Determination of Trace Chloromethane, Chloroethene, and Dichloromethane in Polymer Grade Ethylene & Propylene by Gas Chromatography Mass Spectrometry

UOP Method 1035-19

Scope

This method is for determining trace chloromethane, chloroethene, and dichloromethane in high purity polymer grade ethylene and propylene gas or liquid using a gas chromatograph equipped with a mass spectrometer run in selected ion monitoring mode. The specific instrument is preconfigured and is capable of determining typical impurities in polymer grade ethylene or propylene, however this method only outlines the procedure for determining chloromethane, chloroethene, and dichloromethane. Chloromethane and chloroethene elute on the propylene tail but are readily extracted by unique ions. The lower limit of quantitation for chloromethane, chloroethene, and dichloromethane are 0.02 mol- (or mass-) ppm.

References

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

ASTM Practice D5287, "Automatic Sampling of Gaseous Fuels," 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

Wasson ECE Instrumentation, *Application 460-SP* instrument manual

Wasson ECE Instrumentation, Dynamic Blender instrument manual

Outline of Method

The method requires the use of a dedicated gas chromatographic mass spectrometer system that is configured for automated analysis which is capable, via valving and an on-board vaporizer, of determining impurities in polymer-grade ethylene or propylene gas or liquid. For the trace chloride analysis, a reproducible sample volume is injected into a gas chromatograph (GC) that is equipped with a polar fused silica capillary column (Figure 1, column 2), a mass spectrometer detector, and control and quantitation software. The concentrations of chloromethane, chloroethene, and dichloromethane are determined by a multi-point external standard calibration curve for each

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component that represents the area of each selected ion versus its concentration, analyzed under identical conditions and injection volumes.

Significance and Use

High purity ethylene and propylene are used as feedstocks for production of polyethylene and polypropylene, respectively. The quality of the monomer is critical to successful polymerization. The presence of trace amounts of certain impurities can have detrimental effects on the catalyst and product yields. 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 460-SP "GC/MS Analysis of Impurities in Polymer-grade Propylene", 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. Pre-configured systems are available from Wasson-ECE for determining only chlorides, the application specified can determine other impurities. The Wasson-ECE analyzer includes:

Chromatographic column, 60 meters, PLOT, part# 60 m 2358, Wasson-ECE Instrumentation

Chromatographic column, 60 meters, polar, part# 60 m 2318, Wasson-ECE Instrumentation

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.

Mass Spectrometer Detector, capable of selected ion monitoring and equipped with inert EI source, performance turbo pump, ion gauge controller kit and data system. Agilent Technologies, Model 5977B.

On-board Vaporizer, converts LPG to the gas phase prior to injection, Wasson-ECE Instrumentation

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

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

Dynamic Blender with mass flow controller, model DB302, Wasson-ECE Instrumentation

Flowmeter, Mass/VLM, Agilent Technologies, Model ADM 2000.

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

Regulator, helium, two-stage, high purity, delivery pressure range 30 to 700 kPa (4 to 100 psi), Matheson Tri-Gas, Model 3122-580, Cat. No. SEQ3122A580, 2 required

Regulator, nitrogen, two-stage, high purity, delivery pressure range 30 to 700 kPa (4 to 100 psi), Matheson Tri-Gas, Model 3122-580, Cat. No. SEQ3122A580

Regulator, 2 component chloride blend, two-stage, high purity, delivery pressure range 30 to 1700 kPa (0 to 250 psi), Matheson Tri-Gas, Model 3810-350, Cat. No. SEQ3816A350

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

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.

Calibration blend, Gas, quantitative, containing chloromethane, chloroethene, and dichloromethane at the 10 mol-ppm level in helium, local supply.

Gas purifier, for carrier gases, to remove moisture, VICI Mat/Sen, Cat. Nos. P100-1(helium), P300-1(nitrogen), local supply.

Helium, UHP, 99.9995% minimum purity, total hydrocarbons less than 0.5 ppm as methane, local supply.

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

Procedure

The analyst is expected to be familiar with general laboratory practices, the technique of gas chromatography, mass spectrometry 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, “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 C_3-C_4 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 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.
3. When a major change is made to the system, such as the power to the GCMS is interrupted, the GCMS needs to be tuned in accordance with the manufacturer’s instructions. A new calibration curve should then be established.

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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 Total Ion Chromatogram as shown in Figures 2a and 2b.

Table 1
Recommended Operating Conditions

Carrier gas	**helium**
Mode	**constant flow**
Flow rate	**1.5 mL/min**
Head pressure	**8.2 psig @ 40ºC**
Linear velocity	**31.4 cm/sec @ 40°C**
Split flow	**15 mL/min**
Injection port temperature	**200°C**
On-board Vaporizer temperature	**80°C**
Column temperature program	
Initial temperature	**40°C**
Initial time	**6 min**
Programming rate	**15°C/min**
Final temperature	**150°C**
Final time	**3 min**
Detector	
Ion Source	**EI**
Source temperature	**230°C**
Quad temperature	**150°C**
Transfer line temperature	**280°C**
Fixed Electron energy	**70 eV**
Acquisition Type	**SIM**
Sample size	**1.0 mL, repeatable**

Gas Samples and Blends

1. Choose and load appropriate method for gas sample analysis, ensuring valve 1 is in the on position to bypass the on-board vaporizer, see Figure 1.
2. Connect the sample cylinder or calibration blend cylinder to the sample inlet with Sulfinert tubing and purge the system with the gas to be analyzed for 20 seconds. Stop the flow, allow 5 to 10 seconds for the pressure to equilibrate, and start the analysis.
    - If connecting the dynamic blender to the system, significantly more time (about 60 seconds) should be used to purge the inlet due to the decreased flow rate.
    - The stop flow technique is described however constant flow while injecting can also be used, especially when using the dynamic blender. The technique which provides the best precision between multiple injections should be used.
3. Identify chloromethane, chloroethene, and dichloromethane by matching retention time and their target ion as listed in Table 2. Record the area of each target ion from the extracted ion chromatogram.
    - A typical total ion chromatogram is shown in Figures 2a and 2b for reference.
    - Retention times of components may be influenced by the amount of propylene or diluent in the calibration blend or sample.
4. Repeat steps 1 and 2 for each sample until the peak areas from each run do not deviate by more than 10%.

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