A Honeywell Company

Composition of C_2 through C_5 Hydrocarbon Mixtures by GC

UOP Method 373-08

Scope

This method is for determining individual components in C_2 through C_5 hydrocarbon mixtures. The lower limit of detection for a single component is 0.01 mass-%. C_6 and heavier components, if present, may not be fully quantitated. Trace concentrations of these components can be determined using U899.

References

ASTM Practice D1265, "Sampling Liquefied Petroleum (LP) Gases (Manual Method)," www.astm.org

Scanlon, J. T. and Willis, D. E., *Journal of Chromatographic Science*, 23, 333-340 (1985)

UOP Method 516, "Sampling and Handling of Gasolines, Distillate Fuels, and C_3-C_4 Fractions," www.astm.org

UOP Method 899, "Trace Hydrocarbons in Hydrogen or LPG by Gas Chromatography," www.astm.org

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

Outline of Method

The sample to be analyzed is injected into a gas chromatograph that is equipped with a liquid phase sampling valve, a porous layer open tubular (PLOT) column, and a flame ionization detector (FID). The mass-% or mol-% composition of the sample is obtained by the internal normalization technique, wherein the peak areas are first corrected for differences in response and then normalized to 100%.

Apparatus

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

Chromatographic column, 50m x 0.32mm x 5µm (length, ID, layer thickness) Al_2O_3/KCl, Varian, Cat. No. CP-7515

Gas chromatograph, temperature programmable, built for capillary column chromatography, utilizing a split injection system, equipped with a glass injection port insert, provision for both gas and liquid sampling valves and a flame ionization detector that will give a minimum peak height response of five times the background noise for 0.01 mass-% *n*-butane when operated at the recommended conditions, Agilent Technologies, Model 7890.

Integrator, or data system, electronic, for obtaining peak areas. This device must integrate areas at a sufficiently fast rate so that narrow peaks, typically obtained from a capillary column, can be accurately measured. The integrator must have programmable parameters for controlling baseline events, and have graphics capabilities. ChemStation, Agilent Technologies.

Reducer, Swagelok, Cat. No. SS-200-R-1

Regulator, air, two-stage, high purity, delivery pressure range 30-700 kPa (4-100 psi), Matheson Tri-Gas, Model 3122-590

Regulator, hydrogen, two-stage, high purity, delivery pressure range 30-700 kPa (4-100 psi), Matheson Tri-Gas, Model 3122-350

Regulator, nitrogen, two-stage, high purity, delivery pressure range 30-700 kPa (4-100 psi), Matheson Tri-Gas, Model 3122-580

Regulator, nitrogen or helium, two-stage, high purity, delivery pressure range 70-1700 kPa (10-250 psi), Matheson Tri-Gas, Model 3126-580

Stainless Steel tubing, 1/16" OD x 0.04" ID, Alltech Associates, Cat. No. 30033

Tubing, translucent, FEP Teflon, 3.2-mm (1/8-inch) OD, 1.6-mm (1/16-inch) ID, 3450 kPa (500 psi), Alltech Associates, Cat. No. 45740

Valve, liquid sampling valve, 4-port rotary, with 0.5-µl internal groove, Valco, Cat. No. DCI4UWE.5

Vent Shut-off valve, Swagelok, Cat. No. SS-ORS2 (Shut-off valve for LPG sampling)

Reagents and Materials

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

Hydrocarbon Blends, for calibration, Matheson Tri-Gas

Hydrogen gas purifier, Valco, Cat. No. P-200

Hydrogen, purified chromatographic grade, typically 99.995% purity

Nitrogen, make-up gas, total hydrocarbons less than 0.5 ppm as methane

Procedure

The analyst is expected to be familiar with general laboratory practices, the technique of gas chromatography, and the equipment being used.

Sampling

Obtain the sample by following the procedures described in ASTM Practice D 1265, "Sampling Liquefied Petroleum (LP) Gases (Manual Methods)," UOP Method 516, "Sampling and Handling of

Gasolines, Distillate Fuels, and C3-C4 Fractions," or other reliable technique. The specially coated cylinders described in UOP Method 516 may be used but are not required for this application.

Chromatographic Technique

1. Install the gas purifier in the supply line between the carrier gas source and the carrier gas inlets on the gas chromatograph.
   - Column life is significantly reduced if the gas purifier is not used.
2. Install the LPG sampling valve (see Figure 1).
   - The injection valve should be mounted so that it maintains ambient temperature at the start of the run to keep liquid from bubbling in the valve or injection lines prior to injection.
   - If it is desired to make gas injections, replace the liquid injection valve on the GC with a gas injection valve and refer to the appendix of this method for how to inject a gas sample.
3. Install the fused silica capillary column in the gas chromatograph, according to the column and gas chromatograph manufacturer's instructions.
4. Establish the flow rate and operating temperature specified under Operating Conditions (see Table 1).
   - Caution: Hydrogen leakage into the confined volume of the column compartment can cause a violent explosion. It is, therefore, mandatory to test for leaks each time a connection is made, and periodically thereafter.
5. Program the column oven to 200°C. Maintain this temperature until a stable baseline has been obtained at the required sensitivity.
6. If the sample may contain water or sediment, or is of unknown origin, it must be checked for these contaminants before analysis by releasing a small amount of the sample from the bottom of the cylinder. Place the LPG sample cylinder in a vertical position in a hood or well vented area. If the cylinder has an outage tube, the outage tube must be at the top. Briefly open the bottom valve onto the floor of a hood to check that no water or sediment is present in the LPG. If water or sediment is determined to be present, discontinue the analysis and obtain a clean sample.
7. Pressurize the LPG cylinder containing the sample (or blend) to approximately 1400 to 2000 kPA gauge (200- to 300-psig) with nitrogen or helium.
8. Mount the cylinder in a vertical position.
   - The LPG sample is delivered to the lab at elevated pressure. Make sure to connect the sample vessel securely so LPG flows into the GC sampling valve prior to opening valves on the sample vessel.
   - If the cylinder has an outage tube, the outage tube fitting must be at the top. Connect the bottom valve to the sample injector valve inlet tubing.
   - If the cylinder is fitted with an eductor tube, connect the eductor tube outlet to the sample injection inlet tubing in such a manner that the eductor tube is sampling liquid LPG.
   - The connecting tubing between the cylinder and the injector valve must be as short as possible.
9. Place the injection valve in the fill position.
10. Ensure that the vent shut-off valve is closed.
11. Fully open the bottom valve, or eductor valve of the sample cylinder.
12. Partially open the vent shut-off valve to permit LPG flow through the sampling system.

Table 1

Recommended Operating Conditions

Carrier gas	**hydrogen**
Mode	**constant pressure**
Head pressure	**75 kPa gauge (11 psig)**
Linear velocity @ 85°C	**45 cm/sec**
Equivalent flow @ 85°C	**2.4 mL/min**
Split flow	**300 mL/min**
Injection port temperature	**210°C**
Column temperature program[a]	
Initial temperature	**85°C**
Initial hold time	**2.5 min**
Programming rate A	**2°C/min**
Intermediate 1 temperature	**100°C**
Intermediate 1 hold time	**0 min**
Programming rate B	**5.3C/min**
Intermediate 2 temperature	**135°C**
Intermediate 2 hold time	**0 min**
Programming rate C	**14°C/min**
Final hold temperature	**200°C**
Final hold time	**24.25 min**
Detector	**flame ionization**
Detector temperature	**250°C**
Hydrogen flow rate[b]	**35 mL/min**
Air flow rate[b]	**350 mL/min**
Makeup gas	**nitrogen**
Makeup gas flow rate[b]	**30 mL/min**
Sample size	**0.5 µl for LPG**

[a] The column used for this analysis has an upper limit of 200˚C; do not exceed.

[b] Consult the manufacturer's instrument manual for suggested flow rates.

13. Purge the sample valve with sample, watching the translucent tubing to ensure it is liquid full. Continue the flow until entrained bubbles are no longer observed in the translucent tubing, and inlet lines are adequately flushed of previous sample residuals.
    - CAUTION: Inspect the translucent tubing regularly. Replace at first signs of wear or kinking. Pressure on the translucent tubing must never exceed 2000 kPa (300 psig).
14. Stop the sample flow by closing the vent shut-off valve.
15. Inject the sample immediately by switching the injection valve to the inject position, and start the integrator and the column temperature programming sequence.
    - The injection valve remains in the inject position for the duration of the sample run.
16. Close the LPG cylinder valve and immediately open the vent shut-off valve to vent the sampling system.
17. Identify each component and calculate their concentrations as described in *Calculations*.
    - The C2 through C5 hydrocarbon separation is complete in less than 18 minutes. Additional time is required for heavier components to elute if present.