APPLICATION NOTE

Gas Chromatography

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GC: Determination of CO, CO_2, CH_4 and Total Hydrocarbon Content in Hydrogen in Compliance with ISO 14687 and GB/T3634.2

Introduction

Hydrogen is used in a number of areas, from industrial processes such as pesticide production and the removal of sulfur from petrochemical products to its use as a fuel and in power generation. To ensure the quality of hydrogen, standards such as ISO 14687 and GB/T 3634.2 have been produced which specify the maximum content of certain compounds in hydrogen gas. As such, it is of great importance that hydrogen gas refiners and those using hydrogen gas in various processes have access to a method which allows for quick, accurate and sensitive detection of these compounds. This application note shows the quantitation of carbon monoxide (CO), carbon dioxide (CO_2) and methane (CH_4) in hydrogen. The analysis is performed with a modified configuration to allow for the determination of total hydrocarbon content (THC) or the determination of non-Methane Hydrocarbons (NMHC or C_2+).

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Instrumentation

Analysis of carbon monoxide (CO), carbon dioxide (CO_2) and methane (CH_4) in hydrogen samples was performed with the PerkinElmer Clarus GC Engineered Solution.

The Clarus GC Engineered Solution with THC analysis consists of two analytical channels which include carrier gas input, a hydrogen input for the flame ionization detector (FID) a HayeSep Q analytical column, a restrictor for THC analysis and a methanizer for CH_4 analysis. An important aspect of the analytical method is the backflushing of the analytical HayeSep Q column to speed up the analytical cycle, and to prevent the elution of water, ammonia, sulfur and any hydrocarbons other than methane which have the potential to poison the methanizer catalyst or extend the analytical cycle.

Experimental

CO, CH_4 and CO_4 Analysis

Figure 2 shows the configuration in the ready state, before sample injection. In this state, the HayeSep Q column is being backflushed to vent.

Figure 3 shows the process by which the gas is injected onto the column. In the ON position, the sample loop is exposed to the helium carrier gas from the pressure regulator which pushes it onto the analytical column. CO, CH_4 and CO_2 are separated by the HayeSep Q column before eluting to the FID via the methanizer which converts CO and CO_2 to methane.

Once the final compound of interest (CO_2) has eluted, valve 1 is switched back to the OFF position. This causes backflushing of the column which prevents poising of the methanizer.

THC Analysis

Figure 5 illustrates the THC analysis part of the system in the ready state (Valve 2 OFF).

For sample analysis, the valve is switched to the ON position which exposes the sample loop to the carrier gas, pushing the sample through the THC restrictor to the FID.

Figure 1. Clarus GC Engineered Solution with THC analysis.

Table 1: Gas Chromatography Conditions.

GC Parameters	
Gas Chromatograph	PerkinElmer Clarus GC Engineered Solution
Oven	35 °C for 10 min
Auxiliary Pneumatic Pressure	21.5 psi (Aux 1), 11.4 psi (Aux 2)
FID Detector	H_2 45 mL/min
	Air 450 mL/min
	250 °C
Sample Loop Volume	1.0 cm^3

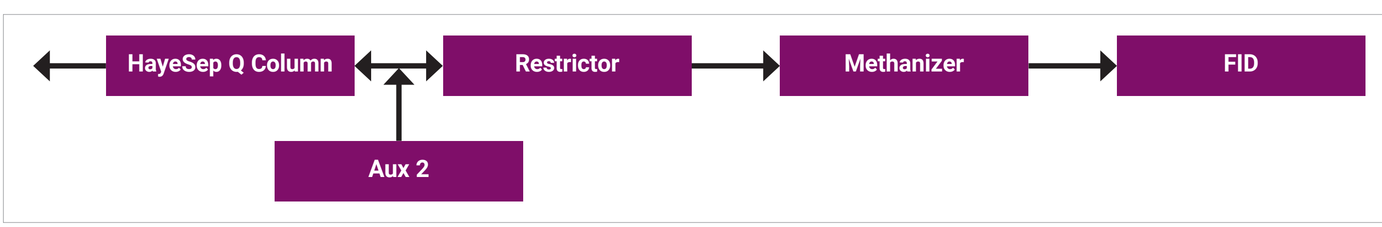

Figure 2. Ready State (valve 1 OFF).

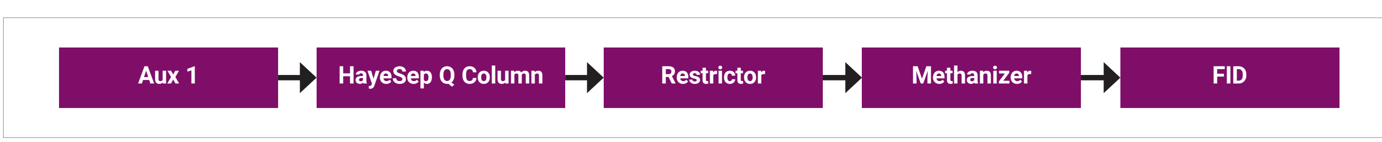

Figure 3. Gas sample injection onto column for analysis.

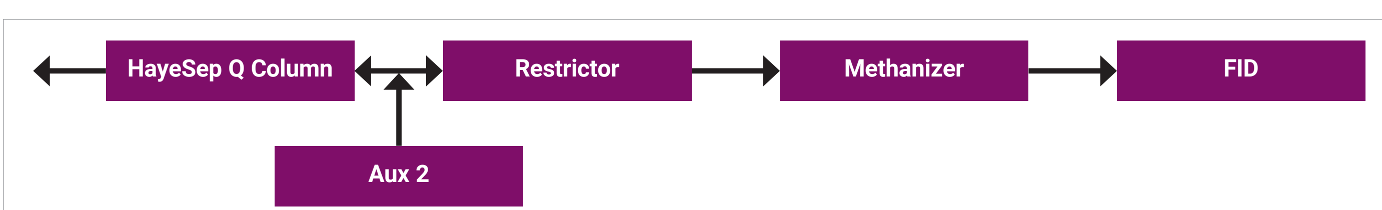

Figure 4. Column Backflush (Valve 1 OFF).

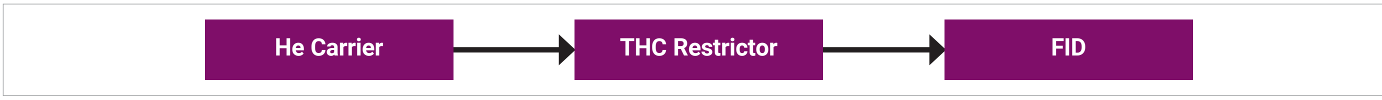

Figure 5. THC Analyzer in Ready State (Valve 2 OFF).

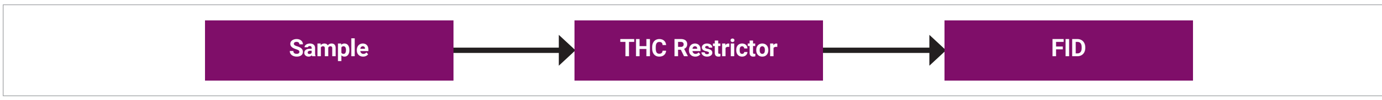

Figure 6. THC Analyzer during sample analysis.

Results and Discussion

A chromatogram of a test gas containing 10 ppm of each component is shown in Figure 7.

This data demonstrates good separation and peak symmetry. The detection limits for this analysis along with the limits for these compounds in hydrogen regulated by ISO 14687 and GB/T 3634.2 are shown in Table 2.

The data demonstrates that the detection limits are far below those required by the relevant standards for hydrogen impurities.

In cases where non-methane hydrocarbon determination is required, the configuration can be modified to include an additional channel and a proprietary silica gel column. Furthermore, for improved sustainability and cost-effectiveness, nitrogen can be used as carrier alternative to helium.

To avoid the ingress of air into the sampling valve, that can cause a false signal for CO_2, this analytical setup has the sampling valve contained in a purged housing. This bathes the valve in a positive pressure of carrier, and it prevents air from entering the valve.

The large capacity methanizer protects against air injection and thus increases the lifespan of the system.

Summary

For the determination of CO_2, CO, CH_4 and THC in hydrogen, the Clarus GC Engineered Solution is a robust ready-to-use set up, enabling reliable and accurate data. It supports compliance with current hydrogen standards with lower limits of detection than

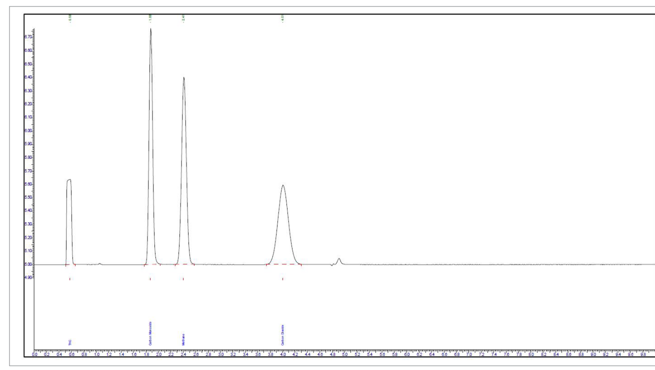

Figure 7. Analysis of 10 ppm test mixture using Clarus GC Engineered Solution with THC modification.

required by the ISO 14687 showing a performance that can help labs future-proofing analysis for any more stringent standards that may be introduced as the use of hydrogen becomes more widespread.

For high-throughput laboratories, the Clarus GC Engineered Solution provides high level of automation, allowing increased lab productivity. Combined with the customization opportunities, that can adapt the system to specific lab requirements, the Clarus GC Engineered Solution is a dedicated solution that help labs face their most challenging analytical requirements.

The Clarus GC Engineered Solution allows for high sample throughput and automated data analysis, allowing increased laboratory productivity. Combined with the customization opportunities, the Clarus GC Engineered Solution is a dedicated solution that can be adapted to specific lab requirements.

Table 2. Detection limits of CO, CO_2, CH_4 and THC using Clarus GC Engineered Solution compared to ISO 14687 and GB/T3634.2 limits for contaminants in hydrogen.

Compound	Clarus GC Engineered Solution Detection Limit	ISO 14687	GB/T 3634.2 - 2011		
			Pure	High Purity	Ultrapure
CO	<0.05 ppm	0.2 ppm	< 5 ppm	< 1 ppm	< 0.1 ppm
CO_2	< 0.05 ppm	2 ppm	< 5 ppm	< 1 ppm	< 0.1 ppm
CH_4	< 0.05 ppm	100 ppm	< 10 ppm	< 1 ppm	< 0.2 ppm
THC	< 0.02 ppm	2 ppm*	-	-	-

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