Analysis of Natural Gas by Gas Chromatography

1. Introduction

A HewlettPackard™[1] 6890 series gas chromatograph (GC) is used to determine the hydrocarbon and non-hydrocarbon composition of natural gases. The GC contains eight columns custom created by Wasson ECE and three detectors so that hydrocarbon and nonhydrocarbon components of interest are analyzed on a single injection. This measurement is commonly used, with other analytical results, to classify and type natural gases. (e.g. Rice, 1993, Schoell, 1983, Whiticar, 1994)

2. Interfaces with Other Methods

None.

3. Materials and Equipment

Hewlett Packard ™ 6890 series gas chromatograph custom configured by Wasson ECE Instrumentation ™
UHP He
UHP N
Oxygen
Air

4. Procedure

Ensure that the GC is in a ready state. Load desired method into the GC and create a sequence in TotalChrom ™ software. Run a system blank (room air) and a check standard. Place appropriate fitting on the inlet to the GC for unknown sample containers. Stainless steel cylinders with ¼" male Swagelok fitting or isotubes are the preferred sample container. Sample pressure must be labeled on the sample container. Evacuate sample loop by manually turning the inlet valve to vent position by opening valve to rough pump. Pump for minimally 15 seconds. Close valve to rough pump, open sample cylinder and allow gas into the sample loop for 30 seconds. Open valve to vent position for 30 seconds for samples under pressure, close valve. For samples at atmospheric

[1] Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

pressure do not open valve to vent position. Continue to run samples. Run a sample with a known composition at the end of the sample set. Refer to instrument manual for advice with issues. (Gas Chromatography Systems and Products, HP6890 Manuals). See Table 1, Table 2 and Table 3 for typical GC parameters. These parameters are only meant to be altered by trained personnel and are included here for informational purposes only.

Table 1: Typical components analyzed with approximate retention times. Note that all columns are proprietary columns from Wasson ECE. Retention times may change with age of the column and with the compositional makeup of the gases analyzed.

Component	Detector	Retention Time (mts)	Carrier Gas	Column	Column Type
Helium	TCD 2	1.09	Nitrogen	Columns 5 and 6	packed columns
Hydrogen	TCD 2	1.23	Nitrogen	Columns 5 and 6	packed columns
Carbon Dioxide	TCD 1	2.96	Helium	Columns 3 and 4	packed columns
Ethylene	TCD 1	3.39	Helium	Columns 3 and 4	packed columns
Ethane	TCD 1	3.75	Helium	Columns 3 and 4	packed columns
Hydrogen Sulfide	TCD 1	5.81	Helium	c Columns 3 and 4	packed columns
Argon and Oxygen	TCD 1	10.73	Helium	Columns 3 and 4	packed columns
Nitrogen	TCD 1	11.35	Helium	Columns 3 and 4	packed columns
Methane	TCD 1	12.31	Helium	Columns 3 and 4	packed columns
Carbon Monoxide	TCD 1	13.49	Helium	Columns 3 and 4	packed columns
Ethylene	FID	3.53	Helium	Columns 1 and 2	capillary columns
Propane	FID	3.86	Helium	Columns 1 and 2	capillary columns
Propylene	FID	4.54	Helium	column 1 and 2	capillary columns
iso-Butane	FID	5.14	Helium	Columns 1 and 2	capillary columns
normal-Butane	FID	5.36	Helium	Columns 1 and 2	capillary columns
neo-Pentane	FID	7.19	Helium	Columns 1 and 2	capillary columns
iso-Pentane	FID	7.65	Helium	Columns 1 and 2	capillary columns
normal-Pentane	FID	7.9	Helium	Columns 1 and 2	capillary columns
sum of components C_6 and above	FID	>8.0	Helium	Columns 1 and 2	capillary columns

Table 2. Typical parameters for the light natural gas GC. These parameters are unique to the custom designed 6890 light natural gas GC. Parameters may be accessed on the front panel of the 6890 GC. Only experienced personnel should change any parameters.:

OVEN			**BACK DETECTOR (TCD)**	
init oven temp	75		temp	150
init time	4		ref flow	30
rate 1	15		makeup (He)	0
final temp	180		filament	on
final time	4		output	24
rate 2	off		neg polarity	off
FRONT INLET			**SIGNAL 1**	
temp	125		type	front
pressure	86.5		value	12.2
total flow	43.8		zero	off
BACK INLET			range	4
mode	split		attn	0
temp	125		**SIGNAL 2**	
pressure	37.6		type	back
split ratio	23.7		value	22.9
split flow	710		zero	off
total flow	743		range	4
gas saver	off		attn	0
COL 1			**COL COMP 1**	
dimensions unknown			no data	
pressure	86.5		detector	front
flow	43.1		start	comp run
mode	constant flow		start	comp 1&2run
COL 2			**COL COMP 2**	
dimensions	50m 530v		no data	
pressure	37.6		detector	back
flow	30		start	comp run
velocity	44		start	comp 1&2run
mode	ramped flow		**FRONT DETECTOR FID**	
init flow	5		temp	250
init time	2		H2 flow	35
rate 1	10		air flow	300
final flow	30		mode	column+makeup=constant
final time	0		combined flow	30
rate 2	off		makeup (He)	25.7
AUX			flame	on
1 or 2	thermal		output	12.2
3,4,5	pressure			

Table 3. Typical Run Table Parameters for light natural gas GC. Run Table parameters describe the opening and shutting of valves on the GC. Run tables may be accessed on the front of the 6890 GC. Only experienced personnel should change any parameters.:

Run Table 1		**Run Table 5**		**Run Table 9**	
Time:	0.01	Time:	1.00	Time:	9.40
Type:	Valve #1	Type:	Valve #5	Type:	Valve #3
Setpoint:	on	Setpoint:	on	Setpoint:	off
Run Table 2		**Run Table 6**		**Run Table 10**	
Time:	0.01	Time:	1.50	Time:	9.50
Type:	Valve #2	Type:	Valve #2	Type:	Valve #4
Setpoint:	on	Setpoint:	off	Setpoint:	off
Run Table 3		**Run Table 7**			
Time:	0.01	Time:	2.15		
Type:	Valve #7	Type:	Valve #4		
Setpoint:	on	Setpoint:	on		
Run Table 4		**Run Table 8**			
Time:	0.25	Time:	2.35		
Type:	Valve #7	Type:	Valve #1		
Setpoint:	off	Setpoint:	off		

5. Calibration and Quality Control Samples

Instrument was calibrated when installed. Minimally an air blank should be run at the start of every day. Check standards are run, minimally, at the beginning and end of each batch of samples, typically once a day when samples are being analyzed.

6. Limits, Precautions and Interferences

This method is intended for gases at room temperature. Ideally 6 cc of gas should be released from the sample container when opened to obtain an analysis; the sample loop size is 5cc. Note that this is the minimum required for this analysis only, additional gas is required for other analyses.

Air blanks are acceptable if no compounds other than nitrogen, argon, oxygen and carbon dioxide are present. Run a second blank if other compounds are present. If there are other compounds still present after a second run, determine cause and remedy before running unknowns.

With each batch of samples minimally one check standard is run at the beginning and end of a batch. If values are acceptable, (±10% relative or ±0.5 mol % absolute, whichever is greater) the calibration is valid and samples may be analyzed.

Instrument is recalibrated by appropriate laboratory personnel if the check standard(s) do not meet acceptance criteria. If laboratory personnel are unable to recalibrate the instrument, it is recommended an engineer from Wasson recalibrate the instrument.

Refer to instrument manuals for advice with issues.

Import data into locked Excel ™ spreadsheet and create proper format for the database.

Though it is desirable to bracket each component with standards, it is not always possible. Due to the large number of components determined and the wide range of compositions examined, one point calibrations are typically used. FID's and TCD's are typically linear over 4-6 orders of magnitude.

Air is a common contaminant frequently introduced during sample collection. Care is given to minimize the introduction of air to samples during the analytical procedure as components making up air are analytes in these measurments.

Frequently the gas produced under laboratory closed system pyrolysis conditions contains components that are not identified. These components are in trace quantity (total amount < 1 mol %) and it is not the intent of this analysis to identify these unknown components.

Lower detection limits: 0.006 mol% for hydrocarbons, 0.03 mol% for permanent gases, 0.15 mol% for H2S. Limits were determined by Wasson ECE Instrumentation ™ and not by EGL staff. It is not the intent of this method to determine components near the stated lower detection limits.

Follow safe laboratory practices when analyzing samples. Gloves, safety glasses, lab coat and closed toe shoes are minimally required.

7. Acceptance of Data

See 6 above. If the measurement of the check standard is ±10% relative or ±0.5 mol% absolute, data is acceptable.

8. Data Handling and Transfer

See step 6 above. Results are validated in the database by the analyst and approved by appropriate laboratory personnel.

9. References

Gas Chromatography Systems and Products, Wasson-ECE, Fort Collins, 1997

HP 6890 Series Gas Chromatograph Operating Manual Vol. 1 General Information, 1996

HP 6890 Series Gas Chromatograph Operating Manual Vol. 2 Inlets, 1996

HP 6890 Series Gas Chromatograph Operating Manual Vol. 3 Detectors, 1996

HP 6890 Series Gas Chromatograph Service Manual, 1995

Rice, D. D., 1993, Biogenic gas: controls, habitats, and resource potential, in D.G. Howell, ed., The Future of Energy Gases-U.S. Geological Survey Professional paper 1570, Washington, United States Government Printing Office, p. 583-606

Schoell, M., 1983, Genetic characterization of natural gases: AAPG Bulletin, v. 67, p.2225-2238.

Wasson Applications, *http://www.wasson-ece.com/applications/?p=60*

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10. Attachments

None

11. History of Changes

R0: Initial Issue