AC Hi-Speed RGA Repeatability

Keywords: Refinery gas, ASTM D 7833 & EN 15984, repeatability, sample shut-off valve

- Refinery gas analysis correlating with ASTM D7833 & EN 15984
- Unsurpassed repeatability with sample shut-off valve functionality
- Analysis time less than 6 minutes

REFINERY GAS

Refinery gas streams vary considerably in composition. Determining individual components of each gas stream is a challenge. An exact measure of stream components is essential in achieving optimum control and assuring product quality. AC Analytical Controls offers the Hi-Speed Refinery Gas Analyzer, the high-speed solution that determines and reports the composition of refinery gas streams.

The AC Hi-Speed RGA system characterizes:

- C1 - nC6, C6+ hydrocarbons
- Inert gases: nitrogen, hydrogen, helium, oxygen, carbon monoxide, carbon dioxide
- Hydrogen Sulfide
- BTEX (benzene, toluene, ethylbenzene, xylenes), using the RGA extended method with a total analysis time under 30 minutes

Typical products that can be analyzed on the AC Hi-speed RGA include fuel gas, atmospheric overhead, FCC overhead, recycle gas, desulfurizer gas, and finished products such as LPG, propane or butanes streams. Optionally, the system can also be configured for hydrocarbon trace analysis as well (e.g. propylene impurities).

A repeatable sample introduction plays a crucial role in the overall performance of the system. Fluctuation in the amount of sample introduced translates into a fluctuation in peak area. If a sample is introduced under different conditions than the calibration gas the quantification might be incorrect.

The amount of sample gas (n) introduced is based on the “Ideal Gas Law”: pV = nRT), and is dependent on three factors:

- **Volume (V):** the sample loop size on the gas sample valve is fixed so the sample volume is constant.
- **Temperature:** GSVs are mounted in a heated valve box, ensuring that they are always at constant temperature.
- **Pressure (p):** this is the only parameter that can vary between analyses.

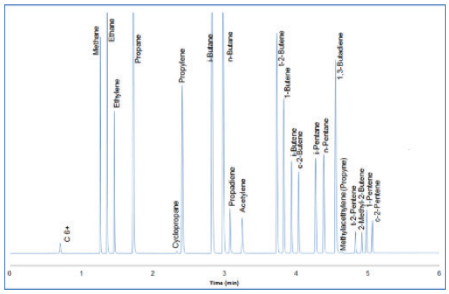
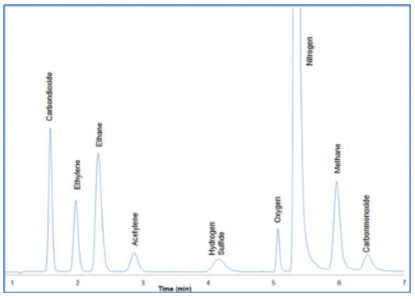
It is critical to maintain a consistent pressure inside the sample loop, preferable atmospheric. To ensure consistent measurements, all AC Analytical Controls gas analyzers are configured with a sample shut-off valve, which ensures repeatable sample introduction.

EN 15984 states that the results can be normalized when the sum of all the mole fractions of the components are not smaller than 0.98 or greater than 1.02. Summed results being out of the listed range clearly indicate that there is a difference for either the sample amount or the amount of calibration gas introduced and will require a duplicate analysis, which costs extra time and effort (assuming there is still sample gas available).

An alternative method for sample introduction at atmospheric pressure is maintaining a constant flow through the sample loop at the moment of sampling. In practice, however, this is not a very robust and reliable method, especially with multiple operators working on the same system.

HARDWARE DESCRIPTION

The AC Hi-Speed RGA system contains six columns and is subdivided into three separate analytical channels. One channel separates the hydrocarbons on the PLOT column using the FID for detection, while the second channel is used to determine oxygen, nitrogen, carbon monoxide, carbon dioxide and hydrogen sulfide using TCD. The third channel determines helium and hydrogen, also using a TCD for detection.

Channel 1	Channel 2	Channel 3
		
C1 – C6+ Hydrocarbons Backflush for C6 and Heavier HCs	Oxygen, Nitrogen, Carbon Dioxide, Carbon Monoxide & Hydrogen Sulfide	Helium & Hydrogen
Capillary in GC oven	Micro-packed in isothermal oven	Micro-packed in isothermal oven
FID	TCD	TCD

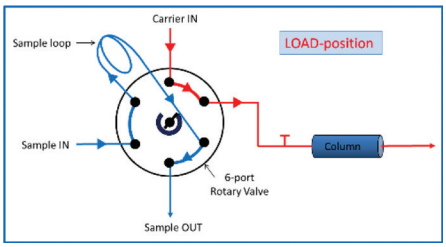
Micro-packed columns for the separation of the inerts or non-condensable gases are mounted in a separate iso-thermal oven, located in the dedicated left-side compartment. Valves are also mounted in an isothermal compartment in the left-side compartment, and, together with the default automated shut-off valve, make the analyzer extremely repeatable and robust. Use of Sulfinert tubing ensures optimal resistance to corrosive materials. Optionally, the Hi-Speed RGA can be configured with a liquid sampling valve dedicated to the hydrocarbon analysis of liquefied samples (like commercial LPG).

SAMPLE SHUT-OFF VALVE PRINCIPLE

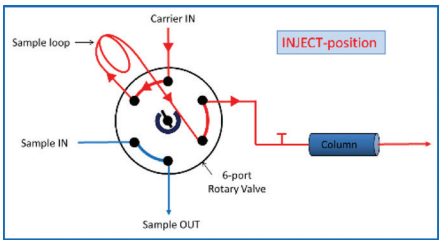
In the AC Hi-speed RGA, the sample is introduced into the columns by a gas sampling valve (GSV), which is a rotary valve with a sample loop, which is a short length of tubing with a fixed volume.

The GSV uses a rotating element to switch port connections between the sample gas stream, carrier gas stream, and column.

In the "LOAD" position the sample stream flows through the sample loop to the sample out port.



In the "INJECT" position the volume of sample gas held in the sample loop gets injected into the column by a flow of carrier gas. The purpose of the sample loop tube is to act as a holding reservoir for a fixed volume of sample gas.



When the sample valve switches to the sample position, at the start of the analysis, the carrier gas will flush the content of the sample loop toward the column.

If the gas sample valve is switched while there is still sample gas flowing at (non-ambient) pressure, more sample is introduced compared to when the pressure inside the loop is atmospheric. This will result in non-repeatable analysis or incorrect quantification. Common practice to overcome this issue is to allow sufficient time between stopping the sample flow and switching the gas sampling valve. This should result in an atmospheric pressure inside the sample loops at the moment they are switched.

The sample shut-off valve automates this process, as it is installed in the sample line just before the sample loops and will be closed at the moment the method run is started. The pressure inside the loop will stabilize to atmospheric, which will only take a few seconds. At a fixed time (eg 5-10 seconds) after the run is started the GSVs are switched to the inject position, thereby introducing the content of sample loops (being at atmospheric pressure) into the columns.

This procedure reduces the operator errors like switching the GSVs too while there is still pressure and/or flow inside the loops.

Other advantages of the sample shut-off valve include:

- The sample flow is stopped just before the GSVs so it takes less time to stabilize the pressure inside the loops to atmospheric (the sample line itself does not have to empty/stabilize as well), which can take a long time.
- Ability of running repetitive analysis from the same sample without user intervention.

Connect sample and open to flush the sample loops

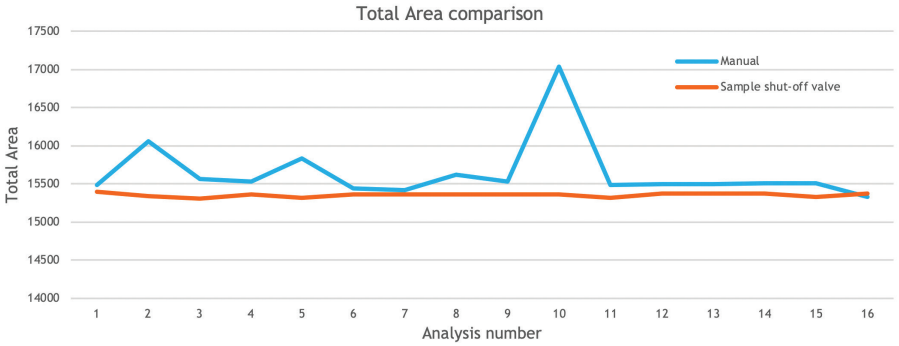
After sufficient flushing start the run

Sample shut-off valve will stop sample flow and allow pressure inside the loop to stabilize to atmospheric

After a fixed time GSVs will be actuated introducing sample into the columns

RESULTS

The results below show the total area repeatability for 16 analyses run without the use of the sample shut-off valve (manual) and a comparable set of analyses with the use of the sample shut-off valve (automated).



A few conclusions can be drawn from these results:

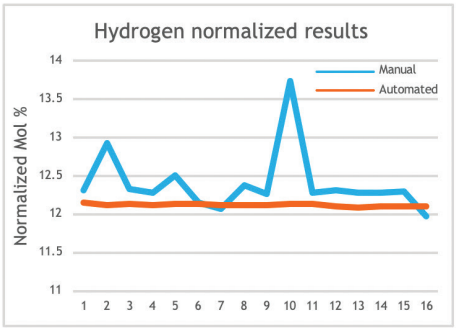
- There is significant higher RSD on the manual results: 2.53% vs 0.15% for the automated analysis.
- The total area for a significant number of manual analyses is higher than for the automated analysis. This indicates that there was still a higher than atmospheric pressure in the sample loops at the moment of switching the GSVs.

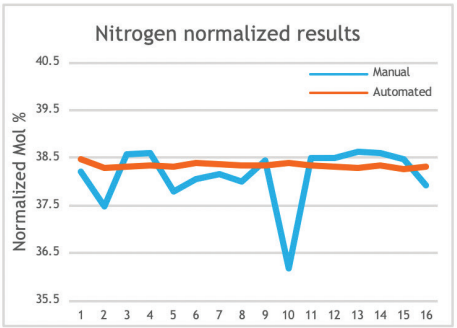
The graphs below show the calculated mol percentage for three components based on an external calibration and normalized results. Each component is analyzed on a different channel.

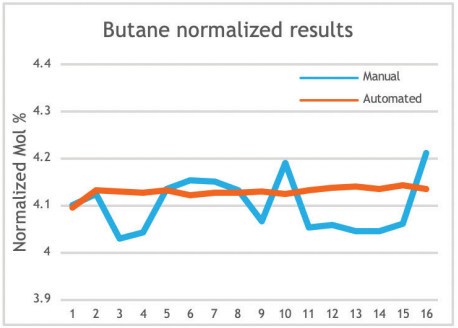
One can conclude from these results that normalizing calculated results does not fix the issue of non-repeatable sample introduction or introducing the sample under (varying) pressure. Hydrogen can be reported at a too high concentration, while nitrogen seems to be reported at a lower concentration.

This can be explained by a pressure gradient in the sample line: high pressure at the sample-in position and lower/atmospheric at the sample-out position. The higher total area for some analyses, together with a too high hydrogen (first loop in line close, to the sample in) and too low nitrogen (last loop in line, close to sample out), clearly shows that pressure inside the sample loops was not stable or constant for some or most of the manual analysis.

So, without the use of the sample shut-off valve, a relatively simple error can be made (like not taking sufficient time to let the pressure reduce to ambient pressure), which may result in a significant error in the end result (>2% at 39 mol% level for nitrogen). The sample shut-off takes out this risk by automating the process of sample introduction.







CONCLUSION

The AC Hi-speed RGA is an analyzer designed for robust and repeatable gas analysis. It features a sample shut-off valve to ensure a constant method of introducing the sample in all three channels at atmospheric pressure.

Normalization of the calculated concentration (based on an external calibration) does not correct for errors due to introducing the sample into the columns while there is still some pressure inside the sample line.