

Chemical Analysis in Fuel Cell Systems: Application of the Agilent 5000A Real-Time Gas Analyzer

Application

Fuel Cells

Author

Roger L. Firor
Agilent Technologies, Inc.
2850 Centerville Road
Wilmington, DE 19808-1610
USA

Abstract

The accelerating pace of fuel cell development is placing new demands on diagnostic and monitoring tools that can help lower costs and improve efficiencies. Rapid quantitative chemical measurement can aid in the understanding and design of all aspects of fuel cell systems including fuel processors and fuel cell stacks. A new quadrupole mass spectrometer based gas analyzer provides near real-time chemical measurement for fuel cell gases and impurities. The Agilent 5000A Real-Time Gas Analyzer based on the Agilent 5973N Mass Selective Detector is easily interfaced to a process through a specialized two-stage gas interface. Customized control charting and data logging software is provided for continuous process analysis.

Introduction

Today, fuel cells offer the promise of reliable power for a wide range of applications with

reduced emissions, better efficiency, and less reliance on fossil fuels. Applications include such diverse areas as backup power generation, distributed power, cogeneration, residential, automotive/public transportation, military, and consumer appliance. Fuel cells will play an important role as the worldwide demand for energy approximately doubles over the next 20 years.

Fuel cell processors that produce hydrogen from hydrocarbons will be a necessary component of most fuel cell systems until means are developed and an infrastructure is built for economic storage, transportation, and generation of hydrogen. This includes both stationary and vehicular on-board systems.

As a summary, Table 1 lists attributes of common fuel cell types, including catalysts and fuel requirements [1]. Fuel processors are complex systems that must be optimized for efficient and trouble-free operation of the overall fuel cell system. Most fuel cell developers agree that initial products for portable and stationary fuel cells applications will rely on fossil fuels. The generation of hydrogen from these fuels is a critical first step in fuel cell development.

The task of fuel processors or fuel reformers is to produce a gas mixture with high hydrogen content



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Table 1. Common Fuel Cell Types

	PAFC*	MCFC*	SOFC*	PEMFC*
Catalyst	Platinum	Nickel	Perovskites	Platinum
Electrolyte	Phosphoric acid	Molten carbonate salt	Ceramic	Polymer
Operating temperature	190 °C	650 °C	1000 °C	80 °C
Fuels	Hydrogen reformat	Hydrogen/CO reformat	H ₂ /CO ₂ /CH ₄ reformat	Hydrogen reformat
Reforming	External	External/Internal	External/Internal	External
Oxidant	O ₂ /Air	CO ₂ /O ₂ /Air	O ₂ /Air	O ₂ /Air
Efficiency (HHV)	40–50%	50–60%	45–55%	40–50%

* PAFC: Phosphoric Acid Fuel Cell, MCFC: Molten Carbonate Fuel Cell, SOFC: Solid Oxide Fuel Cell, PEMFC: Proton Exchange Membrane Fuel Cell.

without harmful levels of impurities that will poison the downstream fuel cell system. Potential fuels include natural gas, gasoline, diesel, methanol, ethanol, and biomass. In reality, the reformat obtained from processors can contain many compounds along with the desired hydrogen content. Also, electrochemical efficiencies depend on the amount and quality of hydrogen produced. These are a few of the reasons why chemical monitoring is essential to understanding and optimizing a given fuel cell system [2].

Fuel processors can consist of six basic operations that include: 1. Fuel vaporization, 2. Fuel pretreatment, 3. Desulfurization, 4. Hydrogen production, 5. Carbon monoxide reduction (partial oxidizers, shift reactors), and 6. Combustion of tail gases. Chemical composition of fuel and oxidant can be used to predict performance and efficiency of fuel cell systems. Thermal and partial oxidation reformer design and operation can also benefit from chemical measurements. Various purification technologies are used in fuel cell systems. Chemical monitoring can assist in developing better systems. Some current technologies include: CaO adsorbent beds for CO₂ removal, membranes (palladium/silver) for hydrogen purification, ZnO, and other supported metal catalysts for desulfurization.

Reformers inherently dilute the hydrogen stream. Lower H₂ concentrations can increase the risk of CO anode poisoning. High CO₂ and N₂ concentrations can lower performance near the stack exit. Introduction of inert gases like N₂, while not harmful, do alter the hydrogen concentration and can affect performance. Monitoring of these gases may assist in reformer optimization.

Fast chemical measurements can also assist in the development and understanding of fuel cell stacks, particularly Proton Exchange Membrane (PEM) systems that operate at low temperatures. Some areas where chemical measurements are useful include model development and validation, impurity tolerance studies, and water management [3]. In general, the lower the operating temperature of the stack, the greater the demand for fuel purity.

While methanol powered fuel cells are attractive, much development work remains. Chemical measurements can assist in understanding CO₂ management. In direct methanol fuel cells, CO₂ is the primary reaction product of methanol oxidation at the anode. Large amounts of CO₂ can accumulate in the stack and lower cell efficiency. Methanol crossover between anode and cathode can also be studied through real-time chemical monitoring [3].

The Real-Time Gas Analyzer (RTGA) can assist in solving the current technical challenges associated with fuel processor and fuel cell stack design. This system, based on Agilent's 5973N high-performance quadrupole mass spectrometer, provides chemical quantitation and speciation with wide dynamic range in near real time. It provides a level of mass axis stability, dynamic range, speed of response, and calibration ease that is not possible with residual gas analyzers (RGAs).

In Figure 1, a diagram of a typical fuel cell system with external reforming appears, highlighting areas where chemical measurements would be useful among the various sub systems, and within the stack itself. This paper focuses on an overview of the RTGA system while demonstrating performance with gases commonly encountered in fuel cell systems. A separate paper focuses on impurities, such as sulfur, in fuel cell streams.

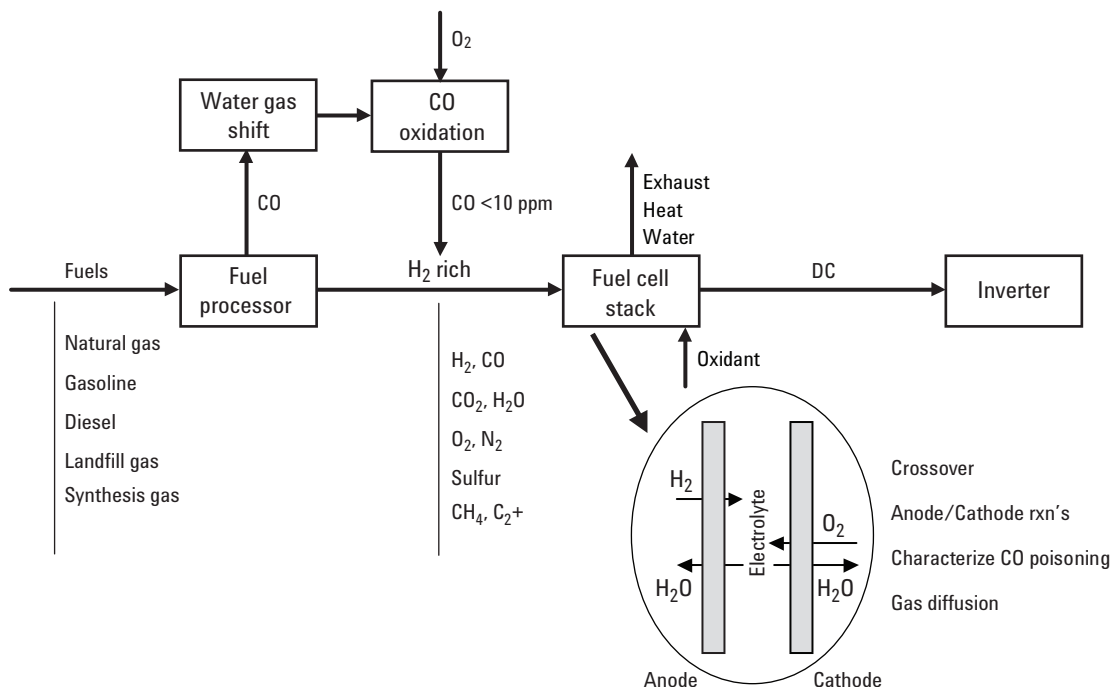


Figure 1. General fuel cell system overview with external fuel processor.

Experimental

RTGA Overview

The RTGA system consists of a modified 5973N mass spectrometer, specialized hardware gas interface system, and control software. The two-stage gas interface and control/monitoring software (MS Sensor 2.0) were developed by Diablo Analytical, Inc. 1110 Burnett Ave., Suite C, Concord, CA 94520. Agilent MSD ChemStation software must be present prior to installation of MS Sensor 2.0. Modifications to the 5973N for enhanced performance with fuel cell gases include a low gauss magnet and modified ion source components. This allows linear calibration of hydrogen and other gases of interest over the concentration ranges needed for fuel cell research and development.

A schematic of the two-stage interface appears in Figure 2. Unlike GC/MS systems, no separation of the chemical components occurs prior to entering the mass spectrometer (mass spec). Control of the material entering the mass spec source is managed by a two-stage system consisting of two precision sized orifices connected to a common cross fitting. Also attached to the cross is a 12-liter per minute fore pump and a pressure transducer. An isolation valve is included to allow easy servicing/changing of orifices and process connections without venting of the 5973N. The mass spec and pressure transducer are interfaced to a personal computer through LAN and RS-232 interfaces, respectively.

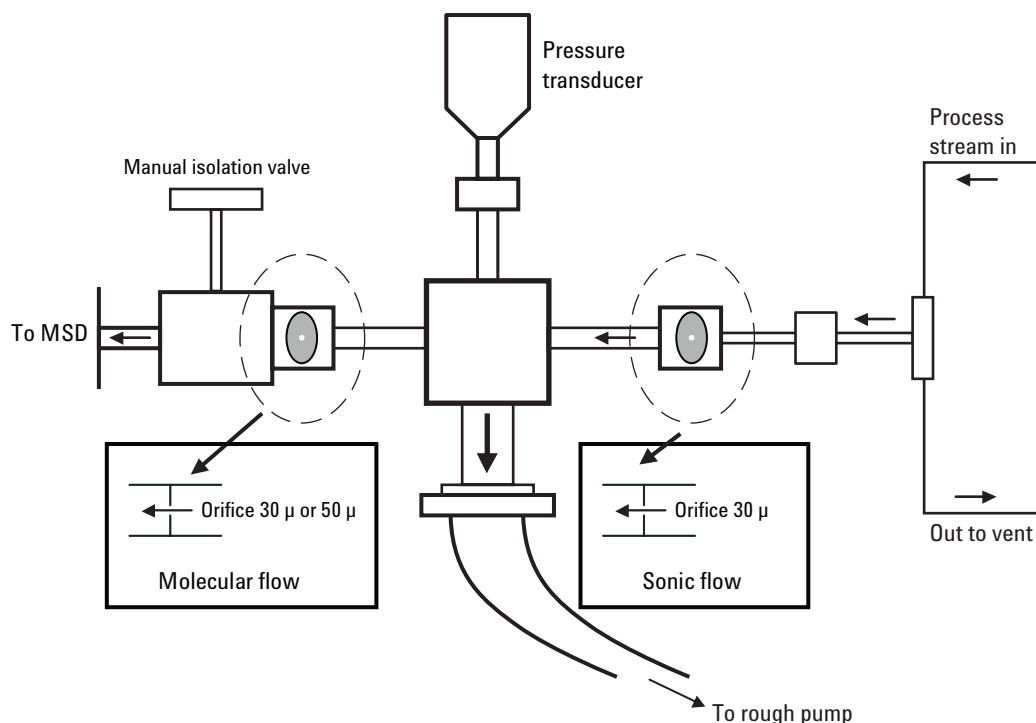


Figure 2. Diagram of the two-stage gas interface system.

Calibration of the pressure transducer is required once at initial setup. This is performed by capping off the process gas entrances to the interface and the interface foreline pump connections, followed by pumping down the interface and transducer with the 5973N vacuum system. The zero is then set from the transducers controller/display front panel as per supplied instructions.

In operation, the process gas is pulled through the first-stage orifice under sonic flow conditions using the 12-liter/min pump. Using the 30-micron orifice, approximately 25- to 30-mL/min flow is required to satisfy system demands. Pressure at this point in the cross, which is dependent on gas composition and process inlet pressure, can be monitored using the optional capacitance manometer. A small amount of material, regulated by the size of the second-stage orifice, enters the mass spec source under molecular flow conditions.

Ions are selected, calibrated, and monitored using custom control software that is installed after installation of the parent mass spec ChemStation software. Information is displayed in up to six display windows that support real-time monitoring of the defined signals (usually an ion representative of a single or group of compounds). Data is also sent to a CSV file for later processing in Microsoft® Excel, for example.

Calibration of the system was performed using a dynamic blending system. This system has been described in detail in previous Agilent publications [4]. Fuel cell gas standards were diluted in various matrices, such as helium, nitrogen, and natural gas, at point of use and time of use for the purpose of establishing calibration curves over the concentration ranges of interest. Gas mixtures were obtained from DCG Partnership, 4170 A. Main, Pearland, TX 77581.

Instrumental hardware details, operating conditions, and software versions are given in Table 2. The RTGA interface is also available in a “basic” version, which does not include the heater assembly or pressure transducer.

Table 2. RTGA Configuration and Conditions

Real-Time Gas Analyzer	
Mass spectrometer	5973N
Pump	Standard turbo
Ionization mode	Electron impact
Mass range	1.6 to 800 u (0.1 u steps)
Resolution	1 amu
Source temperature	230 °C
Quad temperature	150 °C
Typical scan range	1.6 to 50 amu
Threshold	100
Samples (2 [^])	4 Typical
Tune (typical)	Htune, custom
5973 ChemStation software	G1701DA
Gas inlet system	
First stage orifice	30 micron
Second stage orifice	30 or 50 micron
Fore pump	Edwards 12 l/m
Inlet temperature	100 °C
Pressure transducer	MKS Capacitance manometer
Heater assembly	100 °C
Temperature controller	Agilent 19265
Process stream in pressure	Atmospheric pressure
Process stream in flow	30 mL/min minimum
Gas mixtures	
Fuel cell mix	50% H ₂ , 10 % CO ₂ , 5% CH ₄
Natural gas	70% CH ₄ , 9% C ₂ , 6% C ₃ , 3% iC ₄ , 3% nC ₄ , 1% IC ₄ , 1% nC ₄ , 1.5% CO ₂
Other gases (as pure gases)	H ₂ , O ₂ , N ₂ , CO ₂ , CO
RTGA Software	
Operating system	Microsoft® Windows 2000
RTGA Control	Diablo MS Sensor 2.0

Results and Discussion

Inlet Setup

The gas interface was installed with 30- and 50-micron orifices for stage 1 and stage 2, respectively. This combination is suitable for concentration ranges from about 0.1% to 100% for most fuel cell gases such as H₂, O₂, and CO₂. In general, orifice sizes of 30 micron to 50 micron for the second-stage work well for per cent level gas analysis. For trace analysis the second-stage orifice can be changed to 350 micron. Also, if 25 to 30 mL/min of total flow is not available from the process being monitored, the first-stage orifice can be smaller to accommodate lower flow rates.

All material entering the mass spec interface must be in the gas phase. In some cases, this may require the user to supply and interface additional sample conditioning hardware upstream of the system (for example, a vaporizer).

The pressure transducer's response is independent of gas type. However, the flow rate through the orifices and, hence, pressure in the cross is dependent on gas type due to differences in viscosity and

process inlet pressure. This is illustrated in Figure 3 where cross pressure is plotted for He and N₂ at a series of process inlet pressures.

Because response of the mass spec is dependent on sample pressure, the transducer's pressure measurement can be used to correct a given ion signal.

This may be useful if the inlet process pressure is subject to fluctuation or when gas calibrations cover a very wide viscosity range. The pressure reading is treated in the same way as defined chemical masses (m/z values) are in the software. A basic method consists of defined ions representative of unique masses for each compound to be monitored and the pressure reading if desired. For example, a simple pressure corrected hydrogen signal can be defined in the software as: $(\text{Sig1.Raw})/(\text{Sig2.Raw})$, where Sig1 is mass 2 for hydrogen and Sig2 is pressure.

The MS Sensor software allows user-defined formulas to be applied to any defined instrument signal in real-time for custom calculations, signal ratios, normalization, background corrections, etc. This gives the user a great deal of flexibility in customizing the method for a particular task.

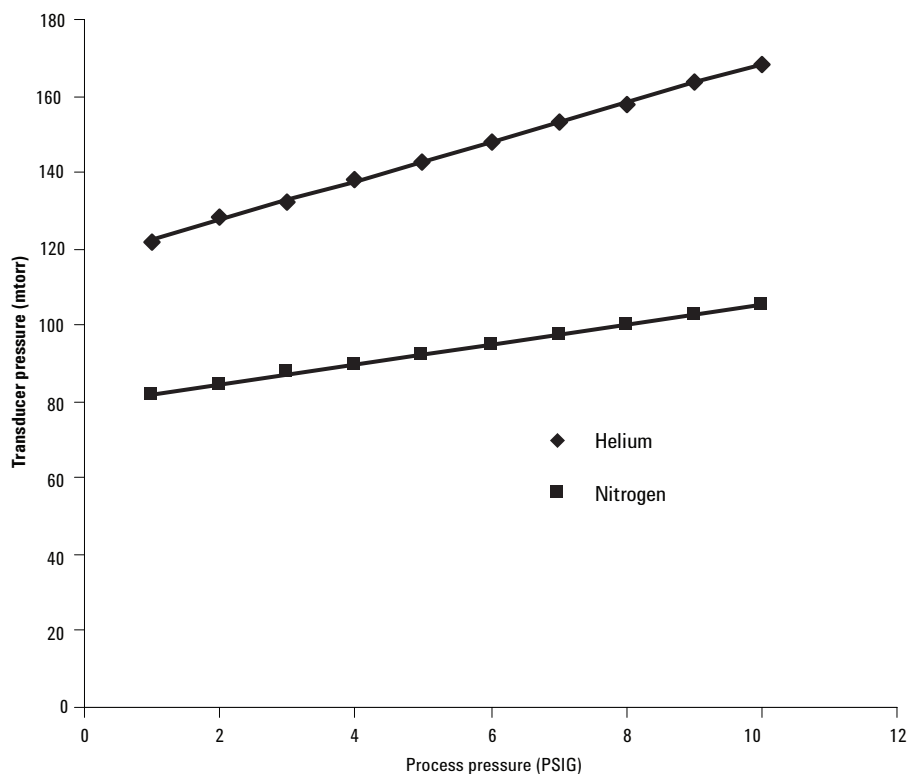


Figure 3. Affect of gas type and process pressure on cross pressure.

Tuning the Mass Spectrometer

Several automated tuning procedures are available with the RTGA system that make mass axis calibration and signal optimization easy and straightforward for the user. Three tunes that are useful for fuel cell applications are listed below. The Atune is a general-purpose tune and a good place to start when the system is initially setup or after hardware maintenance. For best performance and linearity over a wide concentration range for all common fuel cell gases (hydrogen to carbon dioxide through common light sulfur compounds), the hydrogen (Htune) is recommended. To cover a higher mass range up to 250 amu, without optimized hydrogen response, the Ltune is provided. Once tuned, the 5973N will not require re-tuning for many weeks or months depending on the particular set of operating conditions and input process stream.

Custom tunes can also be developed by the user to meet specific needs of the application (for example, trace analysis). These are easily constructed from within the 5973N software by starting with parameters from one of the standard tune files.

Tune file	Purpose
Atune	General mass spec tune (full scan range)
Ltune	Optimized for mass ranges to approximately 250
Htune	Optimized for hydrogen and other fuel cell gases
Custom	Optimized for application (user developed)

Ion Monitoring

Figure 4 is representative of the real-time signal display that is a core software feature. Here, five signals were defined and plotted in one window. Masses defined as separate signals were 2, 16, 27, 30, 43, and 44, for H₂, CH₄, C₂ to C₅'s, ethane, C₃ to C₅'s, and CO₂, respectively. Unique ions exist for hydrogen, methane, ethane (very small contribution from other hydrocarbons at mass 30), and carbon dioxide, while for C₂–C₅, a composite mass is required because a significant unique mass for each hydrocarbon is not available. This figure is intended to illustrate a generic application with many of the compounds that might be found in a fuel cell reformer feed or reformer output. Also, note the step change that occurs when simulated hydrogen production startup occurs. The system is able to capture and record very rapid changes in a process that may be missed by other measurement techniques.

The monitoring of hydrocarbons, in addition to the common fuel cell gases, can be useful to check conversion percentages and monitor potential for carbon deposition in MCFC systems, for example.

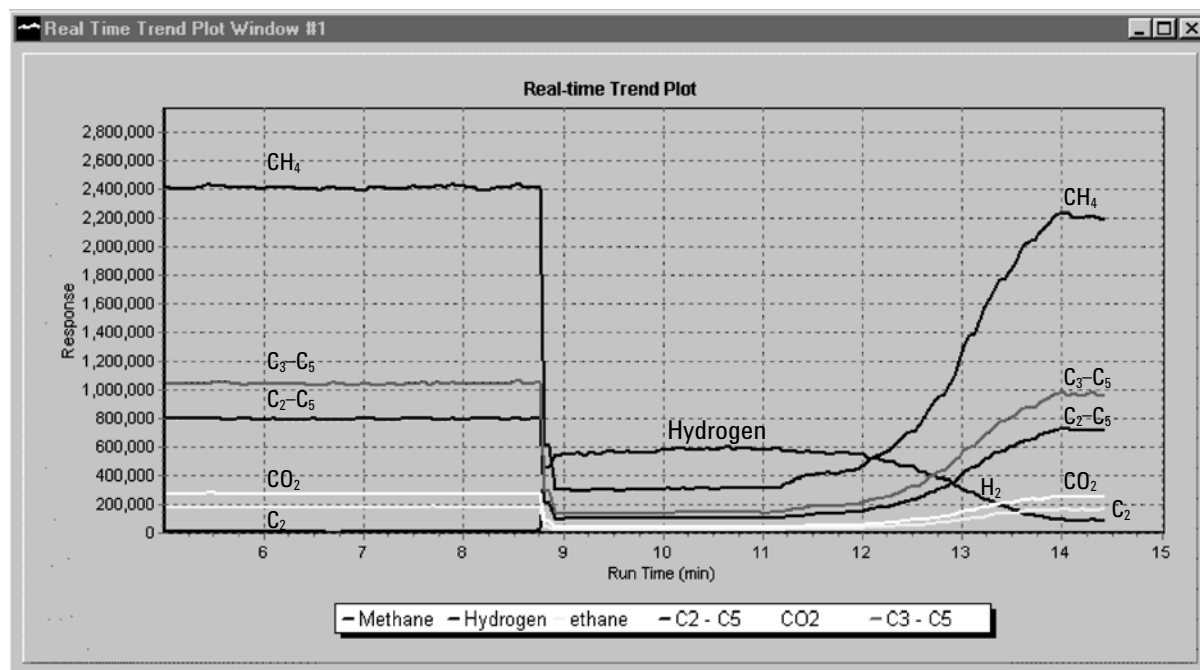


Figure 4. Graphical display of five signals: methane, C₃-C₅ hydrocarbons, C₂-C₅ hydrocarbons, carbon dioxide, ethane, and hydrogen. Scan range: 12–46 amu.

Speed of Response

Three variables are primarily responsible for system response time: amount of time spent collecting signal at a given mass, number of masses in the method, and distance and tubing size used to interface system to the process. For example, in a typical fuel cell method monitoring five ions (scan range 1.6 to 46 amu) that are expected to be present in the percent level range, response to a perturbation will be registered by the RTGA in a few seconds. For trace level analysis at ppm and ppb levels, longer times are required for data collection at each mass, translating to times of 5 seconds to 45 seconds to record each new data point.

Signal Calibration

In nearly all cases, linear calibrations can be constructed for the common fuel cell gases over the concentration ranges that can be encountered during the R&D, prototype, or pilot phases of fuel cell development. The software is designed to make the calibration process easy and straightforward. The user inputs, for a given defined signal, a series of responses and concentrations from calibration runs. The software then calculates the linear equation to be used. An example is shown in Figure 5 for methane calibration. Amounts and responses were input for a three-point calibration into a pop-up window that is available under the Edit Signal menu. The linear equation is calculated and automatically applied to the CH₄ signal in this example. This process is repeated for each ion.

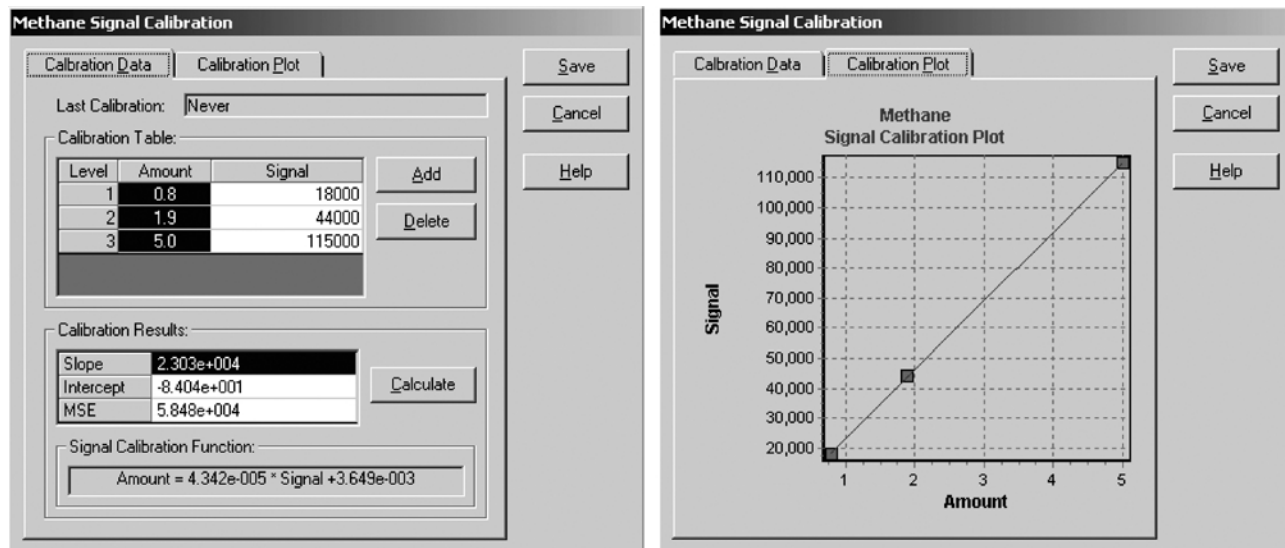


Figure 5. System calibration screen. Methane in fuel cell mix.

Carbon Monoxide and Nitrogen

Carbon monoxide is a well-known poison at levels to 1 ppm in fuel cells, competing with hydrogen for platinum active sites, for example, in PEM fuel cell systems. Because both nitrogen and carbon monoxide have a mass of 28, they cannot be differentiated using the RTGA. Carbon dioxide also has a small fragment ion at 28 amu. Figure 6 shows a calibration of CO performed in the absence of N_2 and CO_2 . The background signal present at mass 28 obtained from measuring a 99.999% helium stream was subtracted. However, in most practical situations, N_2 or CO_2 at some level are likely to be present rendering the RTGA unsuitable. In these cases, the Agilent 3000 Micro gas chromatograph is recommended as it can quantitate CO to approximately 1 ppm with an analysis time of under 90 seconds [5].

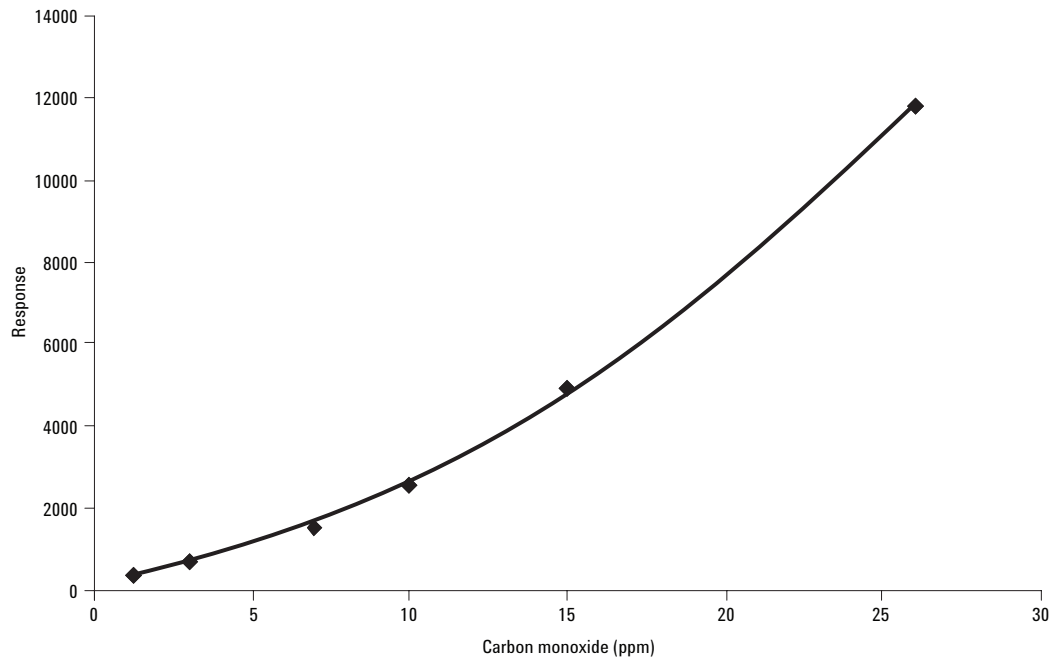


Figure 6. Parts-per-million level carbon monoxide in N_2 and CO_2 free stream. Scan 1.6 to 32 amu.

Performance and Calibration: H₂, CO₂, O₂, N₂, CH₄

The use and performance of any chemical measurement system is enhanced if quantitative information is easy to obtain. In the study of fuel cell systems, including processors and cell stacks, quantitative chemical analysis may be required in addition to qualitative trending. Knowledge of the electrochemical reaction gases and diluent concentrations can be valuable to fuel cell development

efforts. For example, maintaining oxidant composition in the proper (or above) stoichiometric ratio will increase fuel cell performance. Calibration plots are shown in Figures 7 and 8, for H₂ in nitrogen and helium, respectively. Both show good linearity over a wide concentration range indicating that simple two-point calibrations could be performed as described earlier in the “Signal Calibration” section. Correlation coefficients are better than 0.99.

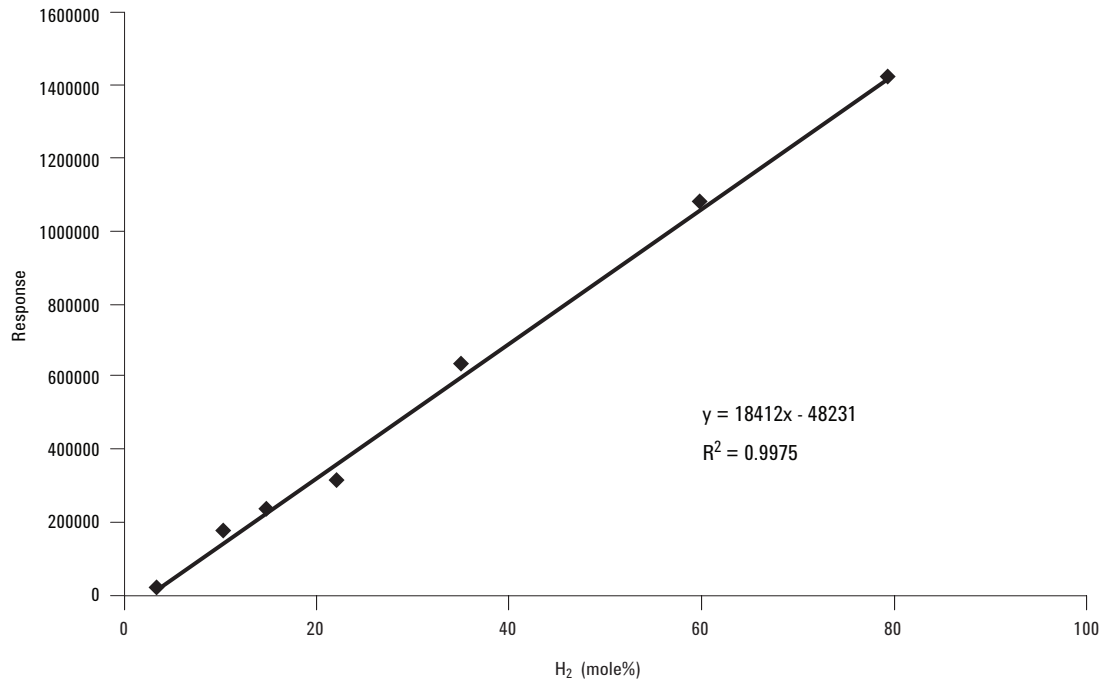


Figure 7. Calibration of hydrogen in nitrogen diluent.

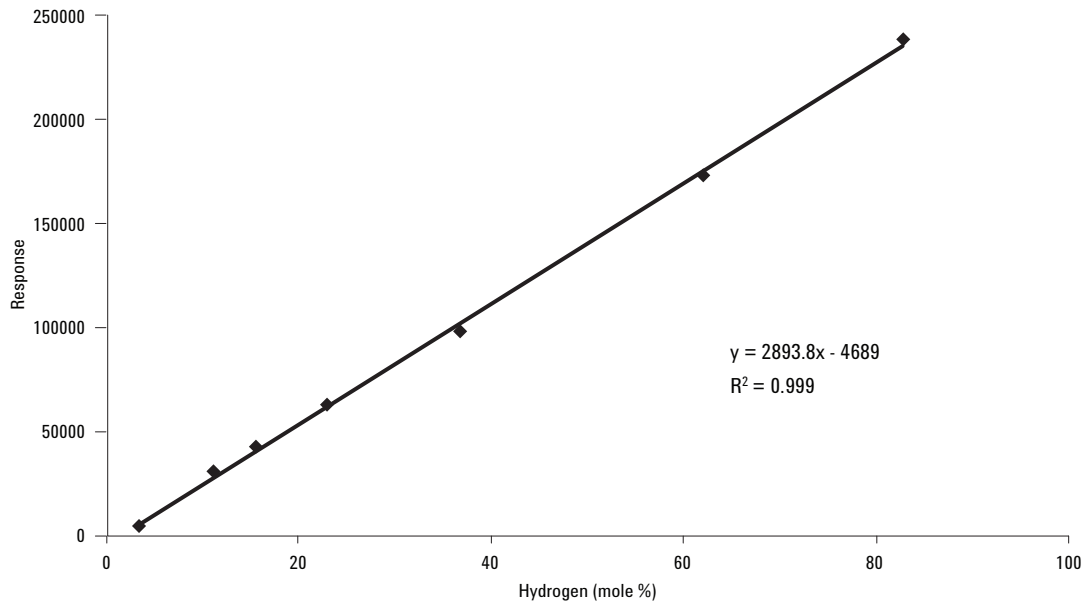


Figure 8. Calibration of hydrogen in helium diluent.

A calibration plot for CO₂ over concentration ranges of 2% to 20% is shown in Figure 9. Carbon dioxide measurements can be important in the development of CO₂ tolerant alkaline fuel cell systems and in monitoring the performance of other fuel cell types. Finally, calibrations are shown respectively for oxygen, nitrogen and methane, in Figures 10, 11, and 12.

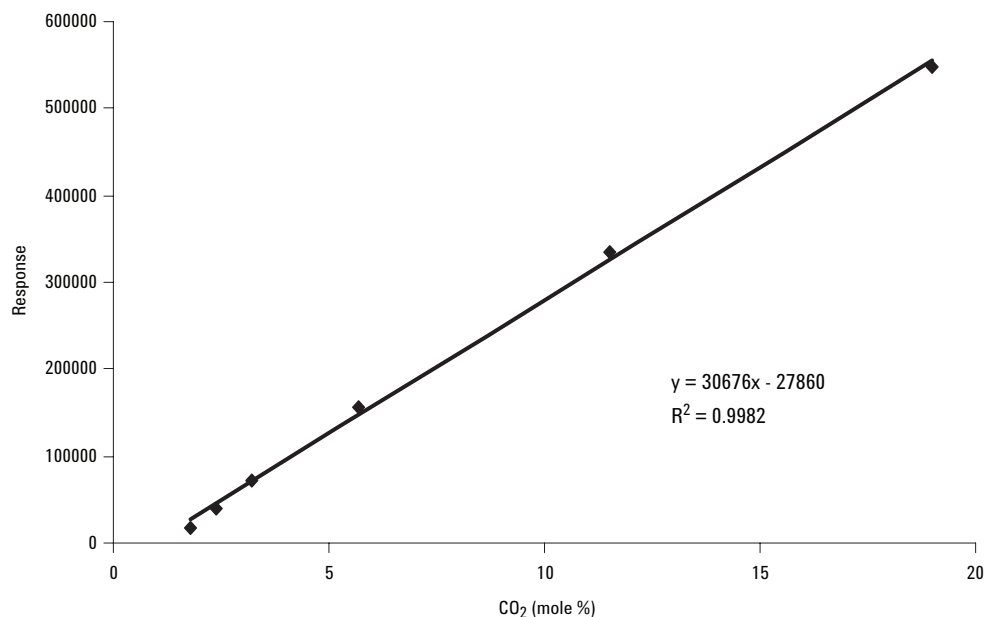


Figure 9. Calibration of carbon dioxide. Stage 1 and stage 2 orifices 30 micron. Ion 44 monitored.

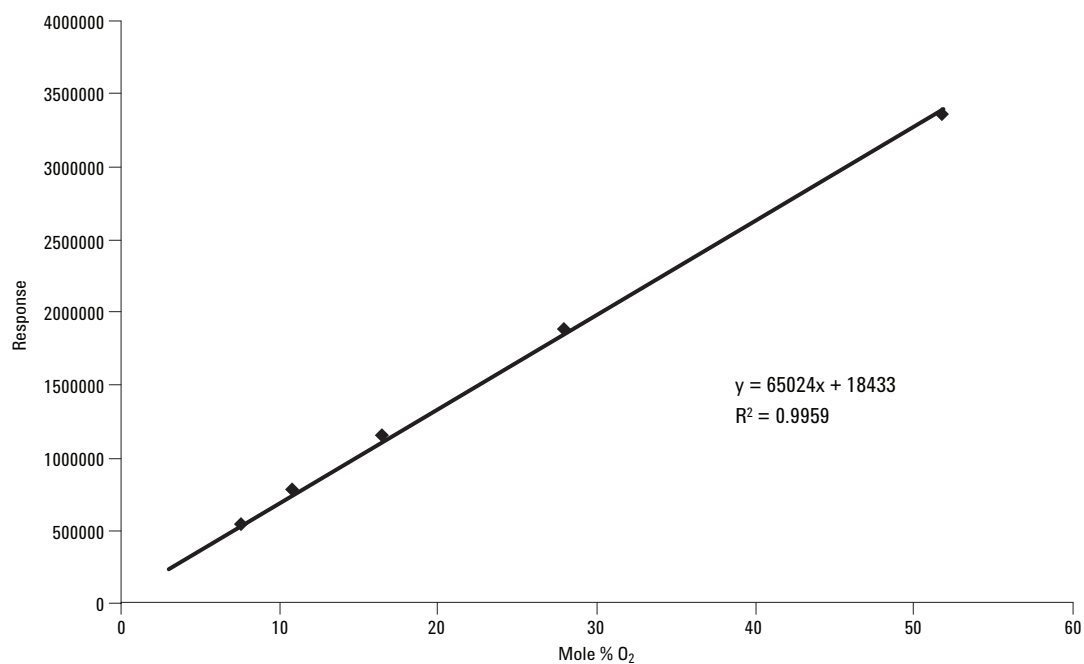


Figure 10. Calibration of oxygen in helium.

These calibrations all show reasonably good linearity over the plotted concentration ranges, making it possible to calibrate a gas with just two data points. These points should be chosen so that the calibration range is representative of the expected concentrations whenever possible. All calibrations were performed with mass spec parameters from an automated fuel cell tune using a scan range from 1.6 to 46 amu. No background correction was applied.

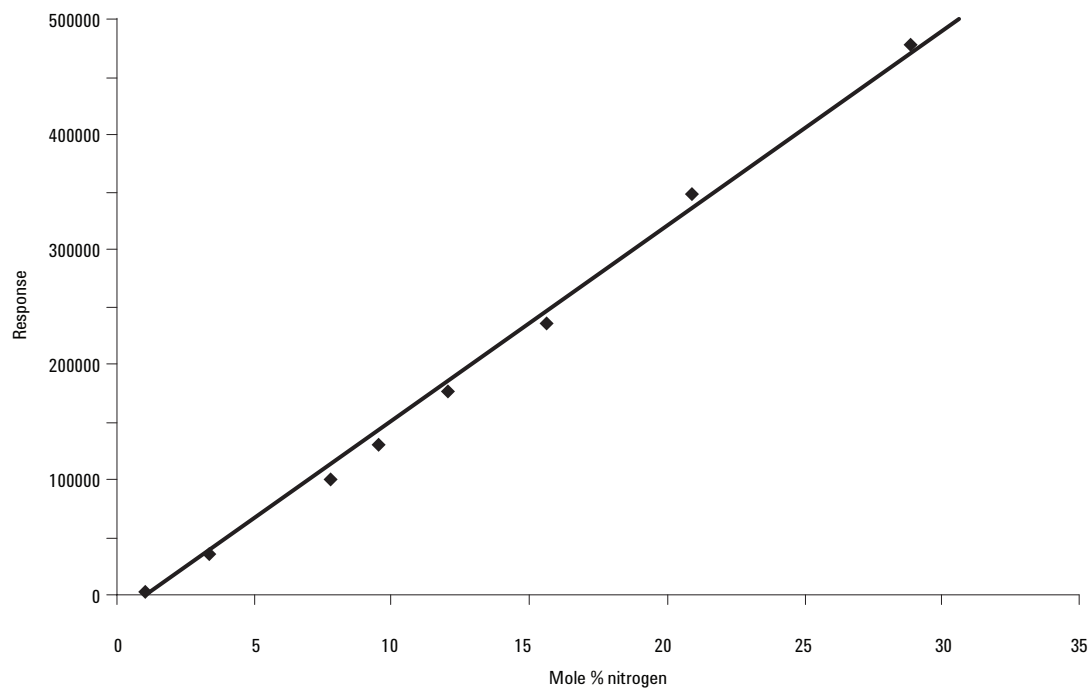


Figure 11. Calibration of nitrogen in hydrogen.

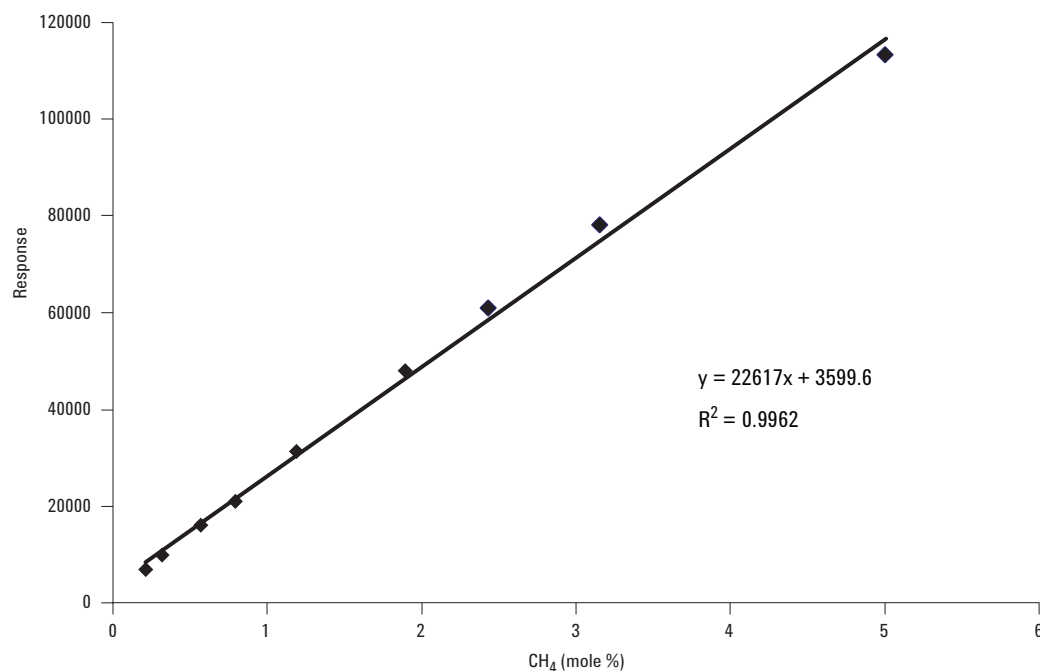


Figure 12. Calibration of methane in fuel cell mix.

Measurement of Low-Level Impurities

Monitoring and quantitation of low-level impurities, especially sulfur-containing compounds is a significant area of study in fuel cell and related catalyst development. For example, odorants present in natural gas feed to a fuel processor must be removed to levels well below 1 ppm using activated carbon beds, in many cases, prior to steam reforming. Although this is the subject of a separate paper, an example is included here to complete the RTGA overview. Figure 13 shows the calibration of dimethyl disulfide to demonstrate typical performance capability in the ppb range. Actual detection limits will be matrix dependent.

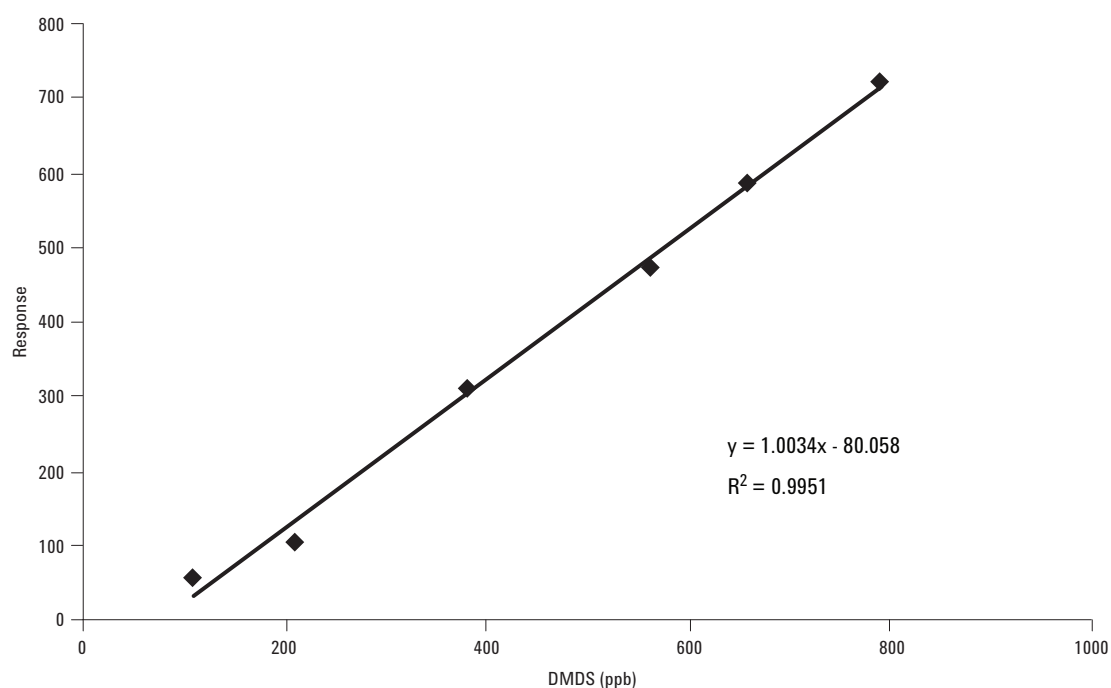


Figure 13. Calibration of dimethyl disulfide at the ppb level. Ion 94 monitored. Dilution in helium.

Conclusions

One key challenge to successful fuel cell commercialization is cost reduction. To this end, there is increasing focus on fuel processor design and catalyst optimization. With the level of development effort intensifying in all fuel cell and fuel processor technologies, any tools that can assist with this challenge are being used. Detailed, real-time, qualitative, and quantitative chemical analysis can be powerful tools when applied to fuel cell development and optimization. This applies to the incoming fuels, processed fuels, reformer output, partial oxidation system gases, and fuel cell stack electrochemical reaction gases.

The RTGA provides a stable, reliable, and quantitative solution to continuous chemical monitoring in fuel cell systems that is not possible with RGAs. Good linearity is seen for hydrogen and other gases that are encountered in fuel cell systems over a wide concentration range from ppb to percent levels, making calibration of the system straightforward. For qualitative chemical trending, the RTGA system can be running in a matter of minutes after simply selecting the ions of interest in the software method screens. With a response time of 2 to 5 seconds, the system can monitor and capture rapid transients that can be missed by other monitoring equipment.

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