High-Pressure Liquid Injection Device for the Agilent 7890A and 6890 Series Gas Chromatographs

Application

Hydrocarbon Processing

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Abstract

In gas chromatography, sampling and representative analysis of highly volatile liquefied hydrocarbons with high precision and accuracy can be challenging. In the solution described here, a unique sample injection device based on a needle interface and liquid rotary valve has been designed for sampling light petroleum matrices with broad boiling point distributions. The 7890A GC-based system consists of a 4-port liquid valve, a deactivated removable needle, and auxiliary flow. The needle is directly installed on one port of the valve. This compact device is installed directly over the top of a split/splitless inlet. The unit is operated automatically just like a typical liquid autosampler; however, the needle is not withdrawn. Various pressurized liquid samples have been run on this device, such as liquefied natural gas (calibration standard), ethylene, propylene, and butadiene. Excellent repeatability is obtained with RSDs typically below 1% in quantitative analyses.

Introduction

There are several known techniques for injecting volatile liquefied hydrocarbons in gas chromatographs. The simplest tools are high-pressure syringes. However, the pressure limit is not high enough to analyze light hydrocarbons such as liquefied natural gas and ethylene. The traditional methods [1, 2] include the use of vaporizing regulators and rotary sampling valves. During sampling, discrimination of the analytes will take place for samples with wide boiling points due to condensing of heavy components and selective vaporization of light components in transfer lines. Recently, piston sampling valves were introduced and are commercially available [3]. These can suffer from discrimination and short service lifetimes at high vaporization temperatures or high sample pressures.

Combining the advantages of simple syringes and high-pressure rotary valves, a unique sample injection device has been designed. The system consists of a 4-port liquid sampling valve, a Siltek deactivated needle, and a split/splitless inlet. This compact device is installed directly over the GC inlet. This unit is operated just like a typical liquid autosampler; however, the needle is not withdrawn. The maximum limit of sample pressure is 5,000 psig. Various pressurized gas samples have been evaluated on this device such as liquefied natural gas (calibration standard), ethylene, propylene, and butadiene. Excellent repeatability is obtained with 0.47% to 1.09% RSD in quantitative analyses. Wide boiling point hydrocarbon samples (C5 to C40) have also been analyzed using this injector, with excellent quantitative results.

Experimental

Injection Device

The high-pressure liquid injection (HPLI) device consists of components as shown in Figure 1.

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- **Valve:** Internal sample valve from Valco Instruments Co. Inc. 4-port equipped with a sample volume of 0.06 µL. Other rotor sizes are available from Valco Instruments Co. The valve works under 75 °C and 5,000 psi.
- **EPC:** An auxiliary flow from a 7890A Aux module is connected to port P. In sample analysis, the flow can be set at 50 mL/min to 200 mL/min. The higher auxiliary flow gives better peak shape.

The following components are recommended. These are not supplied in the option or accessory kit.

- **Filter:** To remove particles from samples, it is necessary to install a filter between the sample line and port S.
- **Restrictor:** To maintain sample pressure, a metering valve (Agilent PN 101-0355) is connected to the end of the sample exit line tubing. Restrictor is not included in option or accessory kit.

Guideline for choosing Aux flow source

7890AGC

G3471A Pneumatic Control Module (PCM) or

G3470A Aux EPC module

6890GC

G1570A Aux EPC or

G2317A PCM module

The PCM is the preferred source for both GCs.

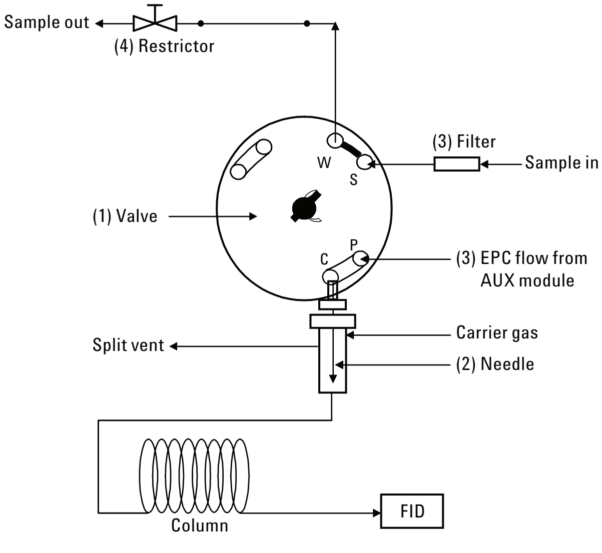


Figure 1. Flow diagram of the HPLI device.

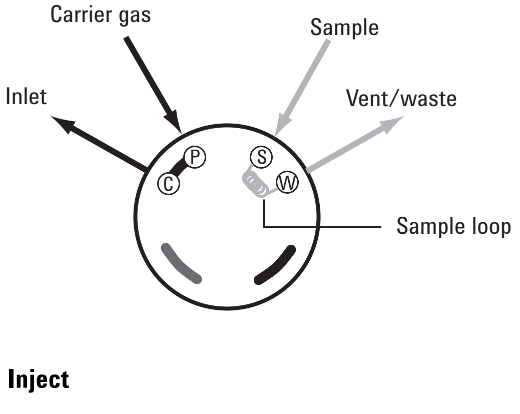
Samples for System Evaluation

- Liquefied natural gas: Calibration standard, 1,200 psi, with nC7-nC9 (0.102%–0.0503%)
- Liquefied ethylene: Purity 99.5, 1,200 psi
- Pressurized propylene: Grade C. P., purity 99.0%, 200 psi
- Pressurized propane + n-butane: 50.0%:50.0%, 200 psi
- Pressurized 1, 3-butadiene: Purity 99.5%, 180 psi
- n-Hexane + 1.0 % 2# BP standard (Agilent PN 5080-8768, nC5–nC18)
- nC5–nC40 D2887 1# BP standard (Agilent PN 5080-8716, diluted by CS_2)
- Glycols, including monoethylene glycol, diethylene glycol, and triethylene glycol
- C8 to C16 hydrocarbons at 100 ppm each

Operating Process

The valve is operated with an Agilent pneumatic air actuator. To load the sample, the valve is set at the OFF position (Figure 1). The sample is loaded from port S and vented to port W. The pneumatic and sample paths in load and inject positions are shown in Figure 2. To maintain the sample in the liquid phase and to avoid “bubbles” in the sample line, it is important to adjust resistance of the metering valve and check for possible leaks at the connections. To inject, the valve is switched to the

Load



Inject

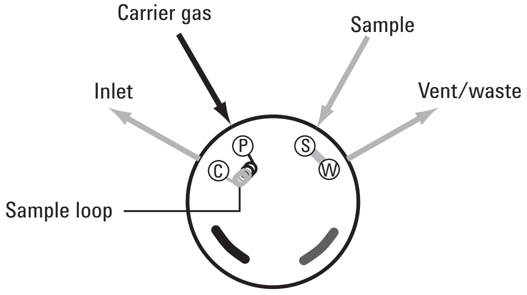


Figure 2. Pneumatic and sample paths in load and inject positions.

ON position. A 2- to 3-second injection time should be used.

The system should always be carefully checked for leaks before introduction of high-pressure hydrocarbons. Instrumental conditions and application-specific columns are shown in Table 1 and Table 2, respectively.

When the valve is actuated, a stream of carrier gas from the Aux EPC or PCM will enter the inlet and combine with the inlet carrier flow; the combined flow will vent through the split vent. Therefore, the actual split ratio will be higher than the value set from ChemStation. The actual split ratio can be calculated by measuring the split vent flow.

Figure 3. Agilent pneumatic air actuator/valve assembly installed on the 7890A.

Table 1. Instrumental Conditions

Gas chromatograph	Agilent 7890A
Injection source	HPLI device at near ambient temperature
Injection port	Split/splitless, 250 °C (350 °C for C5–C40)
Sample size	0.5-µL (0.2 µL for C5–C40) device supplied with 0.06-µL rotor
Carrier gas	Helium
Aux or PCM	150 mL/min (Helium)
FID	250 °C (350 °C for C5–C40) H_2, 35 mL/min Air, 400 mL/min

Table 2. Columns and Parameters

Samples	Columns	Column flow mL/min	Split ratio	Temperature program	Sample pressure psig
Natural gas	30 m × 0.53 mm × 0.5 µm DB-1 #125-1037	8	40:1	35 °C, 1 min 20 °C/min to 180 °C, 1 min	1200
Ethylene	50 m × 0.53 mm × 15 µm AL2O3 PLOT/KCL + 30 m × 0.53 mm × 5 µm DB-1, #19095P-K25 and #125-1035	8	20:1	35 °C, 2 min 4 °C/min to 160 °C, 3.8 min	1100
Propylene	50 m × 0.53 mm HP AL2O3 PLOT + 30 m × 0.53 mm × 5 µm DB-1	7	25:1	35 °C, 2 min 4 °C/min to 160 °C, 1.8 min	180
Propane + n-butane	30 m × 0.53 mm × 1.0 µm DB-1, #125-103J	5	50:1	35 °C	150
1,3-Butadiene	50 m × 0.53 mm AL2O3 PLOT/KCL	10	15:1	35 °C, 2 min 10 °C/min to 195 °C, 15 min	180
n-Hexane	30 m × 0.53 mm × 1.0 µm DB-1	5	50:1	45 °C	N/A
nC5-nC40	10 m × 0.53 mm × 0.88 µm HP-1, #19095Z-021	10	15:1	35 °C, 1 min 15 °C/min to 350 °C, 5 min	N/A
Glycols	30 m × 0.25 mm × 1.0 µm HP-1 ms	1.8	15:1	50 °C, 3 min 15 °C/min to 250 °C, 2 min	

Results and Discussion

Check for Carryover

A set of normal hydrocarbons was used to perform a basic check of the system, looking for good peak shape and lack of carryover.

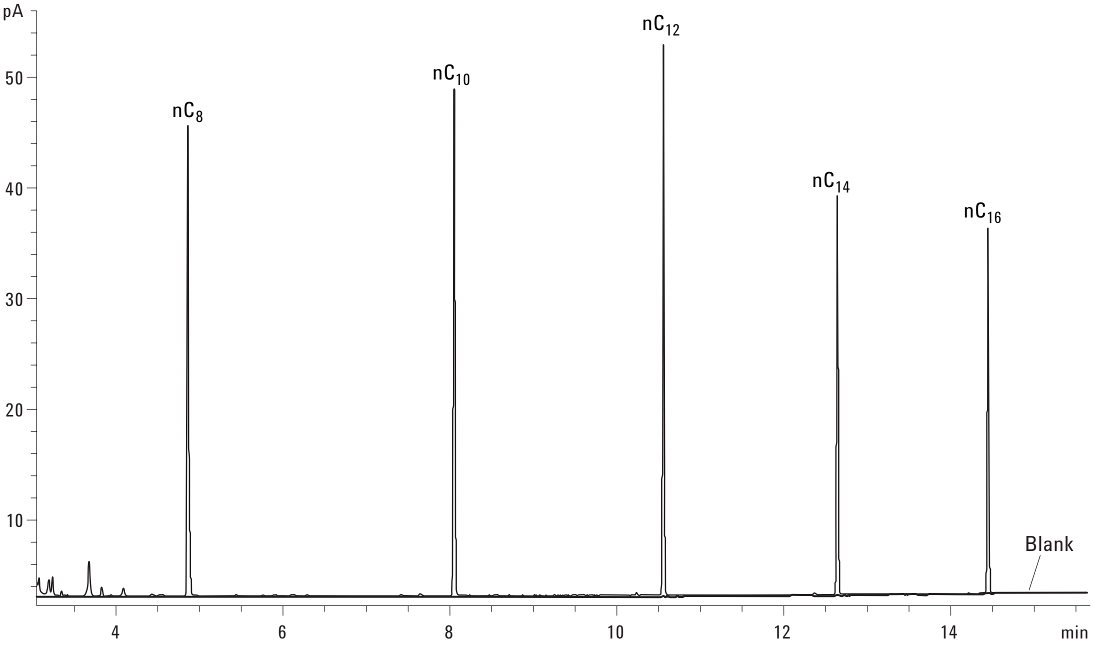


Figure 4. Overlay of standard versus blank (100 ppm each in cyclohexane).

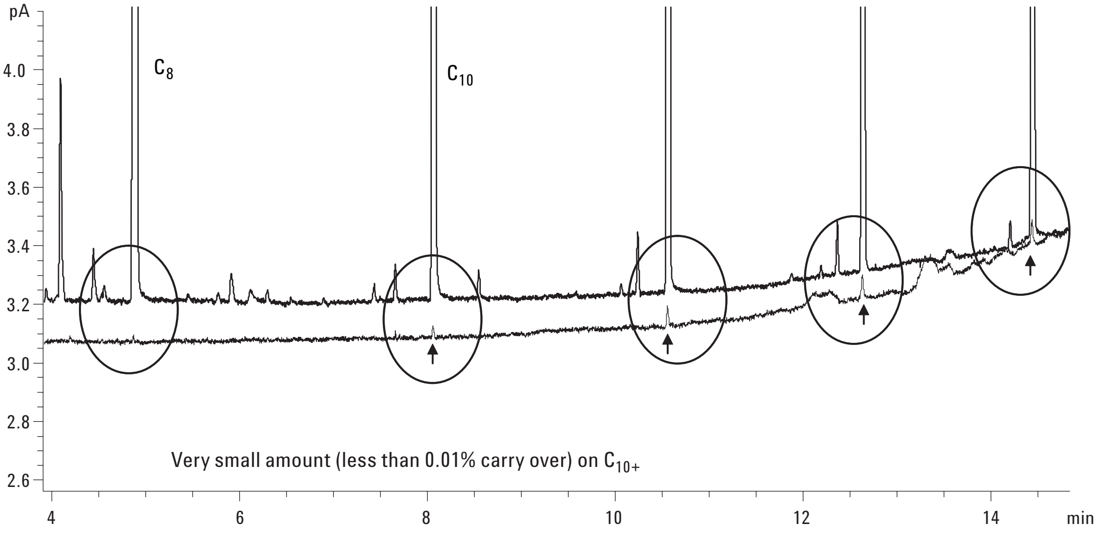


Figure 5. Carryover less than 0.01% on C_{10+}.

Sample Analysis

A series of glycols was used to model performance of the device for highly polar analytes. Minimal peak tailing is seen, due in part to the inertness of the needle interface. Also, carryover is very low.

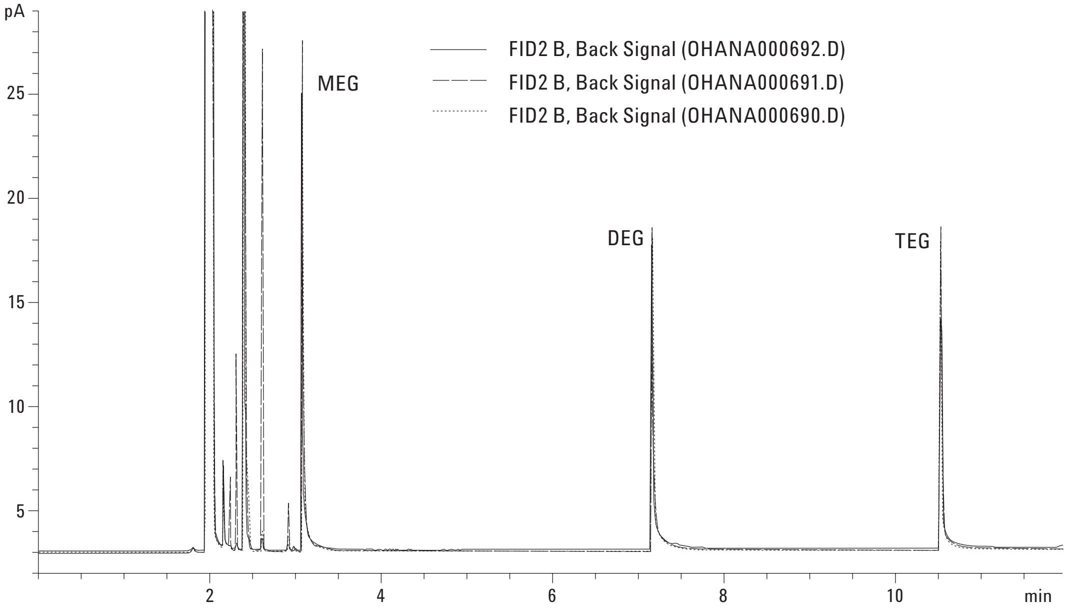


Figure 6. Triplicate run of 100 ppm each of MEG, DEG, and TEG in IPA.

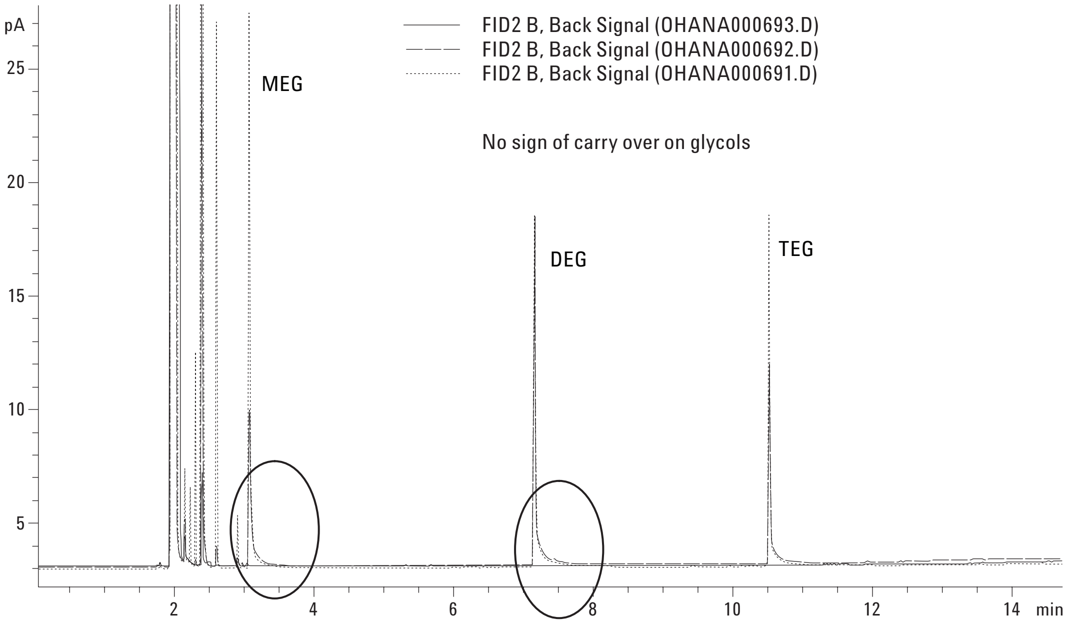


Figure 7. Glycols versus blank. Two standard duplicates, blank run immediately after injection of standard.

A. Liquefied Natural Gas

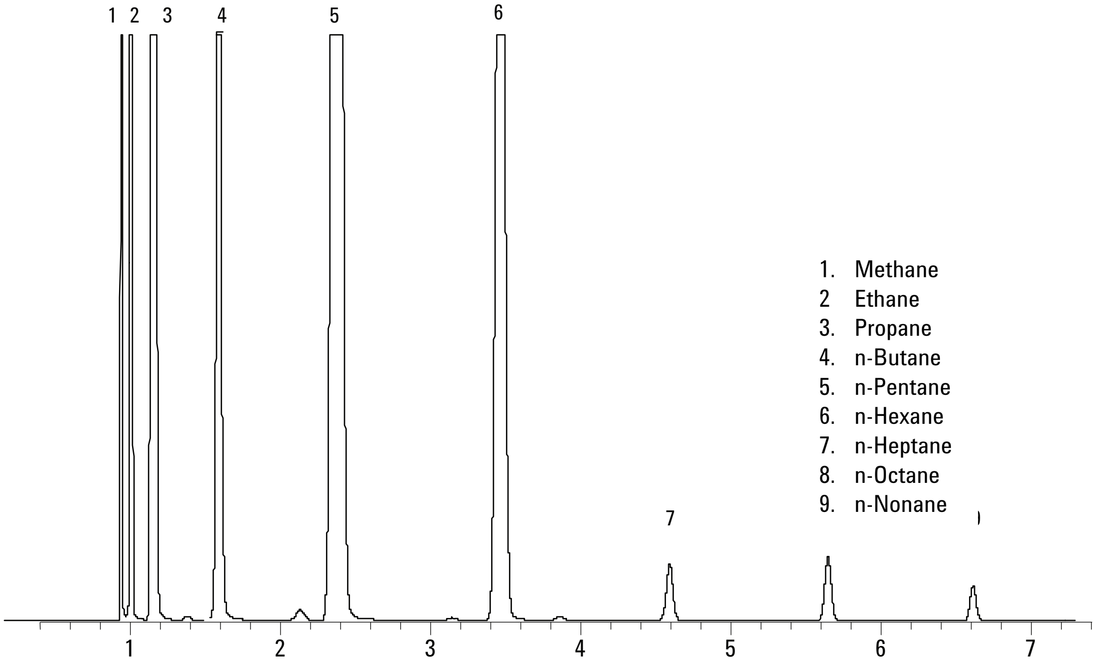


Figure 8. Chromatogram of liquefied natual gas (calibration standard).

Low discrimination is seen in Figure 8 for liquefied natural gas (LNG). Excellent repeatability is obtained with RSDs of less than 1%.

B. Liquefied Ethylene

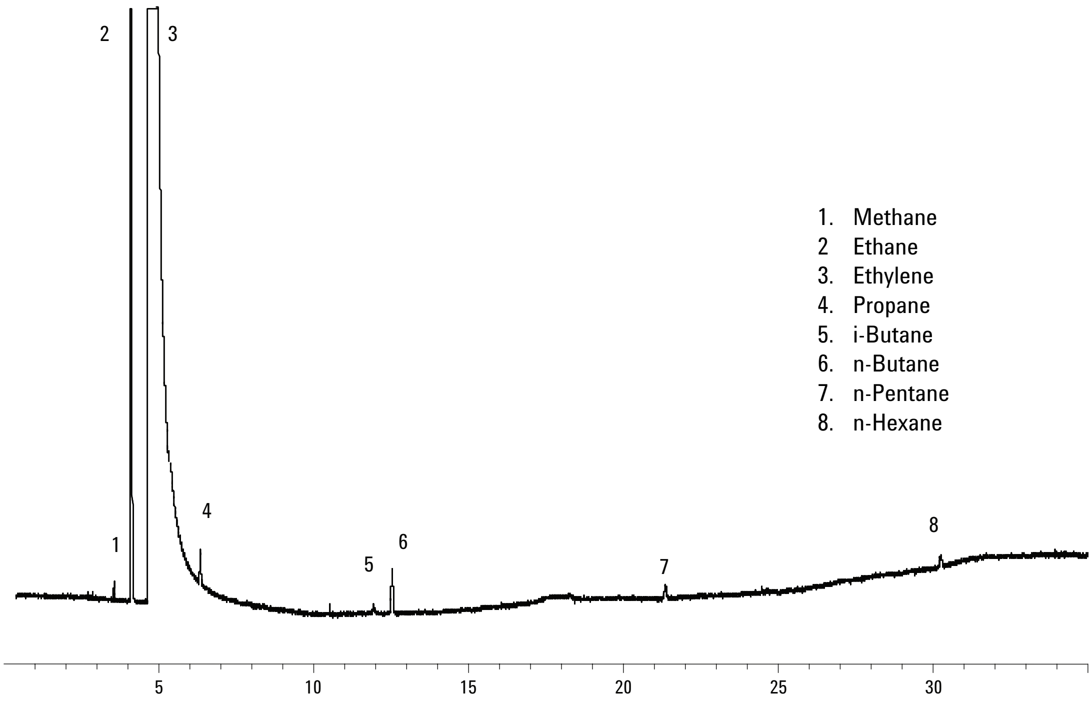


Figure 9. Chromatogram of liquefied ethylene.

The sample in Figure 9 is analyzed by ASTM D6159, “Standard Test Method for Impurities in Ethylene by Gas Chromatography.” The method detection limits (MDLs) for the two methods are listed in Table 3.

The MDL using the HPLI device is 10 times lower than reported in the ASTM method due largely to the lack of peak tailing.

Table 3. MDLs (ppm V) by ASTM D6159 and HPLI

Components	ASTM D6159	HPLI
Methane	5.57–62.3	0.27
Ethane	35.1–338	0.78
Propane	8.07–59.7	0.88
i-Butane	7.74–48.4	0.38
Butane	4.97–56.1	1.61
n-Pentane		0.61
n-Hexane		0.74

C. Pressurized Propylene

This sample is analyzed by the same conditions as in ASTM D6159 (above method for ethylene analysis). The chromatogram is shown in Figure 10.

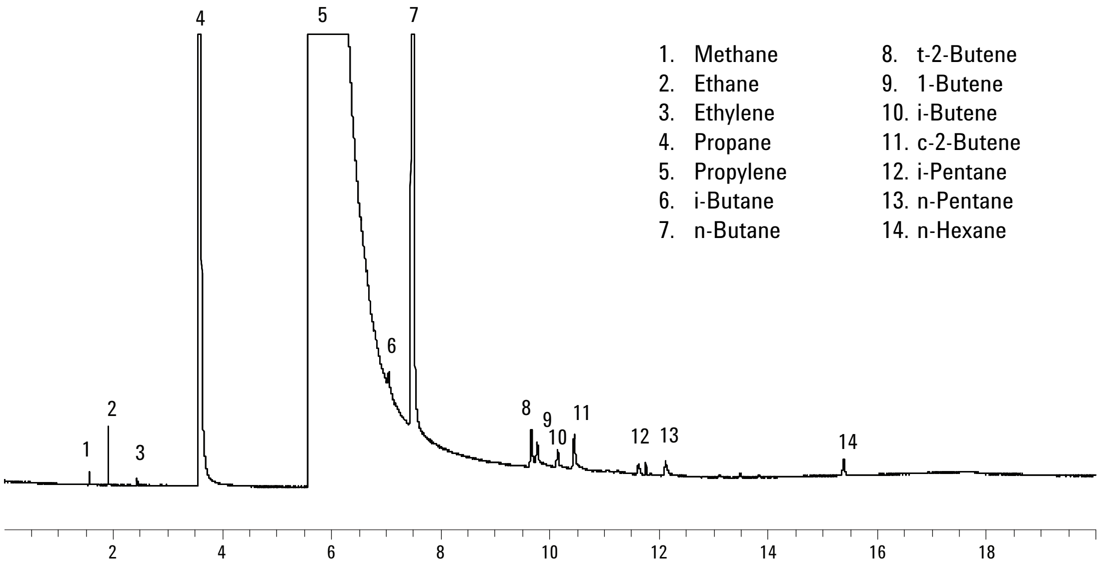


Figure 10. Chromatogram of pressurized propylene.

D. Pressurized 1,3-Butadiene

As an example of C4 hydrocarbons analysis, Figure 11 shows a typical result for 1,3-Butadiene.

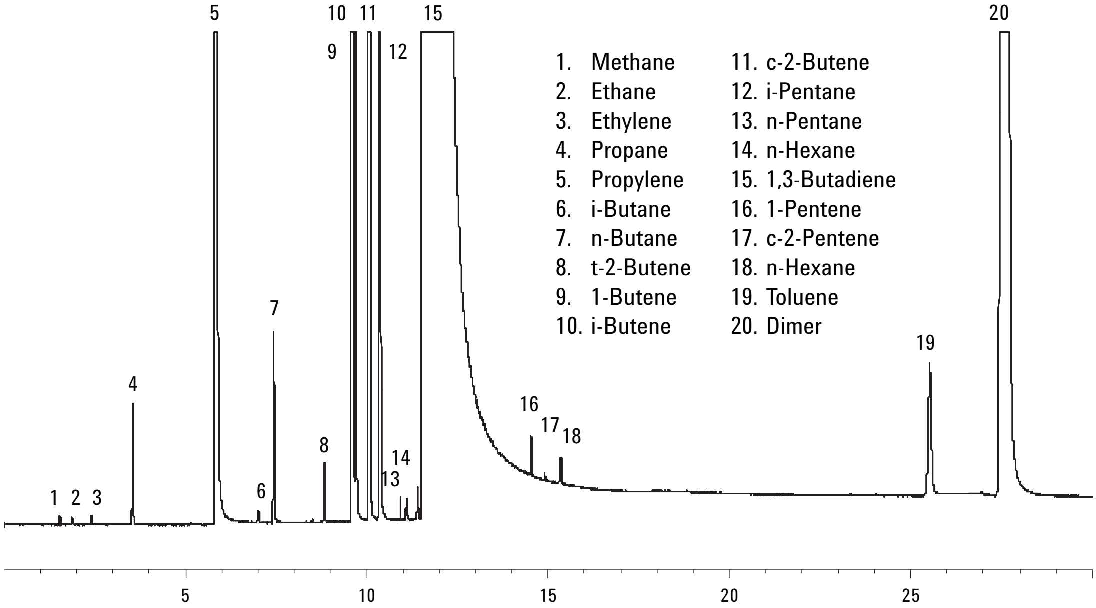


Figure 11. Chromatogram of pressurized 1,3-butadiene.

E. Pressurized Propane + n-Butane

This is a quantitative calibration sample:
Propane:n-Butane = 50%:50%.
The chromatogram is shown in Figure 12 with the results of a quantitative analysis shown in Table 4.

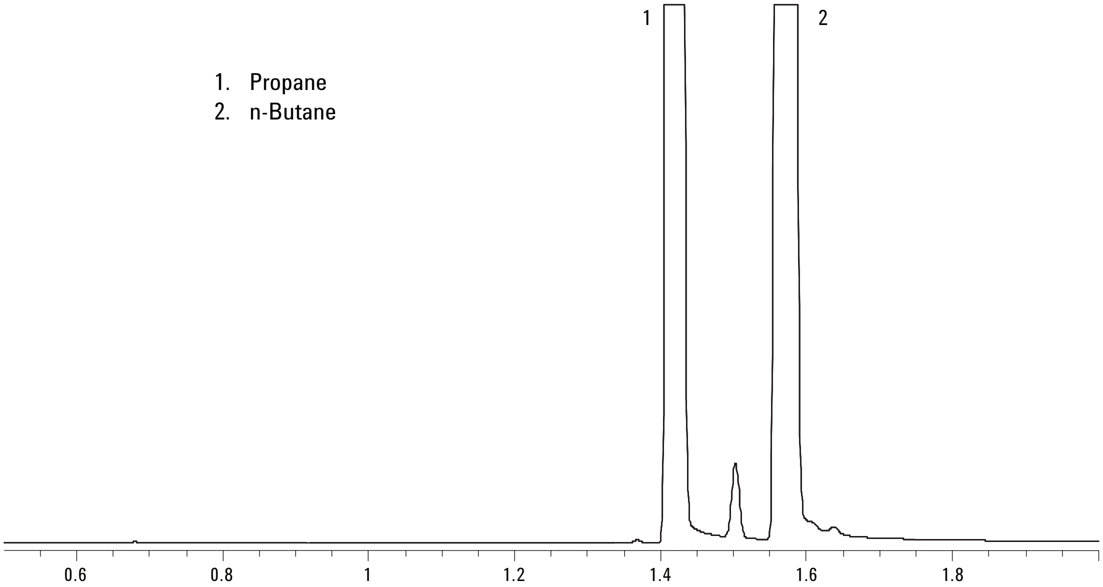


Figure 12. Chromatogram of pressurized propane + n-butane.

Table 4. Quantitative Analysis of Pressurized Propane 50.0% + n-Butane 50.0%. One Percent Difference Between the Blend (actual) and the Analysis Result

	Propane	n-Butane
Response factor	1.03	1.01
Density	0.5139	0.5788
Blend by V%	50.0	50.0
By wt%	47.031	52.969
Analysis		
By area%	45.441	54.559
By wt%	45.927	54.073

F. n-Hexane + 1.0% BP Standard (C5-C18)

To check the quantitative results, a small amount (1.0% BP standard) of C5 to C18 hydrocarbons was added to n-hexane (Figure 13). Table 5 shows the analytical results obtained by adding the C5 to C18 hydrocarbons with both the HPLI device and the automatic liquid sampler (ALS). In Figure 14, chromatograms by HPLI (top) and by ALS (bottom) are shown.

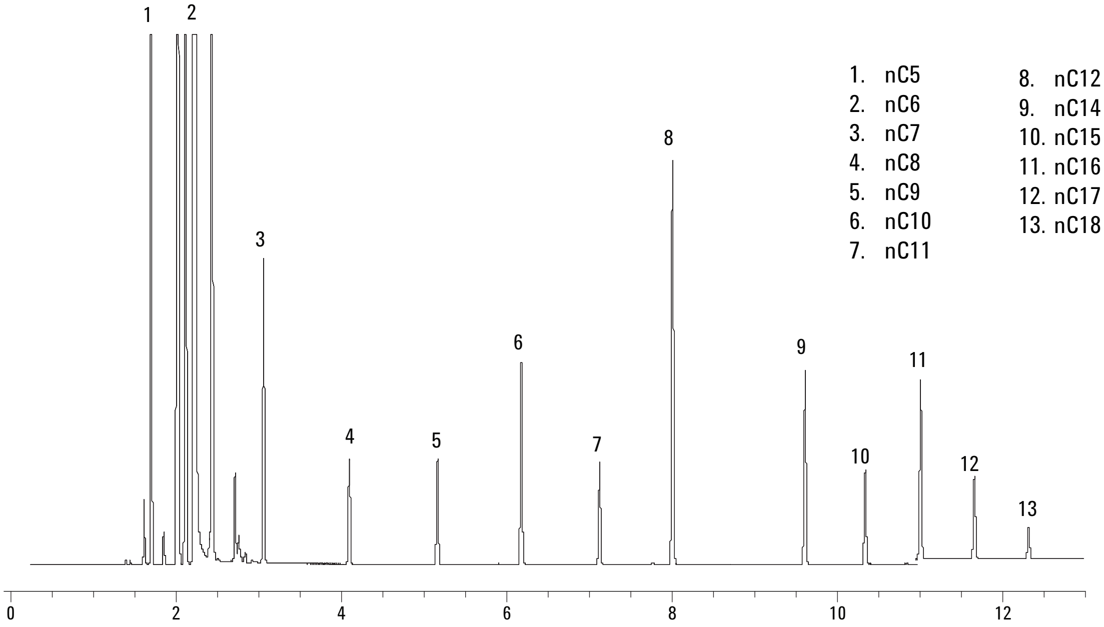


Figure 13. Chromatogram of n-hexane + 1.0% BP standard.

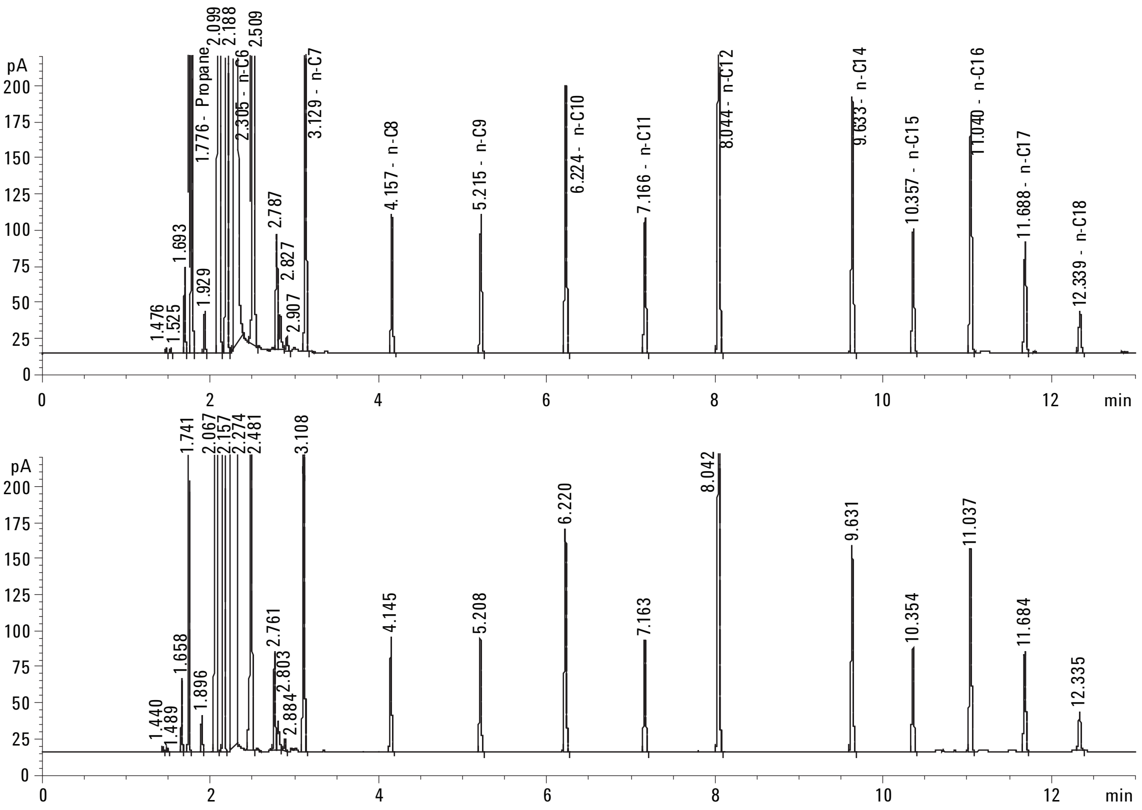


Figure 14. Chromatograms of n-hexane + 1.0% BP standard. Top: HPLI. Bottom: ALS (syringe).

Table 5. Analytical Results for C5-C18 by HPLI and ALS

	HPLI		AUTO INJECTOR	
COMPONENTS	**Area %**	**Width (min)**	**Area %**	**Width (min)**
nC5	0.282		0.279	
nC6	96.950	0.0209	96.922	0.0195
nC7	0.146		0.148	
nC8	0.0524		0.0532	
nC9	0.0537		0.0548	
nC10	0.109		0.111	
nC11	0.0550		0.0559	
nC12	0.219		0.221	
nC14	0.109		0.110	
nC15	0.0532		0.0547	
nC16	0.102		0.109	
nC17	0.0484		0.0546	
nC18	0.0203		0.0239	

The peak width of hexane at top: 0.0209 min
The peak width of hexane at bottom: 0.0195 min

There are no significant differences in quantitative results up to nC14. Compared with the results from an ALS injection, the HPLI device yields results about 10% lower in response above approximately nC16.

G. nC5-nC40 (D2887 BP Standard Diluted by CS_2)

A sample with hydrocarbons (nC5-nC40 D2887 1# BP standard diluted by CS_2) is also run on HPLI. The chromatogram is shown in Figure 15.

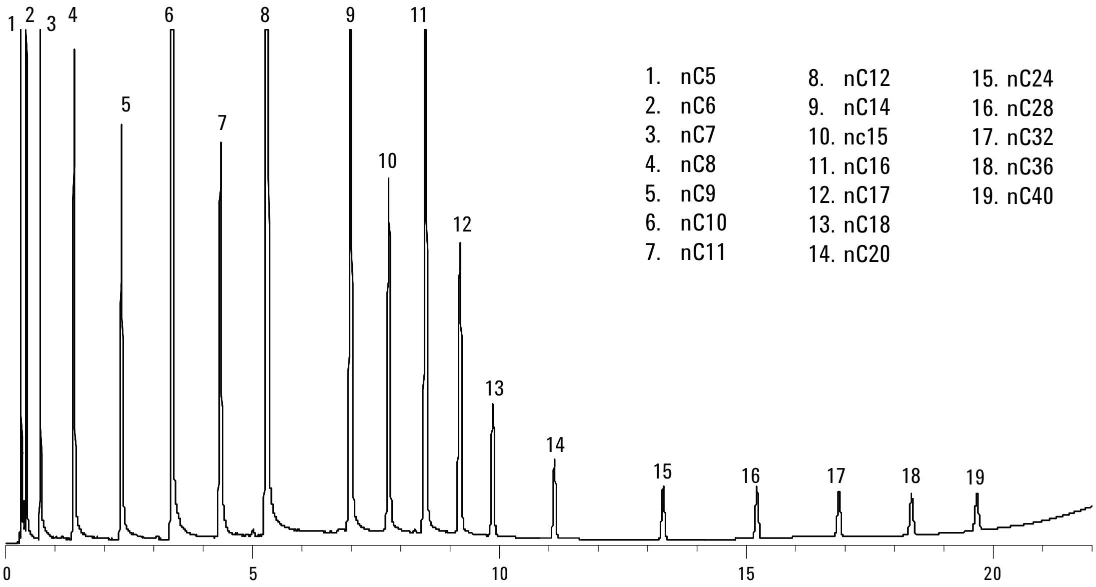


Figure 15. Chromatogram of nC5-nC40 (D2887 BP standard diluted by CS_2).

A lack of discrimination is seen with the HPLI device. In the future, it would be interesting to run some unstable condensates for evaluating the device.

From the above GC evaluation, excellent analytical results could be obtained using the HPLI device. These are summarized below.

1. Excellent repeatability
2. Capable of quantitative results
3. No significant peak width broadening
4. The wide boil point hydrocarbon samples could be analyzed by this device with minimal discrimination.

Conclusions

A unique sample injection device for the Agilent 7890A GC based on a unique deactivated interface and liquid rotary valve has been designed for sampling light petroleum matrices with broad boiling point distributions from methane to as high as C40. It is installed directly over a split/splitless GC inlet. The maximum sample pressure is 3,000 psig, although typical samples will have pressures under 1,500 psig. Various pressurized liquid samples have been tested on this device with high accuracy and precision. The sampler is quick to install and easy to operate. As with all high-pressure sampling systems, appropriate safety precautions must be followed.

References

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2. K. J. Rygle, G. P. Feulmer, and R. F. Scheideman, *J. Chromatogr. Sci.,* 22 (1984) 514–519.
3. Jim Luong, Ronda Gras, and Richard Tymko, *J. Chromatogr. Sci.,* 41 (2003) 550–5.

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