INFICON

APPLICATION NOTE

Analysis of Fuel Cell Reformer Gases in Seconds Using the INFICON 3000 Micro GC

ABSTRACT

Rapid and accurate determination of the composition of gases produced by a catalytic reformer is important for the development and optimization of new fuel cell designs. Gas chromatography, using a micro gas chromatograph and high-resolution columns, produces a complete analysis of fuel cell gases in less than 90 seconds. Connection of the gas chromatograph directly to the output of the reactor provides valuable information for evaluating performance of new catalyst formulations and reformer designs including optimization of reformer operation.

INTRODUCTION

Fuel cells offer the possibility of cleaner, more efficient electrical power for a variety of uses. In stationary, transportation, and portable power applications, fuel cells are likely to be the next technology to revolutionize the way the world is powered. A wide range of researchers, from small startup companies to the multinational oil and automotive companies, are investing billions of dollars to develop and commercialize fuel cells.

Until a hydrogen fuel economy becomes reality, hydrocarbon-based fuels will be the primary source of energy. Hydrocarbon fuels such as natural gas, propane, gasoline, and diesel are typically reformed to hydrogen within the fuel cell system. Proton exchange membrane (PEM) fuel cells require hydrogen as the fuel. While some fuel cell technologies, such as molten carbonate or solid oxide, do not require the fuel to be reformed to hydrogen first, they too benefit from some chemical pretreatment of the inbound fuel.

A simple schematic of a fuel cell system appears in Figure 1. The inbound fuel is first treated to remove sulfur-containing compounds, which are poisons to almost all fuel cell systems. The desulfurized fuel is then reformed to hydrogen and carbon monoxide. For the high-temperature fuel cells, no further processing is necessary as both of these gases are fuel sources at elevated temperatures. For low-temperature fuel cells, such as PEMs, the carbon monoxide (CO) level must be reduced to ppm levels before introduction into the fuel cell stack [1]. CO reversibly poisons the noble metal catalysts in PEMs and must be less than 10 ppm for most systems. For mass balance and system efficiency calculations, the output gas of the fuel cell stack should be measured. At each interface between these subsystems (denoted by an asterix), valuable, informative chemical measurements can be clarified.

Figure 1 Fuel cell schematic
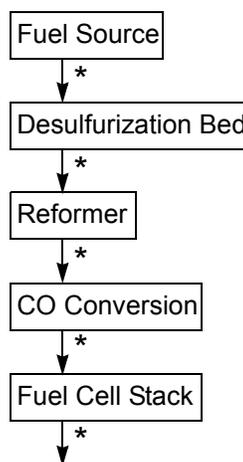
The need for chemical measurements spans fuel cell design, testing, and manufacturing arenas. To reduce costs, optimize designs, and integrate components and subsystems, fuel gas composition needs to be measured throughout the system. The target compounds of interest depend on the fuel cell

technology but are typically hydrogen, carbon monoxide, carbon dioxide, hydrocarbons, and sulfur species. The range of concentrations is from parts-per-million up to 100%, depending on the particular analyte.

Various technologies are available to make these measurements at varying cost and capability. Spectroscopic techniques, such as nondispersive infrared, are useful for measuring a few of the fuel gas components. Mass spectrometry can measure a wider range of the analytes in near-real time and at lower analyte concentrations at higher cost. The micro gas chromatograph offers excellent sensitivity, stability, linearity, and speed for a wide range of analytes, typically at a lower price for applications where real-time transients need not be measured.

The INFICON 3000 Micro GC uses state-of-the-art chromatography components and design to provide reliable, accurate fuel cell gas composition measurements. By employing high speed, independent chromatography channels, the 3000 Micro GC is able to resolve and quantitate fuel cell gas components in 90 seconds or less. A review of the 3000 Micro GC performance herein illustrates its advantages. While this application note focuses on typical product gases associated with hydrocarbon reformers, the 3000 Micro GC can also speciate the inbound gaseous hydrocarbon fuels such as natural gas, propane, and liquid petroleum gas (LPG).

EXPERIMENTAL

Instrumentation

The 3000 Micro GC consists of independent chromatographic channels, each consisting of an injection device, a separation column, and a detector, that optimally analyze a portion of the sample in parallel. For instance, the molecular sieve channel separates and quantitates permanent gases such as hydrogen, oxygen, nitrogen, methane, and carbon monoxide.

Three types of injectors (fixed volume, variable volume, and backflush) are available depending on the measurement need.

The fixed volume injector provides the highest degree of precision with typical peak area precisions of 0.1% relative standard deviation (RSD). The fixed volume injector is used with applications such as natural gas calorific measurements where reproducibility and accuracy are most critical. The variable volume injector allows the largest injection volume for trace analysis. Applications such as trace carbon monoxide in the fuel cell reformer stream can be performed with the variable volume injector. The backflush injector minimizes contact of unwanted or potentially harmful analytes with the analytical column.

The blackflush injector works in the following manner. Two columns are used with a backflush injector. One end of a short precolumn is installed into the injector and the other end into one port of the backflush valve. The inlet to the analytical column is connected then to the second port of the backflush valve. During injection, carrier gas is supplied through the injector rather than through the backflush valve. The sample enters the precolumn and progresses toward the backflush valve. After the analytes of interest elute from the precolumn, the carrier gas supply is switched from the injector to the backflush valve. The analytes of interest continue down the analytical column while the unwanted analytes on the precolumn, such as water on a molecular sieve channel, are backflushed out through the injector. This keeps the analytical column "clean" and allows the system to hold a calibration longer. While the variable and fixed volume injector can certainly do fuel cell analyses, the analytical column will require more frequent thermal cleaning than a blackflush injector performing the same analysis.

When run with a zero-millisecond injection time, the backflush injector behaves like a fixed volume injector. At longer injection times, more sample is introduced to the pre-column and the injector behaves like a variable volume injector. This latter mode of operation improves system detection limits. All channels employ a micro thermal conductivity detector capable of parts-per-million level measurements.

For the experiments described herein, two types of channels were used. The Micro GC configuration is listed in Table 1. The first contained a molecular sieve column and a backflush injector. The second contained

a PLOT U column and a back-flush injector. This second channel was used to separate and quantitate carbon dioxide. The operating conditions are given below in Table 2.

Table 1 Micro GC configuration

Channel A

Column:	Molesieve 5A, 10 m, 0.32 mm
Carrier gas:	Argon
Injector	Backflush 1 µL

Channel B

Column:	PLOT U, 8 m, 0.32 mm
Carrier gas:	Helium
Injector:	Backflush 1 µL

Table 2 Micro GC instrument conditions

Channel A

Sample Inlet Temperature:	110°C
Injector Temperature:	90°C
Column Temperature:	100°C
Sampling Time:	10 or 15 sec
Injection Time:	0 to 200 msec
Run Time:	180 sec
Column Pressure:	30 psi/207 pKa
Column Flow Rate:	2.2 mL/min
Backflush Time:	5.1 sec

Channel B

Sample Inlet Temperature:	110°C
Injector Temperature:	90°C
Column Temperature:	60°C
Sampling Time:	10 or 15 sec
Injection Time:	0 to 200 msec
Run Time:	180 sec
Column Pressure:	30 psi/207 pKa
Column Flow Rate:	2.2 mL/min
Backflush Time:	5.1 sec

Samples

The standards were obtained from DCG Partnership (4170 A. Main, Pearland, TX 77581), Spectra Gases, Inc (Alpha, NJ), and Scott Specialty Gases (Plumsteadville, PA). The compositions appear in Table 3.

Table 3 Sample Compositions

Component	DCG Std no 1	DCG Std no 2	Spectra	Scott no 296	Scott no 297
H2	40.000	49.957		1.00	10.00
O2	0.101	0.0172	0.001		
N2	39.972	35.083	0.750	99.00	90.00
CH4	0.502	4.982			
CO	0.101	0.00496	0.001		
CO2	19.234	9.956	0.001		
He			99.247		

Other concentrations of hydrogen were made using an Agilent 6890 auxiliary electronic pressure control channel to mix the gas streams of hydrogen with nitrogen [2].

Carrier Gases

99.999 grade helium was supplied from our in-house system. Grade 5.0 Argon was purchased from Keen Gas Supply, Wilmington, DE.

RESULTS AND DISCUSSION

Figure 2 shows the separation of typical fuel cell reformer gases in less than 70 seconds. The first channel (molecular sieve column) resolved hydrogen, oxygen, nitrogen, methane, and carbon monoxide. The carrier gas used was argon. The second channel (PLOT U column) separated carbon dioxide and used helium as the carrier gas.

Because carrier gas plays a vital part in detection for thermal conductivity detector (TCD) systems, this parameter was studied in detail. Several important points, such as linearity, sensitivity, and peak shape, need to be considered when selecting the carrier gas for a micro GC. For most routine applications, helium is the carrier gas of choice. Except for hydrogen, helium has the highest thermal conductivity and affords the highest sensitivity for all other analytes.

Figure 2 Separation and detection of typical fuel cell reformer gases

Molesieve 5A PLOT
Flow rate = 2.2 mL/min
Carrier: Ar

PLOT U
Flow rate = 2.2 mL/min
Carrier: He
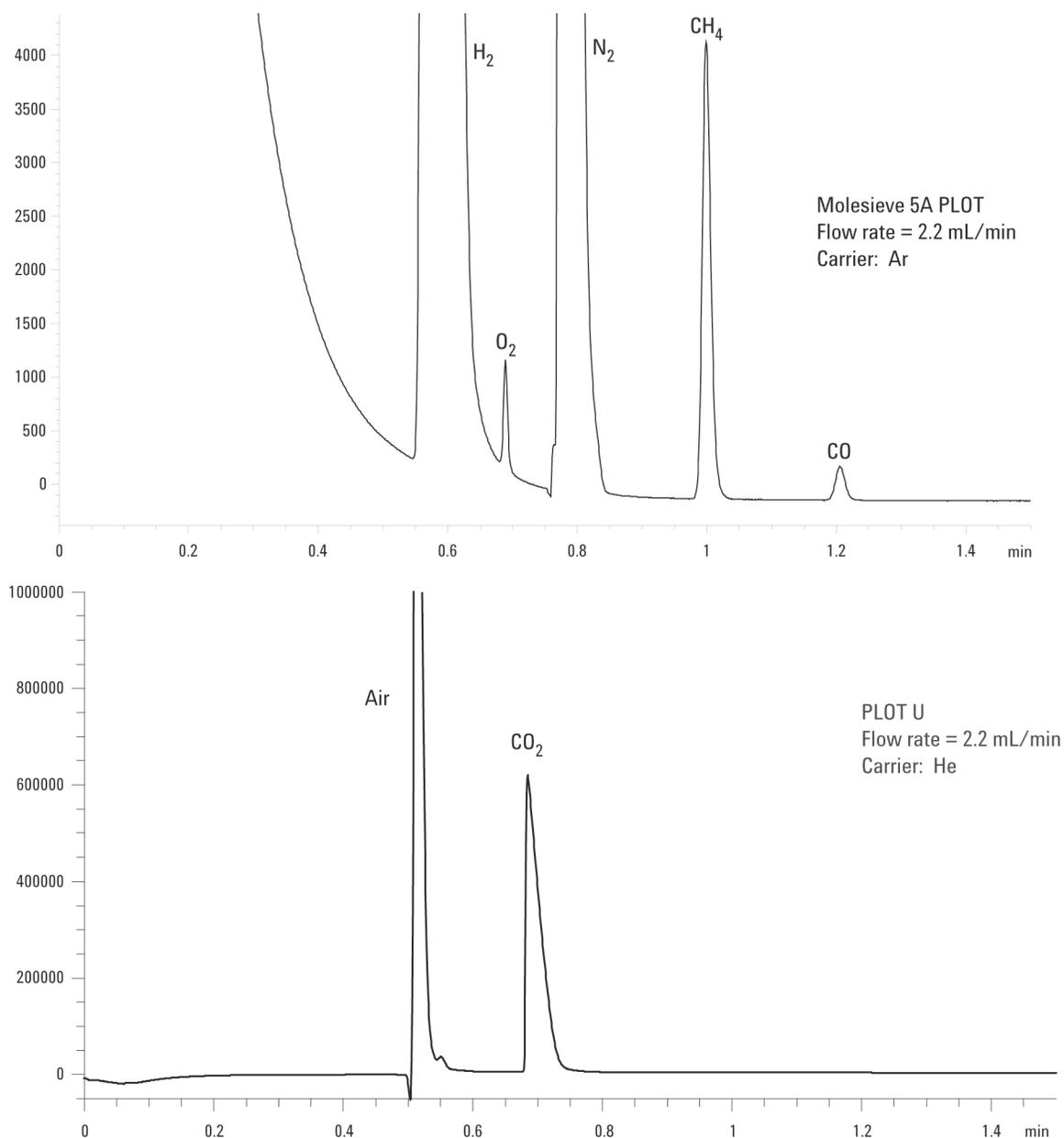
Hydrogen measurements in helium, however, present a problem. At approximately 5 to 10 mole% of hydrogen in helium, the hydrogen peak changes from negative to positive. This complicates quantitation across this concentration region. At concentrations from 10 to 100 mole%, the negative hydrogen peak can be easily and accurately quantitated. For the widest range of linearity and highest sensitivity for hydrogen, argon is the preferred carrier gas. A comparison of carrier gases for fuel cell applications using hydrogen linearity and carbon monoxide sensitivity illustrates the advantages and drawbacks for each.

Figure 3 shows linearity plots for hydrogen in argon and helium carrier gases with a 25-millisecond injection time. Note that the helium carrier gas plot has been multiplied by 10 to achieve a similar response scale. Argon shows the most linear performance and the most sensitivity for hydrogen as anticipated.

Figure 3 Linearity plots for hydrogen using different carrier gases and injection times
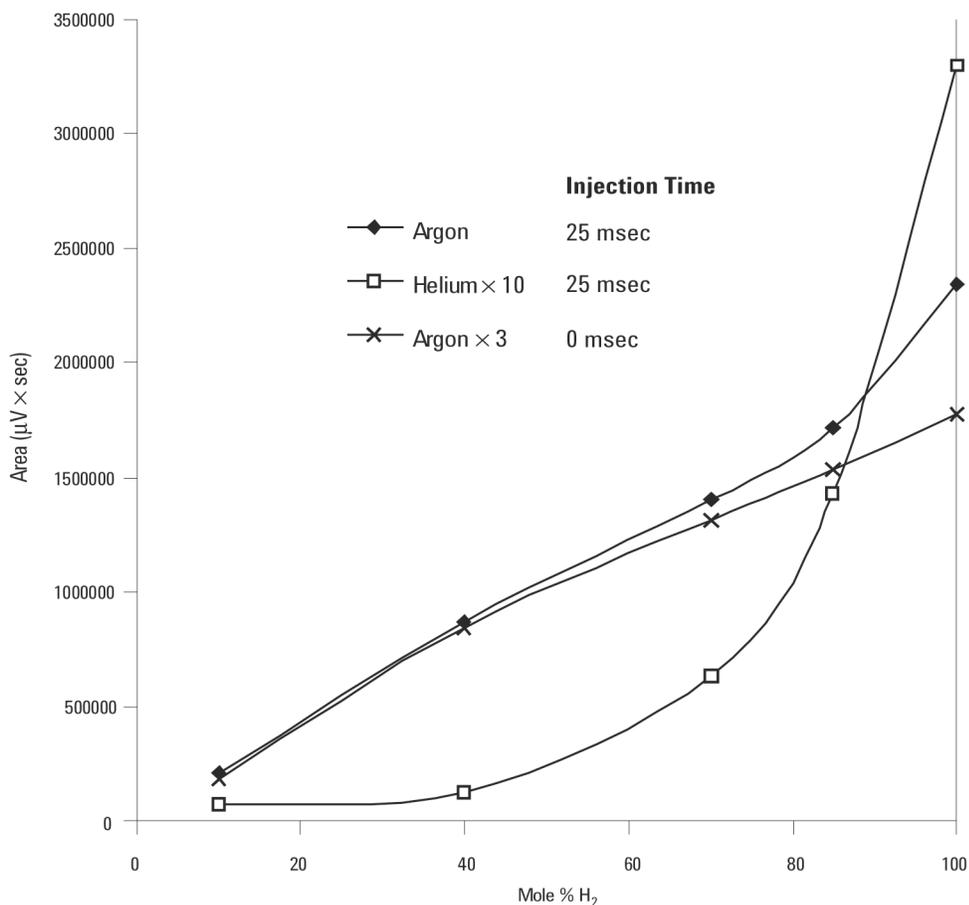
The slight curvature at 100% is due to the change in sample viscosity. Because the sample viscosity changes noticeably near 100% hydrogen, the amount injected has shifted slightly. The third curve for argon as the carrier gas with a zero-millisecond injection time (responses multiplied by 3 to achieve similar scale) introduces a fixed volume of sample into the system. Because this volume injected is independent of the carrier gas or sample viscosity, the plot is linear up to 100 mole%. Similar results are obtained with helium as the carrier gas. Furthermore, argon gives the best sensitivity for hydrogen. This is evidenced by argon having the largest slope, which means the largest response factor, in the linearity plots.

While argon gives the best sensitivity for hydrogen, this is not the case for the other fuel cell analytes. Perhaps the most important analyte for the low-temperature fuel cells is carbon monoxide. This natural by-product of the reforming process is a reversible poison for noble metal catalysts such as platinum. Tests documented in the National Labs Fuel Cell Review '98 [1] show that a transient carbon monoxide spike of 100 ppm can drop the cell output by 90% for 15 minutes. Most carbon monoxide conversion systems are designed to reduce the CO level to 50 ppm or less under steady state conditions. Consequently, the measurement tool must be able to give a reliable answer down to this level. To achieve the desired sensitivity, helium is the preferred carrier gas. Figure 4 shows a 10 ppm CO fuel cell test gas analysis with a 200-millisecond backflush injection using helium as the carrier gas. Excellent signal-to-noise is achieved.

Table 4 shows the minimum detectable levels for carbon monoxide as a function of carrier gas, injection time, and detector sensitivity.

Table 4 Minimum detection levels for carbon monoxide

Inject Time (msec)	Detector sensitivity	Helium ppm	Argon ppm
0	Standard	9.7	170
50	Standard	2.7	26
0	High	10	140
50	High	1.3	21

Helium offers the lowest detection limits for CO, while argon shows approximately an order of magnitude less sensitivity. Clearly, a compromise is needed. For best hydrogen performance, argon carrier gas should be used with the molesieve channel. For best carbon monoxide performance, helium is the carrier gas of choice. For the best performance possible, a different approach offers a solution. In a three-channel instrument, with two channels containing molesieve columns with argon and helium carrier gases and the third channel containing a PLOT U column with helium carrier gas. The new 3-4 channel version of the 3000 Micro GC offers this versatility for the most demanding performance.

Figure 4 10 ppm CO with 200 msec backflush injection

Molesieve 5A PLOT
Carrier: Helium

10 ppm CO
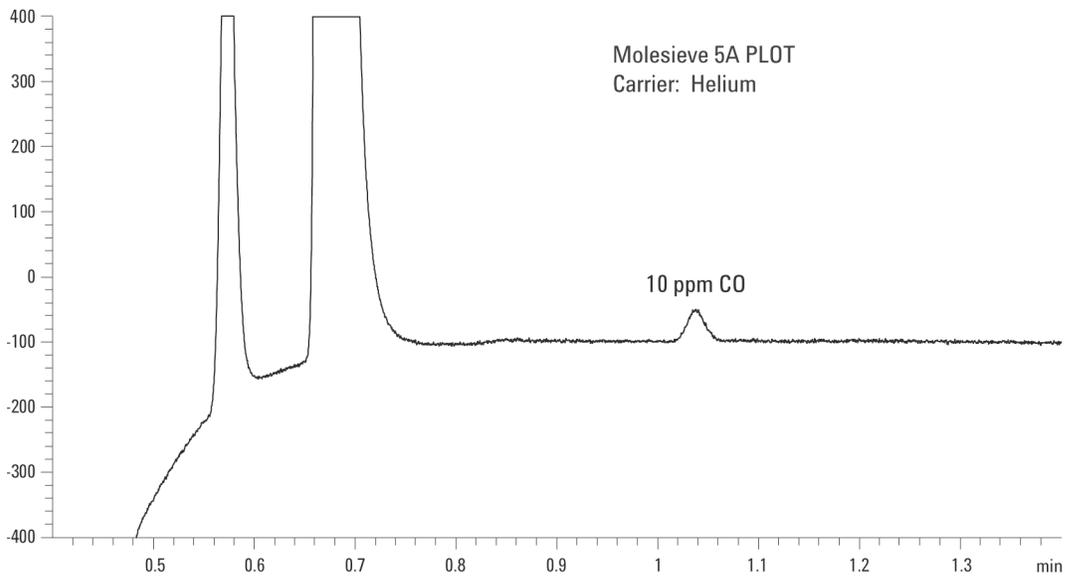
Reproducibility and Stability

Two of the basic metrics for assessing a measurement tool are its run-to-run reproducibility and its long-term stability. Table 5 shows the relative standard deviations for peak area (n = 10) as a function of injection time.

Table 5 RSDs for peak area

Carrier	Sample	0 msec	25 msec	50 msec	100 msec	200 msec
Argon	10% H2	0.16	0.27	0.47	0.30	0.61
Helium	0.1% CO	0.37	0.22	0.12	0.09	0.56

Excellent precision is obtained at all injection times. For a wide range of analyte concentrations, RSDs are typically less than 1% with the majority below 0.5%.

For stability testing, an instrument was calibrated with a 10 ppm CO/7500 ppm N2 standard and then tested under a variety of conditions with a variety of samples. Multiple methods and changes in instrument gas configuration were made between the two sets of data. Two months later, the original instrument conditions were reestablished and the calibration sample was run to assess stability. Table 6 shows the average and standard deviation of peak areas and the average retention times (RT) at the beginning and the end of the 2-month study period. Injection times were 50 milliseconds. The results for carbon monoxide are given in Table 6.

Table 6 Long-term Instrument Stability for Carbon Monoxide

Date	Average RT (min)	Average area	Std dev area
9/21	1.164	24.66	1.07
11/28	1.156	25.16	1.76

CONCLUSION

The INFICON 3000 Micro GC provides accurate, reliable chemical analysis for gaseous components in fuel cell systems. The speed, sensitivity, and stability of the 3000 Micro GC allow fuel cell researchers, fuel cell component manufacturers, and fuel cell system integrators to optimize fuel cell designs. Once configured, the 3000 Micro GC becomes a powerful tool to aid in fuel cell development.

REFERENCES

1. T. Zawodzinski et.al., "Tolerance to CO and Optimized Operation on Reformate," Fuel Cells for Transportation, National Laboratory Annual Progress Report, 1998.

2. R. Firor and B. Quimby, "Automated Dynamic Blending System for the Agilent 6890 Gas Chromatograph: Low Level Sulfur Detection," Agilent Application Note, publication 5988-2465EN, April 2001.

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