Honeywell
UOP

Determination of Trace Propadiene and Methyl Acetylene Impurities in Polymer Grade Propylene by Gas Chromatography

UOP Method 1014-17

Scope

This method is for determining trace methyl acetylene and propadiene (MAPD) in high purity polymer grade propylene liquid or gas using a preconfigured, commercially available gas chromatograph. Other impurities of C3-C5 if present can also be determined. The range of quantitation for each component is 0.2 to 2000 mass- (or mol-) ppm. This method can be used to determine trace impurities in ethylene with appropriate gas injection valve and customized run program. For a full characterization of the C5 minus impurities to a lower limit of quantitation of 2 ppm refer to UOP 899.

References

UOP Method 899, "Trace Hydrocarbons in Hydrogen, Hydrocarbon Gases, or LPG by GC," www.astm.org

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

Wasson ECE Instrumentation, *Application 263-SP* instrument manual

Wasson ECE Instrumentation, Vaporizer instrument manual

Outline of Method

The method requires the use of a dedicated gas chromatographic system that is configured for automated analysis which is capable, via valving and a vaporizer, of determining impurities in polymer-grade propylene gas or liquid.

A reproducible sample volume is injected into a GC configured with a vaporizer (external or on-board), gas sampling valve, split/splitless inlet, flame ionization detector (FID), and control and quantitation software. Through the use of multiple valves, a portion of the sample is injected onto the first column where molecules are separated by boiling point. Next, a portion of the sample, mostly propylene and higher boiling analytes, is cut onto a second column where molecules are separated based on polarity and sent to the FID for detection. The concentrations of methyl acetylene and propadiene (MAPD) in propylene sample matrices are determined by the external standard method of quantitation, wherein peak areas of the sample impurities are compared to peak areas of a calibration blend.

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. SAFETY DATA SHEETS (SDS) 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).

Nonconfidential UOP Methods are available from ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States. The UOP Methods may be obtained through the ASTM website, www.astm.org, or by contacting Customer Service at service@astm.org, 610.832.9555 FAX, or 610.832.9585 PHONE.

Significance and Use

High purity propylene and ethylene are commonly used as the feedstock for production of polypropylene, and the quality of this monomer is critical to successful polymerization. The presence of trace amounts of certain hydrocarbon impurities can have adverse effects on the product quality. This test method is suitable for setting specifications, for use as an internal quality control tool, and for use in development or research work.

Apparatus

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

Analyzer, Wasson-ECE Instrumentation Application 263-SP "Analysis of Impurities in Polymer-grade Propylene" Gas chromatographs are available pre-configured, including a data system, from several suppliers. Confirm with the supplier that the analyzer is appropriate for the stream to be analyzed and the analysis required (see Figure 1 for Analyzer configuration) which includes:

*Chromatographic column 1, 3*0 m of 0.53-mm ID fused silica capillary, internally coated to a film thickness of 0.5-µm (bonded) with poly-dimethyl siloxane, boiling point column. Wasson ECE, Part No. 2337 Code KC79

Chromatographic column 2, 50 m of 0.53-mm ID PLOT fused silica capillary, internally coated to a Film thickness of 9-µm with alumina (GS-Alumina), Wasson ECE, Part No. 2491 Code KC136

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 and flame ionization detector. Three channels of additional electronic pressure control is required. Agilent Technologies, Model 7890.

Vaporizer, model A1034-003, Wasson-ECE Instrumentation, Figure 2 shows Vaporizer flow path.

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

Tubing, stainless steel, 1.6-mm (1/16-inch) OD, 0.76-mm (0.030-inch) ID, Fisher Scientific, Cat. No. AT3003

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

Integrator, or data system, electronic, for obtaining peak areas. This device must integrate areas at a sufficiently fast rate so that narrow peaks typically resulting from use of a capillary column can be accurately measured. ChemStation, Agilent Technologies.

Leak detector, gas, Fisher Scientific, Cat. No. 0.-251-702

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

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

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

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

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

Reagents and Materials

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

Calibration blend, LPG, quantitative, primary Propylene standard, in a piston cylinder, pressurized with nitrogen to 800 psig, containing approximately 3 ppm of each of the following trace components: Isobutane, n-Butane, Propadiene, trans-2-Butene, 1-Butene, Isobutene, cis-2-Butene, Isopentane, Methyl Acetylene, n-Pentane, 1,3-Butadiene in Propylene. Local supply.

Air, zero gas, total hydrocarbons less than 2.0 ppm as methane

Helium, chromatographic grade, typically 99.995% purity

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

Hydrogen, zero-gas, 99.95% minimum purity, total hydrocarbons less than 0.5 ppm as methane

Gas purifier, helium, used to remove oxygen and moisture from carrier gas, VICI Metronics, Cat. No. P100-1

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 reagent, material, 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, "Sampling Liquefied Petroleum (LP) Gases (Manual Method)," ASTM Practice D 5287, "Automatic Sampling of Gaseous Fuels," UOP Method 516, "Sampling and Handling of Gasolines, Distillate Fuels, and C3-C4 Fractions," 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.
    - 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.
3. Place the LPG sample cylinder in a vertical position. If the cylinder has an outage tube, the outage tube must be at the top. Briefly open the bottom valve 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.

- LPG samples are usually contained in a cylinder having valves on both ends or, in some cases, a cylinder where one of the valves is connected to an eductor tube. If the sample cylinder contains an eductor tube, invert the cylinder (both valves on the bottom) and briefly open the valve not connected to the eductor tube to check that no water or sediment is present. See Figure 3 for diagram of common LPG cylinders.

4. Pressurize the LPG cylinder containing the sample to approximately 1400 to 2068 kPA gauge (200 to 300 psig) with nitrogen or helium.
5. Mount the cylinder in a vertical position. If the cylinder has an outage tube, the outage tube fitting must be at the top.
6. Attach the sample cylinder to the appropriate liquid bulkhead on the front of the vaporize
   - 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 vaporizer must be as short as possible.
7. Ensure that the vent purge valve is closed.
8. Ensure the vaporizer temperature is set at desired conditions and all vent and sample lines are connected.
   - Wasson ECE vaporizer temperature is set to 180°C. If using different vaporizer, refer to instrument manual.
9. Fully open the bottom valve, or eductor valve, of the sample cylinder to allow sample to pressurize the sample line.
10. Partially open the liquid purge valve (about one turn counter-clockwise). Wait until the flow emitting from liquid sample vent from the back of the vaporizer become liquid. If it does not, the pressure in the sample cylinder may be too low.
11. Continue the flow until entrained bubbles are no longer observed through the translucent tubing.
    - CAUTION: Inspect the translucent tubing regularly. Replace at first signs of wear or kinking. Pressure rating on the translucent tubing must be rated higher than pressure on sample or blend cylinder.
12. Close the liquid purge valve to block venting liquid.
13. Monitor the vent bubbler, allow about 1 minute for the vaporized sample to sweep through the gas chromatograph gas sampling valve.
14. Inject the sample by switching the injection valve to the inject position, and start the integrator and the column temperature programming sequence.
15. Close the LPG sample cylinder valve and immediately open the vent purge valve to vent the sampling system.
16. Identify each component by comparing the resultant chromatogram with the Typical Chromatogram as shown in Figure 4.

Operating Conditions

It is recommended to use the manufacturer operating conditions for this analysis to produce the required sensitivity and chromatographic separations equivalent to those shown in the Typical Chromatogram.