



A Honeywell Company

## Trace Oxygenated Hydrocarbons in Liquid Hydrocarbon Streams by GC

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### UOP Method 960-06

#### Scope

This method is for determining trace levels of individual oxygenated hydrocarbons, with boiling points up to 138°C, in C<sub>4</sub> liquefied petroleum gas (LPG), light isomerate and naphtha. Mono-oxygenated hydrocarbons determined include C<sub>1</sub> through C<sub>5</sub> alcohols, and C<sub>2</sub> through C<sub>6</sub> carbonyls and ethers. Di-oxygenated hydrocarbons determined include C<sub>2</sub> through C<sub>4</sub> 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](http://www.astm.org)
- ASTM Method D 2163, "Analysis of Liquefied Petroleum (LP) Gases and Propene Concentrates by Gas Chromatography," [www.astm.org](http://www.astm.org)
- ASTM Method D 2598, "Calculation of Certain Physical Properties of Liquefied Petroleum (LP) Gases from Compositional Analysis," [www.astm.org](http://www.astm.org)
- ASTM Method D 4052, "Density and Relative Density of Liquids by Digital Density Meter," [www.astm.org](http://www.astm.org)
- ASTM Practice D 4307, "Preparation of Liquid Blends for Use as Analytical Standards," [www.astm.org](http://www.astm.org)

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UOP Method 373, "Composition of C2 Through C5 Hydrocarbon Mixtures by Gas Chromatography, [www.astm.org](http://www.astm.org)

UOP Method 999, "Precision Statements in UOP Methods," [www.astm.org](http://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- $\mu$ L repeatable volume of sample. An automatic injection system is recommended, Agilent Technologies Model 7683.

*Syringe*, 10- $\mu$ 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.