



Micro Gas Chromatography for Liquid Petroleum Gas's

Class #5400.1

Alejandro Amorin

Louis D'Agostaro

Yvonne Diersche

Alejandro Gonzalez

DCG Partnership 1, Ltd. 4170A S. Main Str.

Pearland, TX 77581



ABSTRACT

For years, micro GC analysis has been useful as a powerful tool for the fast and reliable analyses of natural gas and other gaseous matrices; but, it is yet to prove its capabilities for liquid samples. In this paper, we present a unique gasifying system for volatile liquid sample introduction in a micro GC. The system has been tested with a wide range of different samples: Liquefied gases (ethane/propane blends, volatile liquids (natural gasoline from fractionation plants), butane blends and samples with olefins and C6+'s. Due to the different nature of the samples, a single point calibration was used. The system was designed for simple operation and maintenance. Reducing time and increasing ease of operation when compared to regular Gas Chromatography analyses. All the samples were handled in the same way with the only variation being the response factors applied to each type of sample. Repeatability data will be presented from both calibration standard blends and from real world samples. Also presented are comparisons of the micro GC results with conventional GC data.

INTRODUCTION

Natural gas, refinery gas and liquefied petroleum gas (LPG) compositions can be determined using gas chromatography. A wide range of physical properties such as heating value, specific gravity (or density), compressibility and Wobbe index can be calculated from composition data. Those parameters play an important role in the varied applications of the natural-gas industry because they are of critical importance in determining the commercial value of the natural gas, either purchased or sold, especially in custody transfer situations. They are also particularly important for large volume end users, since even small differences in the calculated values can have a significant financial impact



Those complex samples are often analyzed using conventional multi-column, multi-valve gas chromatographs. However, fast and accurate measurement of the composition can be achieved using a Micro GC. The micro GC is a chip-based instrument with an integrated DCG (Thermal Conductivity Detector) and independent GC Cartridges, containing an injector, detector, column and heating capability up to 180°C. Its miniaturized hardware, low thermal mass, extremely accurate micro liter peak injection and short columns enable fast accurate detection while lowering costs. A complete analysis is made possible without valves and in a fraction of the time required with a conventional GC. The compact system analyzes complex gas samples using the selectivity of independent GC channels. Each GC channel, with a different column phase, simultaneously separates a different subset of sample components. Micro GC usually focuses on natural gas and process applications, (e.g., a BTU analysis is done in less than 20 seconds).

When dealing with pressurized liquid samples the situation changes and sample introduction becomes a critical factor since the instrument has severe inlet pressure limitations. Finding an inlet system suitable for a wide range of sample has become a difficult task. This article shows the results obtained using a new sample introduction device (SID) designed and tested to work with any micro GC.

THE ANALYSIS

All QC laboratories are always looking for fast and reliable ways to analyze samples. This is also the case of Fractionation Plants, QC Labs and process control. Conventional GC analysis ranged from 15 to 60 min without considering oven's cool-down time. Micro GC is capable to make analysis faster, however:

- Micro GC analysis has been extensively used in NG Analyses but not as much for pressurized liquids.
- Micro GC needs the sample in vapor state.
- Micro GC has inlet pressure limitations.



Then, it cannot be used for all types of samples unless a sample introduction system allows us to do that. There are several vaporizer regulators in the market and all are based on the same principle. A known vaporizer regulator was tested with poor results in terms of memory effects and reproducibility when dealing with pressurized liquids.

A Sample Introduction Device (SID) has been designed and tested to meet the requirements of a wide range of different samples from C1 to C4 blends containing Perm Gases, olefins and C6+'s. Tailored methods for each type of sample were also tested and optimized. Due to the nature of each sample, a single point calibration for each type of sample was determined to be the most convenient way for sample quantification. The SID has a vaporizer regulator working continuously and online at fixed and constant temperature and outlet pressure. At a fixed T & P the sample will eventually reach Liquid \longleftrightarrow Vapor equilibrium within the system.

THE SAMPLE:

We seldom deal with pure samples, usually sample are mixtures of different components (A, B, C, ... n) in different proportions (X):

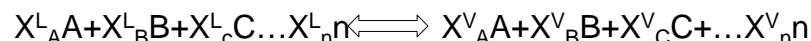
$$X^L_A A + X^L_B B + X^L_C \dots X^L_n$$

In vapor state, sample composition not only depends on several intrinsic properties like boiling point, vapor pressure, density, molecular weight; but also on some external conditions like temperature, pressure, volume, etc.

So the sample's vapor phase composition can be expressed as a function of the properties:

$$F(T, P, Bp, VP \dots) = X^V_A A + X^V_B B + X^V_C C + \dots X^V_n$$

Then, as long as the variables are kept constant the sample will eventually reach liquid-vapor equilibrium. This is what is called a "steady state"





External parameters can be controlled

- Inlet Pressure: Sample and Standards pistons must be kept at constant P.
- Outlet Pressure: SID is set at a fixed outlet pressure.
- Time: Time events are set and fixed through the SID electronics and through the Chromatographic Data Software (CDS)
- Temperature: SID is set at fixed T, lines are insulated, micro GC components at fixed T
- System volume: System geometry is kept constant.
- Injection volume: Determined and fixed by the software.

MATERIALS

A system schematics is shown in fig. 1. The SID has different mechanical and electronic components and it is designed for samples contained in constant pressure cylinders. V3 is a 3 way valve (Swagelok Co.) used for blank injections only. V1 is a 3 port-2 position valve (Valco Instruments Co. Inc.) which selects between the sample and a He source used for blank injections and cleaning the system path. The gasifier is a vaporizing regulator (Controls Corporation of America) which is set at a fixed temperature (250F) and outlet pressure (6psi).

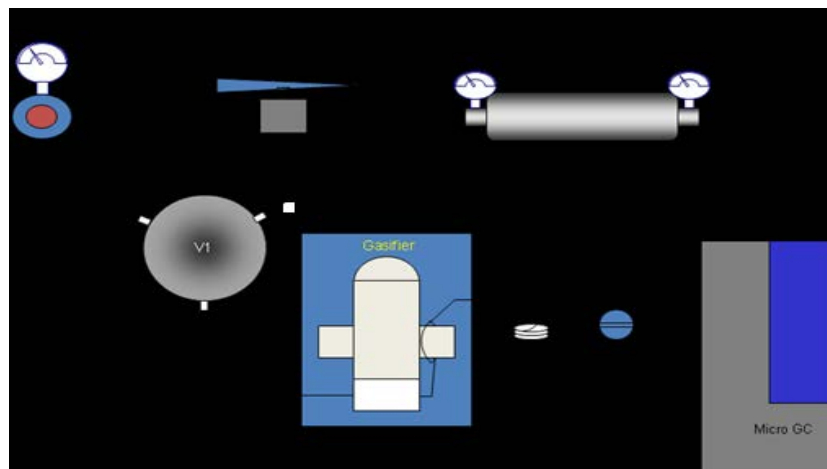


Figure 1. System Schematics

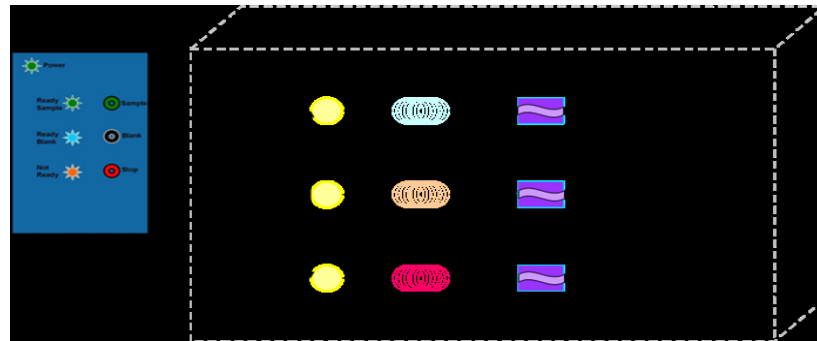
Between the vaporizing regulator and the micro GC there are 2 vents. The so-called controlled vent is a narrow 1/16" tube and V2 is a 3 way solenoid valve (Valcor Engineering Corporation) which is used to flush the system either with sample or He before injection. All wetted parts and lines are stainless steel with the exception of the V1 rotor and the constant pressure cylinder connection line.

The operator connects the constant pressure cylinder to the inlet line, opens the cylinder's valve and starts the SID. After an equilibration time (3 min), the SID indicates when the system is ready. The operator starts injecting sample into the MicroGC through the CDS once the equilibrium is reached.

A 4 channel Varian CP-4900 MicroGC (Varian Inc.) with backflush capabilities was used for all tests. Galaxie software was the CDS used to control chromatographic parameters. Only three channels were used for the tests.



Channel #1 has PoraPlot U capillary column for the separation and determination of permanent gases along with Methane, CO₂ and Ethane. N₂ O₂ and CO are determined as 1 peak (air). Channel #2 has a Al₂O₃ column to separate olefins, when present. Channel # 3 has a CP Sil5 column to separate hydrocarbons by boiling point up to C₁₁.



Experimental

Figure 3 shows a chromatogram of a Y grade Sample obtained from channel #3, showing components peaks up to Toluene which elutes in less than 80 sec.

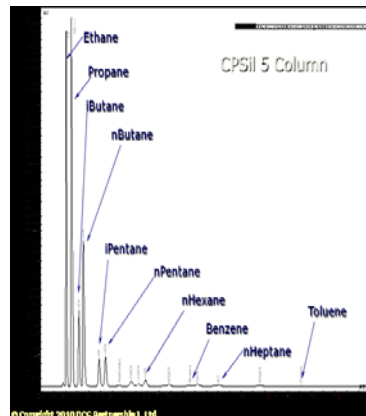




Figure 4 shows a chromatogram of a Propylene sample obtained from channel #1. Depending on the sample (method), Propane may be quantified from the signal on channel #1 or #4. Again, air and carbon monoxide eluted as one peak in this column. To be able to have the permanent gases separated, a MolSieve column may be installed in the 4th channel remaining on the MicroGC. In this case, Propane elutes in less than 90 secs.

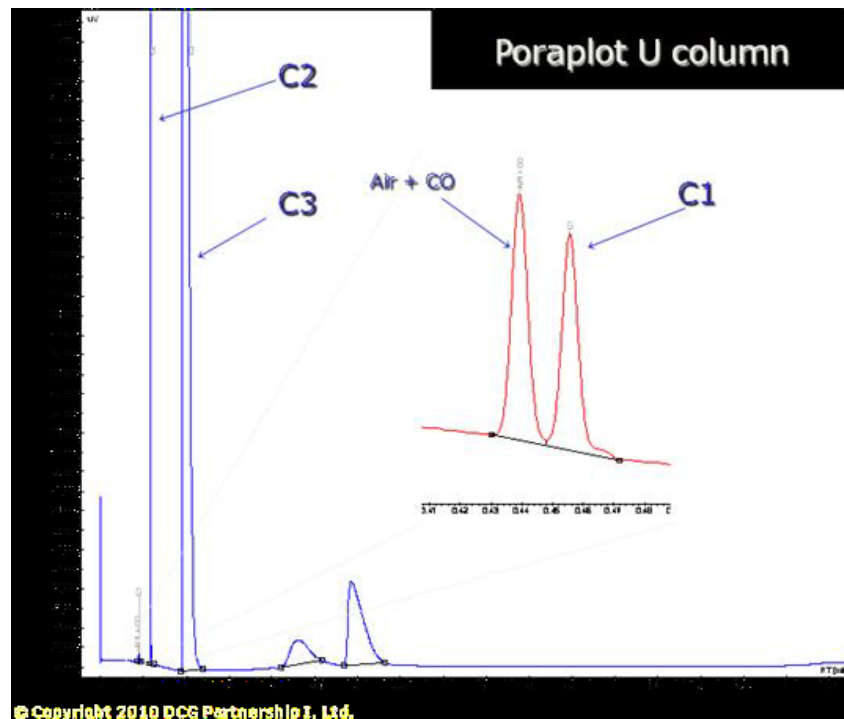


Figure 4. Propylene sample (Channel #1 signal)



Chromatogram obtained from Channel #2 for the same propylene sample is shown in Fig 5. where propylene and C₄ olefins eluted in less than 30 secs. 3BD elutes just after nC₅, if present.

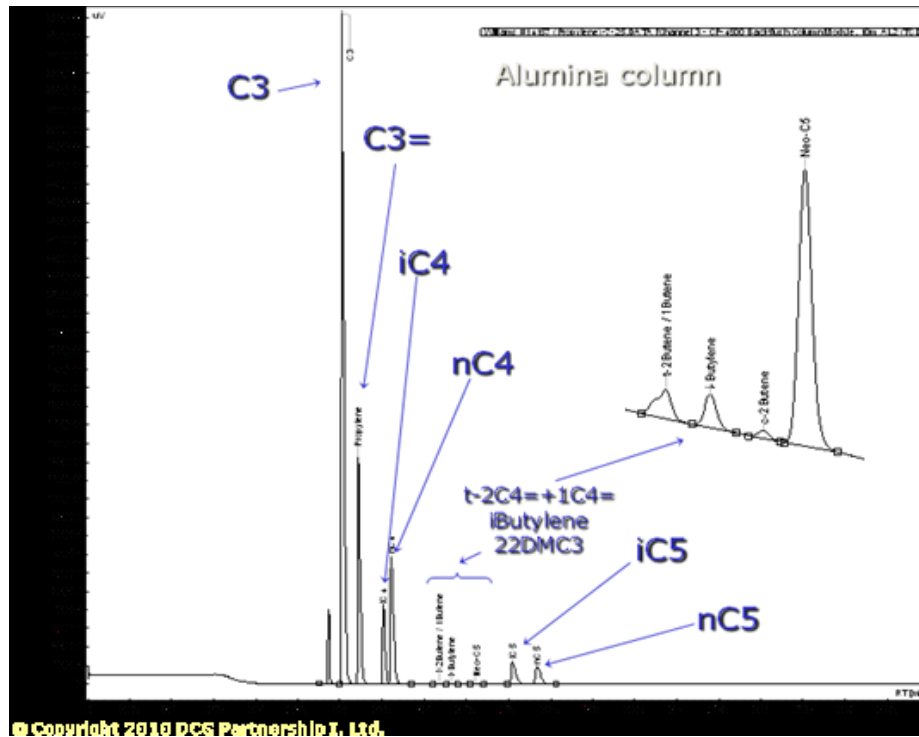


Figure 5. Propylene sample (Channel #2 signal)



Method Comparison

The final step was the comparison of Micro GC results with the ones obtained using a conventional GC. Gravimetrically blended standards and “real world” samples were used on this comparison. First, LPG’s gravimetrically prepared samples were injected in a Hewlett Packard 5890 GC with a Thermal Conductivity detector (TCD), calibrated for this type of samples.

Figures 8 and 9 show the comparison of two “synthetic” samples, a Y grade and an EP Mix respectively. In both cases a good match was found, even for the heavy ends up to 6% Mol. Run time for conventional GC was 45 minutes including cool-down time. Micro GC’s run time was around 4 min and since it is an isothermal run, no cool-down time is needed.

An additional feature when using the SID is that once the system is equilibrated with a sample there is no limit in the amount of injections that can be done for that particular sample.



Repeatability test were made for different samples. Gravimetrically blended standards of EP Mix, Ygrade (5% C6+), Propane, Propylene, iButane and nButane were prepared and injected.

Figures 6 and 7 show a couple of examples, and the results obtained with 95% of confidence.

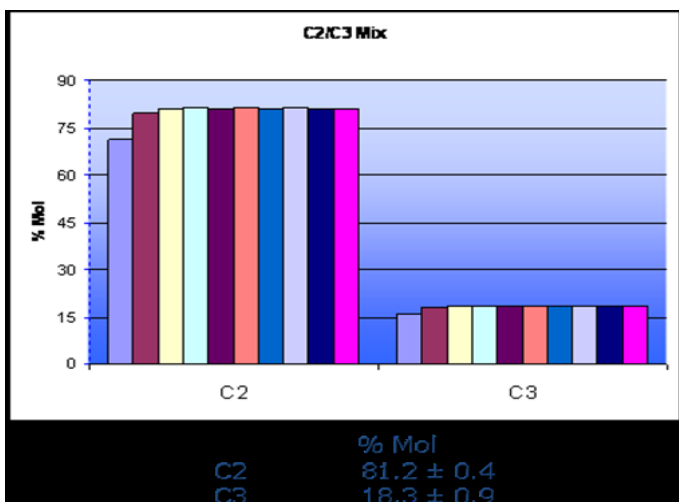


Figure 6. EP Mix Std. Repeatability test.

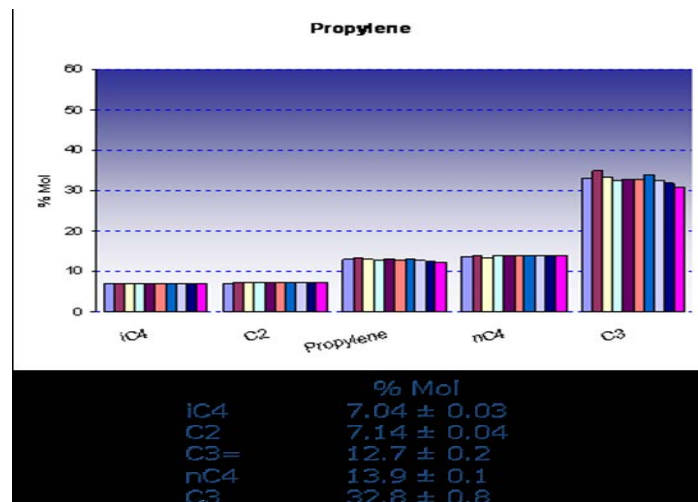


Figure 7. Propylene Std. Repeatability test



The system was installed in a customer's facility and samples were run simultaneously in his instrument HP 5890 (Hewlett Packard). Figure 10 shows the results obtained on each instruments for an EP Sample.

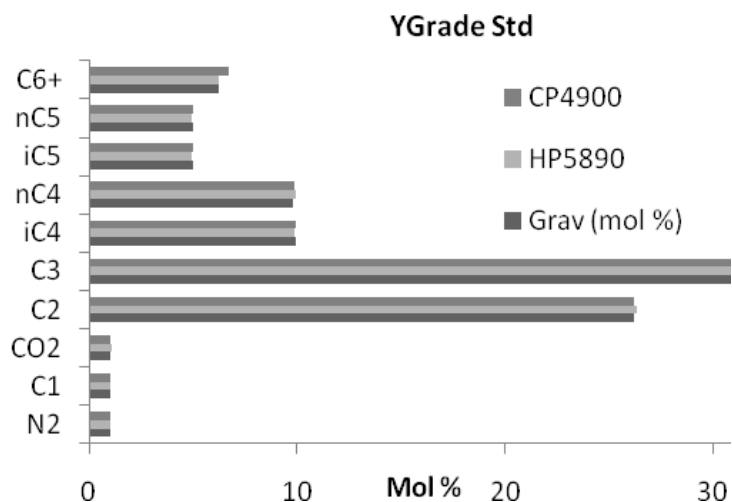


Figure 8. Method Comparison. YGrade Std

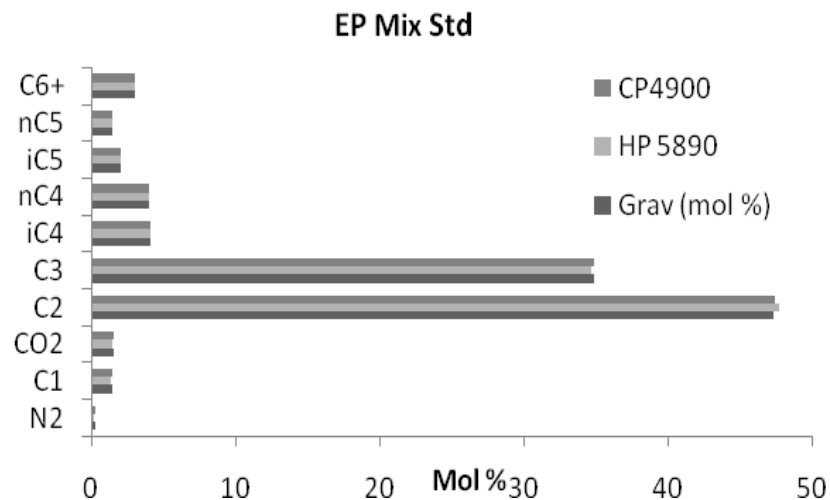


Figure 9. Method Comparison. EP Mix Std

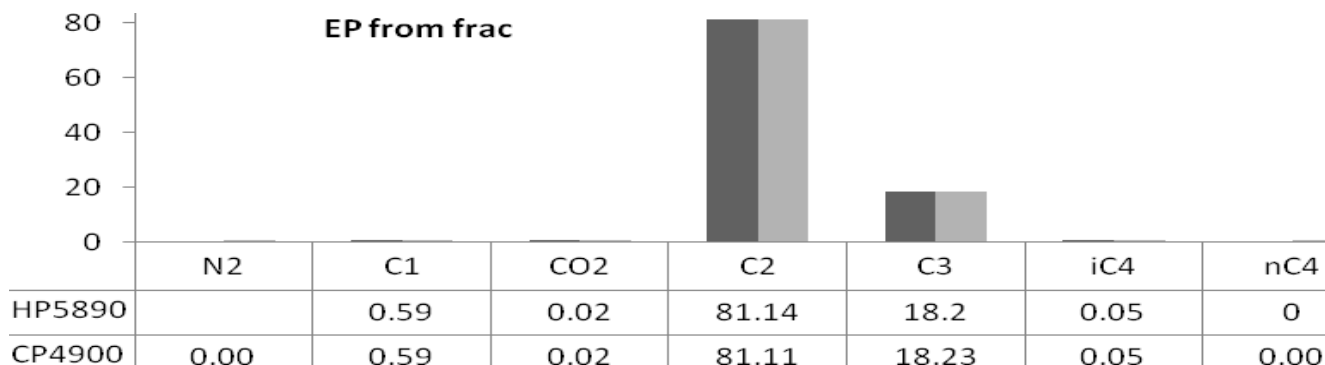


Figure 9. Method comparison. EP Sample from fractionation unit

CONCLUSION

An injection device for LPG samples was designed and thoroughly tested.

Multiple injects can be made without operator supervision.

Run time ranged from 3 to 5 min.

One calibration point is required. However, linearity was checked with the sample's working range.

Method comparison was done with known and unknown samples.

The system is simple, reliable and rugged.

Being an independent unit (no direct interaction with CDS) it can work with any micro GC in the market.

For more information visit us at:

<http://www.dcgpartnership.com/>