior to use and at bimonthly intervals.

5.3.9 SAMPLE LOOP—A sufficient length of SS tubing to obtain 2 cm³ volume (for example, Carle 2 cm³ sample loop, or equivalent).

5.3.10 RESTRICTOR, R1—For controlling the rate of sample flow to purge the sample lines and fill the sample loop (for example, Perkin-Elmer Part Number 009-0211, or equivalent).

5.3.11 RESTRICTOR, R2—For controlling the Porapak column back-flush flow rate so as to approximately equal the fore-flush flow rate (for example, 1200 mm (4 ft) of 0.254 mm (0.010 in) ID stainless steel tubing).

5.3.12 OVEN—To maintain columns, valve, and restrictors at a stable temperature at or near room temperature for analyzer operation, and to condition columns bimonthly at 150°C (for example, Carle Model 4301, or equivalent).

5.3.13 VALVE ACTUATOR—For sample injection and switching valve (for example, Carle Model 4201, or equivalent).

5.3.14 VALVE PROGRAMMER—Timing unit to control valve actuators (for example, Carle Model 4104, or equivalent).

5.3.15 DRYER—To remove water and organic contaminants which might be present in the carrier gas, a filter-dryer containing silica gel and Molecular Sieve is used (for example, Perkin-Elmer Part Number 223-0117, or equivalent). The dryer is reconditioned monthly, after removing it from the analyzer, by flowing 50 cm³/min of dry nitrogen through it while the dryer is heated to 150°C in an oven for 12 h. (This reconditioning procedure assumes the dryer has a metal body.)

5.3.16 FILTER, F4—Sintered metal filter, to prevent grit from entering the valve (for example, Carle Number 3525, or equivalent).

5.3.17 FILTER, F5—Replaceable glass fiber filter, to filter particulates out of sample.

6. Principle of Operation—The methane analyzer (Fig. 1) measures the methane concentration in a sample injected into a carrier gas stream by the valve (V1) from a fixed volume sample loop. The stream enters the Porapak N gas chromatographic column which temporarily retains NMHC, CO₂, and

¹For example, see Federal Register, Vol. 40, No. 126, pp. 27613-27626, Part 86, Subpart B, Sections 86.177-1-86.177-23, June 30, 1975.

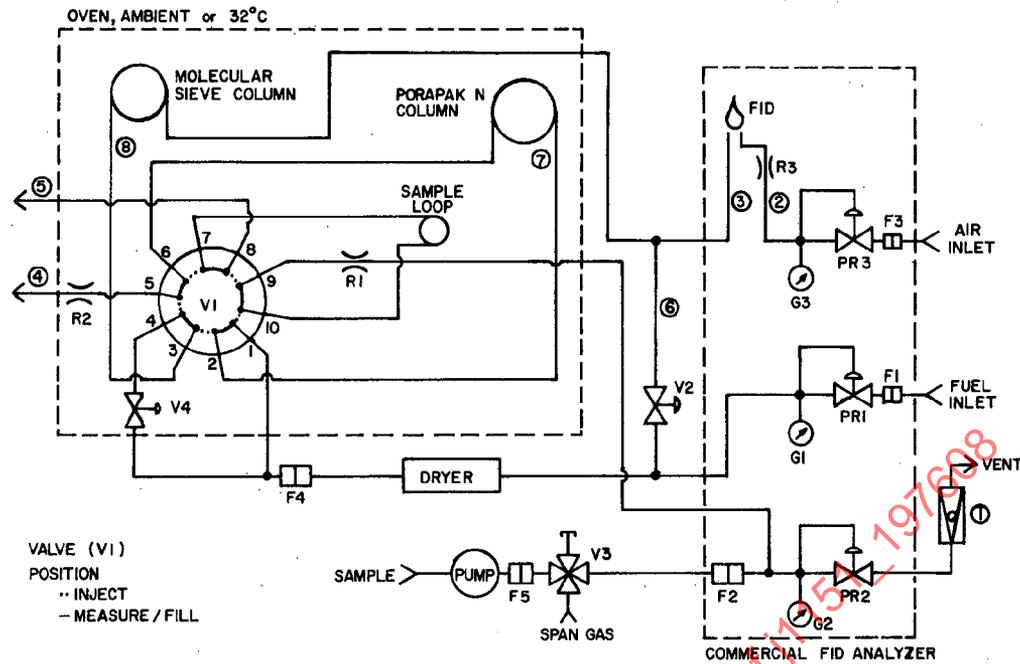


FIG. 1—METHANE ANALYZER

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 back-flushed to waste by switching the valve (V1). 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 to inject the next sample. A complete cycle, from injection of one sample to injection of a second, can be made in approximately 75 s. Automation of injection and back-flush switching assures reproducible peak times and shapes and is easily accomplished.

7. Instrument Operating Procedure—In general, the manufacturer's instructions for operation of the FID HC analyzer should be followed. Optimization of detector response (fuel and air to the flame) should be performed after modification, with carrier gas flowing, as described in paragraph 7.3.3.

7.1 FID Analyzer Modification—The fuel line is disconnected from the burner, the fuel restrictor is removed and the fuel inlet to the burner is plugged. The sample capillary is removed.

7.2 Component Assembly—The assembly of the components for the methane analyzer is shown in Fig. 1. The sample and switching valve V1, restrictor valve V4, sample loop, restrictors, and the two GC columns are installed in the oven. The outlet of restrictor R2 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, the instrument is ready for adjustment of operating parameters.

7.3 Operating Parameters—The timing sequence is determined by the flow rates of the carrier gas, the gas holdup volume of 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 should 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 Column oven temperature—ambient or near ambient (for example, 32°C), but should preferably be in a controlled temperature (heated/air conditioned) location. The temperature control setting that maintains 150°C for use in conditioning columns should be ascertained before column installation.

7.3.1.2 Fuel carrier (Hydrogen/helium mixture—40%/60% or the mixture specified in SAE J254 is recommended, 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 40–65 cm^3/min . The flow is readily measured

TABLE 1—TYPICAL FLOW RATES

Location (Fig. 1)	Valve V1 Position	
	Inject	Measure/Fill
	Flow Rate— cm^3/min (room pressure and temperature)	
1. Sample Bypass Vent	1900	1900
2. Burner Air	350	350
3. Total Burner Fuel	86	85
4. Back Flush	58	58
5. Sample	65	60
6. Makeup Fuel	30	30
7. Porapak N Column	56	58
8. Molecular Sieve Column	56	55

with a soap bubble flow meter. Typically, the pressure regulator PR1 will be set at approximately 140 kPa (20 psig). Turn valve V1 to the measure/fill 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 back-flush flow rate through restrictor R2 to confirm that it is approximately equal (within 25%) to the flow rate through the columns into the FID burner. If the flow rate is not within this range, restrictor R2 needs to be changed. Open valve V2 to provide a total mixed-fuel flow to the FID burner of 80–100 cm^3/min .

7.3.1.3 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 . Typically this pressure regulator, PR3, will be set at approximately 110 kPa (16 psig). Since all FID units are unique, these settings of fuel and air can be adjusted with 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.

7.3.1.4 Sample—Adjust the flow of span gas or sample so that the flow discharged to the vent is about 2000 cm^3/min (4 scfh). With valve V1 in the measure/fill position, adjust back-pressure regulator PR2 so that the flow from port 8 of valve V1 is 40–80 cm^3/min . The pressure reading on gauge G2 should be in the range of 7–35 kPa (1.0–5.0 psig). If it is not in this range, restrictor R1 needs to be changed.

7.3.2 TIMING SEQUENCE—The analysis starts with valve V1 in the measure/fill position. In this position the sample loop is flushed and filled with sample (flow rate 40–80 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 long enough for all the methane to elute from the Porapak N column. If valve V1 is in the inject position too long, CO₂ will also elute from the Porapak N column, pass onto the Molecular Sieve column, be absorbed by and gradually deactivate the Molecular Sieve column. With a typical instrument at a column flow rate of 55 cm³/min, it was found that if valve V1 was manually switched from inject to measure/fill 11 s after injection, the methane peak height was 53% of its ultimate height measured with a later valve switching. If valve V1 was switched 13 s after injection, the methane peak height was 99% of its ultimate height, and if valve V1 was switched 14 s after injection the ultimate peak height was reached. For this instrument, then, valve V1 was programmed to stay in the inject position for 15 s. (A thermal conductivity detector was temporarily inserted between port 3 of valve V1 and the Molecular Sieve column of this typical instrument. With an exhaust gas sample and valve V1 kept in the inject position, the air peak emerged from port 3 at 6 s after injection, the CH₄ peak emerged at 11 s, two extremely small unidentified peaks emerged at 18 and 27 s, and CO₂ started to emerge at 41 s with the peak reached at 50 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. Fig. 2 shows a gas chromatogram obtained with this system. (In normal use a slower chart speed is used.) With valve V1 in the measure/fill 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 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 75 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 rate 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 at six month intervals.

7.4 Calibration—Each six-bag test series is calibrated with a span gas of methane in air.

Typically, a FID analyzer requires only a one-point calibration since response is generally linear with methane content of sample. However, this should be verified for each FID because some instruments at certain conditions are 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. Plot CH₄ peak heights above the baseline against ppm CH₄ of the calibration gas. If a linear response with zero intercept is obtained, no calibration curve will be needed. (A typical instrument was checked with a series of ten span gases whose concentrations ranged from 2.6–120 ppm methane in air. A plot of peak heights against ppm CH₄ yielded a straight line with a zero intercept. The standard deviation from the straight line was equivalent to 0.17 ppm CH₄.) The calibration curve should be re-determined after the FID burner is serviced or at six month intervals, whichever comes first.

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7.5 Emission Measurement Procedure—Six methane analyses may be made in 7.5 min. It is also advisable to include a span gas measured before and after the sample series. All these samples may be handled automatically. The instrument may be located near the CVS in order to minimize the sampling distance. 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. Methane concentrations are measured directly, NMHC concentrations can be determined by the difference between an independent total hydrocarbon concentration measurement and the methane concentration.

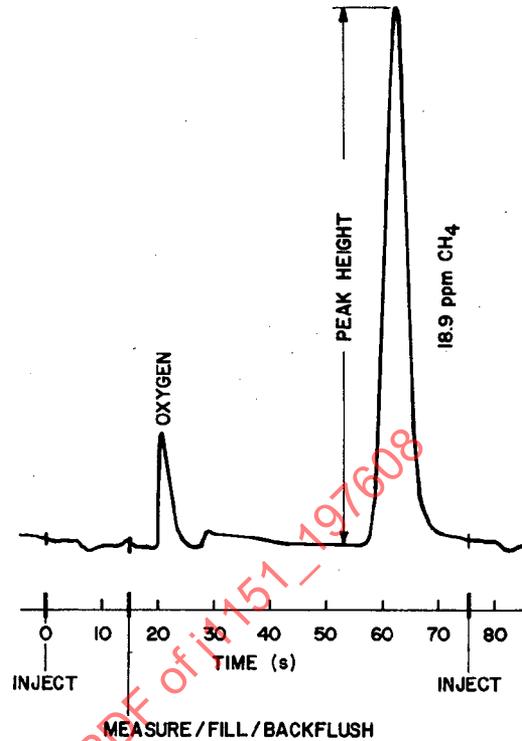


FIG. 2—TYPICAL METHANE ANALYSIS GAS CHROMATOGRAM

7.6.1 METHANE—The following example illustrates the method of calculation:

Span—18.9 ppm C methane—50.0 chart divisions

Bag Analysis

Methane—25.0 chart divisions

Bag Concentration Calculation

$$\text{Methane} = 18.9 \times \frac{25.0}{50.0} = 9.45 \text{ ppm C}$$

For calculating the mass of methane, its density at 20°C (68°F) and 101.32 kPa (760 mm Hg) pressure should be taken to be 667 g/m³ (18.89 g/ft³).

7.6.2 NON-METHANE HYDROCARBON—NMHC data analysis is accomplished with calculation techniques similar to those used for total HC CVS bag emission data analysis. The following example illustrates the method of calculation:

Span—18.9 ppm C methane or

6.3 ppm C₃ equivalent—50.0 chart divisions

Bag Analysis

Methane—25.0 chart divisions

Total HC—27.52 ppm C₃

Bag Concentration Calculations

$$\text{Methane} = 6.3 \times \frac{25.0}{50.0} = 3.15 \text{ ppm C}_3$$

NMHC—(total HC ppm C₃ - methane ppm C₃)

$$= 27.52 - 3.15 = 24.37 \text{ ppm C}_3$$

The exhaust sample and the dilution-air bags should be analyzed and the NMHC concentrations used for calculation of mass emissions as directed in the Federal Register for hydrocarbon.

It can be noted that, in general, the sum of the methane mass emissions and the calculated NMHC mass emissions will not equal the total calculated HC mass emissions. This is because the FID analyzer measures carbon mass and not hydrocarbon mass. The relation between these two masses depends on the carbon/hydrogen ratio of the hydrocarbons in the exhaust gas and this is not determined for each sample. Instead, a nominal value for the carbon/hydrogen ratio is assumed in the Federal Register.

8. Instrument Performance Specifications

8.1 Noise—The instrument shall be run for 20 min with valve V1 remaining in the measure/fill position. The peak-to-peak noise and drift of the baseline shall not exceed the equivalent of 0.16 ppm methane. (With a typical instrument the peak-to-peak noise and drift was 0.07 ppm methane.)

8.2 Precision—A span gas containing about 20 ppm methane in air shall be repeatedly read on the instrument for a period of 40 min. The standard