

GAS ANALYSIS BY GAS CHROMATOGRAPHY USING A TWO - INJECTION TECHNIQUE

UOP Method 709-70

SCOPE

This is a method for determining most of the components, including low concentrations of total $C_6 +$ hydrocarbons, normally found in a wide variety of gaseous hydrocarbon mixtures obtained from refining processes or from natural sources. It may be used as an alternate to UOP Method 539 except when the distribution of ethylene, ethane and carbon dioxide is required. Butene-1 is not resolved from isobutylene by either method and argon is determined as a composite with oxygen. The instrumentation is less elaborate than that described in UOP Method 539 and requires only slight modifications to a standard chromatograph. The lower limit of detection for a single component is 0.1 mol-%.

OUTLINE OF METHOD

All the constituents of a total gas sample cannot be resolved by a single chromatographic column. Therefore, in this procedure, 2 columns are connected in series with appropriate coupling valves to a thermal conductivity detector. Each column is used to separate a specific portion of the total sample. The first column is able to resolve gases in the $C_2 - C_5$ range. The second column separates the light gases: H_2 , $O_2 + A$ (composite), N_2 , CH_4 and CO .

Two injections of sample are required to obtain a complete analysis. The first time, a measured volume of sample is injected into Column 1 only; Column 2 is by-passed. The light gases elute as a single unresolved peak, but the $C_2 - C_5$ components are resolved and recorded. After normal pentane has eluted, the flow through the first column is reversed and the C_5 olefins, along with the $C_6 +$ hydrocarbons, are backflushed through the detector and recorded as a single composite peak.

The sample is injected a second time with Columns 1 and 2 coupled in series. The columns are uncoupled when the light gases have just entered Column 2. The light gases are resolved in Column 2 and recorded while Column 1 is backflushed to the atmosphere.

Quantitative results are obtained from the measured areas of the recorded peaks. The light gases are determined on an absolute basis by utilizing calibration factors obtained from the analysis of a blend of known concentrations. The $C_2 - C_6 +$ components are determined by the application of individual

IT IS THE USER'S RESPONSIBILITY TO ESTABLISH APPROPRIATE PRECAUTIONARY PRACTICES AND TO DETERMINE THE APPLICABILITY OF REGULATORY LIMITATIONS PRIOR TO USE. EFFECTIVE HEALTH AND SAFETY PRACTICES ARE TO BE FOLLOWED WHEN UTILIZING THIS PROCEDURE. FAILURE TO UTILIZE THIS PROCEDURE IN THE MANNER PRESCRIBED HEREIN CAN BE HAZARDOUS. MATERIAL SAFETY DATA SHEETS (MSDS) OR EXPERIMENTAL MATERIAL SAFETY DATA SHEETS (EMSDS) FOR ALL OF THE MATERIALS USED IN THIS PROCEDURE SHOULD BE REVIEWED FOR SELECTION OF THE APPROPRIATE PERSONAL PROTECTION EQUIPMENT (PPE).

response factors, followed by normalization of these corrected areas to 100% minus the total percentage of light gases found.

APPARATUS

Chromatographic columns

Column 1: 15 ft of 1/4-inch OD standard wall Type 316 stainless steel tubing filled with 60-80 mesh Chromosorb "P" impregnated to a 20 wt-% level with dibutyl maleate

Column 2: 6 ft of 1/4-inch OD standard wall copper tubing filled with 20-30 mesh 13X molecular sieves

Flow controller, constant upstream, variable downstream pressures. Brooks Model 8743, with No. 1 needle taper size, available from Brooks Instrument Division, Emerson Electric Co., Hatfield, Pa., 19440, or equivalent

Gas chromatograph, equipped with a thermal conductivity detector and capable of detector operation at 100 C

Recorder, 1-mv, 1-sec full-scale response

Valve, 4-port, aluminum body, Circle Seal, P-1-418, available from Norman Engineering Co., 7659 S. Western Avenue, Chicago, Ill. 60620 (3 required)

Valve, gas sampling. Loenco, Cat. No. L-208-8V, available from Infotronics Instrument Corp., 1062 Linda Vista, Mountain View, Calif. 94040, or equivalent.

Valve, Nupro, fine metering, 1/8-inch Swagelok, SS, Cat. No. SS2MA, available from Dearborn Valve and Fitting Co., 210 Greenwood Ave., P.O. Box 56, Glenview, Ill. 60025, or equivalent (3 required)

REAGENTS AND MATERIALS

Calibration Blends

1. 60 mol-% hydrogen, 10 mol-% nitrogen, 10 mol-% methane, 10 mol-% carbon monoxide, 10 mol-% ethane
2. 80 mol-% hydrogen, 20 mol-% nitrogen
3. 40 mol-% hydrogen, 60 mol-% nitrogen
4. 20 mol-% hydrogen, 80 mol-% nitrogen

Suitable blends may be prepared or purchased from the Matheson Co., Inc., East Rutherford, N.J. 07073

Chromosorb "P", 60-80 mesh

Dibutyl maleate. Available from Chemical Research Services, 14 Industrial Road, Addison, IL 60101

Helium, chromatographic grade

Hydrogen, 99.5% minimum purity

Molecular sieves, Type 13X, 20-30 mesh, regenerated.

PROCEDURE

Operating Conditions

Carrier gas	Helium
Carrier gas flow rate	60 ml/minute
Detector type	Thermal conductivity
Detector block temperature	100 C
Column temperature	Ambient
Recorder chart speed	1/2 inch/minute
Sample size	0.25 ml (gas)

Preparation of Apparatus

Assemble the apparatus as shown in Fig. 1. Position the 4-port valves and columns in the instrument so that all the 1/8-inch OD stainless steel connecting lines are kept as short as possible (to reduce "dead" volume). Establish the specified detector block temperature.

Four separate flow rates must be measured and adjusted so that each is 60 ml/minute. Ascertain the accuracy of these flow rates with care. If flow adjustments 1 and 2, below, differ from each other, a disrupting baseline shift will occur when Columns 1 and 2 are uncoupled during the analysis of the light gases. Refer to Fig. 1 for the following flow adjustments.

Flow adjustment 1: Set the backflush valve in the forward position (solid line) and set coupling valves Nos. 1 and 2 in the solid-line position so that the 2 columns are connected in series. Adjust the flow controller to obtain 60 ml/minute, measured at the detector exit.

Flow adjustment 2: Set the coupling valve No. 1 in the broken-line position and allow coupling valve No. 2 to remain in the solid-line position. Adjust fine metering valve "A" to obtain 60 ml/minute, measured at the detector exit.

Flow adjustment 3: Allow coupling valve No. 1 to remain in the broken-line position and set coupling valve No. 2 in the broken-line position. Adjust fine metering valve "B" to obtain 60 ml/minute, measured at the detector exit.

Flow adjustment 4: Adjust the reference flow with fine metering valve "C" to obtain 60 ml/minute, measured at the detector reference exit.

Recheck flow adjustments 1, 2, and 3 at least once to be certain they are correct.

Chromatographic Technique

C₂ - C₆ Hydrocarbons

Set the gas sampling valve in the "sample inject" position. Set the backflush valve in the forward (solid-line) position and set coupling valves Nos. 1 and 2 in the broken-line position. Allow several minutes for the system to equilibrate. Allow the gas sample to flow through the gas sampling valve at a flow rate of about 20 ml/minute for about 30 seconds. Shut off the sample source and allow several seconds for the gas sampling system to come to atmospheric pressure.

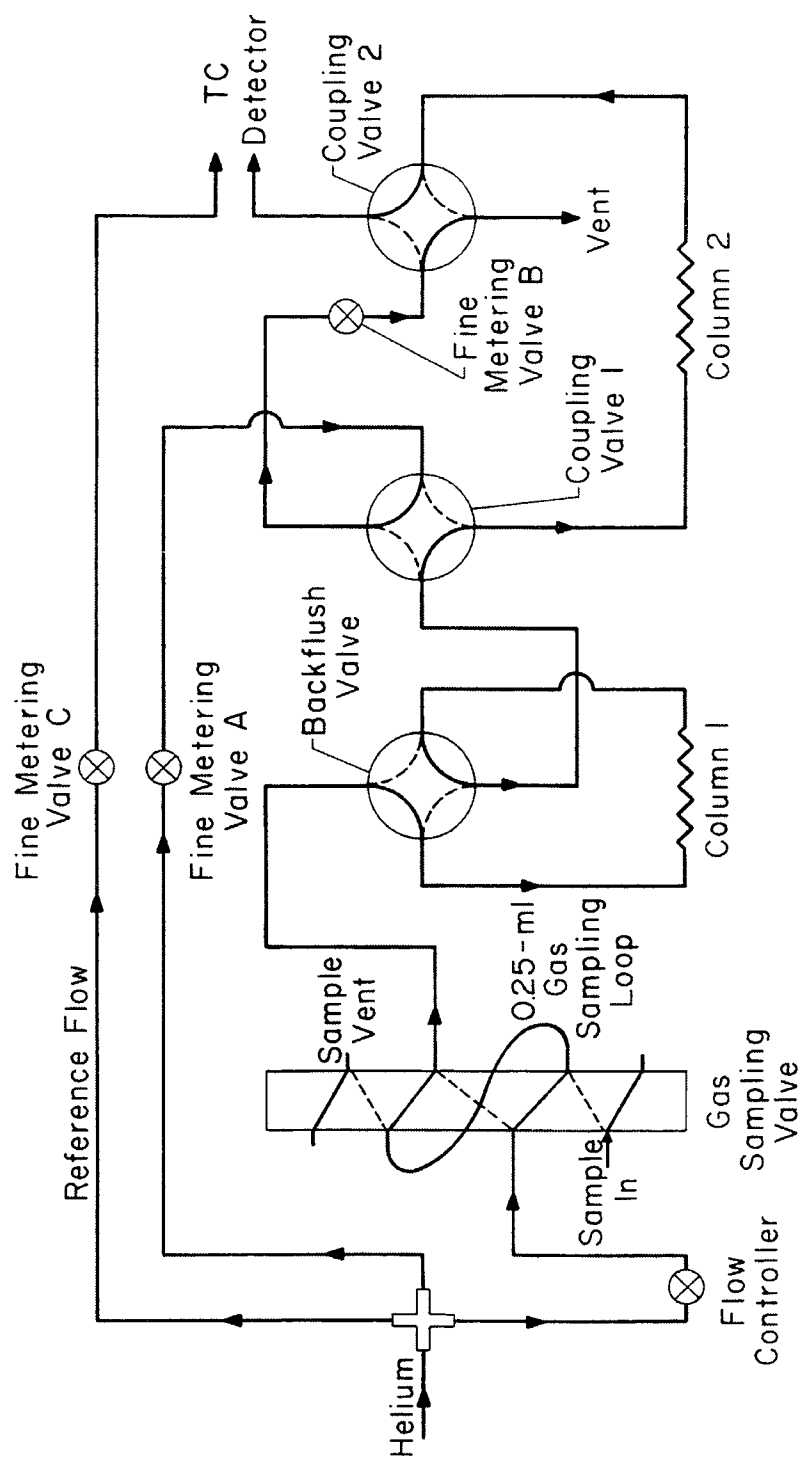


Figure 1
Instrument Flow Diagram

Inject the sample and start the recorder strip chart. The various gases will be eluted as shown in Fig. 2. After the *n*-pentane site has been reached set the backflush valve in the back-flush (broken-line) position. Reset the backflush valve to the forward position after the backflush peak has completely eluted. Measure the areas of each of the $C_2 - C_6 +$ peaks by any satisfactory technique, and, if necessary, adjust the areas for differences in attenuation. The light gas composite is not measured.

Light Gases

The chromatogram of the $C_2 - C_6 +$ portion of the sample will indicate the time at which Column 1 and Column 2 are to be uncoupled. This cut time is also noted in Fig. 2 and occurs immediately after the light gases have entered Column 2, approximately 2.5 minutes after sample injection.

Set the gas sampling valve in the "sample inject" position. Set coupling valves Nos. 1 and 2 in the solid-line position so as to connect Columns 1 and 2 in series. Allow several minutes for the system to equilibrate and then inject the sample in the same fashion described under $C_2 - C_6$ Hydrocarbons. At the time noted above, set coupling valve No. 1 in the broken-line position and then set the backflush valve in the backflush position. The light gases are resolved in Column 2 and recorded as shown in Fig. 3, while the $C_2 - C_6$ components are backflushed to the atmosphere. Measure the area of each light gas peak by any satisfactory technique.

Calibration

$C_2 - C_6$ Hydrocarbons

Factors are required to relate the response of the gases to each other. These factors have been taken from literature (see reference) and are listed in Table 1.

Table 1

<u>Compound</u>	<u>Relative Response Factor</u>
Ethane	1.661
Ethylene	1.771
Carbon dioxide	1.771
Propane	1.318
Propylene	1.318
Hydrogen sulfide	2.238
Isobutane	1.037
<i>n</i> -Butane	1.000
1-Butene	1.044 ^a
Isobutylene	
<i>trans</i> -2-Butene	1.000
<i>cis</i> -2-Butene	0.978
Isopentane	0.833
<i>n</i> -Pentane	0.808
<u>C_5 Olefins &/or $C_6 +$</u>	0.691 ^b

a. Average of 1.051 for 1-butene and 1.037 for isobutylene.

b. Based on the response for *n*-hexane.

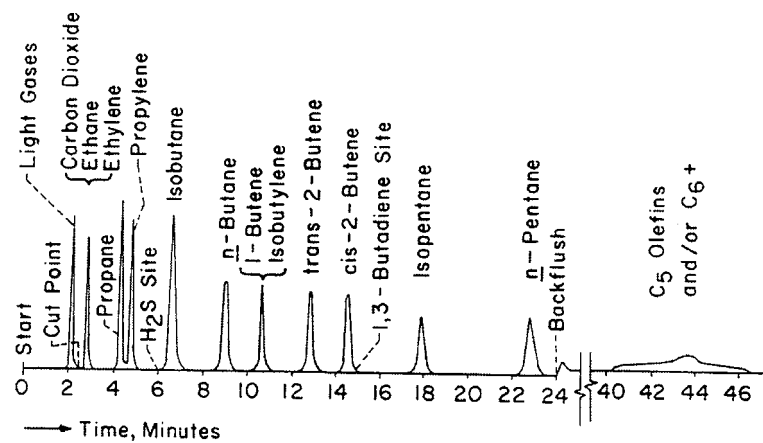


Figure 2
C₂ – C₆+ Chromatogram

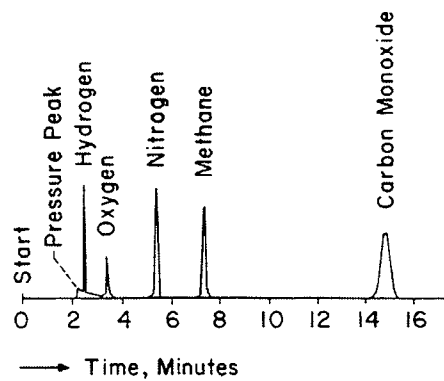


Figure 3
Light Gas Chromatogram

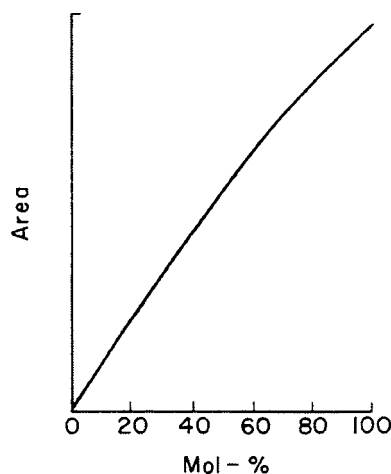


Figure 4

Hydrogen Calibration Curve

Light Gases

Hydrogen does not have a linear response in helium and therefore a calibration curve is required. Analyze each of the calibration blends listed under *REAGENTS AND MATERIALS*, and also pure hydrogen, as described under *Chromatographic Technique – Light Gases*. Determine the area for the hydrogen peak in each run and plot these areas vs. Their respective mol-% concentrations on suitable graph paper. Draw a smooth curve connecting these points. A typical calibration curve is shown in Fig. 4, only for reference, since the actual curve will differ with each individual instrument. If any indication of peak reversal is noted when the pure hydrogen is analyzed, change the sample loop so that a smaller sample volume is injected.

Quantitative results are based on the injection of a reproducible sample volume and the use of response factors to relate the peak areas obtained for the light gases to mol-%. These response factors must be determined prior to each series of analyses or at least once a day. Prepare or purchase a reference calibration blend containing known concentrations of H₂, N₂, CH₄, CO and ethane, as specified under *REAGENTS AND MATERIALS*, Blend 1. Analyze this blend as described under *Chromatographic Technique – Light Gases*. Determine the area of the H₂, N₂, CH₄ and CO peaks by any satisfactory technique, such as electronic integration or peak height times the width at one-half peak height. Calculate the response factor (mol-percent per unit of peak area) for N₂, CH₄ and CO as follows:

$$F = G/H$$

where:

F = response factor for N₂, CH₄ or CO

G = concentration of N₂, CH₄ or CO in the blend, mol-%

H = peak area for N₂, CH₄, or CO in the blend

A calibration adjustment factor for hydrogen must also be determined daily to correct the previously plotted calibration curve for instrument fluctuations. Determine from the calibration curve the area which corresponds to the percent hydrogen present in the calibration blend analyzed. Determine the adjustment factor as follows:

$$A = B/C$$

where:

A = adjustment factor for the hydrogen calibration curve

B = area determined from curve, units consistent with H, above

C = area of hydrogen peak determined from daily calibration blend, units consistent with H, above

Oxygen and argon are eluted as a single peak and are not included in the reference calibration blend. Calibration can be made for this composite peak by analyzing a sample of air which is a convenient blend containing a total of 21.88 mol-% of oxygen plus argon.

CALCULATIONS

Light Gases

Determine the mol-percent hydrogen from the prepared calibration curve after correcting the measured area for differences in daily response as follows:

$$D = EA$$

where:

D = corrected area of hydrogen peak, units consistent with H, above

E = measured area, units consistent with D, above

A = adjustment factor for hydrogen, previously defined

Calculate the mol-percent of each of the other light gas components as follows:

$$\text{Light gas components, mol-\%} = FL$$

where:

F = response factor, previously defined

L = peak area for the respective light gas, units consistent with H, above

C₂ - C₆ Hydrocarbons

Correct the area of each C₂ - C₆ peak for differences in response as follows:

$$M = PN$$

where:

M = corrected peak areas

P = peak area for each C₂ - C₆ component

N = relative response factor from Table 1

Calculate the concentration of each C₂ - C₆ component as follows:

$$\text{Component, mol-\%} = \frac{M(100 - R)}{S}$$

where:

- M** = corrected peak area, defined above
R = sum of all light gas components, mol-%
S = sum of the C₂ - C₆ corrected peak areas

PRECISION

Based on 6 replicate determinations, the estimated standard deviation (esd) in Table 2 was calculated for the gases listed.

Duplicate results should not differ by more than the allowable difference indicated (95% probability).

Table 2

Component	Level, mol - %	esd, mol - %	Allowable Difference, mol - %
Hydrogen	21	0.186	0.68
Nitrogen	7	0.087	0.32
Methane	12	0.180	0.66
Carbon monoxide	8	0.266	0.97
Propane	8	0.077	0.28
Propylene	6	0.203	0.74
Isobutane	7	0.158	0.58
<i>n</i>-Butane	6	0.074	0.27
I-Butene	6	0.264	0.96
Isobutylene			

TIME FOR ANALYSIS

The elapsed time for one analysis is 1.1 hours. The labor requirement is 1.1 man-hours.

REFERENCE

Dietz, W. A., *J. Gas Chromatogr.* **5**, 68 (1967)