

DIOLEFINS IN C₅ OLEFINIC HYDROCARBON STREAMS BY GC

UOP Method 934-94

SCOPE

This method is for determining diolefins in FCC derived C₅ olefinic streams by gas chromatography (GC). The individual diolefins cannot be separated and individually identified, but are eluted and calculated as a composite. 3-Methyl-1,2-butadiene is not determined by this method. 1,2-Pentadiene and 2,3-pentadiene are not expected to be present in C₅ streams and it is not known if they can be determined by this method. The lower determination limit is 10 mass-ppm.

OUTLINE OF METHOD

A two column chromatographic system equipped with a column switching valve and a flame ionization detector is used. A reproducible volume of sample is injected onto a KCl/Al₂O₃ precolumn to separate the C₅ diolefins and C₆+ components from the lighter components. At a predetermined time the diolefin containing cut is backflushed onto a Poraplot Q analytical column that separates the diolefins from the C₆+ material. The individual diolefins are not identified but are eluted and calculated as a composite. The external standard method of quantitation is used.

APPARATUS

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

Balance, readability 0.1-mg

Bulkhead, union fitting, 1.59 cm (1/16-in), Valco Instruments, Cat. No. ZBU 1

Chromatographic column, 50 m of 0.53-mm ID PLOT fused silica capillary, internally coated to a film thickness of 10- μ m with Al₂O₃/KCl, Chrompack, Cat. No. 7518

Chromatographic column, 25 m of 0.53-mm ID PLOT fused silica capillary, internally coated to a film thickness of 20- μ m with Poraplot Q, Chrompack, Cat. No. 7554

Freezer, laboratory, Model C350A, Baxter Scientific, Cat. No. R3815-1A

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Flow meter, Model 520, Fisher Scientific, Cat. No. 11-164-45

Gas chromatograph, having a column switching and backflushing system equivalent to Fig. 1, built for capillary column chromatography, utilizing a split injection system having a glass injection port insert, and equipped with a flame ionization detector that will give a minimum peak height response of 10 times the background noise for 10 mass-ppm total diolefins when operated at the recommended conditions and fitted with an electronic pressure control feature

Integrator, electronic, for obtaining peak areas

Oxygen remover, disposable Getter Cartridge, R&D Separations, Cat. No. GC1

Pipet, Pasteur, disposable, 146-mm, Fisher Scientific, Cat. No. 13-678-20A

Pipet bulb, 1-mL, Fisher Scientific, Cat. No. 13-678-9A

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

Regulator, air, two-stage, high purity, Matheson Gas Products, Model 3122-590

Regulator, helium, two-stage, high pressure, Matheson Gas Products, Model 3122-580

Regulator, hydrogen, two-stage, high purity, Matheson Gas Products, Model 3122-350

Regulator, nitrogen, two-stage, high purity, Matheson Gas Products, Model 3122-580

Restrictor, metering, 1.59-mm (1/16-in) Swagelock, Cat. No. 55-551, available from Dearborn Valve and Fitting

Sample injector, any syringe or injector capable of introducing a reproducible 1.0- μ L volume of sample, such as a Hamilton 701-NWG syringe, Alltech Associates, Cat. No. 80307

Tubing, deactivated fused silica, 1.59-mm (1/16-inch) OD, Alltech Associates, Cat. No. 204330

Tubing, stainless steel, 1.59-mm (1/16-inch) OD, Alltech Associates, Cat. No. 300010

Valve, 10-port, stainless steel, with 1.59-mm (1/16-inch) fittings, manual with standoff, Valco Instruments, Cat. No. C10UWP

Vial, 14.8-mL, with screw cap, Fisher Scientific, Cat. No. 03-339-21J

Vials, scintillation, 20-mL glass, with 22-400 GRI thread finish, Baxter Scientific, Cat. No. R2548-21

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

Cyclopentadiene, distilled from dicyclopentadiene, for procedure see Ref. 1

Dicyclopentadiene, 95% minimum purity, Aldrich Chemical, Cat. No. 11,279-8

Helium, zero-gas, total hydrocarbons less than 2.0 ppm as methane

Hexane, 99.9% minimum purity, Wiley Organics, Cat. No. 3442.00

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

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

1,cis-3-Pentadiene, 99.9% purity, Wiley Organics, Cat. No. 7330.02

n-Pentane, 99.9% minimum purity, Wiley Organics, Cat. No. 7372.40-1

cis-2-Pentene, 99.8% minimum purity, Wiley Organics, Cat. No. 7428.04-1

PREPARATION OF APPARATUS

Chromatographic Technique

1. Install the oxygen remover in the supply line between the carrier gas source and the carrier gas inlets on the gas chromatograph.
 - Column life is significantly reduced if an oxygen remover is not used.
2. Install the 10-port valve and both fused silica capillary columns in the gas chromatograph as shown in Fig. 1.
3. Establish the column and detector flows and temperatures as 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.

Table 1

Carrier gas	helium
Electronic Pressure Control: (EPC)	Channel A, 6 psig (3.3 mL/min) constant flow Channel B, 4 psig (2.8 mL/min) constant flow
Carrier gas head pressure	
Poraplot Q column (analytical column)	42 kPa gauge (6 psig) (Channel A)
KCl/Al₂O₃ column (precursor)	28 kPa gauge (4 psig) (Channel B)
Split flow:	
A	30 mL/min
B	30 mL/min
Injection port temperature	250°C
Column temperature	160°C isothermal
Detector	
Detector temperature*	250°C
Hydrogen flow rate*	38 mL/min
Air flow rate*	275 mL/min
Makeup nitrogen flow rate*	30 mL/min
Sample size	1.0 µL
Chart speed	5 mm/min

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

Flow Adjustments

1. Adjust the 10-port valve to Position A (Fig. 1).
2. Set the EPC Channel B to 28 kPa gauge (4 psig) as specified in Table 1.
3. Attach a flow measuring device to the outlet of Detector B. Measure and record the flow rate through Detector B.
 - The measured flow rate represents the flow through the precolumn.
 - The measured flow should be 2.8 mL/min.
4. Attach a flow measuring device to the B split injector vent and adjust the flow from the split vent using the B flow controller to provide the split flow of 30 mL/min as indicated in Table 1.
5. Set the EPC Channel A to 42 kPa gauge (6 psig) as specified in Table 1.

6. Attach a flow measuring device to the outlet of Detector A. Measure and record the flow rate through Detector A.
 - This represents the flow through the analytical column.
 - The measured flow should be 3.3 mL/min.
7. Attach a flow measuring device to the A split injector vent and adjust the flow from the split vent using the A flow controller to provide a flow as indicated in Table 1.
8. Attach a flow measuring device to the outlet of Detector A.
9. Switch the 10-port valve to Position B (Fig. 2) and adjust the variable restrictor to give the same flow rate set in Step 6.
 - This restrictor adjustment minimizes flow changes when the valve is switched.

Column Conditioning

1. Reset the 10-port valve to Position A.
2. Program the column oven to 200°C and maintain this temperature until a stable baseline has been obtained at the required sensitivity.
3. Cool the column oven to a stabilized 160°C.

Valve Backflush Time

The time to switch the 10-port valve from Position A to Position B will vary slightly for each column system and must be determined experimentally as described below.

1. Prepare a blend containing 1% each of *cis*-2-pentene and cyclopentadiene in *n*-pentane as described in ASTM Method D 4307.
2. Adjust the valve to Position A.
3. Inject 1.0 µL of the blend into Capillary B.
4. Determine the retention times for *cis*-2-pentene and cyclopentadiene on the precolumn.
5. Establish the time (T_1) that should elapse before switching the 10-port valve from Position A to Position B by noting the time that elapses before the elution of cyclopentadiene but after the elution of *cis*-2-pentene from the precolumn.
6. Re-inject the blend and turn the valve to Position B at time T_1 , as determined in Step 5.

7. Ensure that a peak corresponding to the cyclopentadiene appears on the analytical column without any contribution from *cis*-2-pentene.
 - If the valve is switched too soon, lighter hydrocarbons are backflushed and are co-eluted in the C₅ diolefin section of the chromatogram. When the valve is switched to backflush too late, part or all of the diolefin component is lost resulting in an incorrect diolefin measurement.

PROCEDURE

Calibration

Quantitative results are based on the injection of a reproducible volume of a sample and a reference blend. Response factors are then used to relate the peak area obtained for the 1,*cis*-3-pentadiene in the blend to the peak areas of the diolefins in the sample.

1. Prepare a calibration blend containing 1,*cis*-3-pentadiene in hexane to approximate the composition of the samples to be analyzed, as described in ASTM Method D 4307 (Ref. 2).
2. Chromatograph the blend in triplicate daily as described under *Analysis of Samples*, Steps 1 through 4.
 - Fig. 3 is a chromatogram of a calibration blend containing 1,*cis*-3-pentadiene in hexane.
3. Average the 1,*cis*-3-pentadiene peak areas from the triplicate runs.
 - The peak area from each of the three runs should not deviate from the average by more than 3% of the value. If greater deviations occur, make certain there are no problems with the equipment and then make further runs until the required repeatability is obtained on three consecutive runs.
4. Determine a response factor for the 1,*cis*-3-pentadiene to three significant figures using the following formula:

$$F = \frac{C}{A} \quad (1)$$

where:

A = average peak area for 1,*cis*-3-pentadiene in blend, area counts

C = concentration of 1,*cis*-3-pentadiene in blend, mass-ppm

F = response factor for 1,*cis*-3-pentadiene, mass-ppm/area counts

5. Use the 1,*cis*-3-pentadiene response factor for the C₅ diolefin composite.

Analysis of Samples

1. Place the injection valve in Position A.
2. Inject a reproducible 1.0-μL volume of sample into Capillary B of the gas chromatograph, and start the recorder, integrator and column temperature programming sequence.
 - To ensure accurate analysis, the syringe and samples must be kept in a freezer.

3. Switch the valve to Position B at time T_1 determined under *Valve Backflush Time*, to backflush the diolefins to the analytical column.
4. Identify the components of interest by comparing the chromatogram obtained to the Typical Chromatogram (Fig. 4).
5. Sum the peak areas of the identified diolefins to obtain the peak area of the diolefin composite.

CALCULATIONS

Calculate the total concentration of the diolefin composite in the sample using the formula below. Report values above 1000 mass-ppm in mass-% by dividing the mass-ppm value by 10,000. Round all values to two significant figures.

$$\text{Total diolefins, mass-ppm} = \frac{E}{F \cdot G} \quad (2)$$

where:

E = total peak area of diolefin composite in the sample

F = previously defined (Eq. 1)

G = density of hexane divided by the density of the sample, as described in ASTM Method D 4052 (Ref. 3)

PRECISION

Repeatability

Based on two tests performed by each of two analysts on each of two different days (8 tests), the within-laboratory estimated standard deviations (esd) were calculated for the diolefin composite at specific concentrations and are listed in Table 2. Two tests performed in one laboratory by different analysts on different days should not differ by more than the allowable differences shown in Table 2 at the concentrations listed (95% probability).

Table 2

<u>Sample Type</u>	<u>Concentration</u>	<u>Within Lab, esd</u>	<u>Allowable Difference</u>
C₅	1.3 mass-%	0.06 mass-%	0.2 mass-%
C₅	56 mass-ppm	2.6 mass-ppm	9 mass-ppm

Reproducibility

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

TIME FOR ANALYSIS

The elapsed time for one analysis including calibration is 2.7 hours. The labor requirement is 0.35 hour.

REFERENCES

Moffett, *Organic Synthesis*, **Coll. Vol. IV**, 238 (1963)
ASTM Method D 4052, D 4307, www.astm.org

SUGGESTED SUPPLIERS

Aldrich Chemical Co., Inc., P.O. Box 355, Milwaukee, WI 53201 (414-273-3850)
Alltech Associates, Inc., 2051 Waukegan Rd., Deerfield, IL 60015 (708-948-8600)
Baxter Scientific Products, 1430 Waukegan Rd., McGaw Park, IL 60085-6787 (708-689-8410)
Chrompack, 1130 Route 202 South, Rariton, NJ 08869 (908-722-8930)
Dearborn Valve and Fitting Co., 1540 N. Old Rand Rd., Wauconda, IL 60084 (708-526-6900)
Fisher Scientific, 711 Forbes Ave., Pittsburgh, PA 15219 (412-562-8300)
Matheson Gas Products, Inc., P.O. Box 96, Joliet, IL 60434 (815-727-4848)
R&D Separations, Inc., 11358 Sunrise Gold Circle, Rancho Cordova, CA (916-635-2763)
Valco Instruments Co., P.O. Box 55603, Houston, TX 77255 (713-688-9345)
Wiley Organics, 1245 S. Sixth St., Coshocton, OH 43812 (614-622-0755)

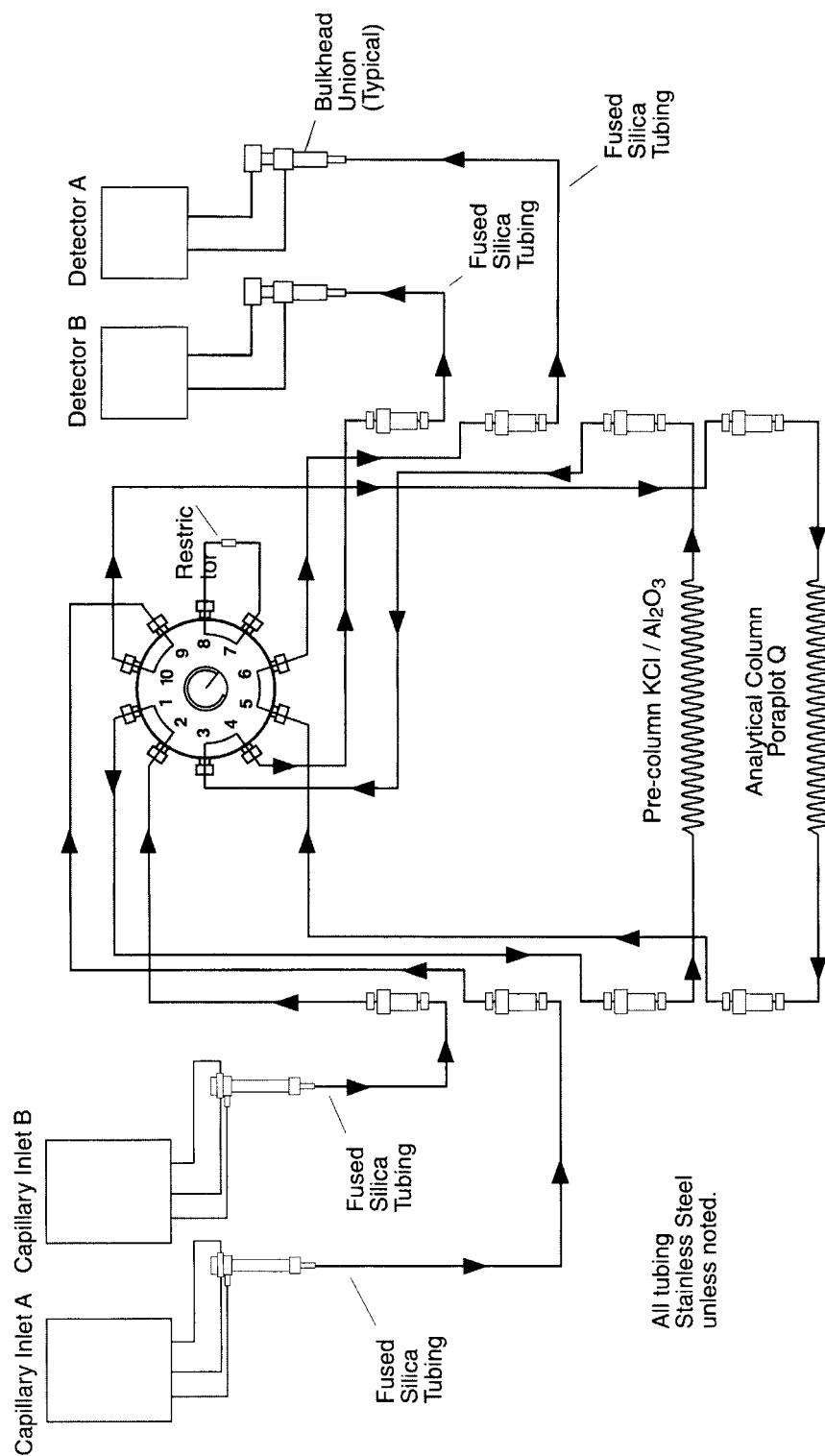


Figure 1
Valve Position A

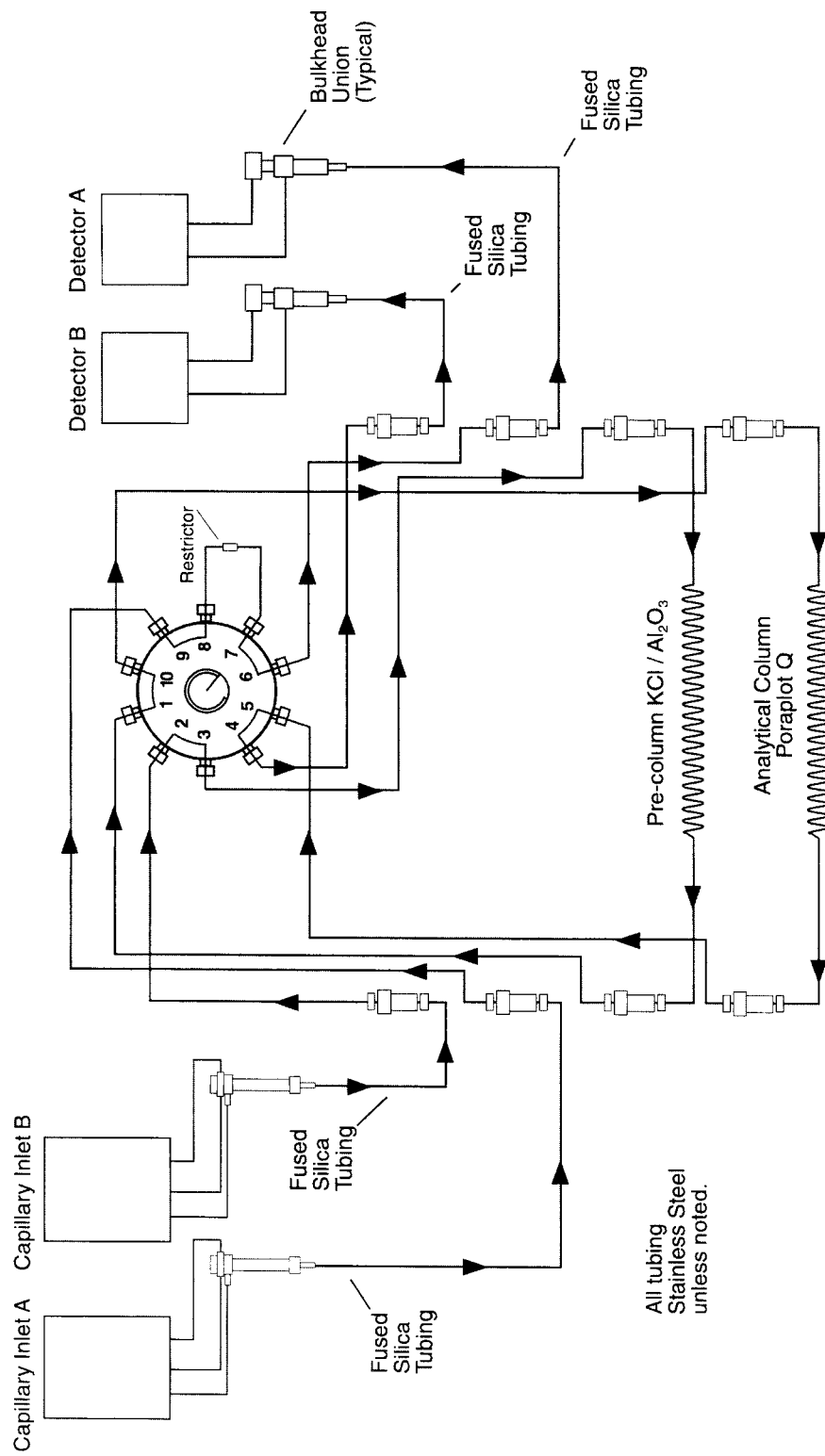


Figure 2
Valve Position B

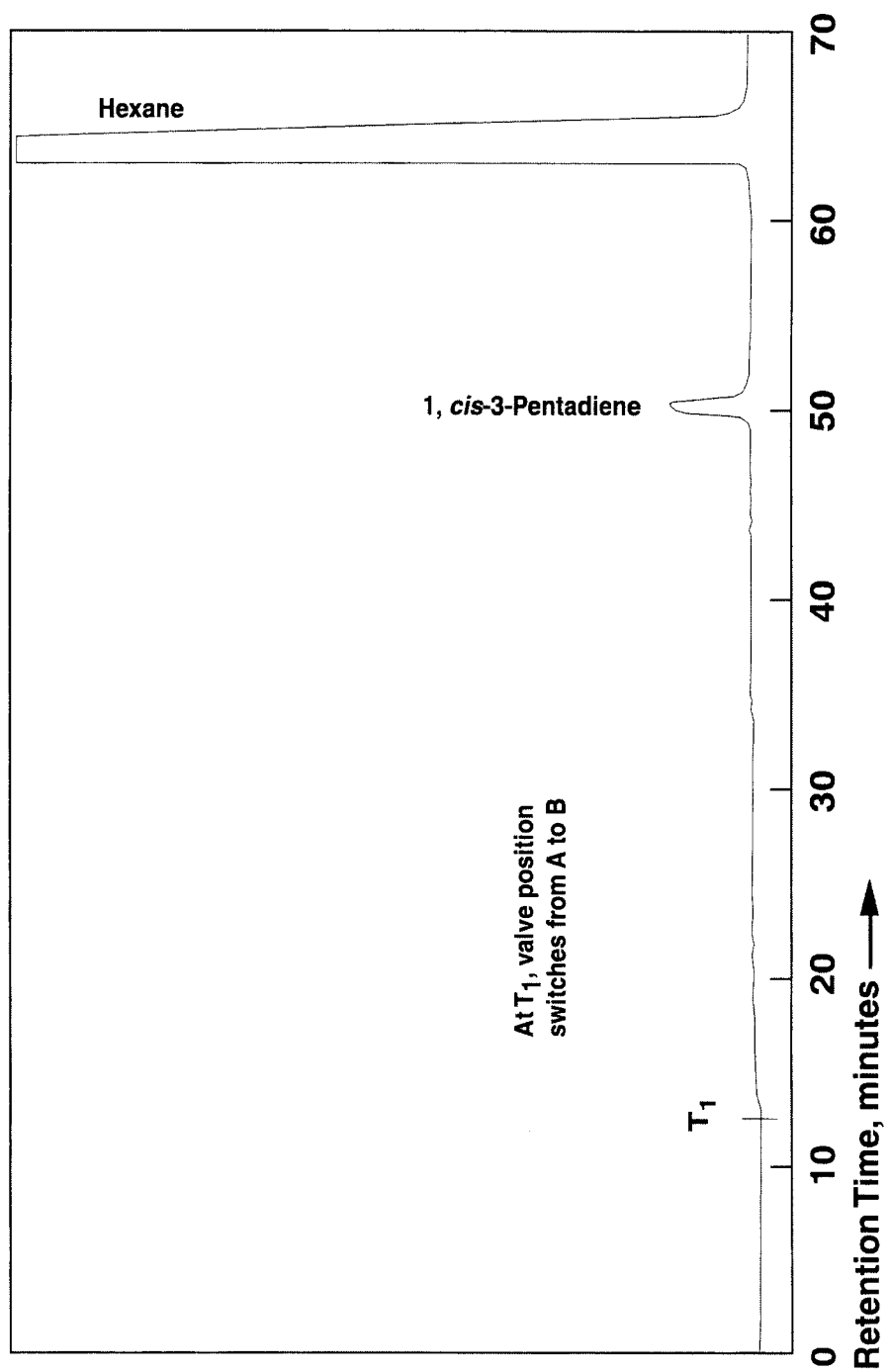


Figure 3
Calibration Blend of 1, *cis*-3-Pentadiene in Hexane

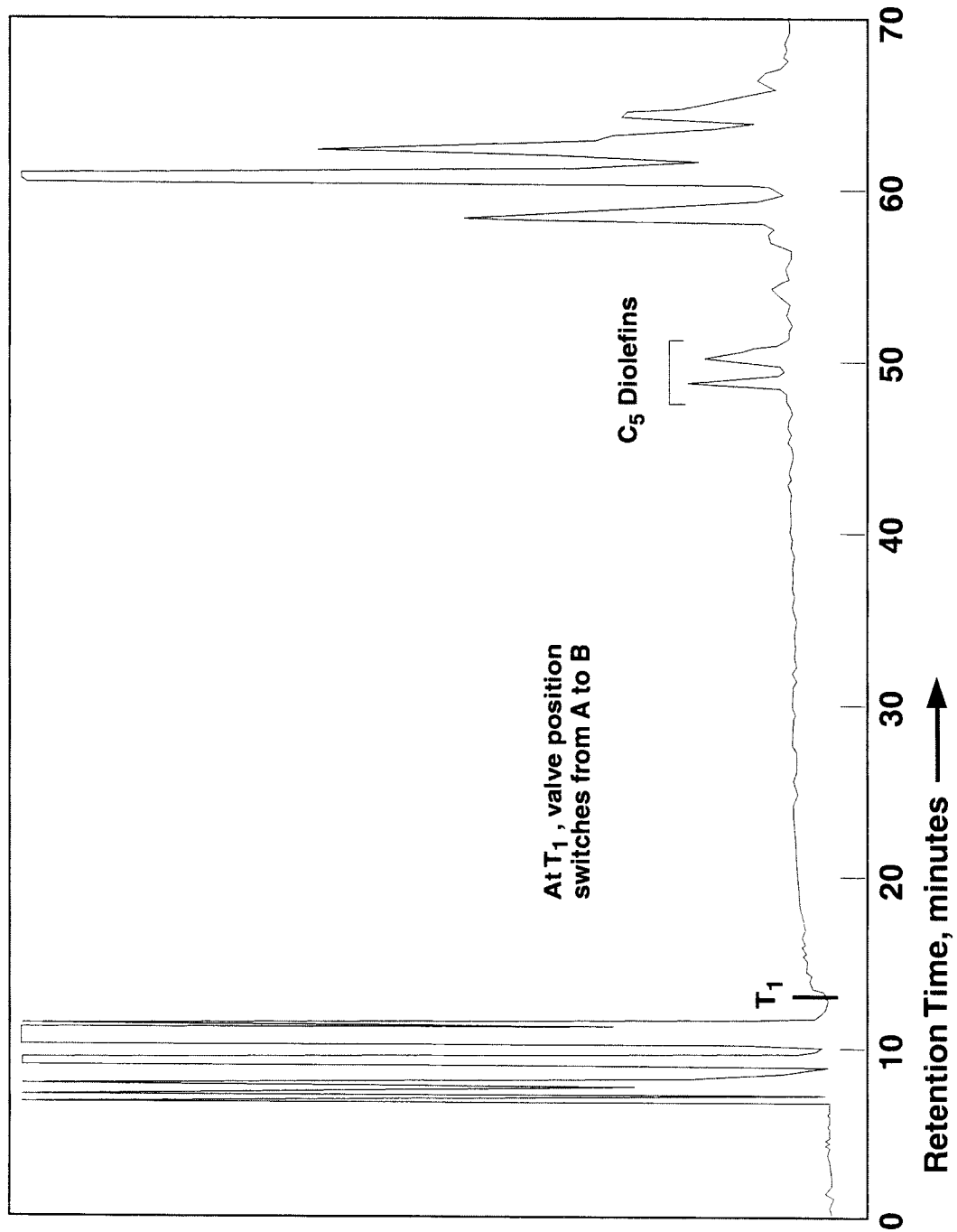


Figure 4
Typical Chromatogram