

CARBON STRUCTURE OF C₉ AND LOWER BOILING HYDROCARBONS BY GAS CHROMATOGRAPHY

UOP Method 832-83

SCOPE

This method is for determining the carbon structure of C₉ and lower boiling hydrocarbons in cyclic-free, liquid olefinic samples. The endpoint of these samples should not exceed 216 C. Complete hydrogenation of olefins to paraffins is accomplished directly within the chromatographic injection system enabling a carbon structure determination to be made. Components in the C₁₀ to C₁₂ range that may be present in the sample are not individually identified, and are reported as a summation. The lower limit of detection for any single hydrogenated component is 0.05 mass-%.

OUTLINE OF METHOD

A sample is injected into the chromatograph through a catalytic hydrogenation reactor where olefinic hydrocarbons are completely converted to paraffinic hydrocarbons. The resulting mixture is then resolved into individual components through the use of a fused silica capillary column. The mass-% composition of the sample is obtained by using the internal normalization technique of quantitation wherein the peak areas are first corrected for differences in response and then normalized to 100%.

APPARATUS

Balance, readable to 0.1 mg

Beaker, Griffin type, 100-mL, Sargent-Welch Scientific, Cat. No. S-4675H, or equivalent

Chromatographic column, 30 m of 0.25 mm ID fused silica capillary internally coated to a thickness of 1.0 μ m with cross linked (bonded) methyl silicone DB-1, J & W Scientific, Cat. No. 122-1033, or equivalent

Cylinder, graduated, 100-mL, Sargent-Welch Scientific, Cat. No. S-24663E, or equivalent

Dish, evaporating, 195-mL, Sargent-Welch Scientific, Cat. No. S-25525-F, or equivalent

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Gas chromatograph, temperature programmable, built for capillary column chromatography utilizing a split injection system that has a glass injection port insert that may be packed with hydrogenation catalyst, and equipped with a flame ionization detector that will give a minimum peak height response of 30 μV for 0.1 mass-% of *n*-octane when operated at the stated conditions. Background noise at these conditions is not to exceed 3 μV .

Hot plate, magnetic stirrer, Sargent-Welch Scientific, Cat. No. 41001-A, or equivalent

Integrator, electronic, or equivalent equipment for obtaining peak areas. This device must integrate areas at a sufficiently fast rate so that narrow peaks typically resulting from a capillary column can be accurately measured.

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

Regulator, air, two-stage, high purity, Matheson, Model 3104-590, or equivalent

Regulator, hydrogen, two-stage, high purity, Matheson, Model 3104-350, or equivalent

Regulator, nitrogen, two-stage, high purity, Matheson, Model 3104-580, or equivalent

Sample injector, any syringe or injection system capable of injecting a 0.5 μL volume of sample. A Hamilton 701-SN-WG syringe with 2.5-cm (one-inch) needle, Point Style No. 2, Alltech Associates, has been found satisfactory.

REAGENTS AND MATERIALS

All reagents shall conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, when such specifications are available, unless otherwise specified.

Air, zero gas, total hydrocarbons less than 2.0 ppm as methane

Chromosorb P NAW, 60-80 mesh, Alltech Associates, Cat. No. 2301, or equivalent

Glass wool, silanized, Alltech Associates, Cat. No. 4037, or equivalent

Hydrocarbon standards, as necessary for component identification, see *Chromatographic Technique*, Wiley Organics, or equivalent

Hydrogen, zero gas, total hydrocarbons less than 0.5 ppm as methane

Methanol, absolute

Nickel (II) nitrate hexahydrate, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ crystals, 99.5% minimum purity

2-Methylbutane, (isopentane), 99% minimum purity

2-Methyl-2-butene, 99% minimum purity

Nitrogen, zero gas, total hydrocarbons less than 0.5 ppm as methane

Normal paraffins, C_6 through C_{10} and C_{12} , 99.5 mass-% minimum purity

PROCEDURE

Preparation of Hydrogenation Catalyst

Prepare the catalyst 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 P. Warm the mixture to 65 C on a hot plate, and in a hood or vented area evaporate the methanol with constant stirring until the mixture appears dry.

Place a sufficient quantity of the prepared catalyst in the glass injection port insert so that the packed portion, when the insert is installed in the injector, is completely heated and does not obstruct the syringe needle upon injection of the sample. Retain the packing in the insert with silanized glass wool plugs. Place the insert in the injection port and pass hydrogen carrier gas at a flow rate of approximately 100 mL/min through the catalyst. Raise the temperature by means of the injection port heater to 350 C. Treat the catalyst at these conditions for approximately 3 hours to ensure that it has been completely reduced after which the catalyst can be used repeatedly without further treatment unless exposed to air. Vent the excess hydrogen from this operation in a safe manner to avoid fire hazard to personnel or equipment.

Confirm the successful preparation and conditioning of the hydrogenation catalyst by analyzing a 50:50 mixture of 2-methylbutane and 2-methyl-2-butene as described in *Chromatographic Technique*. If the catalyst is functioning properly the 2-methyl-2-butene will be completely hydrogenated to 2-methylbutane and only one peak will appear on the chromatogram. If the catalyst is not functioning properly, two peaks will result.

Operating Conditions

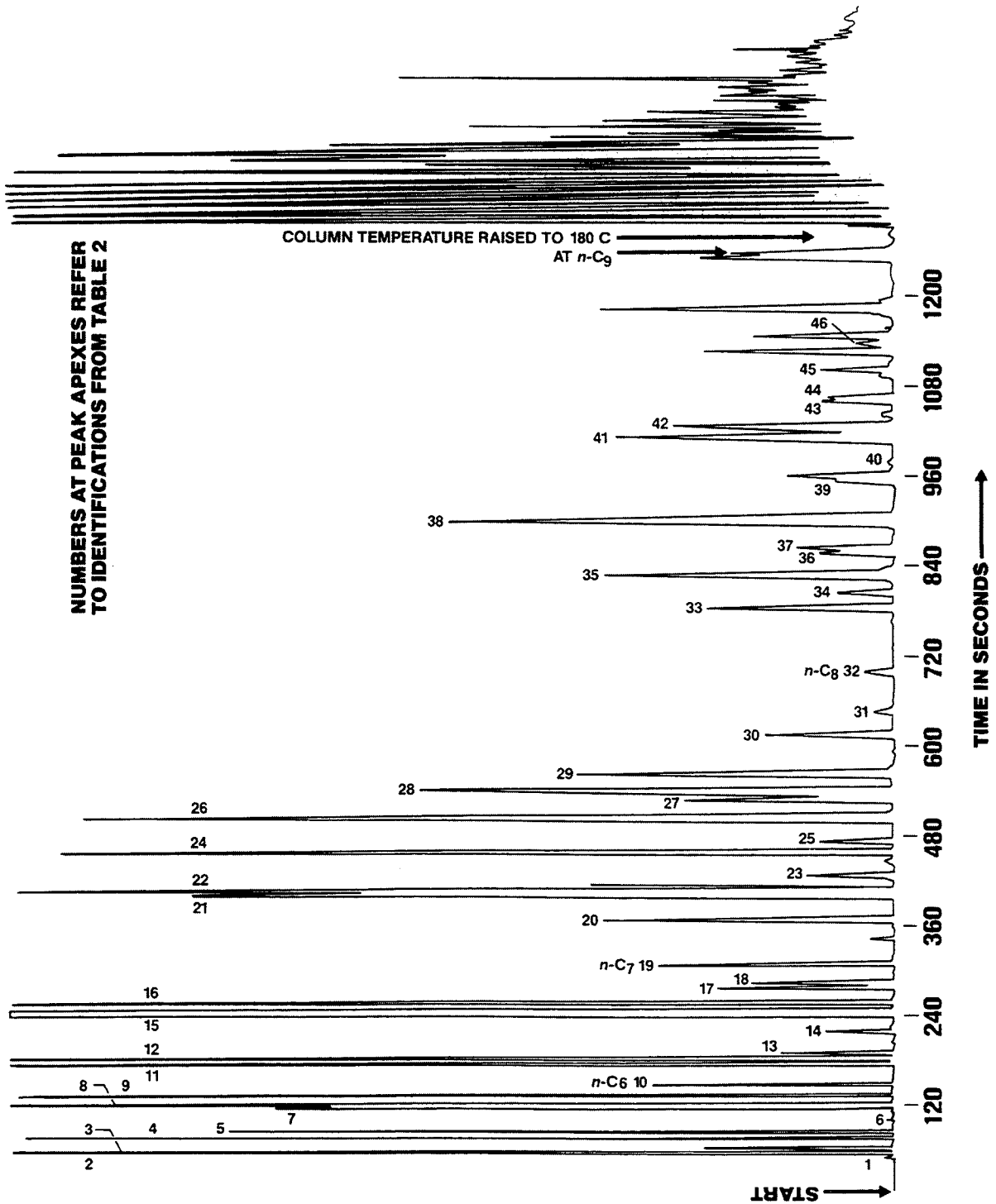
The operating conditions for this analysis are given in Table 1.

Table 1

Carrier gas	hydrogen
Carrier gas linear velocity (in the column)	34 cm/sec (1mL/min flow rate)
Detector temperature	260 C
Detector Gasses	
Hydrogen flow rate^a	30 mL/min
Air flow rate^a	300 mL/min
Make-up gas	nitrogen
Make-up flow rate^a	30 mL/min
Injection port temperature	260 C
Split ratio	50:1
Column temperature program	
Initial temperature	40 C
Initial time	10 min
Program rate^b	2 C/min
Final temperature	180 C
Sample size	0.5 μL

^a Optimum flow rates may depend upon the specific gas chromatograph.

^b After the *n*-nonane has eluted immediately raise the column temperature to 180 C. This may be automated if the gas chromatograph has a multi-level programmer.



Typical Chromatogram

Chromatographic Technique

Pack the injection port insert with hydrogenation catalyst and pretreat as described in *Preparation of Hydrogenation Catalyst*. Install the column and establish the specified operating conditions. Purge the column with hydrogen and program the column oven at 2C/min to 180 C. Maintain this temperature until a stable recorder baseline has been established at the required sensitivity. Cool the column oven to 40 C. Inject 0.5 μ L of sample and immediately start the recorder, integrator and column temperature programming sequence. After the elution of *n*-nonane, immediately raise the column temperature to 180 C. Hold at this temperature until all components are eluted.

Identify the component peaks from the resultant chromatogram. A typical chromatogram is shown in the attached figure. Retention times of identified components are listed in Table 2. Although the retention order should remain the same, absolute retention times can be expected to vary between chromatographic systems. Since all possible isomers, especially in the C₉ range, have not been identified, use hydrocarbon standards as necessary to confirm specific retention sites.

Table 2
Retention Times of Identified Compounds

Compound	Peak Number on Figure	Absolute Retention Time, sec.	Compound	Peak Number on Figure	Absolute Retention Time, sec.
Propane	1	58	2,3,3-Trimethylpentane	25	481
Isobutane	2	63	2,3-Dimethylhexane	26	485
<i>n</i> -Butane	3	67	2-Methylheptane	27	537
Isopentane	4	84	4-Methylheptane	28	549
<i>n</i> -Pentane	5	95	3-Methylheptane	29	571
2,2-Dimethylbutane	6	109	2,2,5-Trimethylhexane	30	623
2,3-Dimethylbutane	7	128	2,2,4-Trimethylhexane	31	654
2-Methylpentane	8	130	<i>n</i> -Octane	32	706
3-Methylpentane	9	142	2,3,5-Trimethylhexane	33	791
<i>n</i> -Hexane	10	156	2,2-Dimethylheptane	34	812
2,2-Dimethylpentane	11	183	2,2,3,4-Tetramethylpentane and/or		
2,4-Dimethylpentane	12	191	2,4-dimethylheptane	35	835
2,2,3-Trimethylbutane	13	198	4,4-Dimethylheptane	36	864
3,3-Dimethylpentane	14	227	2,6-Dimethylheptane	37	871
2,3-Dimethylpentane	15	254	2,5-Dimethylheptane	38	908
3-Methylhexane	16	265	2,2,3,3-Tetramethylpentane	39	960
2,2,4-Trimethylpentane	17	284	3,3,4-Trimethylhexane	40	984
3-Ethylpentane	18	291	2,3-Dimethylheptane	41	1020
<i>n</i> -Heptane	19	316	2,3,3,4-Tetramethylpentane	42	1034
2,2-Dimethylhexane	20	375	4-Methyloctane	43	1067
2,5-Dimethylhexane	21	408	2-Methyloctane	44	1072
2,4-Dimethylhexane	22	415	3-Ethylheptane and/or		
3,3-Dimethylhexane	23	435	3,3-dimethylheptane	45	1109
2,3,4-Trimethylpentane	24	467	3-Methyloctane	46	1119
			<i>n</i> -Nonane	47	1259

CALIBRATION

The response of flame ionization detectors is directly proportional to mass for saturated liquid hydrocarbons. However, some capillary inlet splitters do not split the sample linearly across a wide boiling range. Therefore, response factors for each carbon number must be determined from a blend and applied to components of the same respective carbon number in the sample.

Prepare a quantitative blend containing C₆ to C₁₀ normal paraffins by weighing approximately equal quantities of each to the nearest 0.1 mg. Dilute this blend approximately 1:10 in *n*-C₁₂. Chromatograph the diluted blend as described under *Chromatographic Technique*. From 3 replicate runs determine the average area of each C₆ to C₁₀ normal paraffin. Calculate the relative response factor for these components with *n*-decane as reference using the following formula.

$$F = \frac{AB}{CD}$$

where:

- A** = *n*-paraffin of given carbon number, mass-%
- B** = area of *n*-decane peak
- C** = *n*-decane, mass-%
- D** = area of *n*-paraffin of given carbon number, units consistent with B, above
- F** = relative response factor

Determine the relative response factors monthly and whenever instrument changes are made. For the carbon structure of compounds in the C₃ to C₅ range, use the C₆ relative response factor. For compounds in the C₁₀ to C₁₂ range use the relative response factor for C₁₀.

CALCULATIONS

Obtain the peak area for each component through carbon number C₉. Obtain an area summation for C₁₀, C₁₁ and C₁₂ components. The mass-% composition of the sample is calculated to the nearest 0.1 mass-% using the following formula:

$$\text{Component, mass-\%} = 100 \frac{PF}{T}$$

where:

- P** = single component area (C₃-C₉) or summation (C₁₀-C₁₂)
- F** = relative response factor for a specific carbon number
- T** = sum of the products PF for all components in the sample

PRECISION

Based on 9 replicate determinations, the estimated standard deviation (esd) was calculated for 8 selected compounds at the concentrations listed in Table 3.

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

Table 3
Precision Data

Compound	Concentration, mass-%	esd, mass-%	Allowable Difference, mass-%
Isobutane	1.2	0.038	0.12
Isopentane	2.7	0.036	0.11
3-Methylpentane	0.2	0.008	0.03
2,3-Dimethylpentane	14.7	0.033	0.42
3-Ethylpentane	29.1	0.257	0.82
2,4-Dimethylhexane	2.2	0.089	0.29
4-Methylheptane	0.3	0.007	0.02
2,2,5-Trimethylhexane	1.0	0.011	0.04

TIME FOR ANALYSIS

The elapsed time and labor requirement for one analysis are identical, 0.8 hour.

SUGGESTED SUPPLIERS

Alltech Associates, 2051 Waukegan Rd., Deerfield, IL 60015

J & W Scientific Inc., 3871 Security Park Dr., Rancho Cordova, CA 95670

Matheson, P. O. Box 96, Joliet, IL 60434

Sargent-Welch Scientific Co., 7300 N. Linder Ave., Skokie, IL 60077

Wiley Organics, 4654 Kenny Rd., Columbus, OH 43220