

TRACE SATURATES IN HIGH PURITY AROMATICS BY GC

UOP Method 868-88

SCOPE

This method is for determining trace paraffins and naphthenes by carbon number from C₃ through C₁₀ in olefin-free C₆, C₇ or C₈ aromatics or mixtures thereof (see Note 1). The range of detection for C₃ to C₈ paraffins or naphthenes is 2 to 2,000 mass-ppm. The range of detection for C₉ and C₁₀ paraffins and naphthenes is 100 to 2,000 mass-ppm.

OUTLINE OF METHOD

A repeatable sample volume is injected into a gas chromatograph that is equipped with a two-column chromatographic system and a flame ionization detector. The first column is polar, packed with OV-275 on Chromosorb, and the second column is selective, packed with specially treated 13X molecular sieves. Initially, the two columns are connected in series. Immediately before the elution of benzene from the polar column, the polar column is backflushed to vent while the eluted saturated hydrocarbons are analyzed on the selective column. The external standard method of quantitation is used.

APPARATUS

Balance, readability 0.1-mg

Chromatographic columns:

Column 1: 3 m of 2-mm ID (1/8-inch OD) stainless steel tubing, packed with 30% OV-275 on 60-80 mesh Chromosorb PNAW, Alltech Associates, or equivalent

Column 2: 1.6 m of 2-mm ID (1/8-inch OD) stainless steel tubing, packed with specially treated 13X molecular sieves, Analytical Controls, Part No. 50.06.530

Gas Chromatograph, built for dual packed column operation, with dual flow controllers, pressure gauges and a single flame ionization detector, capable of column temperature programming to 400 C, and equipped with a separate isothermal heated zone large enough to contain 2 rotary valves, 2 restrictor valves and a column. The detector must be capable of producing a minimum peak height response of 10 times the background noise for 2 mass-ppm of *n*-hexane when operated at the recommended conditions (see Note 2).

Integrator, electronic, or equivalent for obtaining peak areas

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).

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

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

Restrictor, fine metering valve, Nupro, Cat. No. SS-1-SG, or equivalent, 2 required (see Note 2).

Sample injector, any syringe or injection system capable of injecting a 1.0- μ L volume of sample, such as a Hamilton 701-NWG syringe, Alltech Associates, or equivalent

Stopwatch, electronic, digital, Alltech Associates, Cat. No. 4061, or equivalent

Valve, 6-port rotary, Valco Instruments Co., Model C6UWP, or equivalent, 2 required (see Note 2).

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 water mean deionized or distilled water, except where noted.

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

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

Butylcyclohexane, 99.9% minimum purity, Wiley Organics, Cat. No. 0419.71-1, or equivalent (C₁₀ naphthene)

Cyclohexane, 99.9% minimum purity, Wiley Organics, Cat. No. 0679.02, or equivalent (C₆ naphthene)

n-Decane, 99.9% minimum purity, Wiley Organics, Cat. No. 0812.57, or equivalent (C₁₀ paraffin)

Ethylcyclohexane, 99.9% minimum purity, Wiley Organics, Cat. No. 2442.00, or equivalent (C₈ naphthene)

n-Heptane, 99.9% minimum purity, Wiley Organics, Cat. No. 3111.00, or equivalent (C₇ paraffin)

n-Hexane, 99.9% minimum purity, Wiley Organics, Cat. No. 3442.00, or equivalent (C₆ paraffin)

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

Methylcyclohexane, 99.9% minimum purity, Wiley Organics, Cat. No. 4082.00, or equivalent (C₇ naphthene)

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

n-Nonane, 99.5% minimum purity, Wiley Organics, Cat. No. 6782.00 or equivalent (C₉ paraffin)

n-Octane, 99.9% minimum purity, Wiley Organics, Cat. No. 7056.50, or equivalent (C₈ paraffin)

Propylcyclohexane, 99.8% minimum purity, Wiley Organics, Cat. No. 8260.05-1, or equivalent (C₉ naphthene)

Toluene (methylbenzene), 99.9% minimum purity, Wiley Organics, Cat. No. 3829.90, or equivalent

PROCEDURE

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

The recommended operating conditions for this analysis are given in Table 1. Other conditions may be used provided they produce the required sensitivity and chromatographic separations equivalent to those shown in the Typical Chromatogram (Fig. 2).

Table 1
Operating Conditions

Carrier gas	hydrogen
Carrier gas flow rate	15 mL/min
Detector	flame ionization
Detector temperature	250 C
Injection port temperature	200 C
Hydrogen flow rate*	15 mL/min
Air flow rate*	400 mL/min
Makeup gas	nitrogen
Makeup gas flow rate*	30 mL/min
Column 1 temperature	120 C
Column 2 temperature program	
Initial temperature	100 C
Programming rate	6 C/min
Final temperature	400 C
Final time	10 min
Chart speed	0.5 cm/min
Sample size	1.0 μL repeatable

***Consult the manufacturer's instrument manual for suggested flow rates.**

Preparation of Apparatus

Instrument Set-up

Install Column 1 (OV-275), the rotary and restrictor valves in a separately heated zone with the flows configured as shown in Fig. 1. In the oven of the gas chromatograph install Column 2 (molecular sieve). ***CAUTION: Leakage of hydrogen into the confined volume of the column and valve compartments can cause a violent explosion. It is, therefore, mandatory to test for leaks each time a connection is made and periodically thereafter.*** All connecting lines are to be of minimum diameter and length and must be heated. The restrictors are required to minimize any flow disruption when the flow positions of the rotary valves are changed and must be set to provide the same back pressure as Column 2.

Establish the column flows in the following manner. Rotate Valve No. 1. to the broken-line position and fully open Restrictor No. 1. Measure flow through Column 1 (OV-275) at the vent exit of Valve No. 1. Adjust Flow Controller No. 1 to produce the recommended flow rate of 15 mL/min. Measure the flow through Column 2 (molecular sieve) at the inlet to the FID. Adjust Flow Controller No. 2 to produce the same flow as Column 1. Return Valve No. 1 to the solid-line position and proceed with the restrictor adjustment.

Restrictor Adjustment

Start with Valve No. 1 and No. 2 in the solid-line position. Note the pressure reading on Pressure Gauge No. 1. Rotate Valve No. 2 to the broken-line position and adjust Restrictor No. 2 until Pressure Gauge No. 1 indicates the same value as noted earlier. Return Valve No. 2 back to the solid-line position and rotate Valve No. 1 to the broken-line position and note the pressure reading on Pressure Gauge No. 2. Return Valve No. 1 to the solid-line position and adjust Restrictor No. 1 until Pressure Gauge No. 2 indicates the same value as noted earlier.

Column Conditioning

With Valve No. 1 in the broken-line position, condition Column 2 (molecular sieve) at 100 C for one hour. Then program the column temperature up to 400 C at 6 C/min and hold that temperature until a stable recorder baseline is established at the required sensitivity. At the same time condition Column 1 (OV-275) at 120 C in the heated zone. Allow Column 2 to cool to 100 C and rotate Valve No. 1 to the solid-line position.

Cut-Time Determination

With Valve No. 1 in the solid-line position and Valve No. 2 in the broken-line position, inject 1.0 μL of benzene into Injection Port 1. Determine the time from injection at which benzene begins to elute, and subtract six seconds from this value. This time is defined as T. Redetermine time, T, daily during the first week of operation and weekly thereafter.

Chromatographic Technique

Inject a repeatable volume of sample, nominally 1.0 μL , into Injection Port 1 of the gas chromatograph with both valves in the solid-line position. Immediately start the temperature programmer, integrator and recorder. At time T, rotate Valve No. 1 to the broken-line position. A typical chromatogram is shown in Fig. 2.

Determine the relative density of the sample by ASTM Method D 4052 or other suitable technique.

Calibration

The external standard technique is used for calibration. Quantitative results are based on the injection of a repeatable volume of sample and standard, and the use of response factors to relate peak areas obtained to mass-ppm. Prepare a calibration blend as described in ASTM Method D 4307 to contain representative paraffin and naphthene components (see *REAGENTS AND MATERIALS*) in toluene at approximately the concentrations expected in the samples. Determine the relative density of the blend by ASTM Method D 4052 or other suitable technique. Analyze the blend in duplicate as described under *Chromatographic Technique* and determine the average area for each paraffin and naphthene peak. In the same manner analyze the toluene and make appropriate corrections to the blend if any paraffins and naphthenes are present in the toluene. Calculate the mass response factor for each component using the following equation:

$$F = \frac{A}{B}$$

where:

- A** = concentration of component in blend, mass-ppm
- B** = average peak area of component
- F** = response factor for component, mass-ppm/unit area

Determine response factors, as directed above, daily for each instrument used. Use the response factor of C₆ paraffins for C₃, C₄ and C₅ paraffins. Use the response factor of C₆ naphthenes for C₅ naphthene.

CALCULATIONS

Calculate the concentration of each component to the nearest mass-ppm using the following equation:

$$\text{Component, mass-ppm} = \frac{EFS}{D}$$

where:

- D** = relative density of sample
- E** = component peak area
- F** = response factor, previously defined
- S** = relative density of calibration blend

NOTES

1. C₃ and C₄ paraffins can be calculated but the determined concentrations may be in error due to the instability of these compounds in the sample. If samples are known to contain C₃ and C₄ paraffins, and a reliable value is required, precautions must be taken in the handling of the sample to maintain its integrity.

2. A suitable gas chromatograph is a Hewlett-Packard Model 5880A with HP 19358D Option 601. This option includes the separate isothermal heated zone, the two required valves and one of the two required restrictors. This gas chromatograph also includes a recorder and, if the Level 4 option is specified, an integrator.

PRECISION

Repeatability

Based on two tests performed by each of two analysts, on each of two days (8 tests) in one laboratory, the within-laboratory estimated standard deviations (esd) were calculated for components at specific concentrations and are listed in Table 2. Two tests performed in the one laboratory by different analysts on different days should not differ by more than the allowable difference values listed in Table 2 at the concentrations shown.

Table 2

Component	Concentration, mass-ppm	Within-Lab esd, mass-ppm	Allowable Difference, 95% Probability, mass-ppm
C₅ Paraffins	29	1.5	5
C₆ Naphthenes	96	1.9	6
C₆ Paraffins	100	2.4	8
C₇ Naphthenes	180	3.3	11
C₇ Paraffins	201	4.9	16
C₈ Naphthenes	207	3.7	12
C₈ Paraffins	307	5.1	17
C₉ Naphthenes	334	3.7	12
C₉ Paraffins	477	5.3	17
C₁₀ Naphthenes	451	5.7	19
C₁₀ Paraffins	378	7.0	24

Reproducibility

There is insufficient data to calculate the reproducibility of the test at this time.

TIME FOR ANALYSIS

The elapsed time for one analysis is 1.4 hours. The labor requirement is 0.6 hour.

REFERENCE

ASTM Methods D 4052 and D 4307, www.astm.org

SUGGESTED SUPPLIERS

Alltech Associates, Inc., 2051 Waukegan Rd., Deerfield, IL 60015
 Analytical Controls, Inc., 3448 Progress Dr., Bensalem, PA 19020
 Hewlett-Packard, 1200 E. Diehl Road, Naperville, IL 60566
 Matheson, P.O. Box. 96, Joliet, IL 60434
 Nupro Company, 4800 East 345th St., Willoughby, OH 44094
 Valco Instruments Co., Inc., P.O. Box 55603, Houston, TX 77055
 Wiley Organics, Inc., 4654 Kenny Road, Columbus, OH 43220

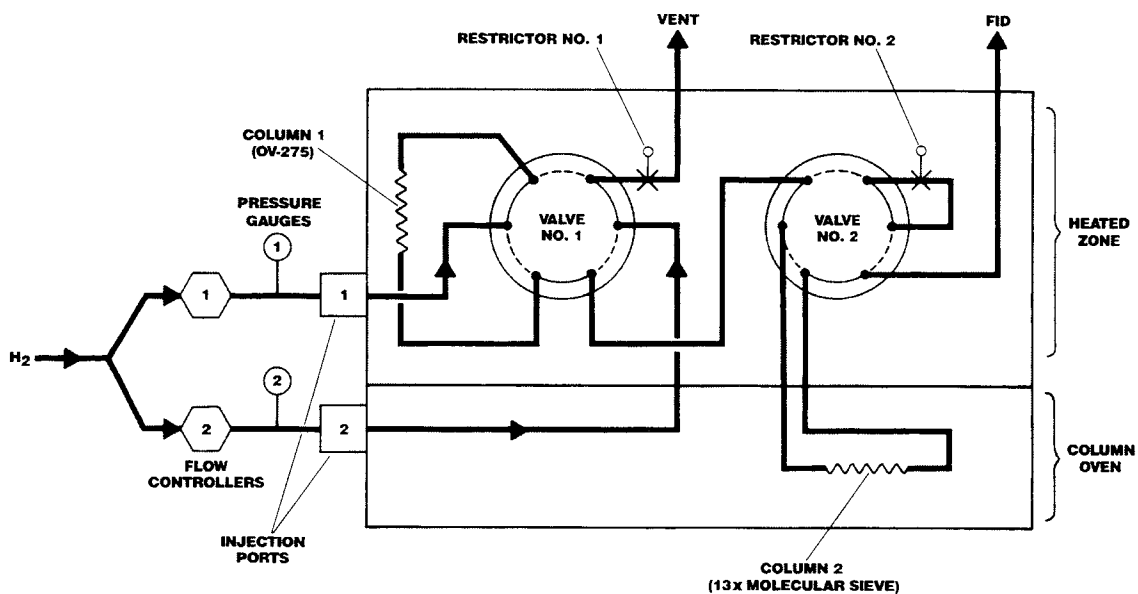


Figure 1
Flow Diagram

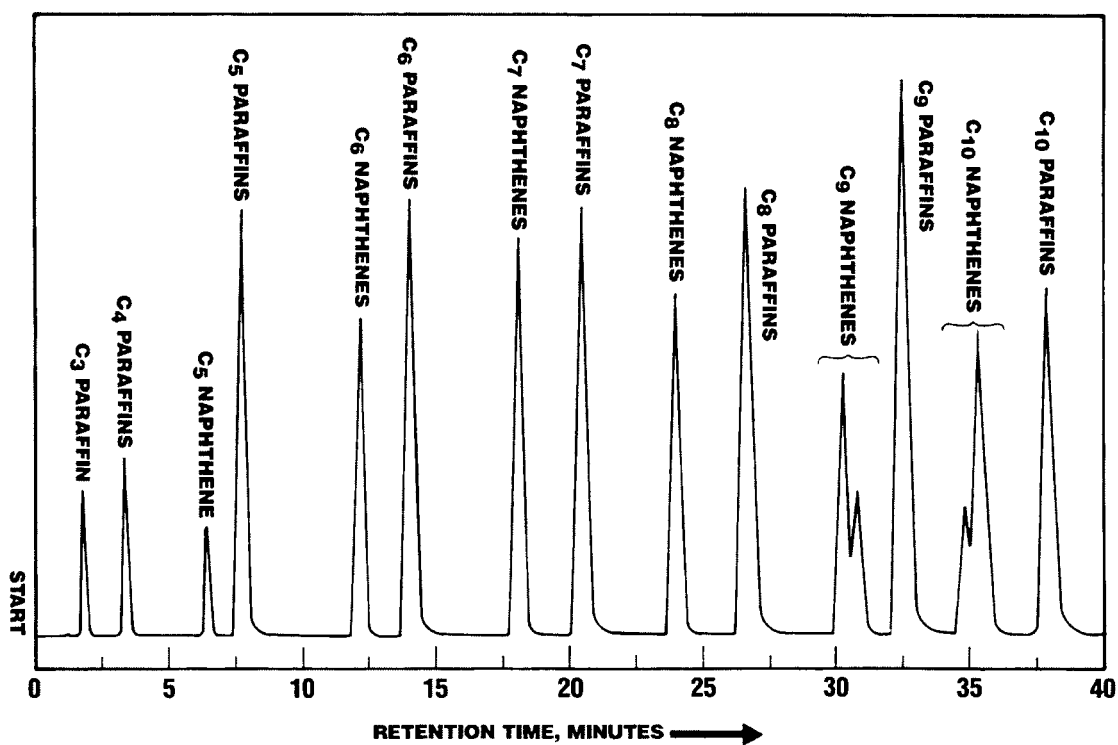


Figure 2
Typical Chromatogram