

CARBON STRUCTURE OF C₇ AND LOWER BOILING HYDROCARBONS IN OLEFINIC SAMPLES BY HYDROGENATION AND CAPILLARY COLUMN GAS CHROMATOGRAPHY

UOP Method 670-68

SCOPE

This method is for determining the carbon structure of C₇ and lower boiling compounds in debutanized olefinic samples. Complete hydrogenation is accomplished directly in the chromatograph injection system, enabling a carbon structure determination to be made. The limit of detection for any single carbon structure is 0.1 wt-%. Quantitative results are obtained through the use of an internal standard.

OUTLINE OF METHOD

A sample is injected into the first column of a 2-column, 2-detector system, connected in series through a backflush valve. The first column is employed as a fractionator to separate the sample into C₇-minus and C₈-plus fractions, respectively. The C₇-minus components pass through a catalytic hydrogenation reactor where the olefins are completely saturated, then are collected and held in a trap until introduced into a capillary column analytical system. The C₈-plus fraction is backflushed out of the fractionation system. Quantitative results are obtained by comparing the peak area obtained for the internal standard to the areas obtained for the components in the sample.

APPARATUS

Beaker, aluminum, 500-ml

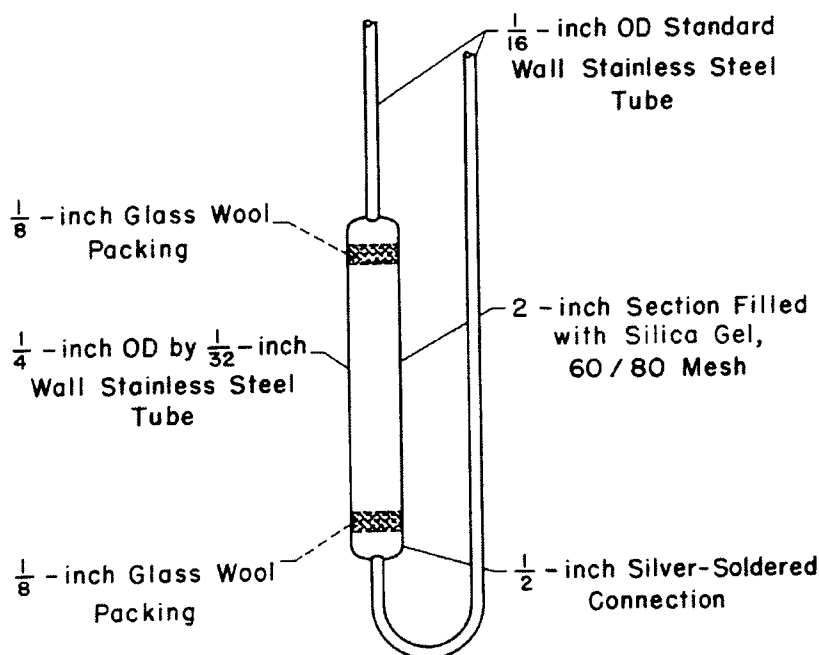
Chromatographic columns

Column No. 1: 10 ft of 1/4-inch OD standard wall copper tubing filled with 60-80 mesh silanized Chromosorb "W" which has been impregnated to the 20 wt-% level with silicone rubber (SE 30)

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**Figure 1**

Collecting Trap

Column No. 2: 200 ft of Type 316 stainless steel 0.062-inch OD x 0.010-inch ID tubing coated with a mixture of 2 parts *n*-hexadecane and 1 part "Kel F-10" by weight. (See *Preparation and Calibration of Apparatus* for preparation of the coating solution). Type 316 stainless steel Chromat ID annealed capillary tubing, available from Handy & Harman Tube Co., Inc., 25 W 753 Durfee Rd., Wheaton, Ill., is satisfactory. See *PREPARATION OF CAPILLARY COLUMN*, page 5.

Collecting trap, 2-inch x 1/4-inch OD Type 316 stainless steel packed with 60-80 mesh silica gel (see Fig. 1)

Flask, Dewar, wide mouth, pint size

Gas chromatograph. A combination of 2 chromatographs is employed. A unit equipped with a thermal conductivity detector is required for the fractionating unit. A unit equipped with a flame ionization detector and a linear splitter for capillary columns is required for the analytical unit.

Hot plate magnetic stirrer, Catalog No. S-40990, obtainable from E. H. Sargent & Co., Chicago, Ill., 60630, or equivalent

Hydrogenator insert tube, 4 inches of 1/4-inch OD Type 316 stainless steel tubing packed with 1 inch of suitable hydrogenation catalyst (see Fig. 2)

Recorder, 1-mv full scale, with dipole switch

Sample injector, any syringe or injection system capable of injecting 0.1 to 5 μ L of sample

Transformer, variable. "Powerstat", Catalog No. S-30940, obtainable from E. H. Sargent & Co., Chicago, Ill., 60630, is satisfactory.

Valve, backflush, 7-port, obtainable from Micro Tek, Baton Rouge, La., or equivalent

Valve, constant pressure. Norgren type 2AB, obtainable from Norgren Co., Denver, Colo., is satisfactory.

REAGENTS AND MATERIALS

Acetone, technical grade

Air, compressed

Chromosorb, 60-80 mesh, silanized "W"

Chromosorb "P", 60-80 mesh

Cyclohexane, 99.9% minimum purity

Dry ice

Hydrogen, purified chromatographic grade

Hydrogenation catalyst. Prepare this in the following manner: Weigh 20 ± 0.1 g of nickel nitrate hexahydrate into a 100-ml beaker. Add 40 ml of methanol. Weigh 20 ± 0.1 g of Chromosorb "P" into an evaporating dish. After the nickel nitrate crystals have dissolved, slowly pour the solution over the Chromosorb. Warm the mixture to 65 C on a hot plate and evaporate the methanol with constant stirring until the mixture appears dry.

Place approximately 3 g of the resulting mixture in the hydrogenator insert tube and hold it in position with glass wool at each end as shown in Fig. 3. Pass hydrogen carrier gas at a flow rate of approximately 60 mL/minute through the catalyst and raise the temperature by means of the cartridge heater to 350 C. Treat the catalyst at these conditions for approximately 3 hours to ensure that it has been completely reduced. After reduction, the catalyst can be used repeatedly without further treatment. Vent the excess hydrogen from this operation in a safe manner to avoid fire hazard to personnel or equipment.

Kel F-10

Methanol, CP grade

Nickel nitrate hexahydrate, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, CP grade

Nitrogen, extra dry

n-Heptane, 95% minimum purity

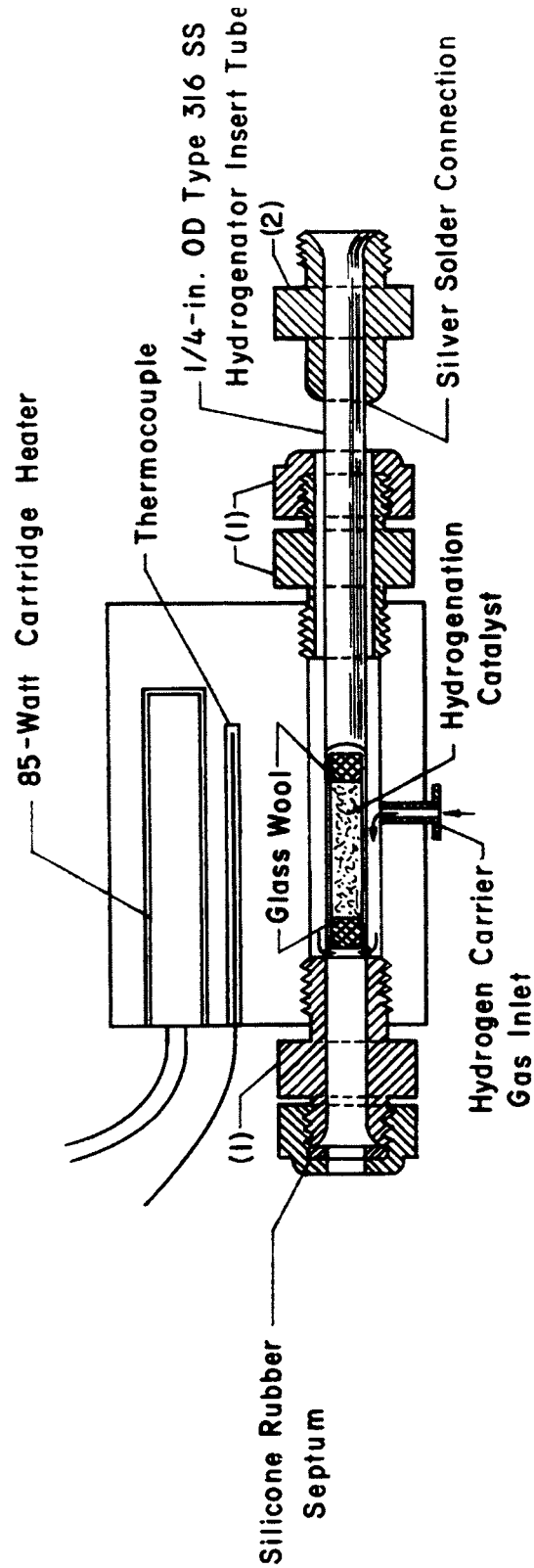
n-Hexadecane

n-Pentane, 95% minimum purity

Silica gel, 60-80 mesh

Silicone fluid, obtainable from General Electric Co., Silicone Products Dept., Waterford, N.Y.

Silicone rubber, SE 30



LEGEND

- (1)-1/4x1/8-in.NPT Swagelok Connector Drilled Out 17/64in.
- (2)-1/8x1/8-in.NPT Swagelok Connector Drilled Out 17/64in.

Figure 2

Injection Port 2 and Hydrogenator

PREPARATION OF CAPILLARY COLUMN

The following method has been found satisfactory for coating capillary columns. Connect a reservoir, 1 ft x 1/4-inch OD Type 316 stainless steel tubing (the volume of which is approximately 7 ml), to the end of a 200-ft coiled capillary column. Connect a 40-ft section of capillary tubing to the other end. Clean the capillary tubing by passing 25-30 ml of *n*-pentane through it, refilling the reservoir as required. Use sufficient nitrogen pressure, about 150 psi, to force the *n*-pentane through at a rate of 40-60 drops per minute. After the column is cleaned, release the pressure and wait 3 to 5 minutes for the pressure in the tubing to equilibrate to atmospheric.

Prepare the column coating solution as follows: Weigh 0.5 ± 0.0001 g of Kel F-10 into a 20-ml vial. Add 1.0 ± 0.0001 g of *n*-hexane and 8.5 ± 0.0001 g of *n*-pentane. Fill the reservoir with this coating solution and promptly connect it to the nitrogen cylinder. Pass the coating solution through the capillary tubing with enough pressure to obtain an elution rate of 40-60 drops per minute. When elution stops release the pressure and wait 5 minutes for the pressure within the column to equilibrate to atmospheric. Disconnect the reservoir and the 40-ft section of tubing from the capillary tubing. Stabilize the column by attaching the downstream end of the inlet of the chromatograph and pass carrier gas through it at the flow rate specified under *Operating Conditions*. Do *not* connect the exit of the column to the flame detector during stabilization since to do so will cause the detector to become contaminated. After 2 hours connect the exit end of the column to the detector and establish a stable recorder baseline.

PROCEDURE

Operating Conditions

Chromatograph 1 (Fractionating section)

Carrier gas	hydrogen
Carrier gas flow rate	60 ml/minute
Detector type	thermal conductivity
Detector block temperature	90 C
Injection port temperature	200 C
Column temperature	90 C
Recorder chart speed	1/2-inch/minute
Recorder range	1 mv full scale
Sample size	5 μ l

Chromatograph 2 (Analyzing section)

Carrier gas	hydrogen
Carrier gas flow rate	1.7 ml/minute
Detector type	flame ionization
Makeup hydrogen flow rate	15 ml/minute
Air flow rate	600 ml/minute
Detector block temperature	325-350 C
Column temperature	ambient
Hydrogenator temperature	220 C
Splitter gas flow rate	600 ml/minute
Oil bath temperature	200 C

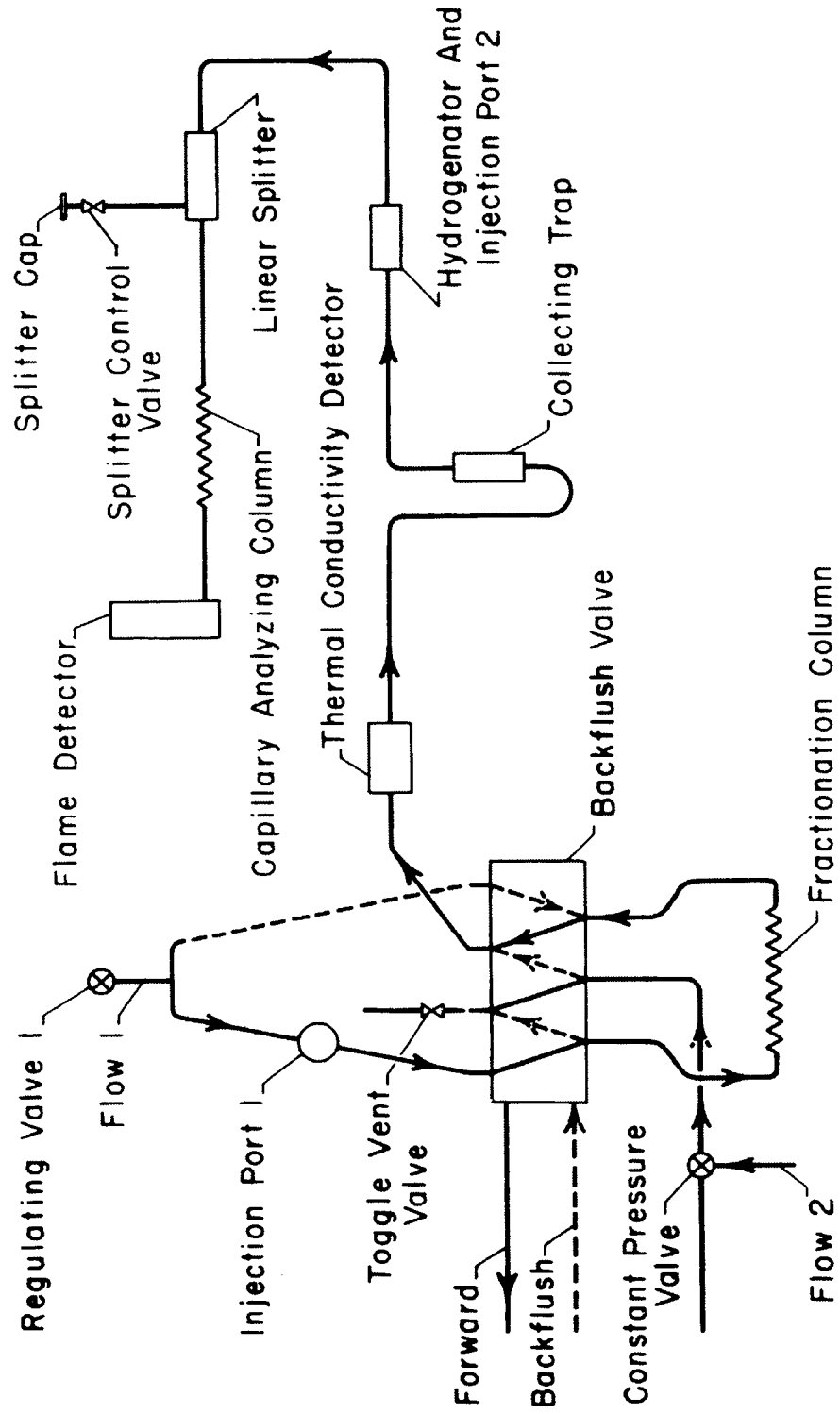


Figure 3

Schematic Diagram of Assembled Apparatus

Preparation and Calibration of Apparatus

Assemble the apparatus as shown in Fig. 1, and establish the operating conditions listed above. Adjust the flow for the fractionating column by setting the backflush valve in the back-flush position (dotted line), then open the vent valve, and adjust regulating valve No. 1 to obtain the specified flow as measured at the vent valve.

Adjust the flow through the analyzing column by setting the backflush valve in the back-flush position, then open the vent valve, disconnect the analyzing column from the flame detector, place the splitter cap on the splitter control valve, and adjust the constant pressure valve to obtain the specified flow rate as measured at the exit of the analyzing column. Reconnect the analyzing column to the flame detector. Adjust the splitter flow rate by removing the splitter cap and adjust the splitter control valve to obtain the specified flow rate as measured at the exit of the splitter control valve. The specified air flow and makeup hydrogen flow rates are set by adjusting the proper valves on the instrument.

Run a reference sample of *n*-heptane, as described in the *Chromatographic Technique* section, through the chromatograph to determine the C₇-minus cut point on the fractionating column. The fractionating column retention time for *n*-heptane has been found to be 7.5 minutes but should be checked for each specific installation. Prior to the chromatographic analyses, weigh to the nearest 0.0001 g approximately 5 wt-% of cyclohexane into the sample as an internal standard. It has been experimentally determined that response factors are not required to relate the peak area of the components determined to the peak area of the internal standard.

Chromatographic Technique

Condition the columns at operating temperatures until a stable recorder baseline is obtained. See Fig. 3 for nomenclature used in the following instructions. Prior to sample injection (1) set the backflush valve in the forward position (solid line), (2) close the vent valve, (3) place the collecting trap in the dry ice and acetone bath, (4) remove the splitter cap and (5) switch the dipole switch on the recorder to Chromatograph 1. Inject a 5- μ l sample containing the previously added internal standard into injection port No. 1 and record the start of the analysis on the recorder strip chart. After 7.5 minutes, or that period which has been determined as the C₇-minus cut point (see *Preparation and Calibration of Apparatus* section), the C₇ - minus components have passed through the hydrogenator and into the collecting trap. At this time (6) open the vent valve, (7) set the backflush valve in the backflush position (dotted line), (8) switch the dipole switch on the recorder to Chromatograph 2, (9) immerse the collecting trap in the hot oil bath and mark the start of the analysis on the recorder strip chart. After 30 seconds, (10) remove the hot oil bath from the collecting trap, and (11) wait 30 seconds more before replacing the splitter cap on the splitter control valve. The C₇-minus has been introduced into the capillary analyzing column.

The absolute retention time for the last of the C₇-minus components to be eluted from the fractionating column used to develop this method is 7.5 minutes. Table 1 lists the absolute retention times of the heptane and lighter components as recorded on the capillary analyzing column used in developing this method.

Table 1

Compound	Absolute Retention Time, minutes	Compound	Absolute Retention Time, minutes
Isobutane	4.1	2,2,3-Trimethylbutane	13.5
<i>n</i> -Butane	4.3	Cyclohexane	
Isopentane	5.2	(internal standard)	14.5
<i>n</i> -Pentane	5.7	3,3-Dimethylpentane	15.7
2,3-Dimethylbutane	8.1	2-Methylhexane	17.3
2-Methylpentane	8.3	2,3-Dimethylpentane	17.7
3-Methylpentane	9.1	3-Methylhexane	18.7
<i>n</i> -Hexane	10.2	3-Ethylpentane	19.9
2,2-Dimethylpentane	12.4	2,2,4-Trimethylpentane	21.5
2,4-Dimethylpentane	12.9	<i>n</i> -Heptane	23.6

The retention times listed should be used only as a guide. The actual retention times should be obtained experimentally for each specific chromatographic system.

CALCULATIONS

Measure the peak area of each component and calculate the respective concentration as follows:

$$\text{Component, wt-\%} = \frac{100 \text{ CW}}{\text{SA}}$$

where:

C = component peak area

W = weight of cyclohexane internal standard added to the sample, g

S = weight of sample prior to addition of internal standard, g

A = internal standard peak area

PRECISION

Based on the mean range for 7 replicates, the estimated standard deviation (esd) was calculated for 5 carbon structures at the concentrations listed in Table 2.

Duplicate results should not differ by more than the allowable difference indicated in Table 2 (95% probability).

Table 2

Carbon Structure	Concentration, wt-%	esd, wt-%	Allowable Difference, wt-%
<i>n</i> -Butane	3	0.31	1.06
2-Methylpentane	2	0.12	0.43
2, 4-Dimethylpentane	6	0.41	1.40
2, 3-Dimethylpentane	20	1.21	4.18
3-Methylhexane	6	0.39	1.34

TIME FOR ANALYSIS

The elapsed time for an analysis is 0.75 hour. The labor requirement is 0.75 man - hour.