TRACE HYDROCARBONS IN HYDROGEN, HYDROCARBON GASES, OR LPG BY GC

UOP™ Method 899-04

SCOPE

This method is for determining individual trace C_5 minus hydrocarbon impurities in hydrogen or liquefied petroleum gas (LPG), where the specific trace components are sufficiently resolved from the major components, typically propane/propylene or ethane/ethylene. Components eluting after ethyl acetylene are grouped and reported as heavies. The range of quantitation for each component is 2 to 3000 mol- (or mass-) ppm; however, the lower limit of quantitation increases when major components interfere with the resolution of the impurities.

REFERENCES

ASTM Practice D 1265, "Sampling Liquefied Petroleum (LP) Gases (Manual Method)," www.astm.org

ASTM Practice D 5287, "Automatic Sampling of Gaseous Fuels," 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 999, "Precision Statements in UOP Methods," www.astm.org

OUTLINE OF METHOD

A reproducible volume of gas sample is injected into a gas chromatograph equipped with an alumina PLOT (porous layer open tubular) capillary column, a capillary injection port, a flame ionization detector (FID), and a gas or LPG sampling valve. An LPG sample may be expanded and analyzed as a vapor, or analyzed directly in the liquid phase (see *NOTE*). The concentrations of the hydrocarbon impurities are determined by the external standard method of quantitation, wherein peak areas are compared to the area of a calibration blend containing a known concentration of isobutane. For

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. MATERIAL SAFETY DATA SHEETS (MSDS) 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).

UOP Methods are available through ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 194428-2959, United States. The 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.

For samples containing C_5 olefins, a second analysis, under a different column temperature program, is necessary to resolve methyl acetylene from an interfering C_5 olefin.

APPARATUS

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

Chromatographic column, 50 m of 0.53-mm ID PLOT fused silica capillary, internally coated to a film thickness of 9-µm with alumina (GS-Alumina), J&W Scientific, Cat. No. 115-3552. Columns from other suppliers, commonly called Al_2O_3/Na_2SO_4, provide similar separation but may not be quantitative for diolefins and acetylenes, and their use is not recommended when analysis of these components is necessary.

Gas chromatograph, capable of temperature ramping, equipped with electronic pressure control, built for capillary column chromatography utilizing a split injection system, having a glass injection port insert, a heated valve box, and an FID that will give a minimum peak height response of 5 times the background noise for 2 mol-ppm of isobutane when operated at the recommended conditions, Agilent Technologies, Model 6890

Injection apparatus, gas, for injection of gas or expanded LPG samples, see Figure 1:

Fitting, internal union, for connecting injection port to 6-port sampling valve, Valco Instruments, Cat. No. ZU1T

Valve, 6-port, stainless steel, 1.59-mm (0.0625-inch) fittings, manual with standoff, Valco Instruments, Cat. No. C6UWE

Sample loop, stainless steel, 100-µL, Valco Instruments, Cat. No. SL100CUW

Tubing, stainless steel, 1.6-mm (1/16-inch) OD, 0.76-mm (0.30-inch) ID, Alltech Associates, Cat. No. 300010

Injection apparatus, LPG, for injection of LPG samples in the liquid phase, see Figure 2:

Fitting, CGA, for blend cylinder, CGA No. 510, Matheson Gas Products

Fitting, internal union, for connecting injection port to 4-port sampling valve, Valco Instruments, Cat. No. ZU1T

Fitting, reducing union, 3.2-mm (1/8-inch) to 1.6-mm (1/16-inch), Swagelok, Cat. No. SS-200-6-1

Tubing, stainless steel, 1.6-mm (1/16-inch) OD, 0.76-mm (0.30-inch) ID, Alltech Associates, Cat. No. 300010

Tubing, translucent, FEP Teflon, 3.2-mm (1/8-inch) OD, 1.6-mm (0.062-inch) ID, 3450 kPa (500 psig), Alltech Associates, Cat. No. 45740

Valve, 4-port, stainless steel, 0.5-µl internal sample volume, 1.59-mm (0.0625-inch) fittings, manual with standoff, Valco Instruments, Cat. No. CI4UWE.5

Valve, vent shut-off, Swagelok, Cat. No. SS-ORS2

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

LPG expansion apparatus, for quantitative expansion of LPG from a liquid to a gas phase, see Figure 3:

Fitting, male connector, stainless steel, 0.25-inch tube fitting to 0.25-inch male NPT, Swagelok, Cat. No. SS-400-1-4. Sample cylinders having an outlet fitting other than 0.25-inch female NPT will require a different fitting.

Fitting, port connector, stainless steel, 0.25-inch tube fitting, Swagelok, Cat. No. SS-401-PC, 2 required

Fitting, union tee, stainless steel, 0.25-inch, Swagelok, Cat. No. 400-3

Tubing, stainless steel, Type 304, 0.25-inch OD x 0.210-inch ID, Alltech Associates, Cat. No. 30301

Vacuum pump, capable of achieving a vacuum of 0.1-mm Hg, Fisher Scientific, Cat. No. 01-115-2

Valve, stainless steel, 0.25-inch, Swagelok, Cat. No. SS-1RS4

LPG expansion cylinder, sample cylinder for containing expanded LPG sample:

Cylinder, 4- x 6-inch, 316 stainless steel, 1380 kPa (200 psi) internal pressure, double connection, 0.25-inch pipe hex bored through, Arthur Harris, Cat. No. B-270

Fitting, hex nipple, stainless steel, 0.25-inch NPT, Swagelok, Cat. No. SS-4-HN, 3 required

Fitting, tee, stainless steel, 0.25-inch NPT, Swagelok, Cat. No. SS-4-T

Gauge, stainless steel, vacuum-pressure, -100 to +200 kPa gauge (-15 to +30.0 psig) range, Matheson Gas Products, Cat. No. 63-2204

Valve, stainless steel, 0.25-inch NPT inlet, 0.25-inch tube fitting outlet, Whitey, Swagelok, Cat. No. SS-1RM4-S4, 2 required

Regulator, air, two-stage, high purity, delivery pressure range up to 690 kPa (100 psi), Matheson Gas Products, Model 3122-590

Regulator, helium, two-stage, high purity, delivery pressure range up to 690 kPa (100 psi), Matheson Gas Products, Model 3122-580

Regulator, hydrogen, two-stage, high purity, delivery pressure range up to 690 kPa (100 psi), Matheson Gas Products, Model 3122-350

Regulator, nitrogen, two-stage, high purity, delivery pressure range up to 690 kPa (100 psi), Matheson Gas Products, Model 3122-580

REAGENTS AND MATERIALS

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