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Trace Oxygenated Hydrocarbons in Liquid Hydrocarbon Streams by GC

UOP Method 960-06

Scope

This method is for determining trace levels of individual oxygenated hydrocarbons, with boiling points up to 138°C, in C₄ liquefied petroleum gas (LPG), light isomerate and naphtha. Mono-oxygenated hydrocarbons determined include C₁ through C₅ alcohols, and C₂ through C₆ carbonyls and ethers. Di-oxygenated hydrocarbons determined include C₂ through C₄ methyl esters and 1,4-dioxane. The range of quantitation for 2-butanone is 0.2 to 250 mass-ppm (mg/kg). The range of quantitation for other components may be estimated by multiplying the relative response factor of the component from Table 2 times the above values. Inorganic compounds containing oxygen, such as water, are not determined. Carbon monoxide and carbon dioxide are not determined. Unsaturated oxygenated hydrocarbons may be detected but are not identified. Oxygenated hydrocarbons containing other heteroatoms such as nitrogen, chlorine or sulfur are not determined. Certain oxygenated hydrocarbons are not separated and are reported as composites. See Table 2 for a list of all identified compounds and composites. Some sulfur and nitrogen compounds are known to elute in the oxygenate region of the chromatogram; Figures 2A and 2B show elution times of some identified sulfur and nitrogen compounds.

References

- ASTM Method D 1657, "Density or Relative Density of Light Hydrocarbons by Pressure Hydrometer," www.astm.org
- ASTM Method D 2163, "Analysis of Liquefied Petroleum (LP) Gases and Propene Concentrates by Gas Chromatography," www.astm.org
- ASTM Method D 2598, "Calculation of Certain Physical Properties of Liquefied Petroleum (LP) Gases from Compositional Analysis," www.astm.org
- ASTM Method D 4052, "Density and Relative Density of Liquids by Digital Density Meter," www.astm.org
- ASTM Practice D 4307, "Preparation of Liquid Blends for Use as Analytical Standards," www.astm.org

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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UOP Method 373, "Composition of C2 Through C5 Hydrocarbon Mixtures by Gas Chromatography, www.astm.org

UOP Method 999, "Precision Statements in UOP Methods," www.astm.org

Outline of Method

A repeatable volume of sample is injected into a specially modified gas chromatograph (GC) that is equipped with two megabore capillary columns operating at different temperatures. The first column, a non-polar column, fractionates interfering sample components from the system. The second column, a selective CP-Lowox column, separates and analyzes the oxygenates. The non-polar column operates isothermally inside an auxiliary oven, and the CP-Lowox column resides in the main GC oven. Initially, the columns are connected in series, and after the elution of components of interest from the non-polar column, the non-polar column is backflushed. The CP-Lowox column is maintained in foreflush and temperature programmed, eluting compounds to a flame ionization detector (FID). Two sample injections (fractionations) may be required.

1. Fractionation A is used to determine all oxygenates other than methyl ether.
2. Fractionation B is used to determine methyl ether.

Quantitative results are obtained by the external standard method of quantitation wherein the peak areas for the components of interest are compared to peak areas of a calibration standard.

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

Bracket, nut plate assembly, for mounting bulkhead fittings in GC oven, Agilent Technologies, Cat. No. 05890-80660

Chromatographic column, 10 m of 0.5-mm ID CP-Simdist Ultimetel, Varian, Cat. No. CP7592

Chromatographic column, 10 m of 0.53-mm ID CP-Lowox, Varian, Cat. No. CP8587

Electronic leak detector, Gow-Mac Mini gas leak detector, 115 volt, Restek, Cat. No. 21640

Fittings, CGA, for blend cylinder, CGA No. 510, Matheson Tri-Gas

Fittings, internal union, bulkheads for transfer lines, 4 required, VICI Valco Instruments, Cat. No. ZBU1

Fittings, fused silica adapters to connect to bulkheads, 4 required, VICI Valco Instruments, Cat. No. FS1.8-5

Fittings, internal union, for connecting front injection port to 4-port sampling valve, 1 required, VICI, Cat. No. ZU1T

Fused silica tubing, 10 m of 0.53-mm ID, methyl deactivated, Varian, Cat. No. CP4076

Gas chromatograph, capable of temperature ramping, equipped with two electronic pressure controlled injection ports, a separate isothermal heated zone, built for capillary column chromatography, utilizing a split injection system capable of pressure pulsed injection and equipped with an FID that will give a minimum peak height response of five times the background noise for 0.1 mass-ppm of 2-butanone when operated at the recommended conditions, Agilent Technologies, Model 6890

Integrator, electronic, for obtaining peak areas. This device must be capable of graphically displaying chromatograms and peak integration, Agilent Chemstation or equivalent.

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

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

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

Regulator, methyl ether, Aldrich, Cat. No. Z14,670-6

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

Regulator, nitrogen, two-stage, high purity, high pressure delivery to pressurize LPG sample and blend cylinders, Matheson Tri-Gas, Model 3020-580

Sample injector, syringe or injector capable of injecting a 4- μ L repeatable volume of sample. An automatic injection system is recommended, Agilent Technologies Model 7683.

Syringe, 10- μ L, for qualitative mixture preparation, Hamilton 701NF, 2 required, Restek, Cat. No. 20167

Tubing, 1/16-inch Silcosteel™, for transfer lines from valves to GC oven, Restek, Cat. No. 20531

Tubing, Teflon™, 1/8-inch for LPG injection, Supelco, Cat. No. 2-0532

Valve, backflush, VICI Valco Instruments, Model C6UWE

Valve, LPG injection, with actuator, VICI Valco Instruments, Model ACI4UWE2

Valve, vent shut-off, for LPG injection, Swagelok, Cat. No. SS-ORS2

Valve, shut-off, for blend cylinder, Swagelok, Cat. No. SS-1RF4

Valve box (heated with actuator and solenoid), Wasson ECE

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 ppm as methane

Blend, LPG, quantitative, certified standard, containing 50 mass-ppm of 2-butanone and 1 mass-ppm of 2-methyl-2-propanol in research grade isobutane, contained in an aluminum Ultra-Line cylinder with a stainless steel valve, Matheson Tri-Gas. A 250-psig nitrogen head pressure should be maintained on the LPG blend.

Bottle, glass, 500-mL, with cap, for qualitative blend preparation, Fisher Scientific, Cat. No. 03-320-6

Cyclohexane, anhydrous, 99.5+%, Aldrich, Cat. No. 227048. The anhydrous cyclo-hexane is kept under a nitrogen blanket between uses to prevent contamination.

Ethyl methyl ether, 90+%, TCI America, Cat. No. M0110

Gas purifier, hydrogen carrier gas purifier, VICI Mat/Sen, Cat. No. P200-1

Gas purifier, air (for detectors), VICI Mat/Sen, Cat. No. P400-1

Gas purifier, nitrogen, for detector makeup gas, VICI Mat/Sen, Cat. No. P300-1

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

Inlet liner, Silcosleeve™ metal inlet liner with fused silica wool, Restek, Cat. No. 21700-200.1

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

Oxygenated hydrocarbons, see Table 2

Toluene, 99.8% purity, Aldrich, Cat. No. 270377

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

p-Xylene, 99+%, Aldrich, Cat. No. 240451

Vials, glass, 20-mL, with caps, Fisher Scientific, Cat. No. 03-3386

Procedure

Preparation of Apparatus

Refer to Fig. 1 when making all tubing and column connections.

1. Install the gas purifiers in the supply line between the instrument gases and the gas chromatograph.
 - Low detection limits are required for the analysis. Purifiers are essential for all gases used, and must be routinely replaced to be effective. Follow the vendors recommended replacement schedule.
2. Install the 6-port backflush valve in the Wasson valve box onto the Valve 1 actuator.
3. Mount the 4-port LPG injection valve on the external left side of the Wasson valve box. Connect the valve actuator lines to the Valve 2 solenoid connections. Connect 6 inches of Teflon tubing between the sample vent connection of the LPG injection valve and the inlet of the 1/8-inch shut-off valve. The outlet of the 1/8-inch shut-off valve must be directed to a laboratory fume hood.
4. Install bulkheads on brackets inside the oven of the GC.
5. Make valve connections between valves and bulkheads using 1/16-inch Silcosteel tubing. Tubing exiting the valve box must lay flush along the heated channel provided by Wasson ECE.
6. Make connections between the front injection port and the 4-port sampling valve. Cut the carrier flow inlet line to the front injection port. Connect the carrier flow line from the injection port flow module to the carrier gas port on the 4-port sampling valve. Use 1/16-inch Silcosteel tubing and 1/16-inch internal unions for all connections. All lines should run through the Wasson valve box and lay in the heated channel.
7. Install the Silcosleeve metal inlet liner into the front injection port according to the instrument manufacturer instructions.
 - The Silcosleeve liner has equivalent inertness to glass sleeves but, has greater total volume, allowing the large injections of LPG and volatile liquids to be contained in the injection port.
8. Install the CP-Simdist column in the valve box. The column must rest on the front ledge inside the valve box for the box to close properly. Connect the column to the 6-port backflush valve using the fused silica adapters.
9. Install deactivated fused silica tubing between the front injection port, the back injection port, and the associated bulkhead fittings.

10. Install the remaining deactivated fused silica tubing in the GC oven between the bulkhead and Valve 1, Port 1, and the bulkhead and either the vent or back FID detector, if present.
11. Install the CP-Lowox column in the GC oven. The inlet end of the column connects to a bulkhead, the outlet end of the column connects to the “front” detector.
12. Check all fittings for leaks using an electronic leak detector.
 - Do not use liquid leak detector on capillary lines.
 - **CAUTION:** Hydrogen gas leakage into the confined volume of the column oven can cause a violent explosion. It is, therefore, mandatory to check for leaks each time a connection is made and periodically thereafter.
13. Establish the operating conditions as given in Table 1.
 - Initially, the injection port should be conditioned for 24 hours at 250°C to clean the Silcosteel injection port liner. Then, the injection port temperature should be reduced to operating temperature.
 - Other conditions may be used provided they produce the required sensitivity and chromatographic separations equivalent to those shown in the Typical Chromatogram (Figs. 2A and 2B) .
14. Put the cover on the Wasson ECE valve box, and allow the temperature to equilibrate for a minimum of one hour.
15. Condition the CP-Lowox column according to the manufacturer’s instructions.
 - Maintain the CP-Lowox column at 200°C with carrier gas flowing when it is not used.
16. Check all fittings in the GC oven for leaks after the CP-Lowox is conditioned.

Fractionation Time Determination

1. With the instrument operating at the established conditions, set Valve 1 to the “off” position. See Figure 1.
2. Set up a run table on the GC with Valve 1 “on” at 1.00 minute and Valve 1 “off” at 29.5 minutes.
3. Prepare a qualitative mixture of oxygenates in cyclohexane by the following procedure. This mixture is used to determine retention times of the oxygenates.
 - Fill a 500-mL bottle with 450 mL of cyclohexane
 - Add 1 mL each of toluene and *p*-xylene
 - Add 5 µL each of the oxygenates in Table 2, mix well
 - Methyl ether is a compressed gas. It should be bubbled into the blend bottle by flowing it through a section of 1/16-inch tubing that is immersed in the cyclohexane, for 3 to 4 seconds.
4. Inject 4 µL of the qualitative mixture, start the GC and integrator and compare to Figures 2A and 2B to identify peaks.
 - The qualitative mixture determines retention times for all possible components and is used to set fractionating cut times. Peak separations and shapes should be similar to chromatograms in Figures 2A and 2B. If the chromatogram is not comparable make appropriate repairs until it is.
 - It is not expected that samples for this analysis will contain all oxygenates found in the qualitative mixture.
5. Reduce the Valve 1 “on” time by 0.05 minute increments until the *p*-xylene peak is no longer seen on the chromatogram and the 1-pentanol peak does not diminish in size (see Figures 2A, 2B and 4). Record this value as the cut time for Fractionation A.
6. Reduce the Valve 1 “on” time further until the toluene peak is no longer seen on the chromatogram and the methyl ether peak does not diminish in size (see Figure 3). Record this value as the cut time for Fractionation B.

Table 1
Recommended Operating Conditions

Carrier gas	hydrogen
Front Inlet	
Temperature	120°C isothermal
Column head pressure @ 50°C	5.5 kPa gauge (0.8 psig)
Equivalent flow	5.0 mL/min
Flow mode	constant flow
Pressure pulse	34.4 kPa gauge (5.0 psig)
Pulse time	0.25 min
Split ratio	1.0
Split flow	5.0 mL/min
Back Inlet	
Temperature	120°C
Column head pressure @ 50°C	5.5 kPa gauge (0.8 psig)
Equivalent flow	5.0 mL/min
Flow mode	constant flow
Split ratio	5.0
Split flow	25.1 mL/min
Auxiliary 1 temperature (Wasson ECE valve box)	150°C isothermal
Auxiliary 2 temperature (heated channel)	150°C isothermal
Main oven temperature programming	
Initial temperature	50°C
Initial time	0 min
Programming rate	10°C/min
Final temperature	250°C
Final time	10 min
Front Detector	FID
Temperature	250°C
Hydrogen flow rate*	30 mL/min
Air flow rate*	400 mL/min
Makeup nitrogen flow rate*	25 mL/min
Constant makeup mode	
Back Detector (if installed)	FID
Temperature	250°C
Hydrogen flow rate*	30 mL/min
Air flow rate*	400 mL/min
Makeup nitrogen flow rate*	25 mL/min
Constant makeup mode	
Run Table	
Valve 1 "on" at	
Typical for Fractionation A	0.35 min
Typical for Fractionation B	0.25 min
Valve 1 "off" at	29.5 min
For LPG samples add:	
Valve 2 "on" at	0.01 min
Valve 2 "off" at	0.1 min
Sample size	
Liquids	4.0 µL (syringe)
LPG	2.0 µL (valve)

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

Calibration Blends - Liquid Samples

Prepare a calibration blend as described in ASTM Method D 4307, "Preparation of Liquid Blends for Use as Analytical Standards," to contain approximately 50 mass-ppm of 2-butanone in cyclohexane. Run the calibration blend in triplicate daily when samples are analyzed as described under *Chromatographic Technique*. The lifetime of this calibration blend is estimated at one week.

- Peak areas from each of the triplicate runs should not deviate from the average by more than 5% of the value. If greater deviations occur, make certain that there are no problems with the equipment, then make additional runs until the required repeatability is obtained on three consecutive runs.

Calibration Blends - LPG samples

A blend containing approximately 50 mass-ppm of 2-butanone and 1 mass-ppm of 2-methyl-2-propanol in high-purity isobutane is required for calibration. Run the calibration blend in triplicate daily when samples are analyzed as described under *Chromatographic Technique*. The lifetime of this calibration blend is estimated at two years.

- Peak areas from each of the triplicate runs should not deviate from the average by more than 5% of the value. If greater deviations occur, make certain that there are no problems with the equipment, then make additional runs until the required repeatability is obtained on three consecutive runs.

Chromatographic Technique

Use the time determined for Fractionation A as the Valve 1 "on" time.

1. Inject 4 μ L of pure cyclohexane and start the integrator and GC programming sequence.
2. Monitor the baseline for peaks in the oxygenate region of the chromatogram.
3. Make repeat injections of the cyclohexane until no peaks are detected in the oxygenate region of the chromatogram, or the resulting chromatogram looks similar to Fig. 5.
4. Run the appropriate calibration blend. For LPGs, use the 50 mass-ppm 2-butanone LPG blend, for liquids use the 50 mass-ppm liquid blend.
5. For LPG, follow Steps 6 through 9. For liquid injection by autosampler, proceed to Step 10.
6. Pressurize the cylinder to 250 psig with high purity nitrogen.
 - Confirm that the sample container can handle the desired pressure, prior to pressurizing.
 - Confirm that the cylinder is not liquid full by venting a small amount of the contents into a laboratory fume hood.
7. Connect the LPG to Valve 2 sample inlet.
8. Flush the LPG for several seconds through the sample inlet line on Valve 2 and out to vent.
9. Slowly close the Valve 2 vent shut-off valve. Visually monitor the liquid stream in the Teflon tubing for bubble formation. When no bubbles are left in the line, close the Valve 2 vent shut-off completely.
10. Start the GC and integrator.
 - The Valve 2 "on" and "off" commands must be loaded into the GC for LPG injections, and must NOT be loaded into the GC for liquid syringe injections.
 - The calibration standard is run to determine system response for 2-butanone. The LPG calibration standard also contains 1 mass-ppm of 2-methyl-2-propanol. With the 2-methyl-2-propanol peak properly integrated, the operator should confirm that it is at minimum 20 times higher than the baseline noise. This ensures that the instrument has sufficient sensitivity. Calibrations are done in triplicate on any day samples are run.
11. Inject an identical volume of sample, by repeating Steps 5 through 10.

12. Confirm the presence of oxygenated compounds, by first comparing the sample chromatogram to the cyclohexane chromatogram. Any peaks in the oxygenate region that are of the same intensity and common to the two chromatograms should not be calculated for sample result purposes, as they are likely to be artifacts and not oxygenates. Then compare the sample chromatogram to the chromatogram of the qualitative mixture to identify oxygenated compounds in the sample. Be sure that all peaks are properly integrated, small peaks are detected, and baseline noise is not integrated. Separate peaks that are not completely resolved from each other using a perpendicular drop to the baseline unless they are obviously on the tail of a much larger peak; see Figures 2A and 2B
13. Obtain the density of liquid samples using ASTM Method D 4052, "Density and Relative Density of Liquids by Digital Density Meter." The relative density of LPG samples may be determined by ASTM Method D 1657, "Density or Relative Density of Light Hydrocarbons by Pressure Hydrometer," or by calculation from composition using ASTM Method D 2163, "Analysis of Liquefied Petroleum (LP) Gases and Propene Concentrates by Gas Chromatography," or UOP Method 373, "Composition of C₂ Through C₅ Hydrocarbon Mixtures by Gas Chromatography," and ASTM Method D 2598, "Calculation of Certain Physical Properties of Liquefied Petroleum (LP) Gases from Compositional Analysis."

For the analysis of dimethyl ether, use the time determined for Fractionation B as the Valve 1 "on" time, and repeat the steps above.

Calculations

For either LPG injection or liquid injection, calculate the 2-butanone response factor to four significant figures using Equation 1. Use the average 2-butanone peak area from triplicate blend runs.

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

where:

A = concentration of 2-butanone in blend, mass-ppm

B = average area of 2-butanone peak

F = response factor for 2-butanone

Calculate the amount of an individual component in an LPG sample using Equation 2. Report to one significant digit below 1.0 mass-ppm, two significant digits from 1.0 to 100 mass-ppm, and to three significant digits above 100 mass-ppm.

$$C = FGH \frac{0.563}{J} \quad (2)$$

where:

C = amount of component in sample, mass-ppm

F = previously defined, Equation 1

G = peak area of sample component

H = component response relative to 2-butanone as found in Table 2. If the components are a composite peak, use the highest listed response factor in the composite to calculate.

J = relative density of sample at 15.6°C (60°F) (from ASTM D 1657 or by calculation from composition)

0.563 = relative density of isobutane at 15.6°C (60°F)

Calculate the amount of an individual component in a liquid sample using Equation 3. Report to one significant digit below 1.0 mass-ppm, two significant digits from 1.0 to 100 mass-ppm, and to three significant digits above 100 mass-ppm.

$$C = FGH \frac{0.778}{K} \quad (3)$$

where:

C = amount of component in sample, mass-ppm

F = previously defined, Equation 1

G = previously defined, Equation 2

H = previously defined, Equation 2

K = density of sample, g/mL (from ASTM D 4052)

0.778 = density of cyclohexane, g/mL

For either liquid or LPG samples, if a component is unidentified and eluting in the oxygenate region of the chromatogram, use a value of 1.000 for variable H and report the component as equivalent to 2-butanone.

Results may also be expressed as mass-ppm elemental oxygen for any component identified. Use Equation 4 and report to one significant digit below 1.0 mass-ppm, two significant digits from 1.0 to 100 mass-ppm, and to three significant digits above 100 mass-ppm.

$$M = 0.01 CP \quad (4)$$

where:

C = previously defined, Equations 2 and 3

M = mass-ppm of elemental oxygen per compound

P = percentage elemental oxygen in component as per Table 2

0.01 = factor to convert percentage elemental oxygen to fraction of elemental oxygen in component

Table 2
Oxygenated Component Properties and Response Times

Peak Number	Component	Retention Time*, minutes	Aldrich Chemical, Cat. No. and Purity	Elemental Oxygen, %	Response Relative to 2-Butanone
1	Methyl ether	5.34	295299 99+%	34.73	1.278
2	Ethyl methyl ether	6.65	**	26.62	1.111
3	Ethyl ether	7.65	346136 99%	21.62	1.028
4	Acetaldehyde	7.90	110078 99%	36.32	1.222
5	Methyl formate	8.59	291056 99%	53.33	1.666
6	<i>tert</i> -Butyl ethyl ether	8.69	253898 99%	15.69	0.945
7	<i>tert</i> -Butyl methyl ether	8.83	293210 99.8%	18.15	0.978
8	Isopropyl ether	8.92	296856 99%,	15.69	0.945
9	Propylene oxide	8.98	240397 99+%	27.55	1.074
10	<i>sec</i> -Butyl methyl ether	9.05	424463 99%	18.15	0.978
11	Propionaldehyde	9.42	P51451 97%	27.55	1.074
12	Butyl methyl ether	9.50	235377 99%	18.15	0.978
13	<i>tert</i> -Amyl methyl ether	9.80	283096 97%	15.66	0.945
14	<i>n</i> -Propyl ether	9.92	111333 99+%	15.66	0.945
15	Butyl ethyl ether	10.24	268925 99%	15.66	0.945
16	Isobutyraldehyde	10.32	240788 99+%	22.19	1.000
17	Tetrahydrofuran	10.38	270385 99.5%	22.19	0.999

Peak Number	Component	Retention Time*, minutes	Aldrich Chemical, Cat. No. and Purity	Elemental Oxygen, %	Response Relative to 2-Butanone
18	<i>n</i> -Butyraldehyde	10.87	B103284 99%	22.19	1.000
19	Methyl acetate	10.95	296996 99.5%	43.20	1.370
20 (composite)	Tetrahydropyran	11.02	293105 99%	18.58	0.956
	Trimethylacetaldehyde		T71501 97%	18.58	0.956
21	Methyl alcohol	11.47	270474 99.9%	49.93	1.778
22	Acetone	11.69	270725 99.9%	27.55	1.074
23	2-Methylbutyraldehyde	11.83	M33476 95%	18.58	0.956
24 (composite)	Isovaleraldehyde	12.11	146455 97%	18.58	0.956
	Cyclobutanone		C96001 99%	22.86	0.973
25	Methyl propionate	12.20	109258 99%	36.32	1.222
26	<i>n</i> -Valeraldehyde	12.40	110132 97%	18.58	0.956
27	2-Butanone	12.83	270695 99.5%	22.19	1.000
28 (composite)	Ethyl alcohol	13.08	270741 denatured	34.74	1.278
	2-Ethylbutyraldehyde		110094 92%	15.97	0.926
29	3,3-Dimethylbutyraldehyde	13.16	359904 95%	15.97	0.926
30	2-Methylvaleraldehyde	13.23	258563 98%	15.97	0.926
31	Methyl butyrate	13.58	246093 99%	31.33	1.133
32	1,4-Dioxane	13.68	270539 99.9%	36.32	1.222
33	Hexanal	13.74	115606 98%	15.97	0.926
34	3-Pentanone	13.82	127604 98%	18.58	0.956
35	3,3-Dimethyl-2-butanone	14.11	P45605 98%	15.97	0.926
36	2-Pentanone	14.18	448516 99+%	18.58	0.956
37 (composite)	2-Propanol	14.29	270490 99.5%	26.62	1.111
	1-Propanol		293288 99.5%	26.62	1.111
	Cyclopropyl methyl ketone		C120006 99%	19.02	0.934
38	2-Methyl-3-pentanone	14.34	108707 97%	15.97	0.926
39	3-Methyl-2-pentanone	14.77	M67001 99%	15.97	0.926
40	Cyclopentanone	14.97	C112402 99+%	19.02	0.934
41 (composite)	4-Methyl-2-pentanone	15.13	293261 99.5%	15.97	0.926
	3-Hexanone		103020 98%	15.97	0.926
42 (composite)	2-Methyl-1-propanol	15.27	270466 99.5%	21.59	1.028
	2-Methyl-2-propanol		308250 99.5%	21.59	1.028
	2-Butanol		294810 99.5%	21.59	1.028
43	Cyclobutanol	15.42	156434 99.5%	22.19	0.999
44	2-Hexanone	15.58	103004 98%	15.97	0.926
45	1-Butanol	15.72	270679 99.8%	21.59	1.028
46 (composite)	3-Methyl-2-butanol	15.96	110949 98%	18.15	0.978
	Neopentyl alcohol		N7206 99%	18.15	0.978
47	3-Pentanol	16.12	P8025 98%	18.15	0.978
48	<i>tert</i> -Amyl alcohol	16.19	240486 99+	18.15	0.978
49 (composite)	2-Methyl-1-butanol	16.54	133051 99+%	18.15	0.978
	Cyclopentanol		C112208 99%	18.58	0.956
50	2-Pentanol	16.60	P8017 98%	18.15	0.978
51	3-Methyl-1-butanol	16.89	309435 99+%	18.15	0.978
52	1-Pentanol	16.95	138975 99+%	18.15	0.978

* retention times are provided as an example only

** not available from Aldrich Chemical

Precision

Precision statements were determined on two LPG samples using UOP Method 999, "Precision Statements in UOP Methods."

Repeatability

A nested design was carried out for trace oxygenated hydrocarbons analysis with two analysts. Each analyst carried out tests on four separate days, performing two tests each day. The total number of tests was 32. Using a stepwise analysis of variance procedure, the within-day estimated standard deviations (esds) were calculated for the components listed in Table 3. Two analyses performed in one laboratory by the same analysts on the same day should not differ by more than the repeatability allowable differences shown in Table 3 at the concentrations listed with 95% confidence.

Intermediate Precision

A nested design was carried out for trace oxygenated hydrocarbons analysis by two analysts. Each analyst carried out tests on four separate days, performing two tests each day. The total number of tests performed was 32. Using a stepwise analysis of variance procedure, the within-lab estimated standard deviations (esds) were calculated for the components listed in Table 3. Two analyses performed in one laboratory by different analysts on different days should not differ by more than the intermediate precision allowable differences shown in Table 3 at the concentrations listed with 95% confidence.

Table 3
Repeatability and Intermediate Precision, mass-ppm

<u>Component</u>	<u>Concentration</u>	<u>Repeatability</u>		<u>Intermediate Precision</u>	
		<u>Within-Day esd</u>	<u>Allowable Difference</u>	<u>Within-Lab esd</u>	<u>Allowable Difference</u>
Sample 1					
Acetaldehyde	254	2.0	6	3.8	12
Propionaldehyde	8.9	0.08	0.3	0.13	0.5
<i>n</i> -Butyraldehyde	0.9	0.06	0.2	0.07	0.2
Methanol	9.0	0.14	0.5	0.19	0.6
Acetone	12.6	0.13	0.4	0.20	0.7
Ethanol	74	0.8	3	1.1	4
Sample 2					
Diethyl ether	1.1	0.02	0.1	0.03	0.1
Methyl acetate	0.8	0.04	0.1	0.06	0.2
Methanol	0.6	0.05	0.2	0.05	0.2
Acetone	1.1	0.05	0.2	0.05	0.2
<i>tert</i> -Butanol	2.2	0.04	0.1	0.04	0.1

The data in Table 3 are a short-term estimate of repeatability. When the test is run routinely in the field, a control standard and chart should be used to develop better estimates of the long-term repeatability.

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 2.5 hours. The labor requirement is 1.5 hours. For subsequent analyses, the elapsed time is 0.5 hour with the labor requirement of 0.3 hour.

Suggested Suppliers

Agilent Technologies, 2850 Centerville Rd., Wilmington, DE 19808-1610 (302-633-8000)
www.agilent.com

Aldrich, 1000 West Saint Paul Avenue, Milwaukee, WI 53233 (414-273-3850)
www.sigma-aldrich.com

Fisher Scientific, 711 Forbes Ave., Pittsburgh, PA 15219-4785 (412-490-8300) www.fishersci.com

Matheson Tri-Gas, 166 Keystone Drive, Montgomeryville, PA 18936 (215-641-2700)
www.mathesontrigas.com

Mat/Sen, 26272 Twelve Trees #C, Poulsbo, WA 98370 (360-697-9199) www.vici.com

Restek, 110 Benner Circle, Bellefonte, PA 16823 (814-353-1300) www.restek.com

Supelco, 595 North Harrison Road, Bellefonte, PA 16823 (814-359-3441) www.sigma-aldrich.com

Swagelok Company, 29500 Solon Rd., Solon, OH 44139 (440-248-4600) www.swagelok.com

TCI America, 9211 N. Harborside St., Portland, OR 97203 (503-283-1681) www.tciamerica.com

Varian, Inc., 2700 Mitchell Drive, Walnut Creek, CA 94598 (925-939-2400) www.varianinc.com

VICI Mat/Sen, 7806 Bobbitt, Houston, TX 77055 (713-688-9345) www.vicimatsen.com

VICI Valco Instruments, 7806 Bobbitt, Houston, TX 77255 (713-688-9345) www.vici.com

Wasson ECE, 101 Rome Ct., Fort Collins, CO 80524 (970-221-9179) www.wasson-ece.com

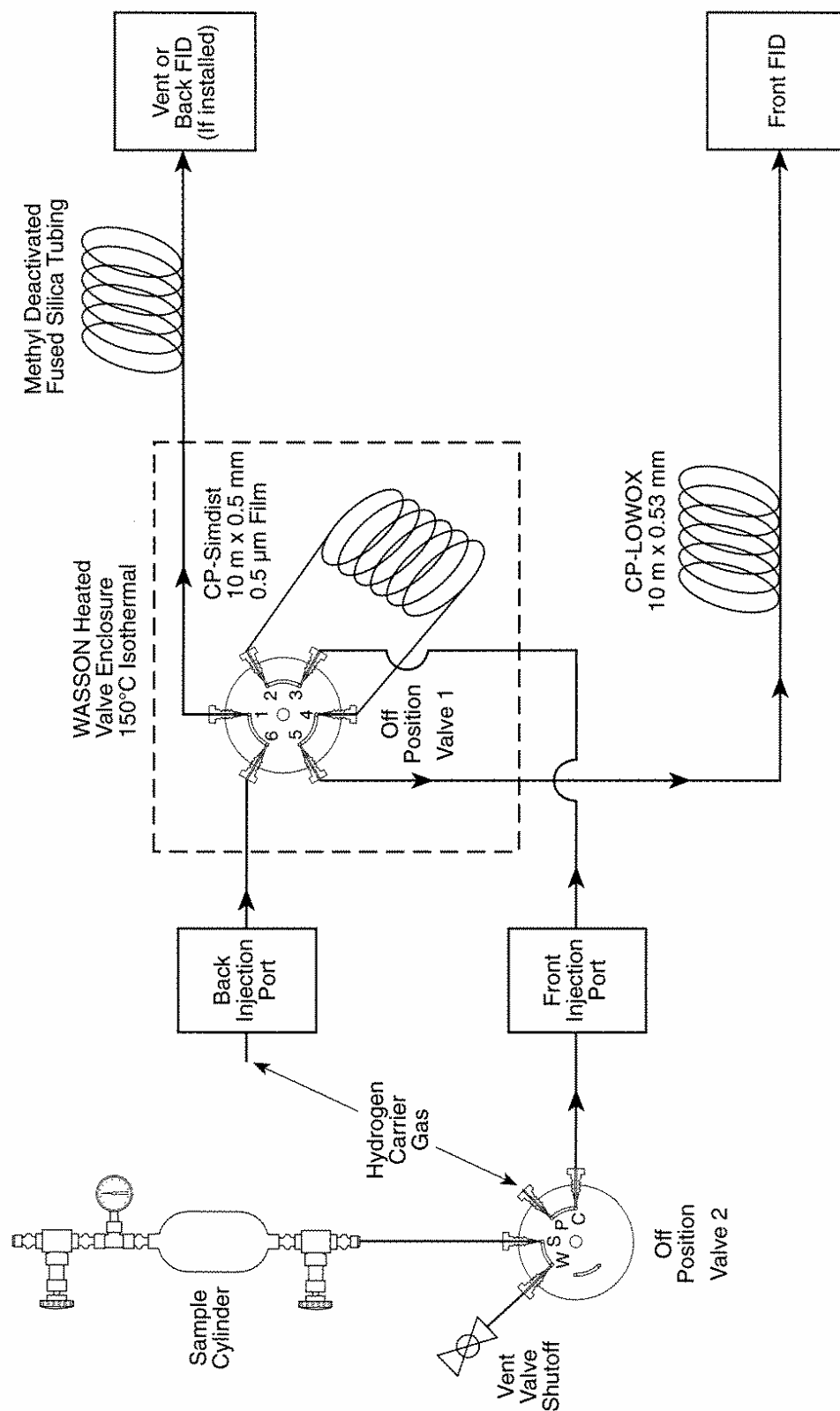


Figure 1
Sampling and Gas Chromatograph Flow Diagram

UOP Method 960

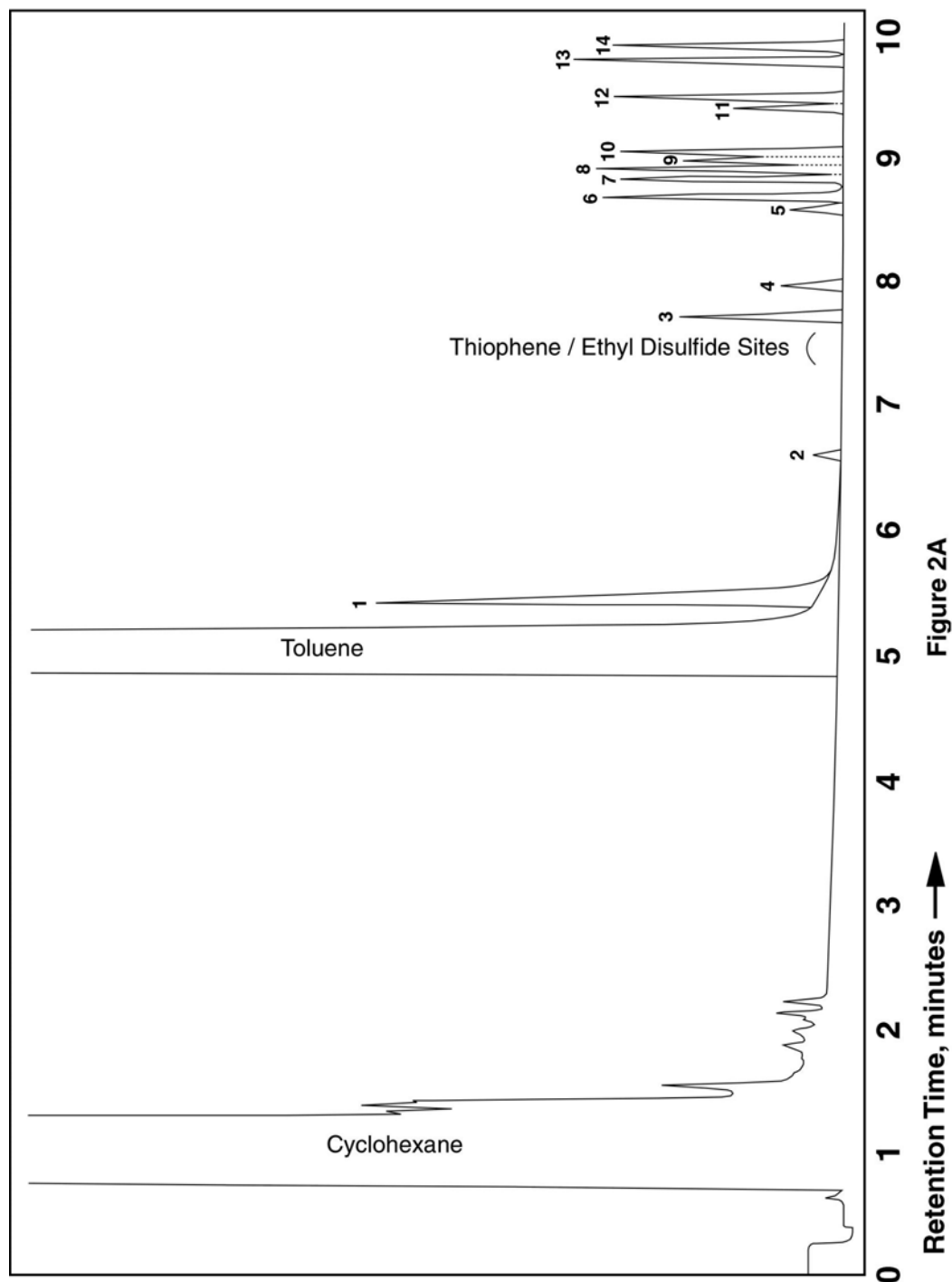
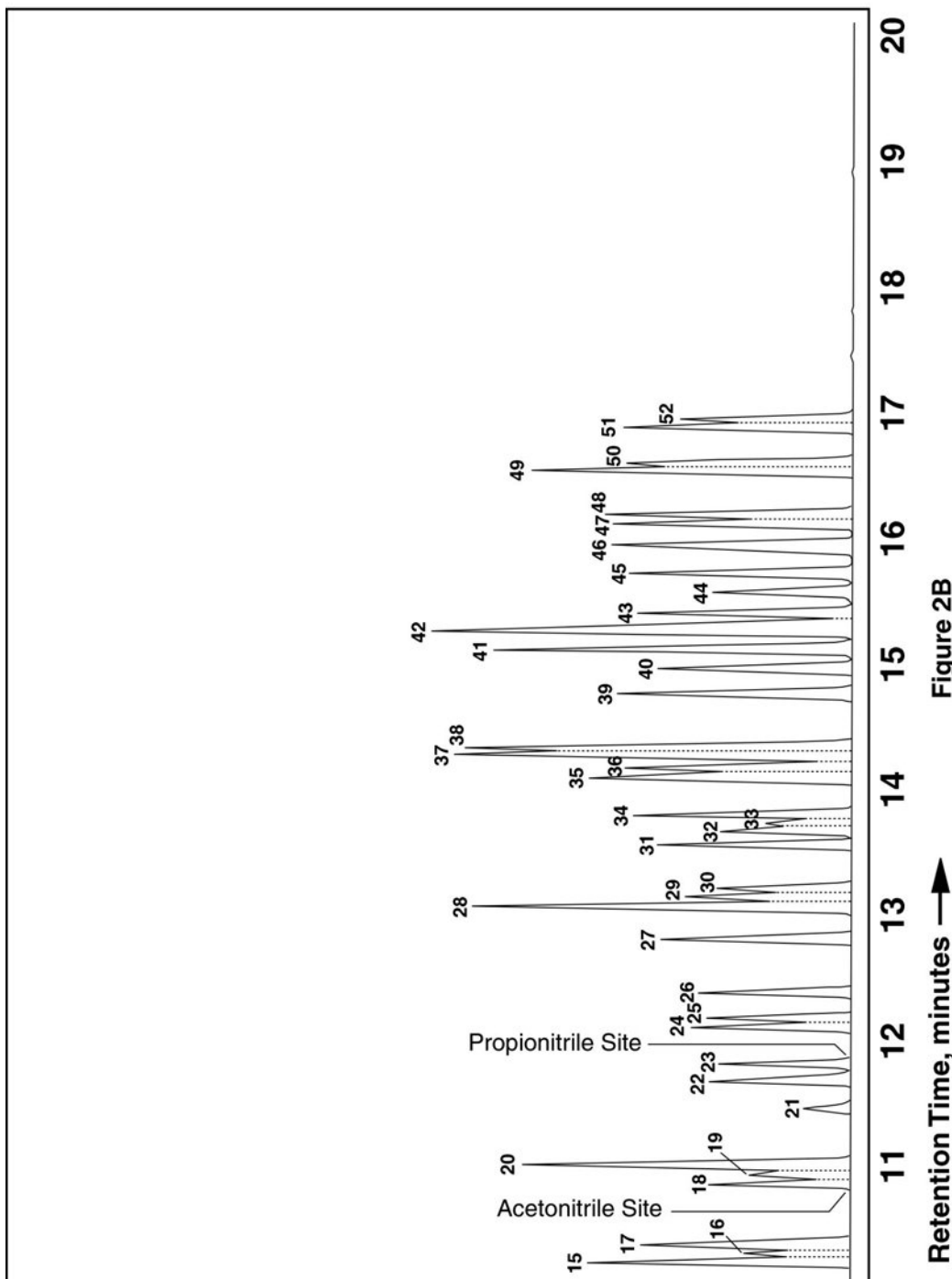


Figure 2A

Typical Chromatogram
Valve 1 "on" at 0.35 Minute

UOP Method 960



UOP Method 960

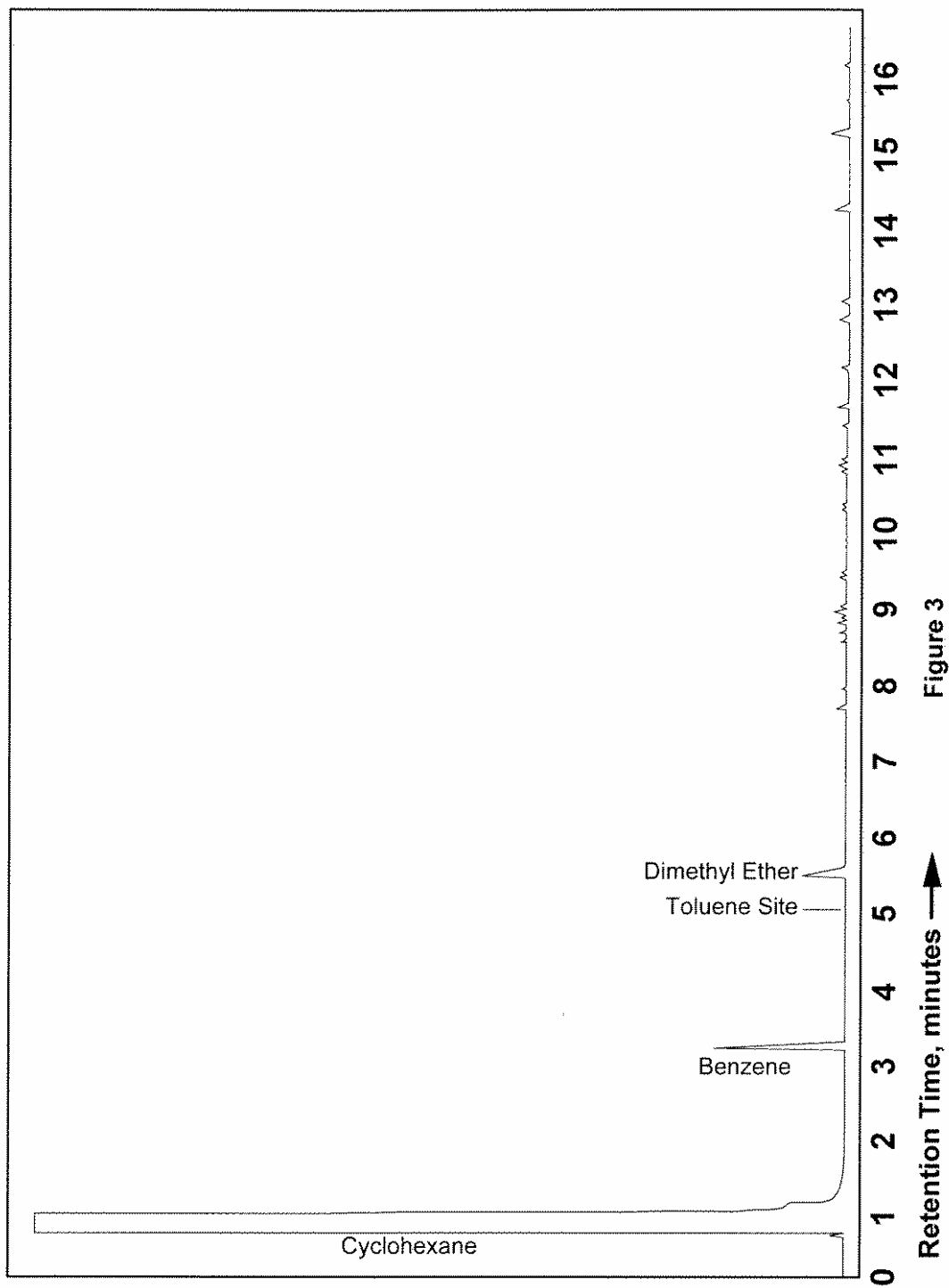


Figure 3

Typical Chromatogram

Fractionation B, Valve 1 "on" at 0.25 Minute

UOP Method 960

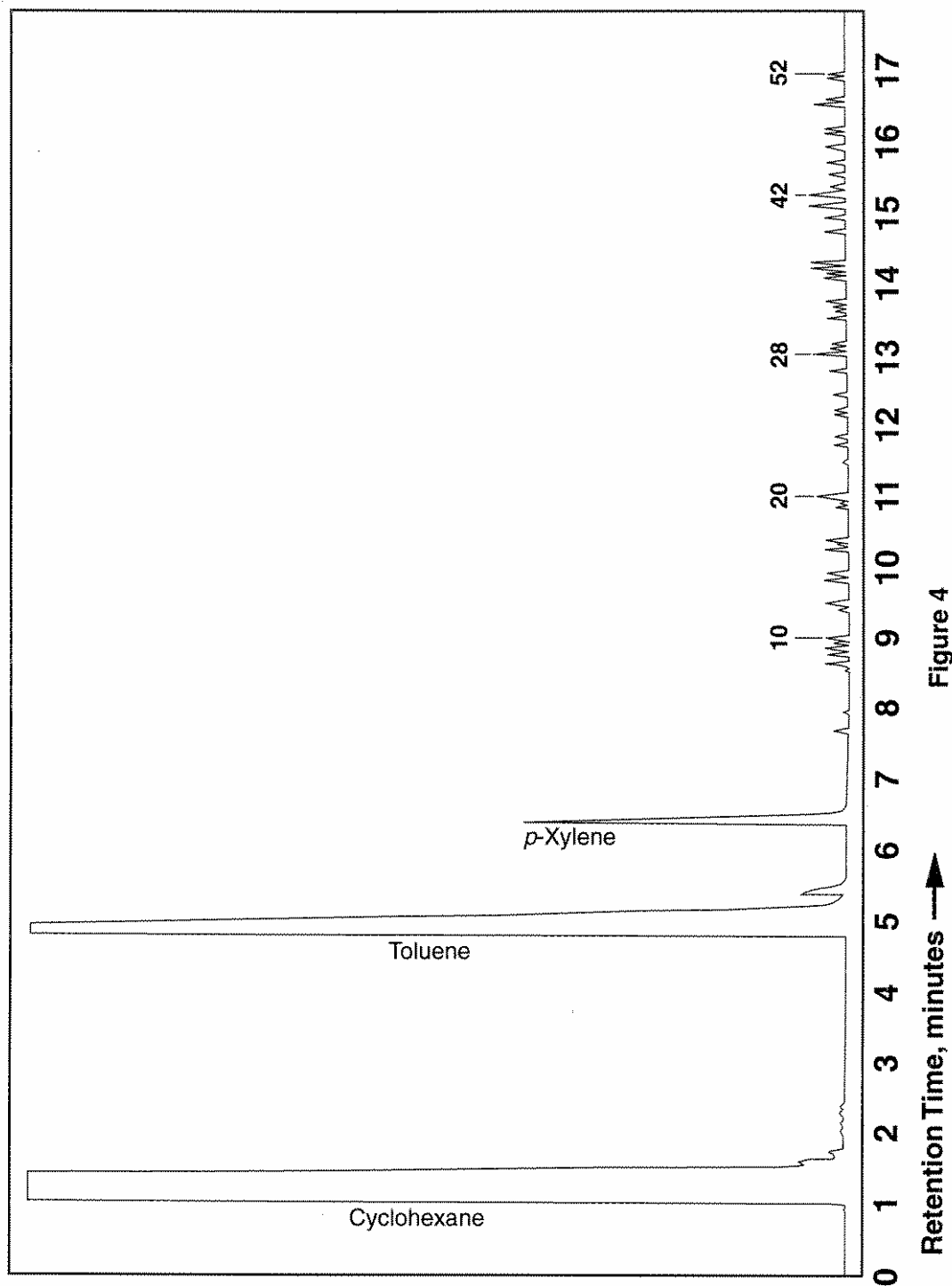


Figure 4

Typical Chromatogram

Fractionation Showing *p*-Xylene Elution, Valve 1 "on" at 1.0 Minute UOP Method 960

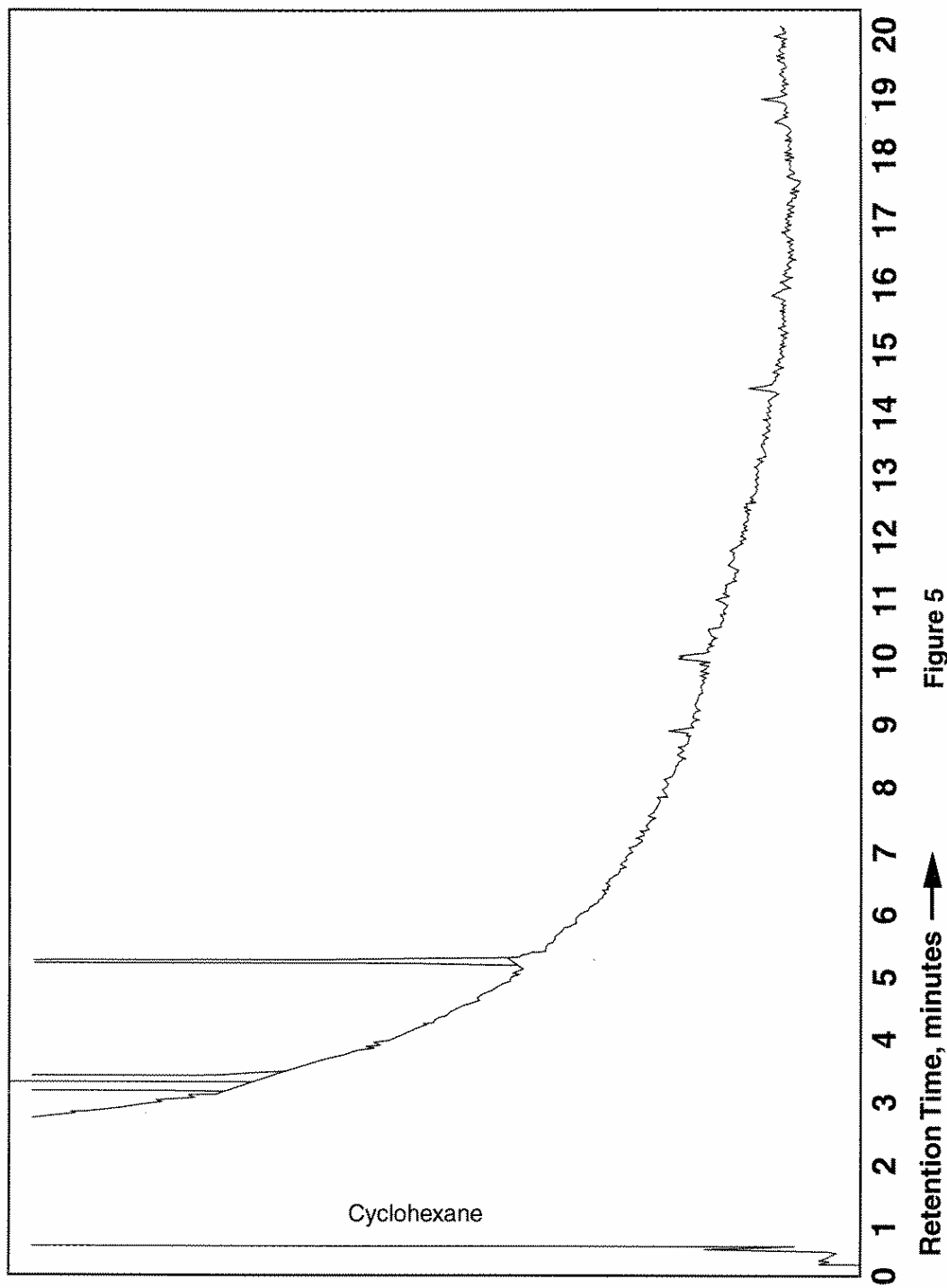


Figure 5
Typical Chromatogram
Anhydrous Cyclohexane

UOP Method 960