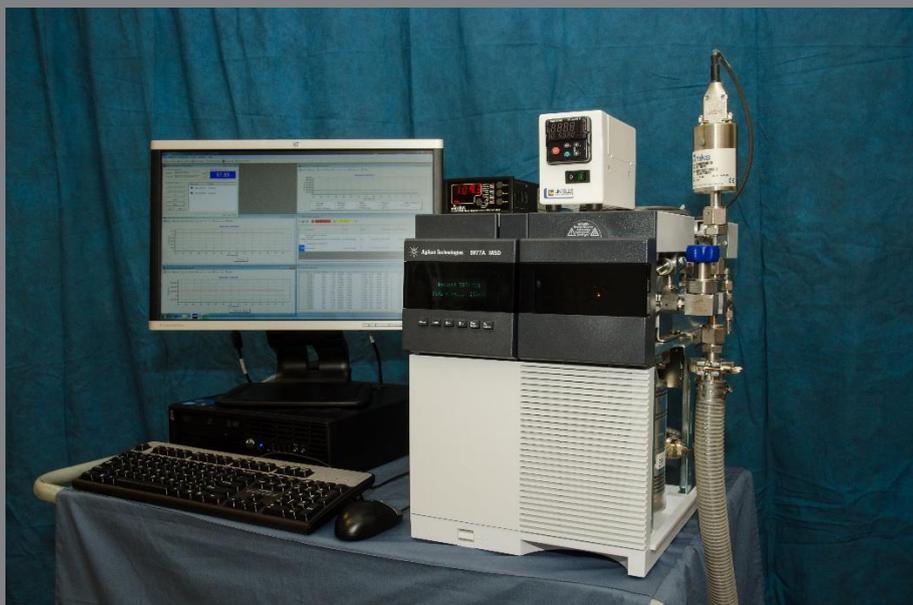


Fast Chemical Analysis for Fuels R&D: Application of the Diablo 5000B Real Time Gas Analyzer

A Diablo Analytical White Paper

The last few years have seen an accelerating pace of new fuel development. This has increasingly led to the need for high performing 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 processing systems.

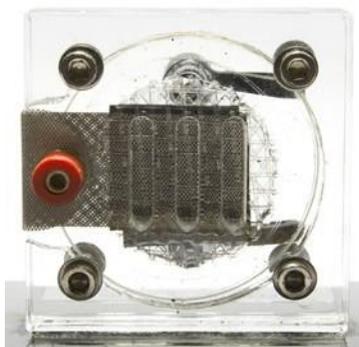
The Diablo 5000B Real-Time Gas Analyzer (RTGA) based on the Agilent 5977 Mass Selective Detector has proven to be a powerful analytical tool for the study and optimization of fuel cell systems and 'syngas' production and use. This white paper will detail how the Diablo 5000B RTGA provides a stable, reliable and quantitative solution to continuous chemical monitoring in fuel processing systems that is not possible with residual gas analyzers.



Gas Generation for Fuel Cells

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.



Until means are developed, and infrastructure built for economic storage, transportation, and generation of hydrogen, fuel processors will be a necessary component of most fuel cell systems. This includes both stationary and vehicular on-board systems.

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 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 reformate 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.



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 examples 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 chemical monitoring. (3)

Diesel Production from Syngas

Generating liquid fuels, such as diesel or alcohols, from Syngas has been very important in the 20th Century. Countries that did not have access to liquid petroleum hydrocarbons have made liquid fuels from other sources like coal. This was done by Germany during World War II to supplement unreliable fuel supplies. In the modern economy of today, this is still a higher cost method to generate liquid fuels, so more study is required to make this a viable business option. It is likely that less liquid petroleum source material will be available in the future. The earth retains vast deposits of Coal and other rocky hydrocarbon formations. Syngas may be one approach to extracting fuels from these difficult hydrocarbon formations.



Natural Gas from Syngas:

In the aftermath of the 1970's oil shortages, the U.S. generated "Syngas" from sources such as coal. The Syngas was used in several ways, including as a gaseous fuel mixture similar in composition to natural gas. Since this time, natural gas production has increase dramatically so this is a less desirable route in the current markets.

High Value Products from Green Sources

Biomass can be used to make Syngas-like materials that can be processed into ethylene, propylene and other feeds for higher value, 'green' polymer production.

Experimental



RTGA Overview

The RTGA system consists of a modified Agilent Technologies 5977 Mass Spectrometer, specialized hardware gas interface system, and control software. The two-stage gas interface and control and monitoring software (MS Sensor 4.0) were developed by Diablo Analytical, Inc. The Agilent MassHunter GC/MS Acquisition software must be present and operational prior to installation of MS Sensor 4.0. Modifications to the 5977 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 1. 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 spectrometer 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 5977. The mass spec and pressure transducer are interfaced to a personal computer through LAN and RS232 interfaces, respectively.

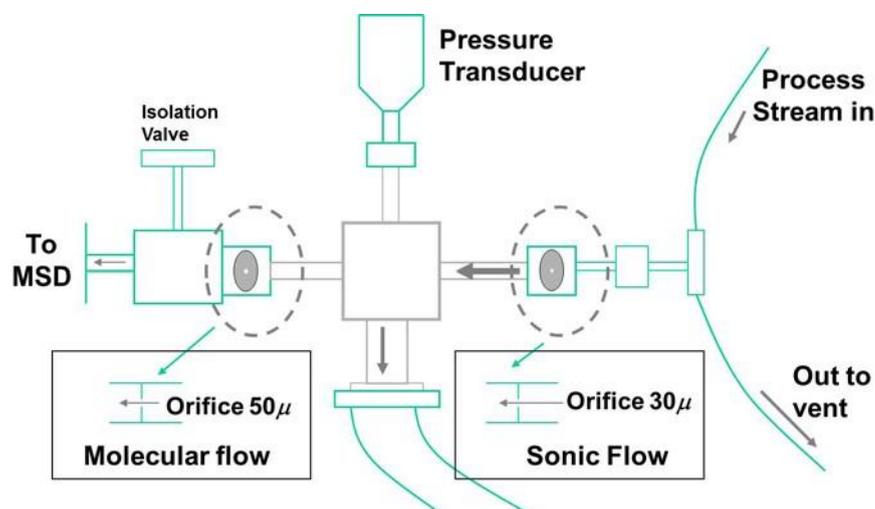


Figure 1:
Diagram of the two-stage gas interface system.

Calibration of the pressure transducer is performed only at initial setup by capping off the process gas and the interface fore-line pump connections, followed by pumping down the interface and transducer with the 5977 vacuum system. The zero is then set from the transducer's 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 8 to 15-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 capacitance monometer. A small amount of material, regulated by the size of the second stage orifice, enters the mass spectrometer source under molecular flow conditions. This interface design as well as the design of the mass spectrometer allows quantitative work to be performed for a wide range of materials over wide dynamic ranges.

Ions are selected, calibrated, and monitored using custom control software that is installed over the parent mass spec MassHunter 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 saved to a data file and can be exported to a CSV file for later processing in Excel, for example.

External standard calibration of the system can be performed using a dynamic blending system, or gas cylinder blend mixtures. Gas standards can be diluted in various matrices such as helium, nitrogen, and natural gas at the point of use and time of use for the purpose of establishing calibration curves over the concentration range of interest. Instrumental hardware details, operating conditions, and software versions are given in Table 1.

Table 1: RTGA Configuration and Conditions

Real Time Gas Analyzer	5977
Mass Spectrometer	5977
Pump	Performance turbo
Ionization mode	Electron impact
Mass range	1.6 - 800 u (0.1 μ steps)
Resolution	1 amu
Source Type	Stainless Steel
Source temperature	230 °C
Quad temperature	150 °C
Typical scan range	1.6 to 100 amu
Threshold	100
Samples (2 [^])	4 Typical
Tune (typical)	Low mass or hydrogen tunes
5977 MassHunter software	G6845
Gas Inlet System	Diablo Analytical 5000B
First stage orifice	30 Micron
Second stage orifice	50 Micron
Fore pump Pfeiffer/Edwards	10 to 12 l/m
Inlet temperature	Ambient to 200 °C
Pressure transducer	MKS Capacitance monometer
Heater assembly	Ambient to 200 °C
Temperature controller	Integrated Watlow
Process stream in pressure	Atmospheric pressure to hundreds of PSI (depends on sampling orifice)
Process stream in flow	30 mL/min minimum (or much more or much less)
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	Windows 10 Professional
RTGA Control	Diablo MS Sensor 4.0

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. For trace analysis the stage orifice can be changed to 300 or 350-micron. Also, if a smaller total flow from the process being monitored is desired, then the sampling orifice can be changed and or a direct, low volume, connection can be used for sample introduction.

All material entering the mass spec interface must be in the gas phase. In some cases, this may require the user to supply and add additional sample conditioning hardware upstream of the system (for example 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. This is illustrated in Figure 2 where cross pressure is plotted for He and N₂ at a series of process inlet pressures.

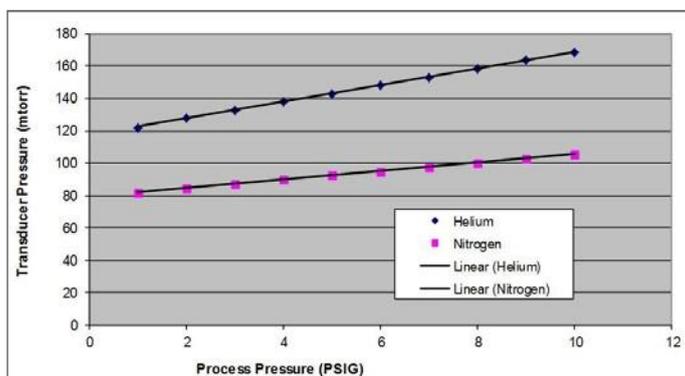


Figure 2: Effect of gas type and process pressure on cross pressure.

Since response of the mass spec is dependent on source 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 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: $(\text{Sig1.Raw})/(\text{Sig2.Raw})^*$ (P-nominal), where Sig1 is mass 2 for hydrogen, Sig2 is pressure and P-nominal is about 0.1 torr (typical) in the interface.

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.

Tuning the Mass Spectrometer

Several automated tuning procedures are available with the 5977 and 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 placebo 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 gases (hydrogen to carbon dioxide through common sulfur compounds up to tetrahydrothiophene), the custom tune (Htune) is recommended. To cover a higher mass range up to 250 amu, without optimized hydrogen response, the "low mass" or Ltune is provided. Once tuned, the 5977 will not require re-tuning for many weeks depending on the particular set of operating conditions and analytical requirements.

Custom tunes can also be developed by the user to meet specific needs of the application. These are easily constructed from within the 5977 software, by starting with parameters from one of the standard tune files.

Tune file	Purpose
Atune or Stune	General mass spec tune
Ltune	Optimized for mass ranges to approx. 250, not H ₂
Htune	Optimized for hydrogen and other fuel or combustion gases
HeTune	Similar to HTune, but Helium is used as the tune gas
Custom	Optimized for application (user developed)

Ion Monitoring

Figure 3 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, and carbon dioxide, while for C₂—C₅ a composite mass is required since 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 hydrogen production startup occurs. The system can 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 related gases, can be useful to check conversion percentages and to monitor the potential for carbon deposition in process systems, for example.

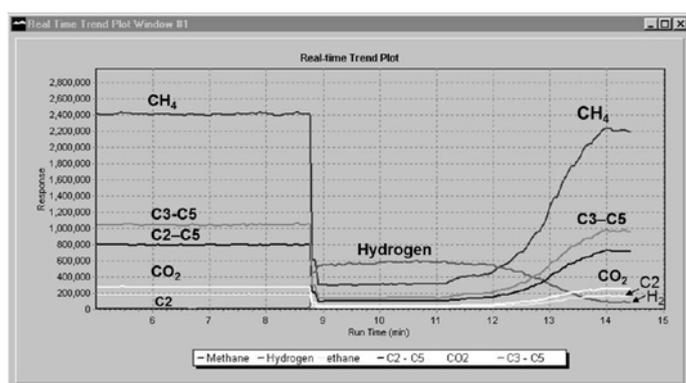


Figure 3: Graphical display of five signals: methane, C₃-C₅ hydrocarbons, C₂-C₅ hydrocarbons, carbon dioxide, ethane, and hydrogen. Scan range: 12 - 46 amu.

Speed of Response

Three variables are primarily responsible for limits on system response time: amount of time spent collecting signal at a given mass; number of masses in the method; distance and tubing size used to interface system to the process.

For example, in a typical fuel related method monitoring five ions that are expected to be present in the percent level range, response to a perturbation will be registered by the RTGA on the seconds time scale. For trace level analysis at ppm and ppb levels, longer response times may require for data collection at longer dwell times.

Trace level gases may also require longer purge times to stabilize. The 5000B RTGA interface is electro-polished high quality stainless steel to minimize any passivation issues. The design of the 5000B RTGA interface allows very fast sample response time on the second time scale for typical applications.

Signal Calibration

In nearly all cases linear calibrations can be constructed for the common fuel related gases over the concentration ranges that can be encountered during the R&D, prototype, or pilot phases. The software is designed to make the calibration process easy and straightforward. The user selects 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 nitrogen in hydrogen calibration. Amounts and responses were input for a three-point calibration into a popup window that is available under the edit signal menu. The linear equation is calculated and automatically applied to the N₂ signal in this example. This process is repeated for each ion.

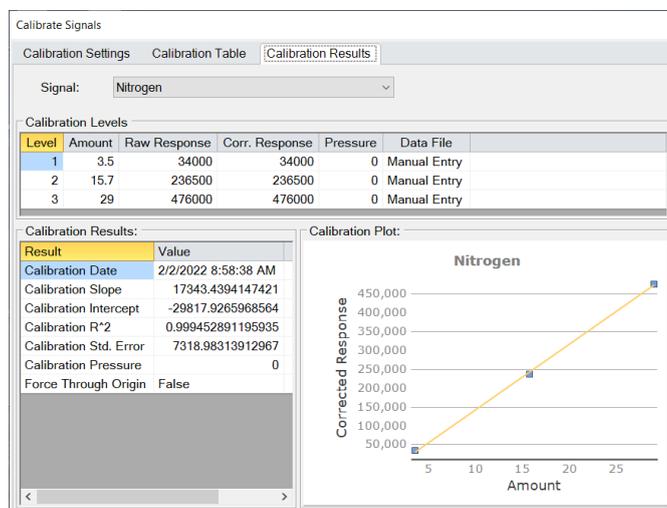


Figure 4: System calibration window. Nitrogen in hydrogen used as example.

Carbon Monoxide and Nitrogen

Both nitrogen and carbon monoxide have a mass of 28, they cannot be differentiated using the RTGA under normal operational modes. Carbon dioxide may also generate a small fragment ion at 28 amu. In most practical situations N₂ or CO₂, at some level is likely to be present, but the concentration level may not interfere for many applications.

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 related systems, quantitative chemical analysis is required in addition to qualitative trending. Calibration plots are shown in Figures 5 and 6, 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 above in the Calibration section. Correlation coefficients are better than 0.99. A more sensitive indication of hydrogen response can be seen in Figure 7 where response factors are plotted for dilution of a fuel cell mix (50% H₂, 10% CO₂, 5% CH₄) in helium. Variation in response over the concentration range used is approximately ±10 %.

Calibration plots for CO₂ over concentration ranges of 5% to 60% and 0.5% to 7% appear in Figures 7 and 8, respectively. Finally, calibrations are shown respectively for oxygen, nitrogen, and methane, in Figures 9, 10 and 11.

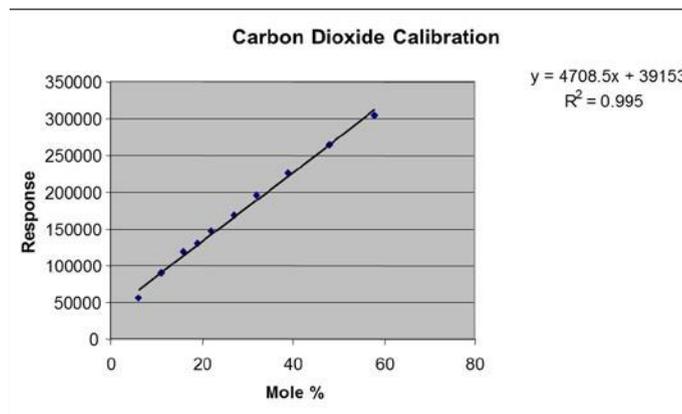


Figure 7: Calibration of carbon dioxide (5 to 60%) in helium.

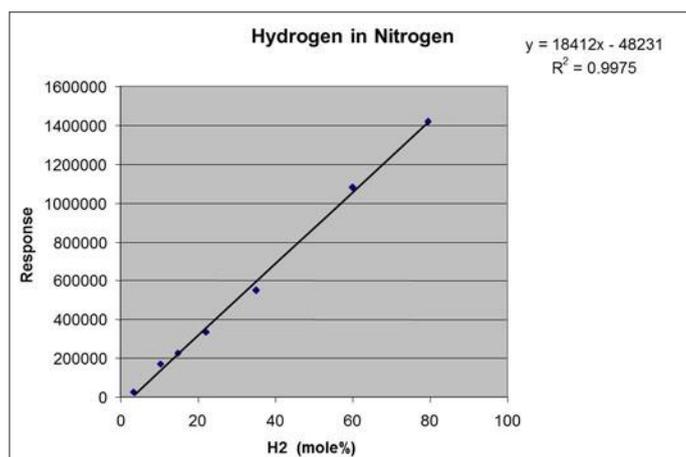


Figure 5: Calibration of hydrogen in nitrogen diluent.

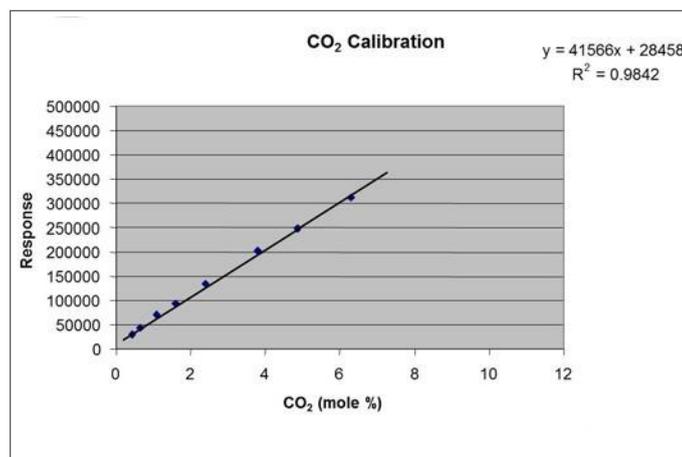


Figure 8: Calibration of carbon dioxide (0.5 to 7%) in fuel cell mix.

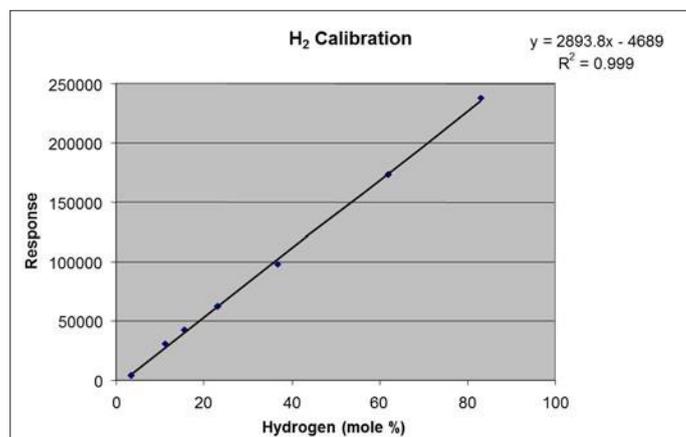


Figure 6: Calibration of hydrogen in helium diluent.

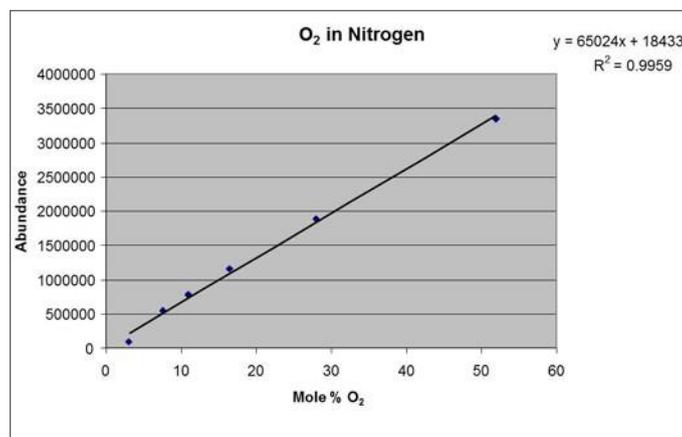


Figure 9: Calibration of oxygen in nitrogen diluent.

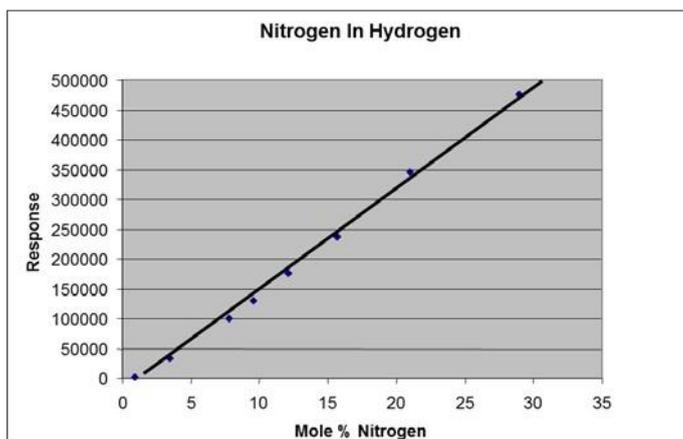


Figure 10: Calibration of nitrogen in hydrogen.

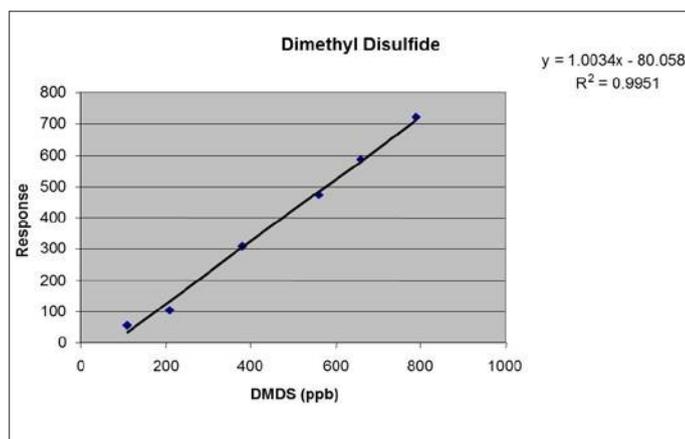


Figure 12: Calibration of dimethyl disulfide at the ppb level. Ion 94 monitored.

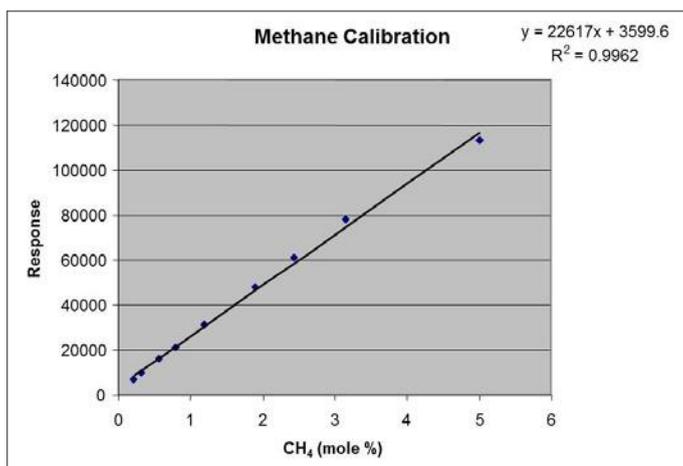


Figure 11: Calibration of methane in fuel cell mix.

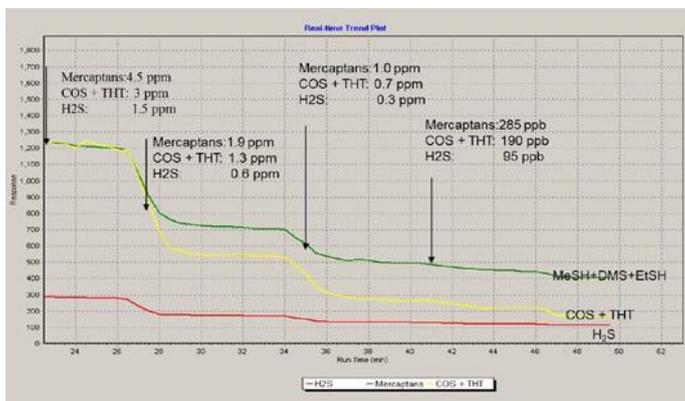


Figure 13: Monitoring stepwise changes in low-level sulfur gases.

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 tune using a scan range from 1.6 to 46 amu.

Measurement of Low-level Impurities

Monitoring and quantitation of low-level impurities, including sulfur containing compounds is a significant area of study in fuel gases and related catalyst development. For example, odorants present in natural gas feed to some fuel processors must be removed to levels well below 1ppm, using activated carbon beds in many cases, prior to steam reforming. Fig. 12 shows the calibration of dimethyl disulfide to demonstrate typical performance capability in the ppb range. Figures 13 & 14 show stepwise changes of low-level sulfur gases, illustrating the inertness of the RTGA interface.



Figure 14: Monitoring stepwise changes in low-level sulfur gases: Step 1: 1.0 ppm (mercaptans) to Step 5: 4.0ppm (mercaptans).

Conclusions

The main challenge to successful alternative fuel commercialization is cost reduction. 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, and quantitative chemical analysis can be powerful tools when applied to alternative fuel 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 Diablo 5000B RTGA provides a stable, reliable, and quantitative solution to continuous chemical monitoring in fuel processing systems that is not possible with residual gas analyzers. 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. With a response time of 1 to 5 seconds, the system can monitor and capture rapid transients that can be missed by other monitoring equipment.

Acknowledgement & References

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Please contact us at:



Diablo Analytical, Inc.

5141 Lone Tree Way

Antioch, CA 94531

T: (925) 755-1005

E: info@diabloanalytical.com