



A Honeywell Company

Refinery Gas Analysis by GC

UOP Method 539-12

Scope

This method is for determining the composition of refinery gas streams or vaporized liquefied petroleum gas (LPG) using a preconfigured, commercially available gas chromatograph. At a minimum, the following components are reported: non-condensable gases, individual C_1 through C_4 hydrocarbons and C_5 paraffins. C_5 olefins and C_6+ hydrocarbons are reported as a composite. Some configurations of the analyzer will separate the C_5 olefins and certain C_6+ hydrocarbons. Oxygen is not separated from argon. Results for hydrogen sulfide, if present, may not be quantitative on some analyzers. The lower limit of quantitation for each component or composite is 0.05 mol-%. If the measurement of lower concentrations of hydrocarbons are needed, use UOP Method 899, "Trace Hydrocarbons in Hydrogen, Hydrocarbon Gases, or LPG by GC." LPG samples may be analyzed by UOP Method 373, "Composition of C_2 through C_5 Hydrocarbon Mixtures by GC," or UOP Method 980, " C_5 and Lower Boiling Dienes, Olefins, and Paraffins in Naphthas by GC." Alternatively, LPG samples may be expanded to the gas phase and run by this method.

References

Analyzer manufacturer's operating manual

UOP Method 373, "Composition of C_2 through C_5 Hydrocarbon Mixtures by GC," www.astm.org

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

UOP Method 980, " C_5 and Lower Boiling Dienes, Olefins, and Paraffins in Naphthas by GC," www.astm.org

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

Outline of Method

The sample is injected into a GC configured for refinery gas analysis with multiple valves and columns, and, usually, more than one detector. The included data system controls the operating sequence, measures the resultant peaks, and performs component quantitation based upon calibration with known gas blends.

Apparatus

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

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).

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Analyzer, refinery gas. Refinery gas analyzers are available pre-configured, including a data system, from several suppliers. A partial list of suppliers is included in *Appendix A*, and includes instrument features as described in the supplier's website, as of publication of this method. Other vendors also supply similar systems. Confirm with the supplier that the analyzer is appropriate for the streams to be analyzed and the analysis required.

Instrument gas supply regulators; not all instruments will require all the regulators listed below.

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

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

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

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

Leak detector, gas, Grace Davison, Cat. No. 60229

Reagents and Materials

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

Calibration blends, as specified by the analyzer operating manual, Matheson Tri-Gas, or local supply. For increased accuracy, one calibration blend should have a composition close to that of the samples to be analyzed, but not less than 1 mol-% of each component of interest. Table 1 lists a set of calibration blends that would be generally applicable to a variety of sample types.

Gas purifier, for carrier gases, to remove oxygen and moisture, VICI Mat/Sen, Cat. Nos. P100-1 (helium), P200-1 (hydrogen), P300-1 (nitrogen), and (optional) indicating oxygen traps, Restek, Cat. No. 22010

Instrument gases, as needed; not all instruments will require all the gases listed below.

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

Argon, 99.99% minimum purity, local supply

Helium, 99.99% minimum purity, local supply

Hydrogen, zero gas, 99.99% 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, and the equipment being used. Dispose of used reagents, materials, and samples in an environmentally safe manner according to local regulations.

Table 1
Calibration Blend Example Concentrations, mol-%

Component	Blend 1	Blend 2	Blend 3
Hydrogen	50.0	---	20.0
Nitrogen	15.0	15.0	45.0
Argon	5.0	---	5.0
Methane	5.0	10.0	---
Ethane	5.0	10.0	---
Ethylene	---	5.0	---
Propane	12.0	12.0	---
Propylene	---	6.0	---
Propadiene	---	1.0	---
<i>n</i> -Butane	3.0	10.0	---
Isobutane	3.0	10.0	---
1-Butene	---	5.0	---
Isobutylene	---	5.0	---
<i>trans</i> -2-Butene	---	5.0	---
<i>cis</i> -2-Butene	---	5.0	---
1,3-Butadiene	---	1.0	---
<i>n</i> -Pentane	1.0	---	---
Isopentane	1.0	---	---
CarbonDioxide	---	---	5.0
CarbonMonoxide	---	---	10.0
Helium	---	10.0	---
HydrogenSulfide	---	---	5.0

If specific components, e.g., hydrogen sulfide, helium, or 1,3-butadiene are known to be not present in the sample types being analyzed, they may be deleted from the blends, and the composition of the other components adjusted to total 100%.

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 gas purifiers are not used. Replace the gas purifiers at intervals determined by good laboratory practice. Indicating oxygen traps may be placed downstream of the gas purifiers. When the indicator shows one-half used, replace both the gas purifier and the indicating trap.
2. Follow the instrument set-up procedure provided by the manufacturer and establish the recommended operating conditions.
 - CAUTION: Hydrogen leakage into the confined volume of the column oven can cause a violent explosion. Therefore, it is mandatory to check for leaks each time a connection is made and periodically thereafter.
3. Connect the sample cylinder or calibration blend cylinder to the sample inlet and purge the system with the gas to be analyzed. If LPG samples are to be analyzed, they must be expanded to the gas phase before analysis, see *Appendix B*.
 - LPG samples that contain significant quantities of C₅+ material may not vaporize quantitatively and are beyond the scope of this method.
4. Stop the flow, allow 5 to 10 seconds for the pressure to equilibrate, and start the analysis.

Calibration

Response factors are required to relate detector response for each sample component to mol-%. Response factors are determined by the analysis of one or more calibration blends as directed by the

analyzer operating manual. Analyze the blends in triplicate or as directed by analyzer operating manual and determine the response factors according to the instructions in the analyzer operating manual.

- For increased accuracy, a calibration blend should have a composition close to that of the samples to be analyzed, but not less than 1 mol-% of each component of interest.
- The peak areas from each of the triplicate blend runs should not deviate from the average by more than 3% (relative) of the value. If greater deviations occur, make certain that there are no problems with the equipment and then make additional runs until the required repeatability is obtained on three consecutive runs.
- Confirm the stability of the chromatographic system by analyzing a reference sample or blend each day when samples are analyzed. If the results differ by more than 5% from the average of previous analyses, a problem has developed with the chromatographic system, and the series of samples must be rerun after the problem is resolved.

Calculations

Component identifications and calculations are performed by the instrument data system. Report each measured component or group of components to the nearest 0.01 mol-%.

Precision

Precision statements were determined using UOP Method 999, "Precision Statements in UOP Methods."

Repeatability, Site Precision, and Reproducibility

A nested design was carried out for determining impurities in a synthetic refinery gas blend on three instruments, each by two analysts, with each analyst performing analyses on two separate days, performing two analyses each day for a total of 24 analyses. Using a stepwise analysis of variance procedure, the within-day, within-lab, and between-lab estimated standard deviations (esd) were calculated at the concentration means listed in Table 2. Two analyses performed in one laboratory by the same analyst on the same day should not differ by more than the repeatability allowable differences shown in Table 2 with 95% confidence. Two analyses performed in one laboratory by different analysts on different days should not differ by more than the site precision allowable differences shown in Table 2 with 95% confidence. Two analyses performed in different laboratories by different analysts on different days should not differ by more than the reproducibility allowable differences shown in the Table with 95% confidence.

Table 2
Repeatability, Site Precision, and Reproducibility, mol-%

Component	Mean	Repeatability		Site Precision		Reproducibility	
		Within-Day esd	Allowable Difference	Within-Lab esd	Allowable Difference	Between-Lab esd	Allowable Difference
Hydrogen	40.12	0.191	0.59	0.193	0.60	0.204	0.63
Oxygen	4.99	0.019	0.06	0.019	0.06	0.019	0.06
Nitrogen	14.95	0.056	0.17	0.062	0.19	0.063	0.19
Carbon Dioxide	1.95	0.016	0.05	0.017	0.05	0.037	0.17
Methane	9.97	0.039	0.12	0.042	0.13	0.046	0.14
Ethane	4.99	0.018	0.05	0.020	0.06	0.021	0.07
Propane	20.96	0.080	0.25	0.083	0.26	0.089	0.27
Isobutane	2.05	0.010	0.03	0.010	0.03	0.110	0.67

The data in Table 2 represent short-term estimates of the repeatability of the method. When the test is run routinely, use of a control standard and a control chart is recommended to generate an estimate of long-term repeatability.

Time for Analysis

The elapsed time for one analysis is 0.9 hour. The labor requirement is 0.3 hour.

Suggested Suppliers

Grace Davison Discovery Sciences, 2051 Waukegan Rd., Deerfield, IL 60015, USA (847-948-8600)
www.discoverysciences.com

Matheson Tri-Gas, 166 Keystone Dr., Montgomeryville, PA 18936, USA (215-641-2700)
www.mathesontrigas.com

Restek, 110 Benner Circle, Bellefonte, PA 16823, USA (814-353-1300) www.restek.com

VICI Mat/Sen, 7806 Bobbitt, Houston, TX 77055, USA (713-688-9345) www.vicimatsen.com

Appendix A

List of Suggested Suppliers for Refinery Gas Analyzers

<u>Suggested Supplier</u>	<u>Model</u>	<u>Features</u>
Agilent Technologies	Refinery Gas Analyzer	Complete range of analyzers for refinery and other petroleum gases containing H ₂ , O ₂ , N ₂ , CO, H ₂ S, CO ₂ and C ₁ -C ₅ plus higher chain length hydrocarbons Expandable to the analysis of liquefied gases with addition of an optional micro-gasifier
	MicroGC Refinery Gas Analyzer	4 channel, multi-dimensional system based on the 490 Micro GC Suitable for sample streams with low sample component concentration
Analytical Controls (PAC)	HiSpeed RGA - Refinery Gas Components	A high speed solution that determines and reports the composition of refinery gas streams in only five minutes
Separation Systems	Refinery Gas Analyzer	Analysis of C ₆ + Individual Analysis up to Benzene Complete Separation of C ₄ Olefins Hydrogen Analysis from 100 ppm to 99.9%
Wasson ECE	Hyper-Extended Refinery Gas Analysis (RGA)	C ₁ – C ₇ , hydrogen, carbon dioxide, hydrogen sulfide, oxygen, nitrogen, carbon monoxide
	Standard Refinery Gas Analysis (RGA)	C ₁ – C ₇ , hydrogen, carbon dioxide, hydrogen sulfide, oxygen, nitrogen, carbon monoxide

Suggested Suppliers

Agilent Technologies, 2850 Centerville Rd., Wilmington, DE 19808-1610, USA (302-633-8000)
www.agilent.com

PAC, 8824 Fallbrook Dr., Houston, TX 77064, USA (281.940.1803) www.pacip.com

Separation Systems, 100 Nightingale Ln., Gulf Breeze, FL 32561, USA (850-932-1433),
www.separationsystems.com

Wasson-ECE Instrumentation, 101 Rome Ct., Fort Collins, CO 80524, USA (970-221-9179)
www.wasson-ece.com

Appendix B

LPG Sampling

Liquefied petroleum gas (LPG) must be carefully expanded to ensure that a representative sample is analyzed. This can be accomplished using an electrically heated pressure reducing vaporizing regulator. The apparatus listed below is one such device.

Apparatus

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

LPG vaporization system, Micro-GC Gasifier, Agilent Technologies, Model CP-4900

Procedure

1. Install the LPG vaporization system according to the manufacturer's instructions, and allow the system to warm up.
2. Connect the LPG cylinder as directed, start the flow of the sample, and start the analysis.
 - The cylinder must be connected so that the sample is taken from the liquid phase.
3. Calibration and calculations are the same as in the body of the method.

Note

LPG samples that contain significant quantities of C5+ material may not vaporize quantitatively and are beyond the scope of this method.