CARBON NUMBER DISTRIBUTION OF PARAFFINS, NAPHTHENES AND AROMATICS BY GC

UOP Method 870-90

SCOPE

This is an automated method for determining the distribution of paraffins, naphthenes and aromatics by carbon number in hydrocarbon fractions having an endpoint of 200 C or less (C_3-C_{11}) (see *NOTE*). C_{12} paraffins and naphthenes at concentrations less than 3% can be determined. C_9+ aromatics are reported as a group. Olefins, if present, are hydrogenated and the resultant saturates are included in the paraffin and naphthene distribution. The lower limit of detection for a single carbon number hydrocarbon type is 0.05 mass- or liquid volume (LV)-%.

OUTLINE OF METHOD

The sample is injected into a gas chromatographic system that is equipped with three packed columns and appropriate valving. The first column is polar, typically packed with OV-275 on Chromosorb; the second column is non-polar, typically packed with OV-101 on Chromosorb and the third column is selective, typically packed with specially treated molecular sieves. Initially, the polar and selective columns are connected in series. After the elution of C_{11} saturates from the polar column, the polar column flow is stopped, holding the aromatics until the paraffins and naphthenes have eluted from the selective column. The aromatics are then eluted from the polar column in 3 fractions, each fraction being separated on the non-polar column.

Internal normalization of peak areas after correction for difference in response is used to obtain a mass- or LV-% distribution of the components.

APPARATUS

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used.

This method requires the use of a dedicated gas chromatographic system that is configured for automated hydrocarbon types analysis and is capable, via valve switching, of multi-column operation. The suggested GC is supplied complete with columns, valves and programming specific to this analysis.

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).

Balance, readability 0.1-mg

Gas chromatograph, Hewlett-Packard, Model 5890 modified by Analytical Controls as PNA analyzer, available from Analytical Controls

Integrator, electronic for obtaining peak areas. An integrator may be included with the gas chromatograph.

Oxygen remover, Oxy-Trap, Alltech Associates, Cat. No. 4001. An oxygen remover in the carrier gas line ensures optimum column life.

Recorder, 1-mv full scale, 1-sec or less full-scale response. A recorder may be included with the gas chromatograph.

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

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

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

Sample injector, any syringe or injector capable of introducing a 0.2-μL volume of sample, such as a Hamilton 701-NWG syringe, Alltech Associates

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.

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used.

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

Benzene, 99.9% minimum purity, Wiley Organics, Cat. No. 0160.84

n-Butylcyclohexane, 99% minimum purity, Wiley Organics, Cat. No. 0419.70 (C_{10} naphthene)

Cyclohexane, 99.9% minimum purity, Wiley Organics, Cat. No. 0679.02 (C_6 naphthene)

Cyclopentane, 99.9% minimum purity, Wiley Organics, Cat. No. 745.05 (C_5 naphthene)

n-Decane, 99.9% minimum purity, Wiley Organics, Cat. No. 0812.57 (C_{10} paraffin)

Ethylbenzene, 99.9% minimum purity, Wiley Organics, Cat. No. 2379.03 (C_8 aromatic)

Ethylcyclohexane, 99.9% minimum purity, Wiley Organics, Cat. No. 2442.00 (C_8 naphthene)

n-Heptane, 99.9% minimum purity, Wiley Organics, Cat. No. 3111.00 (C_7 paraffin)

n-Hexane, 99.9% minimum purity, Wiley Organics, Cat. No. 3442.00 (C_6 paraffin)

Hydrogen, zero gas, 99.95% minimum purity, total hydrocarbons less than 0.5 ppm as methane

Isopropylcyclohexane, 99.7% minimum purity, Wiley Organics, Cat. No. 8260.52 (C_9 naphthene)

Methylcyclohexane, 99.9% minimum purity, Wiley Organics, Cat. No. 4082.00 (C_7 naphthene)

Nitrogen, zero gas, 99.99% minimum purity, total hydrocarbons less than 0.5 ppm as methane

n-Nonane, 99.5% minimum purity, Wiley Organics, Cat. No. 6782.00 (C_9 paraffin)

n-Octane, 99.9% minimum purity, Wiley Organics, Cat. No. 7056.50 (C_8 paraffin)

n-Pentane, 99.9% minimum purity, Wiley Organics, Cat. No. 7372.40 (C_5 paraffin)

Toluene (methylbenzene), 99.0% minimum purity, Wiley Organics, Cat. No. 3829.90

1,2,4-Trimethylbenzene, 99.6% minimum purity, Wiley Organics, Cat. No. 8779.00 (C_9 aromatic)

o-Xylene (1,2-dimethylbenzene), 99.8% minimum purity, Wiley Organics, Cat. No. 1240.02 (C_8 aromatic)

PROCEDURE

Install the oxygen remover in the supply line between the carrier gas source and the carrier gas inlet on the gas chromatograph.

The operating conditions for the analysis are provided in the Instruction Manual received with the instrument.

Chromatographic Technique

Installation, set-up and training are provided by the instrument supplier or its representatives. Follow the chromatographic technique outlined in the manufacturer's Instruction Manual received with the instrument. ***CAUTION: Hydrogen carrier gas leakage into the confined volume of the column oven can cause a violent explosion. It is, therefore, mandatory to test for leaks each time a connection is made and periodically thereafter***. An example of the type of chromatogram to expect is shown in the Figure. Identify each hydrocarbon type by comparison with the calibration blend, see *Calibration*. Separate incompletely resolved hydrocarbon types with a vertical line as shown. Due to column switching, a component, such as benzene, or group of components, such as C_8 aromatics, can elute at multiple retention times and hence the separate peaks or groups of peaks must be summed to obtain a total area for each component or group.

Calibration

Response factors are required to relate instrument response of the various components to mass-or LV-%. Prepare a blend as described in ASTM Method D 4307 containing the paraffin, naphthene and aromatic components at approximately the concentrations expected in the samples. Analyze the blend in duplicate using the chromatographic technique described in the manual and determine the average area for each component peak. Calculate the mass response factor for each component relative to *n*-heptane as follows:

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

where:

A = component in blend, mass-%
B = peak area of *n*-heptane