Honeywell UOP

Determination of Trace Oxygenated Hydrocarbons in Gaseous, LPG and Liquid Hydrocarbon Streams by GC

UOP Method 960-20

Scope

This method is for determining trace levels of select oxygenated hydrocarbons, with boiling points up to 138°C, in refinery gas streams, C_4 liquefied petroleum gas (LPG), light isomerate and naphtha. Mono-oxygenated hydrocarbons determined include C_1 through C_5 alcohols, and C_2 through C_6 carbonyls and ethers. Formaldehyde, if present, is not determined by this method. Di-oxygenated hydrocarbons determined include C_2 through C_4 methyl esters and 1,4-dioxane. The range of quantitation for each individual oxygenate in liquid streams is 0.2 to 250 mass-ppm (mg/kg) and in gas/LPG streams is 1.0 to 250 mass-ppm (mg/kg). Inorganic compounds containing oxygen, such as water, carbon monoxide, carbon dioxide or heteroatoms such as nitrogen, chlorine or sulfur are not determined. Unsaturated oxygenated hydrocarbons may be detected but are not identified. Certain oxygenated hydrocarbons are not separated and are reported as composites. Some sulfur and nitrogen compounds are known to elute in the oxygenate region of the chromatogram.

References

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

ASTM Method D1657, "Density or Relative Density of Light Hydrocarbons by Pressure Hydrometer," www.astm.org

ASTM Method D2163, "Analysis of Liquefied Petroleum (LP) Gases and Propene Concentrates by Gas Chromatography," www.astm.org

ASTM Method D2598, "Calculation of Certain Physical Properties of Liquefied Petroleum (LP) Gases from Compositional Analysis," www.astm.org

ASTM Method D4052, "Density and Relative Density of Liquids by Digital Density Meter," www.astm.org

ASTM Practice D4307, "Standard Practice for Preparation of Liquid Blends for Use as Analytical Standards," www.astm.org

ASTM Practice D5287, "Standard Practice for Automatic Sampling of Gaseous Fuels," www.astm.org

ASTM Method D7423, “Standard Test Method for Determination of Oxygenates in C2, C3, C4, and C5 Hydrocarbon Matrices by Gas Chromatography and Flame Ionization Detection,” www.astm.org

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

UOP Method 516, “Sampling and Handling of Gasolines, Distillate Fuels, and C3-C4 Fractions,” www.astm.org

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

Scanlon, J. T., and D. E. Willis. "Calculation of Flame Ionization Detector Relative Response Factors Using the Effective Carbon Number Concept." *Journal of Chromatographic Science* 23.8 (1985): 333-40. Web.

Outline of Method

The method requires the use of a dedicated pre-configured gas chromatograph equipped with an auxiliary oven that is configured for automated analysis and is capable, via valving, of determining trace oxygenates in refinery gas streams, C_4 liquefied petroleum gas (LPG), light isomerate and naphtha. A reproducible volume of sample is injected into a specially configured 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 Lowox column, separates and analyzes oxygenates. The non-polar column operates isothermally inside an auxiliary oven, and the 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 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. Valve 2 Fractionation A time is used to determine all oxygenates other than dimethyl ether.
2. Valve 2 Fractionation B time is used to determine only dimethyl 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. Effective carbon number (ECN) is used to calculate the relative response factors of the oxygenated components based on the response factor of the reference material. See Table 2 for a list of compounds and composites. Using pure compounds to calibrate each component can result in better accuracy.

Apparatus

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers or newer models may be used. Pre-configured instruments are available.

Analyzer, Wasson ECE Instrumentation, Application No. UOP960. See Figure 1 for Analyzer configuration. Other vendors also supply similar systems. Confirm with the selected vendor that the required separations are provided for the specific sample types to be analyzed. The Wasson-ECE analyzer includes:

Chromatographic column, 10 m x 530 µm ID x 10 µm Lowox, Agilent, Cat. No. CP8587

Fractionation column, 30 m x 530 µm ID x 5 µm MXT-1, Restek, Cat. No. 70179

Fused silica tubing, 2 m x 0.32 mm ID, deactivated, Agilent, Cat. No. CP803210

Gas chromatograph, capable of multiple temperature ramping, built for capillary column chromatography utilizing a split injection system with electronic pressure control (EPC), having a glass injection port insert. Three channels of additional electronic pressure control are required. Agilent Technologies, Model 7890.

Sample injector, syringe or injector capable of injecting a 4-µL repeatable volume of sample. An automatic injection system is recommended, Agilent Technologies Model 7693A.

Balance, readability 0.1-mg

Clamp, for ring stand and sample cylinders, Fisher Scientific Cat. No. 02-217-000

Clamp holder, for ring stand and clamp, Fisher Scientific Cat. No. 02-217-005

Chromatographic Data System, for computerized instrument control of data acquisition and data reduction, ChemStation, Agilent Technologies.

Electronic leak detector, Agilent gas leak detector, Agilent, Cat. No. G3388B

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

Regulator, air, two-stage, high purity, Matheson Tri-Gas, Cat. No. SEQ3122A590

Regulator, hydrogen, two-stage, high purity, Matheson Tri-Gas, Cat. No. SEQ3122A350

Regulator, dimethyl ether blend, two-stage, high purity, Matheson Tri-Gas, Cat. No. SEQ3810A350

Regulator, nitrogen, two-stage, high purity, Matheson Tri-Gas, Cat. No. SEQ3122A580

Regulator, nitrogen, single stage, high purity, high pressure delivery to pressurize LPG sample and blend cylinders, Matheson Tri-Gas, Cat. No. SEQ3538A580

Ring stand, with rectangular base, 140- x 229- mm with 610- mm rod, Fisher Scientific, Cat. No. 14-679Q

Syringe, 10-µL, for qualitative mixture preparation, Hamilton 701NF, Restek, Cat. No. 20167

Tubing, Sulfinert, .030-in ID x 1/16-in OD, Cat# 29230, Restek

Tubing, translucent, FEP Teflon, 3.2-mm (1/8-inch) OD, 1.6-mm (1/16-inch) ID, 3450 kPa (500 psi), Thomas Scientific, Cat. No. 9567K20

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 ppm as methane

Blend, gas, quantitative, certified standard, containing 100 mol-ppm of dimethyl ether in research grade propane, Matheson Tri-Gas.

Blend, LPG, quantitative, certified standard, containing 10 mass-ppm of 2-butanone 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.

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

Cyclopentanol, 99%, Sigma-Aldrich, Cat. No. C112208

Gas purifier, hydrogen carrier gas purifier, VICI Metronics, Cat. No. P200-1

Gas purifier, air (for detectors), VICI Metronics, Cat. No. P400-1

Gas purifier, nitrogen, for detector makeup gas, VICI Metronics, Cat. No. P300-1

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

Inlet liner, Siltek Deactivated, 5.2 mm ID Straight Inlet Liner for Agilent GCs equipped with split/splitless inlets, Restek, Cat. No. 21700

Methyl ethyl ketone (2-Butanone), 99.5%, Sigma-Aldrich, Cat. No. 270695

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

Oxygenated hydrocarbons, Sigma-Aldrich, see Table 2 for Catalog Numbers

Pipet bulb, 1-mL, Fisher Scientific, Cat. No. 03-448-25

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

Vials, glass, 20-mL, with caps, Fisher Scientific, Cat. No. 03-337-14

Procedure

The analyst is expected to be familiar with general laboratory practices, the technique of gas chromatography and the equipment being used. Dispose of used reagents, materials, and samples in an environmentally safe manner according to local regulations.

Sampling

Obtain the sample by following the procedures described in ASTM Practice D 1265, ASTM Practice D 5287, UOP Method 516, or other reliable technique.

Chromatographic Technique

1. Follow the instrument site preparation checklist provided by the manufacturer and arrange for installation by the manufacturer's service engineer to establish recommended operating conditions as listed in Table 1.
   - The Wasson-ECE analyzer comes with on-site installation and training by a Wasson-ECE engineer in the continental U.S., inquire with Wasson-ECE for other locations.
2. 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. Replace the gas purifier at intervals determined by good laboratory practice. An indicating oxygen trap may be placed downstream of the gas purifier. When the indicator shows one-half used, replace both the gas purifier and the indicating trap.
   - 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.
3. Install the Siltek metal inlet liner into the front injection port according to the instrument manufacturer instructions.
   - The Siltek liner has equivalent inertness to glass sleeves but, has greater total volume, allowing the large injections of LPG and volatile liquids will not exceed the vapor volume of the injection port.
   - Initially, the injection port should be maintained at 250°C for 24 hours to condition the Siltek injection port liner.