GREENPIX: THE NEXT GENERATION OF MICRO-GC REDEFINING GAS ANALYSIS

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ABSTRACT

Founded in 2014, APIX Analytics has been at the forefront of developing and commercializing micro gas chromatography (µ-GC) systems, with more than 800 units installed worldwide for applications such as natural gas and biomethane energy content analysis, as well as impurity monitoring. Building on this experience, the European-funded GreenPix project, launched in 2022, has developed a new generation of µ-GC analyzers that preserve advanced technologies like the highly sensitive micro thermal conductivity detector (µTCD) and proprietary nano-gravimetric detector (NGD) while incorporating new features to enhance performance and versatility. These innovations include a silicon-based micro-injector that further reduces instrument size, and a new design that streamlines manufacturing and maintenance while being highly integrable as an OEM (Original Equipment Manufacturer).

Recent proof-of-concept demonstrations have underscored GreenPix's capabilities, including a three-module configuration for rapid gas analysis (encompassing permanent gases and hydrocarbons from C1 to nC5 in less than 25 seconds), and other key impurity applications such as trace-level H_2S detection with state-of-the-art limits of detection using µ-TCD. Each of these advances is easily integrated into OEM configurations, showcasing the platform's adaptability and strong integration potential.

Ongoing developments, such as miniaturized silicon-based GC columns, promise unprecedented compactness and further performance gains in future µ-GC generations. Together, these advancements position GreenPix as a powerful, flexible, and embedded solution that is redefining performance standards in gas analysis.

INTRODUCTION

In the last 20 years, innovative development emerged in the field of miniaturized multi-gas analyzers, breaking from conventional technologies through the application of silicon-based technology. Mainly the disruption comes from the introduction of micro-TCD technology which enables the analysis of permanent and light gases with sensitivity reaching the parts per million (ppm) range. One can cite products from Agilent, Inficon and Qmicro. Very recently APIX introduced on top of that a new silicon detector called the Nano Gravimetric Detector (NGD), facilitating the analysis of heavier compounds (beyond C6) with sub-ppm sensitivity [Reference 1]. With the combination of TCD and NGD technology, it is therefore now possible to measure molecules from H2 up to C12.

Most micro-GC manufacturers integrate multiple columns in their instrument to cover the different applications needs. APIX has proposed a revolutionary approach using plug-and-play analytical modules integrating the three key technological components required for analysis (injector, GC separation column, and detector). These modules are installed in various non-ATEX or ATEX enclosures, enabling diverse applications in laboratories, on-site industrial analysis bays, or ATEX zones. In all cases, these systems provide online, continuous, and real-time analysis with short analysis times of just a few minutes.
The variety of enclosures, capable of integrating up to 2 or 4 analytical modules, along with the broad range of available analytical modules, enables highly modular analysis systems covering a wide range of applications. In addition to offering modular systems, this system architecture strategy also facilitates commissioning and maintenance.

The application fields covered by micro-GC are involved in the energy market for the transactional measurement of the calorific value of biomethane and natural gas, including hydrogen (in compliance with OIML R140, ISO 6976, and WELMEC standards) but also for the biogas quality, the measurement of odorant in natural gas, the quality of CO2 and hydrogen, etc.

In this article we introduce a new micro GC called GreenPix combining TCD and NGD focusing on the easing of assembly process (Reducing manual handling), simplifying the maintenance and offering new levels of performance by introducing a fast temperature programming feature of the column to perform complex analysis up to C10 while allowing backflush of the column, which is particularly important when using Molsieve columns to measure permanent gases.

A NEW MICRO-GC ARCHITECTURE

The strategy for conception of this new system architecture is to automate the instrument's assembly process by using automatic pick and place equipment of all the analytical building blocks, minimizing manual handling tasks as much as possible. Advantages of this strategy are:

- To improve reliability.
- To increase versatility.

- To decrease assembly costs.
- To allow the design of more complex GC architectures (e.g., multi-detectors, multi-GC columns) to offer better performance.

To achieve this goal, the different analytical key building blocks (on/off valves, GC column, silicon detectors) must be mounted on a so-called fluidic manifold. The manifold embeds all the microfluidic pipes interconnecting all these key building blocks to each other.
Following this strategy, MEMS technology is a viable option that allows for the mass production of the various analytical components, such as detectors, columns, and injectors. The assembly of these components can be facilitated by using a fluidic integrated board (manifold) like the way electronic PCBs connect different electronic circuitry. The new design replaces the complex "spaghetti" tubing connections of discrete components in our current GC module with a more structured and dependable system, enhancing reliability and reducing variability in GC system fabrication.

The analytical module, which forms the core of the analysis technology, consists of the following components:

- The silicon injector, which is responsible for sampling a small volume of gas (typically 10 µL), is directed to the GC column. The silicon injector chip is a set of interconnected on/off silicon microvalves and is paired with a glass splitter, whose role is to distribute different gases to the analytical module [FIGURE 1]. Once integrated with the silicon injector, the glass splitter facilitates fluidic interconnections between the injector's valves and the distribution of gases to the columns and detectors, eliminating the need for traditional tubes and capillaries commonly used in such assemblies. The glass splitter also incorporates the sample loop.

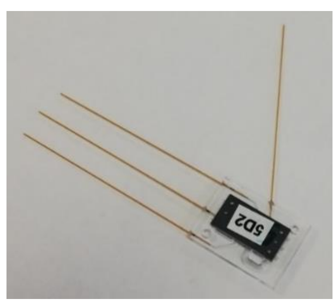


FIGURE 1. SILICON INJECTOR MOUNTED ON MANIFOLD

- The GC oven, which has been developed to house the separation column, is capable of accommodating capillary columns up to 50 meters long and applying a temperature ramp from ambient to 250°C. This design includes a wheel that supports the winding of a copper heating wire, enabling the column to reach the temperature required for analysis, and that then supports the GC column of interest.
- The bulk detector, which analyzes each compound as it exits the separation process. APIX developed individual detectors integrated with fluidic manifolds, enabling the seamless incorporation of these detection components into the

architecture of the analytical module. The proposed architecture utilizes a machined metal manifold to form fluidic channels that connect the vertical outputs of the detector to the horizontal outputs of the GC column, thereby nearly eliminating the need for capillaries.

- The electronic control board which provides autonomous control of the analytical module. The electronics for the analytical module have been designed to control various functions, such as the opening and closing of injector valves, thermal regulation of the GC oven, and monitoring detector responses. Additionally, electronics manage communication with the computer responsible for collecting data from different modules, processing chromatograms (integrating peaks), and delivering gas composition results to the end user

In the current product line, the assembly of our module is primarily done by hand, taking approximately half a day. With the new GreenPix module, manual operations are minimized. Each sub-element, namely the injector, GC oven, and detector, is preassembled using pick-and-place equipment. The assembly of these sub-elements is subcontracted to specialists with strong expertise. Overall, it now takes less than half an hour to assemble the complete module with minimum manual operation.

Several analytical channels were manufactured to address the various applications targeted by APIX. These analytical channels vary based on the type of GC separation column and the detector used (TCD or NGD), which are selected according to the compounds being analyzed:

- The selection of the GC separation column (i.e., the stationary phase) determines the separation efficiency of the compounds based on their interactions with the stationary phase.
- The choice of detector depends on its sensitivity to the compounds of interest: the TCD offers good sensitivity for light permanent gases up to compounds with six carbon atoms, while the NGD is more sensitive to heavier compounds, ranging from six to twelve carbon atoms and extending to 40 carbon atoms for specific petrochemical applications.

The analytical module is thus inserted into a channel base that incorporates the fluidic manifold. The external fluidic manifold is a key component designed to facilitate the efficient assembly of the final instrument, offering a plug-and-play solution for gas line distribution, regardless of the number of analytical channels involved. Each analytical channel is connected to the gas distribution lines via a system of multiple gas connectors, combining both gas inlets and outlets [FIGURE 2]. External manifold also enables multiple analytical channels to be connected, facilitating the distribution of carrier, actuation, and sample gases across these channels [FIGURE 3]. In addition, the external fluidic manifold incorporates the electropneumatic solenoid valves necessary for controlling the silicon injector assembly.

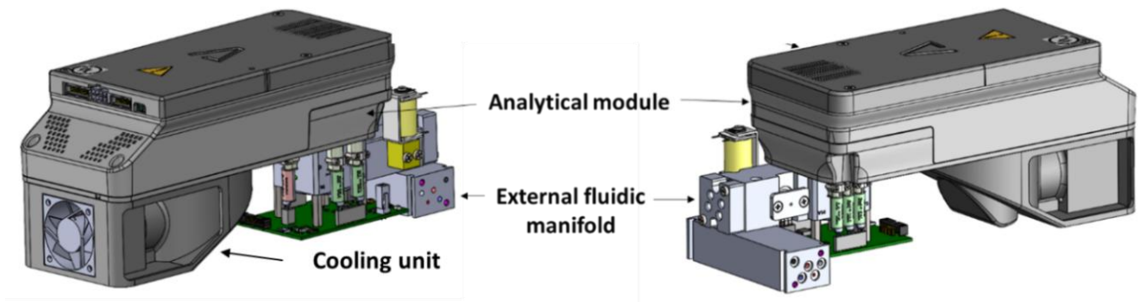


FIGURE 2. GREENPIX ANALYTICAL CHANNEL

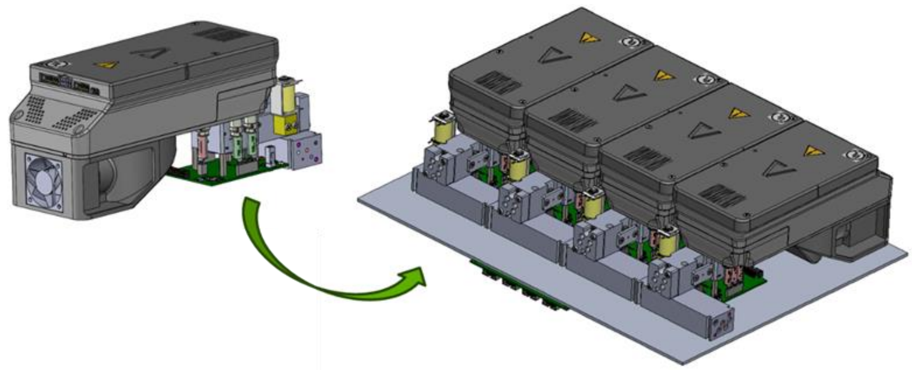
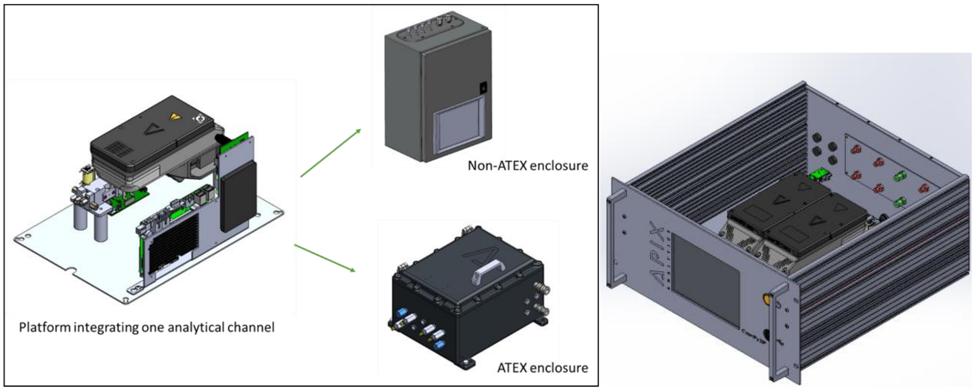


FIGURE 3. ASSEMBLY OF SEVERAL GREENPIX ANALYTICAL CHANNELS

GREENPIX SYSTEMS

The analytical modules are integrated into various systems based on the requirements of the targeted applications and testing environments. The integrations primarily depended on the number of analytical modules needed to fulfill the application's needs.
A plate designed to support a single analytical channel was created for seamless integration into various enclosures, featuring fluidic connections and a PC with an embedded SSD for system control and 512GB internal storage for data. The PC runs the main software which can be accessed through a password protected web interface, as well as auxiliary software such a Modbus server over RTU or TPC/IP. This platform is an immediate solution for the OEM integration of the GreenPix technology by system integrators, enabling them to extend the analytical capabilities of their solution. Integrations have been completed in both a non-ATEX wall-mounted box with a front-facing touch screen and an ATEX box for use in potentially hazardous environments. Integrations of 2 and 3 analytical modules have also been implemented in non-ATEX rack-mounted enclosures and ATEX explosion-proof enclosures [FIGURE 4].



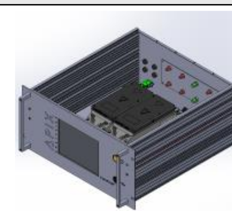
ATEX system (ChromEx 200)	non-ATEX system (wall-mounted enclosure)	non-ATEX system (19'' rack)
		

FIGURE 4. EXAMPLES OF GREENPIX SYSTEMS

The GreenPix system's modular architecture enables it to meet the diverse requirements of these markets, offering certified, high-performance solutions that adapt to evolving energy and gas industry trends. For each application case, a specific system configuration was designed based on the number and type of analytical channels required. These configurations are tailored to meet the unique demands of each market and integrate the analytical channels. Each system is built with a modular approach, allowing easy customization of the number and type of analytical channels based on the requirements of the specific application.

EXPERIMENTAL SET-UP

Several application markets are accessible for GreenPix systems. Some of these, such as the biomethane and natural gas markets, are currently addressed by the company's existing generation of analyzers. However, both these markets, along with emerging sectors like hydrogen and trace analysis, are the focus of new GreenPix systems, offering more competitive solutions in terms of performance and cost. Based on this strategy, the key applications of interest are natural gas, biomethane, biogas, odorization, hydrogen.

The deployment of system tests was conducted in a specially equipped laboratory, outfitted with multiple systems in varying configurations [FIGURE 5]. These configurations are designed to cover most of the market applications of interest. By simulating real-world conditions and testing various system configurations for gas applications, the laboratory ensures that each configuration meets the performance, reliability, and compliance requirements specific to each application, from natural gas and biomethane to hydrogen and biogas analysis. These tests were performed in a temperature-controlled laboratory environment, and other tests in different climatic conditions are to be conducted outside of the scope of this paper.

FIGURE 5. EXPERIMENTAL SET-UP FOR TESTING GREENPIX SYSTEMS

RESULTS

ANALYSIS OF NATURAL GAS

The need for natural gas analysis arises from the necessity to evaluate the composition of this complex mixture, both to assess its quality and to calculate its higher calorific value, which determines the heat released during combustion and, ultimately, the market price charged to the user. This measurement process is governed by metrological certifications. The challenge is to provide accurate, reliable, and efficient analytical solutions capable of separating and quantifying the individual components of natural gas.

For this purpose, two Greenpix modules are required: a PPU10-PPU1-TCD module for analyzing light compounds up to C2, including methane, the primary component of natural gas, and a PDMS15-PDMS2-TCD for analyzing hydrocarbons from C3 to C6, which are present in lower concentrations.
A series of tests was conducted on three natural gas samples across a wide range of concentrations. The chromatograms obtained from both modules for these samples confirmed the system's strong performance in terms of separation over the entire concentration range [FIGURE 6]. The TCD responses exhibited linearity with the intercept forced to zero within the concentration range studied of each compound, typical in natural gas, with coefficients of determination (R^2) of 1 for most compounds, demonstrating the high effectiveness of the linear regression model for all components [FIGURE 7]. After calibration of the system, the concentrations measured by the system are highly accurate,

showing a low relative deviation from the expected values. The calorific value was calculated from the measured concentrations and compared to the theoretical value provided by the sample supplier. The relative deviations between the measured and theoretical calorific values are less than 0.5%, which is within the acceptable limit for certifying a measuring device in the highest accuracy class for transactional measurement of the higher calorific value [FIGURE 8].

Module : PPU10-PPU1-TCD

- Injector temperature : 60 °C
- Column temperature : 70 °C
- Detector temperature : 70 °C
- Column pressure : 0.8 bar(g), Helium
- Sample pressure : 15 psi(g)

- Sampling : 24.0 s
- Injection time : 100 ms
- Foreflush duration : 8.0 s

Module : PDMS15-PDMS2-TCD

- Injector temperature : 60 °C
- Column temperature : 70 °C
- Detector temperature : 70 °C
- Column pressure : 2.5 bar(g), Helium
- Sample pressure : 15 psi(g)

- Sampling : 28.0 s
- Injection time : 400 ms
- Foreflush duration : 15.0 s

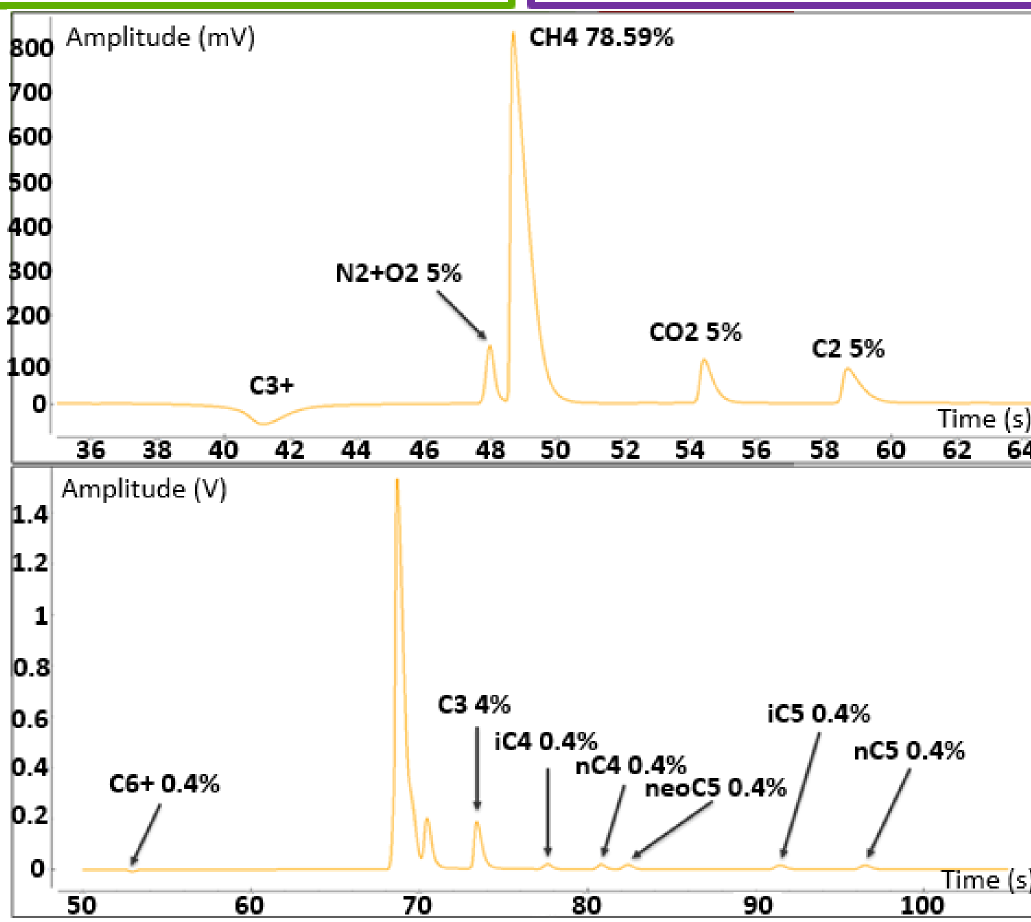


FIGURE 6. EXAMPLE ANALYSIS OF NATURAL GAS AND METHODS

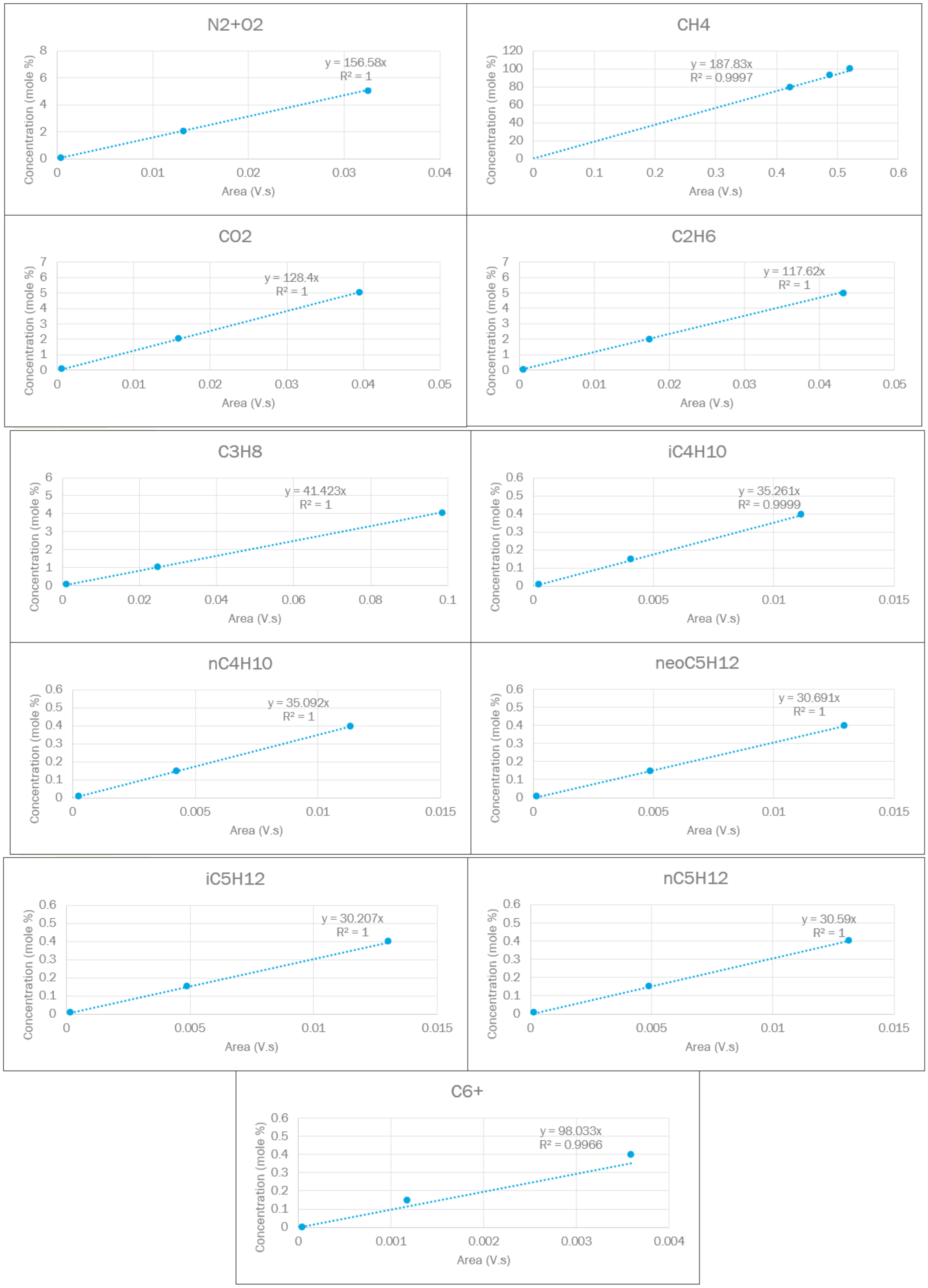


FIGURE 7. TCD RESPONSE LINEARITY

N2+O2							
Standard concentration		Measured concentration		Absolute difference		Rel. difference	RSD%
Mole %	*Mole ppm*	*Mole %*	*Mole ppm*	*Mole %*	*Mole ppm*	*% rel*	*% rel*
0.0501	501	0.0801	801	0.0300	300	59.95%	0.89%
4.9970	49970	5.0497	50497	0.0527	527	1.05%	0.27%
1.9760	19760	2.0812	20812	0.1052	1052	5.33%	0.38%

CH4							
Standard concentration		Measured concentration		Absolute difference		Rel. difference	RSD%
Mole %	*Mole ppm*	*Mole %*	*Mole ppm*	*Mole %*	*Mole ppm*	*% rel*	*% rel*
99.7605	997605	99.7014	997014	0.0591	591	0.06%	< 0.01%
78.5905	785905	78.5375	785375	0.0530	530	0.07%	0.01%
92.1247	921247	91.9459	919459	0.1788	1788	0.19%	0.01%

CO2							
Standard concentration		Measured concentration		Absolute difference		Rel. difference	RSD%
Mole %	*Mole ppm*	*Mole %*	*Mole ppm*	*Mole %*	*Mole ppm*	*% rel*	*% rel*
0.0499	499	0.0800	800	0.0301	301	60.29%	0.66%
5.0050	50050	5.0303	50303	0.0253	253	0.51%	0.06%
1.9990	19990	2.0484	20484	0.0494	494	2.47%	0.01%

C2H6							
Standard concentration		Measured concentration		Absolute difference		Rel. difference	RSD%
Mole %	*Mole ppm*	*Mole %*	*Mole ppm*	*Mole %*	*Mole ppm*	*% rel*	*% rel*
0.0502	502	0.0524	524	0.0022	22	4.29%	0.28%
5.0020	50020	5.0165	50165	0.0145	145	0.29%	0.02%
1.9990	19990	2.0341	20341	0.0351	351	1.76%	0.02%

C3H8							
Standard concentration		Measured concentration		Absolute difference		Rel. difference	RSD%
Mole %	*Mole ppm*	*Mole %*	*Mole ppm*	*Mole %*	*Mole ppm*	*% rel*	*% rel*
0.0499	499	0.0506	506	0.0007	7	1.39%	0.19%
4.0070	40070	4.0498	40498	0.0428	428	1.07%	0.20%
1.0010	10010	1.0328	10328	0.0318	318	3.18%	0.12%

iC4H10							
Standard concentration		Measured concentration		Absolute difference		Rel. difference	RSD%
Mole %	*Mole ppm*	*Mole %*	*Mole ppm*	*Mole %*	*Mole ppm*	*% rel*	*% rel*
0.0099	99	0.0081	81	0.0018	18	18.22%	0.24%
0.3993	3993	0.3894	3894	0.0099	99	2.49%	0.23%
0.1499	1499	0.1437	1437	0.0062	62	4.13%	0.14%

nC4H10							
Standard concentration		Measured concentration		Absolute difference		Rel. difference	RSD%
Mole %	*Mole ppm*	*Mole %*	*Mole ppm*	*Mole %*	*Mole ppm*	*% rel*	*% rel*
0.0101	101	0.0094	94	0.0007	7	6.70%	0.31%
0.3997	3997	0.3936	3936	0.0061	61	1.53%	0.25%
0.1502	1502	0.1495	1495	0.0007	7	0.45%	0.26%

neoC5H12							
Standard concentration		Measured concentration		Absolute difference		Rel. difference	RSD%
Mole %	*Mole ppm*	*Mole %*	*Mole ppm*	*Mole %*	*Mole ppm*	*% rel*	*% rel*
0.0048	48	0.0042	42	0.0006	6	11.78%	0.89%
0.3999	3999	0.3918	3918	0.0081	81	2.02%	0.19%
0.1505	1505	0.1486	1486	0.0019	19	1.24%	0.22%

iC5H12							
Standard concentration		Measured concentration		Absolute difference		Rel. difference	RSD%
Mole %	*Mole ppm*	*Mole %*	*Mole ppm*	*Mole %*	*Mole ppm*	*% rel*	*% rel*
0.0047	47	0.0051	51	0.0004	4	7.73%	0.82%
0.3998	3998	0.3957	3957	0.0041	41	1.02%	0.21%
0.1499	1499	0.1500	1500	0.0001	1	0.07%	0.18%

nC5H12							
Standard concentration		Measured concentration		Absolute difference		Rel. difference	RSD%
Mole %	*Mole ppm*	*Mole %*	*Mole ppm*	*Mole %*	*Mole ppm*	*% rel*	*% rel*
0.0049	49	0.0051	51	0.0002	2	4.06%	0.67%
0.3997	3997	0.3982	3982	0.0015	15	0.39%	0.28%
0.1499	1499	0.1502	1502	0.0003	3	0.23%	0.39%

C6+							
Standard concentration		Measured concentration		Absolute difference		Rel. difference	RSD%
Mole %	*Mole ppm*	*Mole %*	*Mole ppm*	*Mole %*	*Mole ppm*	*% rel*	*% rel*
0.0050	50	0.0036	53	0.0014	3	28.04%	0.98%
0.4001	4001	0.3475	4962	0.0526	961	13.14%	0.61%
0.1499	1499	0.1154	1674	0.0345	175	23.03%	0.41%

HHV							
Standard calorific value		Measured calorific value		Absolute difference		Rel. difference	RSD%
kWh/Nm3	*BTU/Sft3*	*kWh/Nm3*	*BTU/Sft3*	*kWh/Nm3*	*BTU/Sft3*	*% rel*	*% rel*
11.1057	1072.4349	11.0990	1071.7885	0.0067	0.6464	0.06%	< 0.01%
11.8327	1142.6325	11.8804	1147.2453	0.0478	4.6129	0.40%	0.05%
11.2716	1088.4579	11.2736	1088.6510	0.0020	0.1930	0.02%	0.01%

FIGURE 8. ACCURACY RESULTS

In conclusion, the results from the analytical tests confirm the effectiveness of the GreenPix system in delivering precise and accurate separation and quantification of natural gas components. Prolonged tests are currently being performed to conduct a full evaluation as a product on its way to certification on the market. Both the PPU and PDMS modules demonstrated outstanding performance, with fast and clear separation of key compounds such as N_2+O_2, CH_4, CO_2, C_2H_6, and hydrocarbons ranging from C_3 to C_6. Even in challenging separations, like those of n-butane and neo-pentane, the system maintained high resolution and repeatability, highlighting its robustness for natural gas analysis.
The calibration process, based on linear regression coefficients, ensured accurate measurements with low relative deviations from expected concentrations. Furthermore, the system consistently delivered precise calorific value calculations, with deviations from theoretical values remaining below 0.5%. This level of accuracy satisfies the stringent requirements for certifying a device in Class A for transactional measurements of higher calorific value. These results confirm that the GreenPix system is a reliable and effective solution for industrial applications, ensuring accurate compositional analysis and optimized quantification of natural gas components.

ANALYSIS OF NATURAL GAS USING H2 AS A CARRIER GAS

Specific attention has been paid to the analysis of natural gas using hydrogen as a carrier gas. In Europe, natural gas analysis systems based on gas chromatography typically use Helium as carrier gas. However, the natural helium supply is becoming scarce, leading to increasing costs for helium cylinders. As a result, in certain countries, particularly the United States, users are moving away from helium due to these rising supply costs and are opting for hydrogen as a carrier gas instead. Hydrogen is more readily available in cylinders and benefits from multiple production methods, such as water electrolysis, making it more accessible compared to helium, which relies solely on natural sources.

Suppliers now offer hydrogen generators, based on water electrolysis, which produce hydrogen with the necessary purity for use as a carrier gas.

For these tests, two GreenPix module have been used: a PPU10-PPU1-TCD for analysis of light compounds and a PDMS module with a 7-meter column (PDMS7-PDMS2-TCD module), to analyze hydrocarbons from C3 to C6 with a shorter analysis time. The analytical methods developed for this application using the new set of analytical modules are illustrated in FIGURE 9.

Module : PPU10-PPU1-TCD

- Injector temperature : 50 °C
- Column temperature : 60 °C
- Detector temperature : 60 °C
- Column pressure : 0.7 bar(g), Hydrogen carrier gas
- Sample pressure : 15 psi(g)

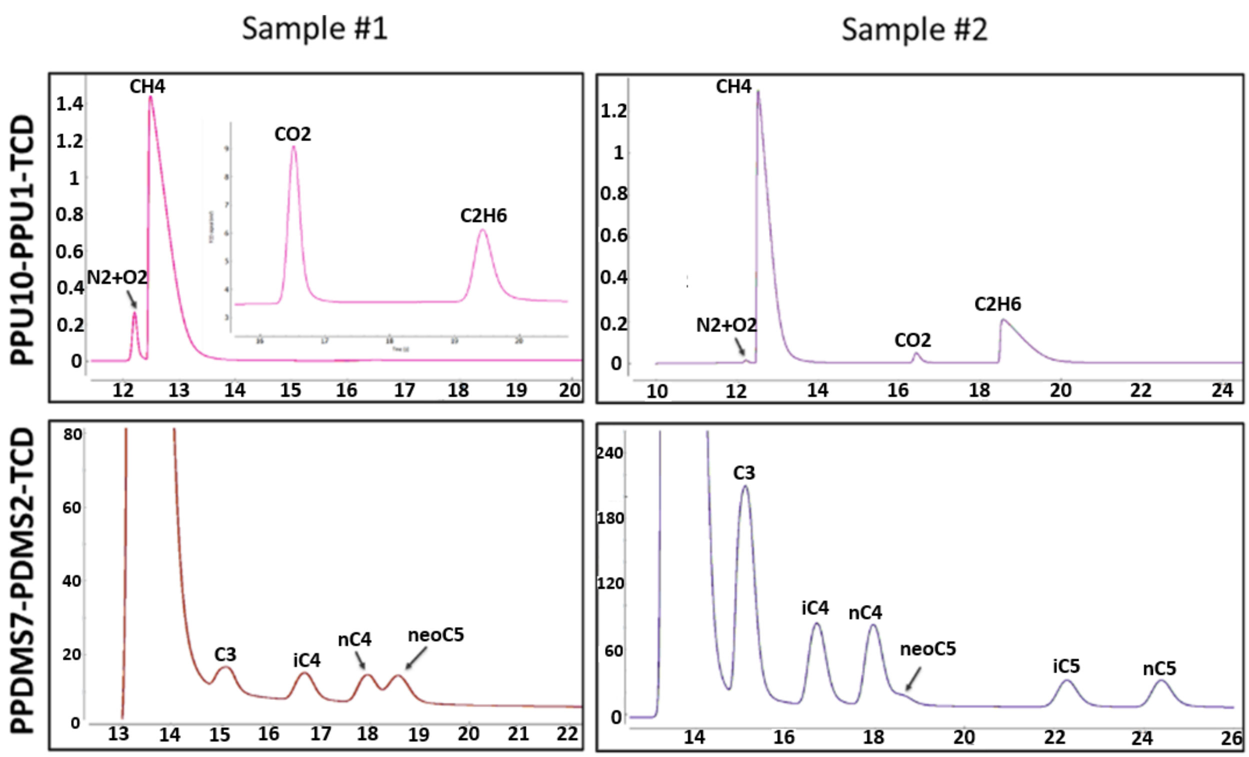
- Sampling : 4.0 s *
- Injection time : 40 ms ***(Partial injection)***
- Foreflush duration : 3.2 s

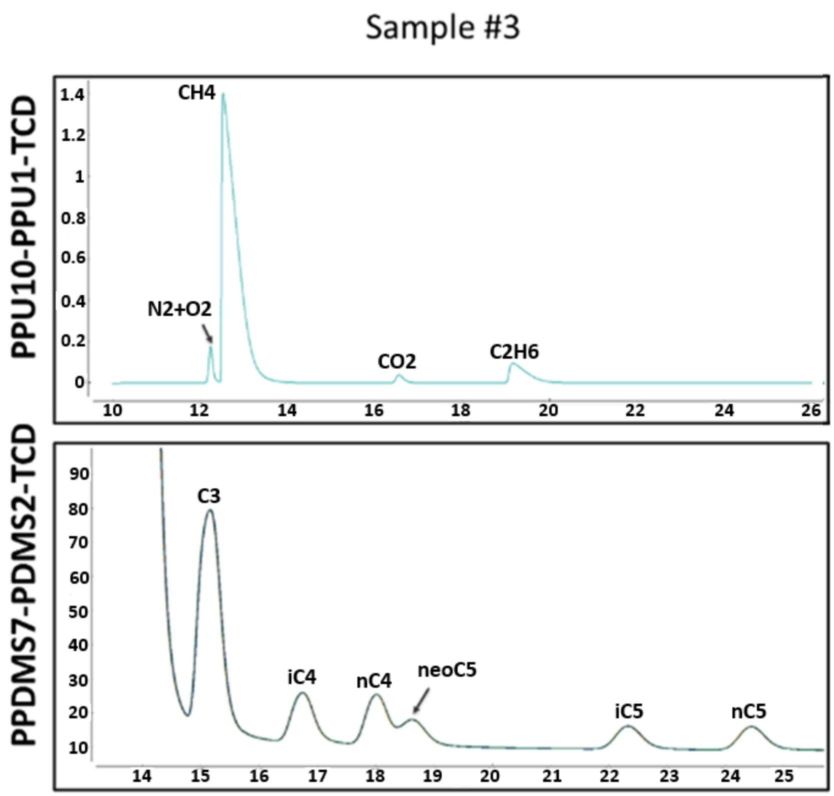
Module : PDMS7-PDMS2-TCD

- Injector temperature : 50 °C
- Column temperature : 60 °C
- Detector temperature : 60 °C
- Column pressure : 1.4 bar(g), Hydrogen carrier gas
- Sample pressure : 15 psi(g)

- Sampling : 8.0 s *
- Injection time : 400 ms ***(Partial injection)***
- Foreflush duration : 25.0 s

FIGURE 9. ANALYTICAL METHOD FOR NATURAL GAS ANALYSIS (WITH H2)





Sample #1

	Concentration	RSD% (RT)	RSD% (Height)	RSD% (Area)
N2+O2	4.01 % mol	0.041%	0.333%	0.229%
CH4	94.1 % mol	0.045%	0.121%	0.204%
CO2	0.101 % mol	0.044%	0.299%	0.401%
C2H6	0.099 % mol	0.042%	0.346%	0.344%
C3H8	0.099 % mol	0.07%	0.19%	0.298%
iC4H10	0.1 % mol	0.034%	0.158%	0.25%
nC4H10	0.099 % mol	0.036%	0.156%	0.181%
neoC5H12	0.099 % mol	0.034%	0.189%	0.209%

Sample #2

	Concentration	RSD% (RT)	RSD% (Height)	RSD% (Area)
N2+O2	0.101 % mol	0.013%	0.188%	0.287%
CH4	73.1 % mol	0.019%	0.143%	0.247%
CO2	1 % mol	0.014%	0.328%	0.421%
C2H6	15 % mol	0.008%	0.172%	0.259%
C3H8	2.99 % mol	0.026%	0.063%	0.129%
iC4H10	1 % mol	0.03%	0.079%	0.142%
nC4H10	1 % mol	0.024%	0.112%	0.131%
neoC5H12	0.1 % mol	0.031%	0.198%	0.175%
iC5H12	0.351 % mol	0.028%	0.133%	0.145%
nC5H12	0.351 % mol	0.024%	0.203%	0.175%

Sample #3

	Concentration	RSD% (RT)	RSD% (Height)	RSD% (Area)
N2+O2	2.7 % mol	0.013%	0.188%	0.287%
CH4	89.57 % mol	0.019%	0.143%	0.247%
CO2	1 % mol	0.014%	0.328%	0.421%
C2H6	5 % mol	0.008%	0.172%	0.259%
C3H8	1 % mol	0.06%	0.098%	0.301%
iC4H10	0.2 % mol	0.055%	0.154%	0.366%
nC4H10	0.2 % mol	0.054%	0.167%	0.329%
neoC5H12	0.1 % mol	0.064%	0.398%	0.601%
iC5H12	0.1 % mol	0.036%	0.249%	0.44%
nC5H12	0.1 % mol	0.035%	0.213%	0.173%

FIGURE 10. ANALYSIS OF NATURAL GAS (WITH H2)

Performance tests were conducted on three natural gas cylinders, each with compositions representing the typical ranges for this application. FIGURE 10 shows the chromatograms obtained for the PPU and PDMS modules for each of these three compositions, along with the repeatability results for the chromatographic peak areas and the measured retention times.
The chromatograms obtained from both modules demonstrate excellent separation of all natural gas components across the studied concentration range, in less than half a minute. Although the separation between n-butane and neo-pentane is not as well-defined on the PDMS15 module, it remains adequate for accurate quantification of both compounds without introducing significant errors in the calculation of calorific value. On this module, which incorporates a shorter GC column, the increased analysis speed comes at the expense of optimal separation of these two compounds. Furthermore, injection times were optimized to obtain a balance between sensibility and column overloading. While peak fronting can be observed on the PPU module, a column known to exhibit such behavior, it is not detrimental to separation and could be reduced by lowering the injection volume. The repeatability values for retention times, peak areas, and peak heights are outstanding.

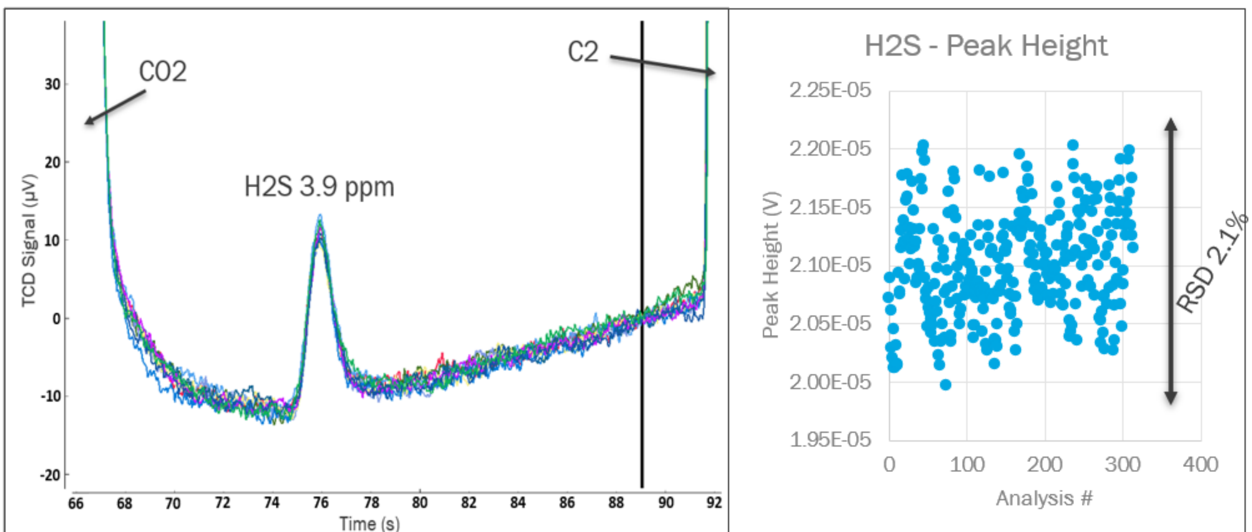
In conclusion, the results obtained from the use of hydrogen as a carrier gas in natural gas analysis demonstrate both high performance and reliability. The developed analytical methods, utilizing the PPU and modified PDMS modules, provide excellent separation of natural gas components, even with a shorter analysis time. The repeatability of retention times, peak areas, and peak heights further confirms the robustness of the system, making it a viable and efficient alternative to helium-based gas chromatography for natural gas analysis.

ANALYSIS OF H2S TRACES

The PPU10-PPU1-TCD module can be adapted for trace analysis by increasing the injected sample volume, achieved by adjusting the injection loop volume. This feature, enabled by the silicon injector developed within the GreenPix program, allows the sample loop volume to be adjusted via the injection time parameter, configurable through the control software, ensuring that the injections remain reproducible regardless of the volumes used. This allows the same module to be used for analyzing both high concentrations and trace levels, simply by modifying the injection time and, consequently, the sample volume.

This strategy was applied to the analysis of H_2S, a pollutant in biogas/biomethane that must be removed due to its corrosive properties before the gas is injected into the network. Accurate detection of H_2S at low concentrations, in the ppm range, is crucial.

FIGURE 11 presents the results of H_2S analysis at 3.9 ppm, quantified on peak height, with a great TCD sensitivity and overnight (14 hours) repeatability tests showing a variation of 2%. This demonstrates a detection limit around 1 ppm for H_2S, confirming the module's suitability for low-concentration pollutant analysis in biogas and biomethane applications. Results are 2 times better than the previous generation of PPU modules.



	Concentration	RSD% (RT)	RSD% (Height)	RSD% (Area)	SNR*	LOQ (SNR = 6)	LOD (SNR = 3)
H2S	3.9 ppm mol	0.072%	2.108%	4.185%	10.5	2 ppm	1 ppm

FIGURE 11. ANALYSIS OF H2S TRACES

ANALYSIS OF HYDROGEN IMPURITIES

Hydrogen, increasingly used as a new energy source when blended with natural gas or biomethane, also plays a crucial role in generating electrical energy via fuel cells, especially for mobility applications. For this use, hydrogen must meet strict purity standards, where compounds like O_2, N_2, CO_2, argon, and helium must be analyzed at concentrations of a few to tens of ppm.

For the hydrogen purity application, two modules have been identified and tested:

- PPU10-PPU1-TCD module for the trace analysis of CO_2 and compounds with two carbon atoms. The results demonstrated excellent sensitivity and repeatability, with a detection limit of 1 ppm for CO_2.
- MS5A15-PPU5-TCD module for the analysis of trace levels of O_2, N_2, CH_4, and CO. Using helium as the carrier gas, the tests showed strong sensitivity for methane and CO detection. this module also performs well in detecting O_2 and N_2.

Both modules exhibit reliable performance, making them well-suited for ensuring the required hydrogen purity in fuel cell applications [FIGURE 12].

In conclusion, the PPU10-PPU1-TCD and MS5A15-PPU5-TCD modules demonstrate excellent performance in detecting trace impurities like CO_2, O_2, N_2, CH_4, and CO in hydrogen, meeting the stringent purity requirements for fuel cell applications. Both modules offer high sensitivity and repeatability, ensuring reliable analysis of critical contaminants down to ppm levels.

Looking ahead, the GreenPix system shows great promise for broader applications in hydrogen production and distribution, particularly as hydrogen becomes a key energy source in mobility and other sectors. Its modular flexibility and precise detection capabilities position it as a valuable tool for ensuring the purity and quality of hydrogen used in fuel cells, contributing to the advancement of clean energy technologies.

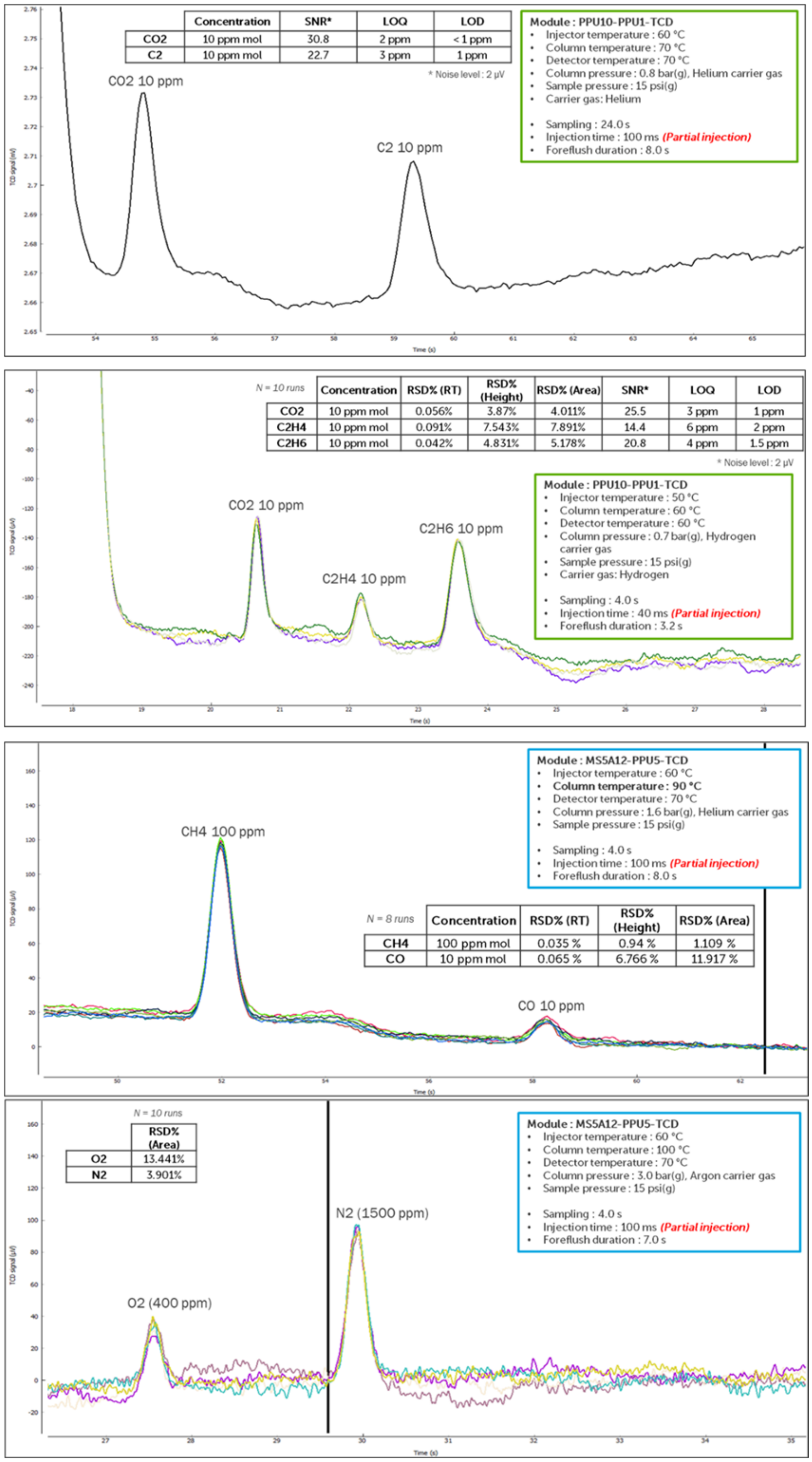


FIGURE 12. ANALYSIS OF HYDROGEN TRACES IMPURITIES

CONCLUSIONS

In conclusion, the testing results for the GreenPix systems in the analysis of natural gas, biomethane, hydrogen, and odorants demonstrate outstanding performance that sets a new benchmark in the industry. These systems provide at least double the efficiency of current generation modules, showcasing significant advancements in the separation of natural gas components and heightened sensitivity. Additionally, improvements in manufacturability have streamlined module assembly to under 15 minutes while reducing material costs by 50%.

The successful implementation of GreenPix in various applications—such as natural gas (C1-C6+), biogas, H_2S trace analysis, THT detection, and hydrogen/CO_2 quality assessment—highlights the versatility and effectiveness of these systems. Key performance indicators, including sharp chromatographic peaks, effective separation, stable baselines, and exceptional repeatability, accuracy, precision, and linearity, further attest to their capabilities. With a rapid cycle time of just 30 seconds for ultra-fast analysis and compatibility with multiple carrier gases (helium, hydrogen, argon), GreenPix caters to a broad spectrum of analytical requirements.

Moreover, the adaptability of GreenPix systems positions them as essential tools in the evolving green energy market, encompassing biogas, biomethane, natural gas, and hydrogen applications. Their ability to provide precise gas composition measurements makes them invaluable across diverse industries. In the smart gas grid market, GreenPix operates effectively as a sensor, negating the need for specialized expertise in gas chromatography. As the most compact temperature-controlled GC covering hydrogen to C_{14}, GreenPix exemplifies state-of-the-art performance, establishing itself as a leading solution in gas analysis technology. With these advancements, GreenPix is well-equipped to revolutionize gas analysis and contribute significantly to the future of energy solutions.

AND BEYOND…

In parallel, miniaturized gas chromatography (GC) columns on silicon substrates were developed for integration into next-generation analytical modules using a fluidic integrated board. This aligns with the GREENPIX project's goal to reduce manufacturing and purchase costs by utilizing MEMS technology for mass production of analytical components. A semi-packed design with cylindrical and elongated pillar arrays offers improved efficiency, higher sample capacity, and reduced dispersion [FIGURE 13].

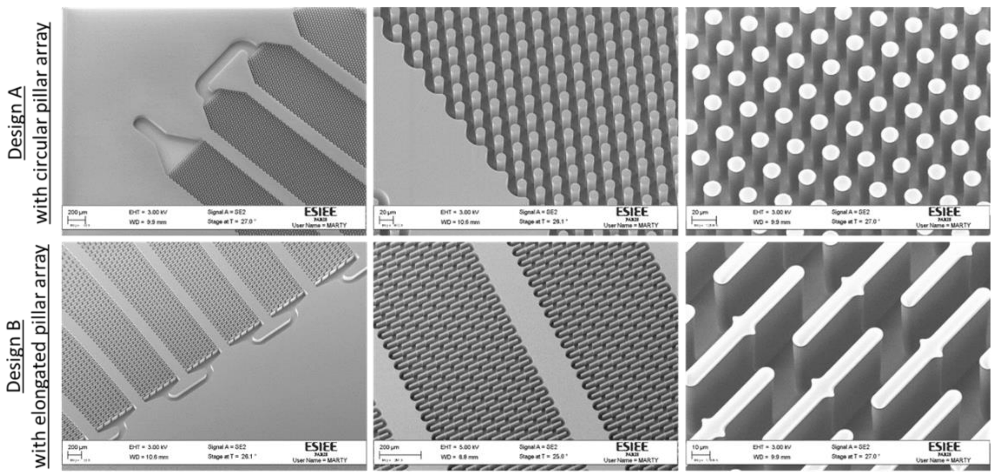


FIGURE 13. SILICON MICRO-GC COLUMNS

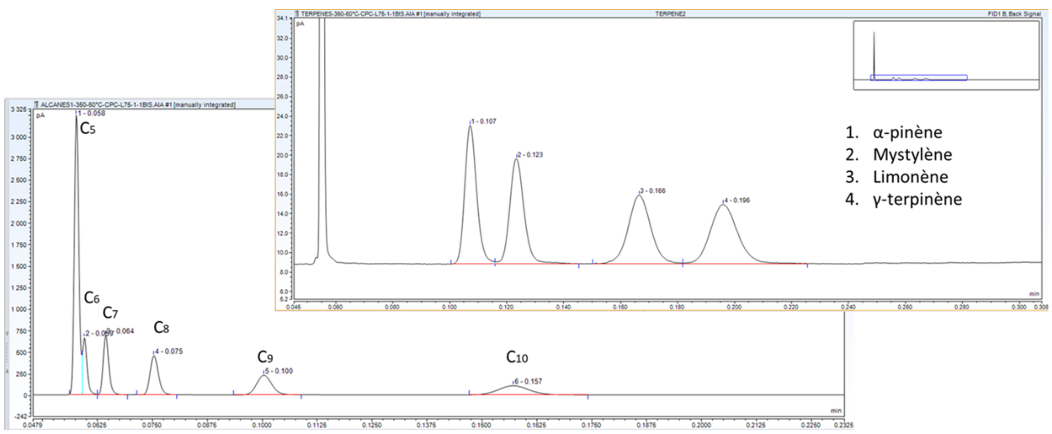


FIGURE 14. SILICON MICRO-GC COLUMNS

After functionalization with PDMS stationary phases, The GC silicon columns demonstrate excellent separation performance for the target compounds (BTEX, terpenes, alkanes, VOCs, etc.), making them particularly suitable for detecting impurities in biogas or biomethane processes [FIGURE 14]. Additionally, these new GC column designs offer analysis times of under one minute, enabling new applications and use cases.

Building on the successful development of GC columns on silicon and the advancements made in the project with silicon injectors on manifolds and detectors on manifolds, a future generation of analytical modules fully integrated on silicon is conceivable. The three silicon components—injector, GC column, and detector—would be assembled on a common fluidic manifold using pick-and-place techniques that have already been developed and validated for assembling injectors and detectors. This new integrated silicon module architecture should enhance its competitiveness compared to the competition [FIGURE 15].

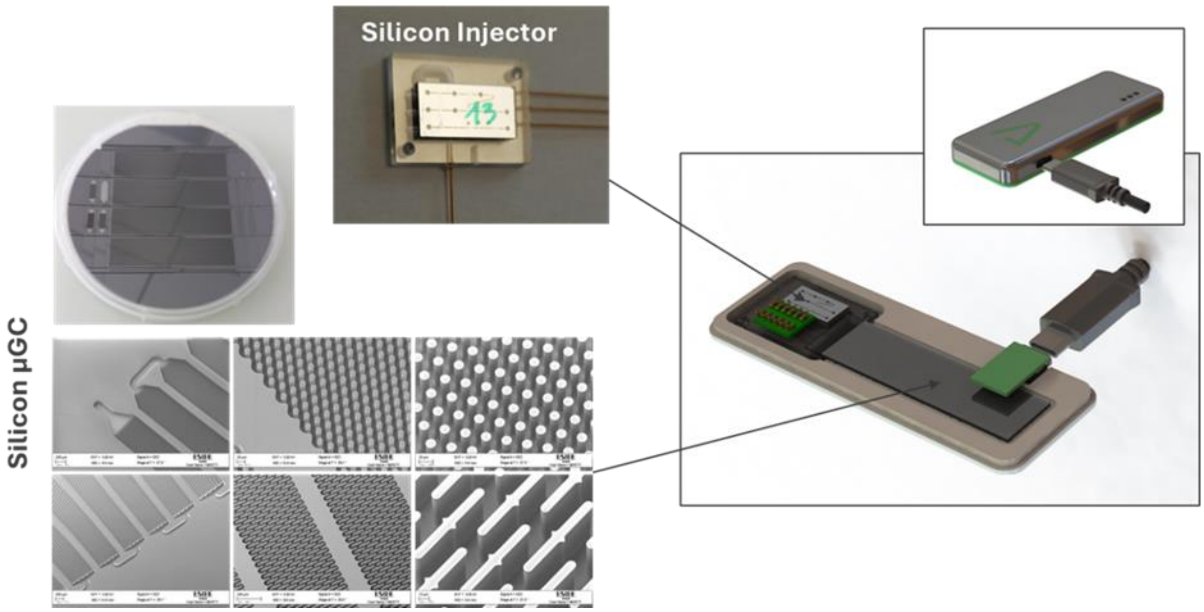


FIGURE 15. SILICON MICRO-GC COLUMNS

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