Chemical Analysis in Fuel Cell Systems: Application of the Agilent 5000A Real-Time Gas Analyzer for Monitoring Low-Level Sulfur

Application

Fuel Cells

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Abstract

All fuel cell technologies are affected in various ways by impurities that can be present in incoming fuels, processed feeds, and oxidants. Monitoring impurities can be particularly important when hydrocarbon-based fuels, such as natural gas, are used as the source of hydrogen. The Agilent 5000A Real-Time Gas Analyzer, based on the 5973N mass selective detector, is used to monitor and quantify low-level sulfur species in natural gas and high hydrogen content feeds that are associated with the operation of fuel processors. Analysis of common natural gas odorants and impurities at the ppb level is discussed and demonstrated.

Introduction

Reforming of hydrocarbon-based fuels will likely be the primary source of hydrogen needed to power fuel cells for the foreseeable future. Natural gas fuels can contain naturally occurring contaminants, such as hydrogen sulfide, and odorants, such as mercaptans or tetrahydrothiophene (THT). These compounds are detrimental to both subsystems within the fuel processor, and to the fuel cell stacks themselves.

Because fuel cell systems employ numerous catalytic processes, they risk suffering significant degradation in performance due to various impurities. Nearly all catalytic materials are poisoned, or reduced in lifetime or conversion efficiency by various chemical species, with sulfur compounds being particularly harmful. Fuel cell systems must deal with these issues, requiring measures to remove or reduce impurities to levels that do not shorten lifetimes or reduce efficiencies. For example, sulfur can poison both steam reforming and various fuel cell electrocatalysts, such as platinum. A summary of fuel cell poisons and tolerances are listed in Table 1 [1]. The values in Table 1 represent current views in the fuel cell industry, however, much lower levels of sulfur in the final fuel to the cell are likely to be necessary. Levels below 300 ppb are desirable, especially in low temperature cells. Total sulfur in hydrogen-rich feeds to molten carbonate fuel cells (MCFCs) is recommended to be below 0.1 ppm [2].

Table 1. Allowed Levels of Impurities in Various Types of Fuel Cells

	PAFC*	MCFC*	SOFC*	PEMFC*
Hydrogen	Fuel	Fuel	Fuel	Fuel
Carbon monoxide	10 ppm	Shifted**	Shifted**	10 ppm
Methane	Diluent	Fuel/Diluent	Fuel	Diluent
Sulfur	20 ppm	<10 ppm fuel***	1 ppm	<1 ppm
Halides	4 ppm	0.1 ppm	1 ppm	
C2+	0.5 Olefins	Coking, 0.2%	Fuel below C5	
Ammonia	0.20%	1%	Fuel <5000 ppm	
CO_2 and H_2O	Diluent	Recirculated	Diluent	Diluent, H_2O management

* PAFC: Phosphoric acid fuel cell, MCFC: Molten carbonate fuel cell, SOFC: Solid oxide fuel cell, PEMFC: Polymer electrolyte membrane fuel cell.

** Water shift gas reaction.

***Sulfur dioxide <1 ppm allowed in oxidant.

Although this work focuses on sulfur impurities, the methods and techniques discussed using the Real-Time Gas Analyzer (RTGA) apply to many other impurities that may be encountered in fuel cell systems. For example, the final purification stage of a fuel processor may require removal of ammonia or halides depending on the nature of the starting fuel. It is essential, therefore, to develop an understanding of trigger levels and magnitude of effects of various impurities during the research, development, and pilot phases of fuel cell commercialization [3].

Experimental

The RTGA consists of a modified 5973N mass selective detector (MSD), specialized two-stage gas interface, and control/monitoring software. Diablo Analytical, Inc. 1110 Burnett Ave., Suite C, Concord, CA 94520, developed the gas interface and monitoring software exclusively for the 5973N MSD. Figure 1 shows a representation of the interface. The amount of gaseous material entering the MSD is carefully controlled through precision orifices in two stages using differential pumping: 1) process orifice, and 2) MSD sampling orifice. Unlike in traditional GC/MS systems, separation of the components does not occur prior to entering the MSD. Compound selectivity is obtained through selected ion monitoring of prominent ions present in the gases of interest. Unique ions are used when available or composite ions when a unique ion is not available. Details can be found in another Agilent publication [4].

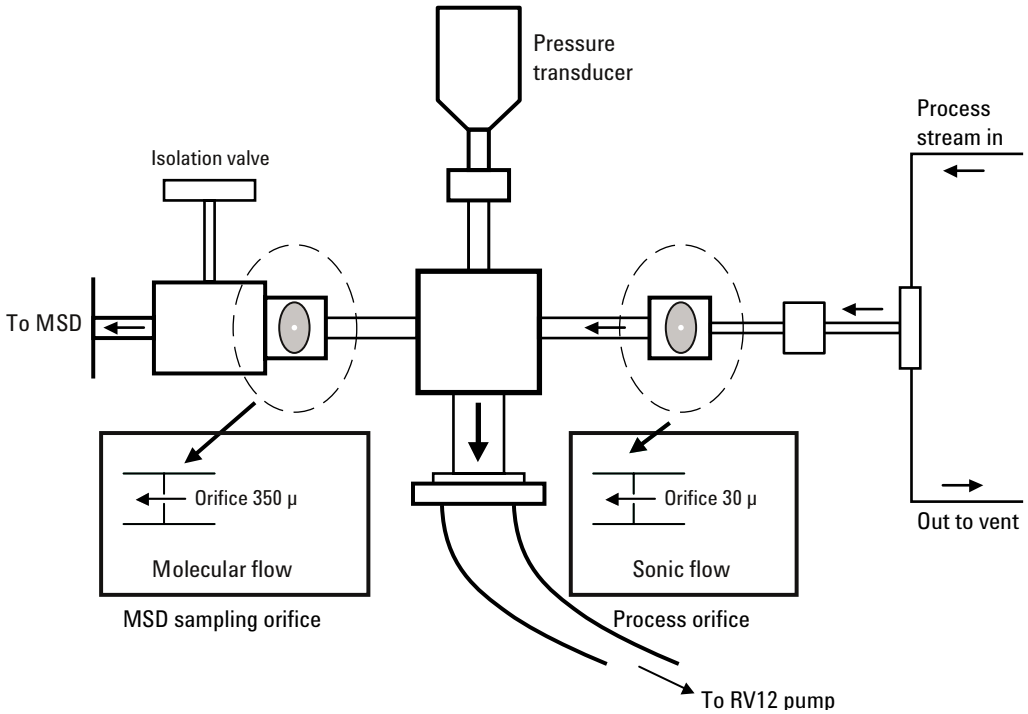

Figure 1. Diagram of the RTGA gas interface.

The RTGA interface normally is configured with 30- and 50-micron orifices for percent-level gas analysis. However, for trace analysis the MSD sampling orifice must be larger to allow a higher flux of sample to enter the source. In this work, a 350-micron orifice was chosen. Orifices larger than 350 micron do not necessarily offer increased sensitivity due to corresponding increases in background noise and higher MS source pressure. In general, larger orifices (over 350 micron) may lead to better sensitivity only in very simple matrices, such as inert gases.

Ions are selected, calibrated, and monitored using control software, developed by Diablo Analytical, Inc., that communicates with the parent ChemStation software. This software "shell" allows the use of the 5973N MSD for continuous process analysis by monitoring unique (*m/z*) values for a given compound. User-defined formulas can be applied to any signal for functions, such as signal summing, normalization, background subtraction, and pressure correction. Six available trend plot (control chart) windows can display graphic results in real time. Data are logged and stored in simple delimited format and are easily imported into other process software like LabVIEW™ and spreedsheet software (Microsoft® Excel).

Table 2 shows instrument details, operating details, and gas mixtures. Dynamic blending was used to prepare low-level sulfur-containing gas feeds in several matrices, such as helium and natural gas. The system allows quantitative blending of ppm- and ppb-level gases from one certified standard mixture. Use and setup of the system is described in detail in another Agilent application note [5]. Gas mixtures including the low-level sulfur standard and fuel cell mix were obtained from DCG Partnership, 4170A Main, Pearland, TX 77581.

Table 2. RTGA Configuration and Conditions

Real-Time Gas Analyzer	
Mass spectrometer	**5973N**
Pump	Standard turbo
Ionization mode	Electron impact
Mass range	1.6–800 amu (0.1 amu steps)
Resolution	1 amu
Source temperature	230 °C
Quad temperature	150 °C
Typical scan range	26 to 90 amu
Threshold	25
Samples setting	7 Typical
SIM mode	4000–7000 ms dwell
Tune (typical)	Htune, custom
5973 ChemStation software	G1701DA
Gas inlet system	
First stage orifice	30 micron
Second stage orifice	350 micron
Fore pump	Edwards 12 L/sec
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 balance N_2
Natural gas	70% CH_4, 9% C_2, 6% C_3, 3% i-C4 3% n-C4, 1% i-C5, 1% n-C5, 1.5% CO_2, balance N_2
Sulfur mix (5 ppm per component)	H_2S, COS, CH_3SH, EtSH, DMS, CS_2, tButylSH, THT
Other gases (as pure gases)	H_2, O_2, N_2, CO_2, He

Discussion

Matrix gases

Sulfur compounds were studied in three different matrices. These included inert gases (N_2 and He), fuel cell mix, and natural gas. Simple inert gas matrices were used to characterize and optimize the overall system for trace analysis, while fuel cell, and natural gas matrices were used to simulate more realistic real-world conditions. The eight-component sulfur mix used in this work contains most of the low-level compounds that might be found in a natural gas feed to a fuel processor. Of course, in any given feed, only one or two of these are likely to be present, simplifing the measurement. Odorants and naturally occurring impurities were included.

Orifice size

For trace analysis, the orifice next to the MSD must be larger than the standard 50-micron size to allow a higher flux of sample to enter the source. However, as the orifice is made larger, a point is reached where pressure increases in the source and subsequent increases in background noise begin to degrade performance. The optimal orifice size is highly matrix dependent. An orifice of 350 microns offered the best overall performance compromise in terms of sensitivity and stability when hydrocarbon matrices were used. These matrices produce a high degree of fragmentation and neutral species that will reduce sensitivities. Better sensitivities for impurities in hydrocarbon matrices may be possible if positive chemical ionization is used as an alternative to electron impact. The softer ionization, with ammonia as the reagent gas, should suppress hydrocarbon fragmentation producing a cleaner background.

Analysis modes

Both scan and selected ion monitoring (SIM) modes can be used. Scan, with samples set to 7, or SIM with dwell times of 4000 to 7000 ms were found to yield approximately the same sensitivities. If SIM is employed, data points are recorded less frequently. For example, with a dwell of 7000 ms per ion and a total of six ions in the method, a unique data point can be recorded approximately every 45 seconds. Signal to noise improves as samples or dwell settings are increased. However, response to process transients slow.

Trace sulfur results

Monitoring and quantitation of low-level impurities, especially sulfur-containing compounds, is a significant area of study in fuel cell and related catalyst development. Many fixed-bed catalytic processes are involved in fuel processors; all are affected by sulfur. In addition, all fuel cell technologies are poisoned to varying degrees by H_2S and organo-sulfur [2]. In particular, proton exchange and phosphoric acid fuel cells are extremely sensitive due to the use of platinum in electrode assemblies. Odorants present in natural gas feed to a fuel processor must be removed to levels well below 1 ppm in low-temperature fuel cells, using activated carbon beds in many cases, prior to reforming [3]. Sulfur removal is a critical step in the conversion process, improving the performance of subsequent steps, such as catalytic or autothermal reforming. Figure 2 shows the monitoring of three signals: a) hydrogen sulfide H_2S, b) methyl (MeSH) and ethyl mercaptan (EtSH), plus dimethyl sulfide (DMS), c) carbonyl sulfide (COS) and tetrahydrothiophene (THT) in the low ppm range. Concentrations are shown in Table 3.

Table 3. Concentrations (ppm) of Sulfur Compounds Plotted in Figure 2

Step	H_2S	MeSH, EtSH DMS	COS, THT
1	2.0	6	4.0
2	2.5	7.5	5.0
3	2.8	8.4	5.6
4	3.5	10.5	7.0
5	4.0	12.0	8.0

Figure 3 shows results using helium as the matrix for seven sulfur compounds. Dimethyl disulfide is shown separately in Figure 4. Impressive sensitivities can be achieved with the RTGA when a simple inert gas matrix is used.

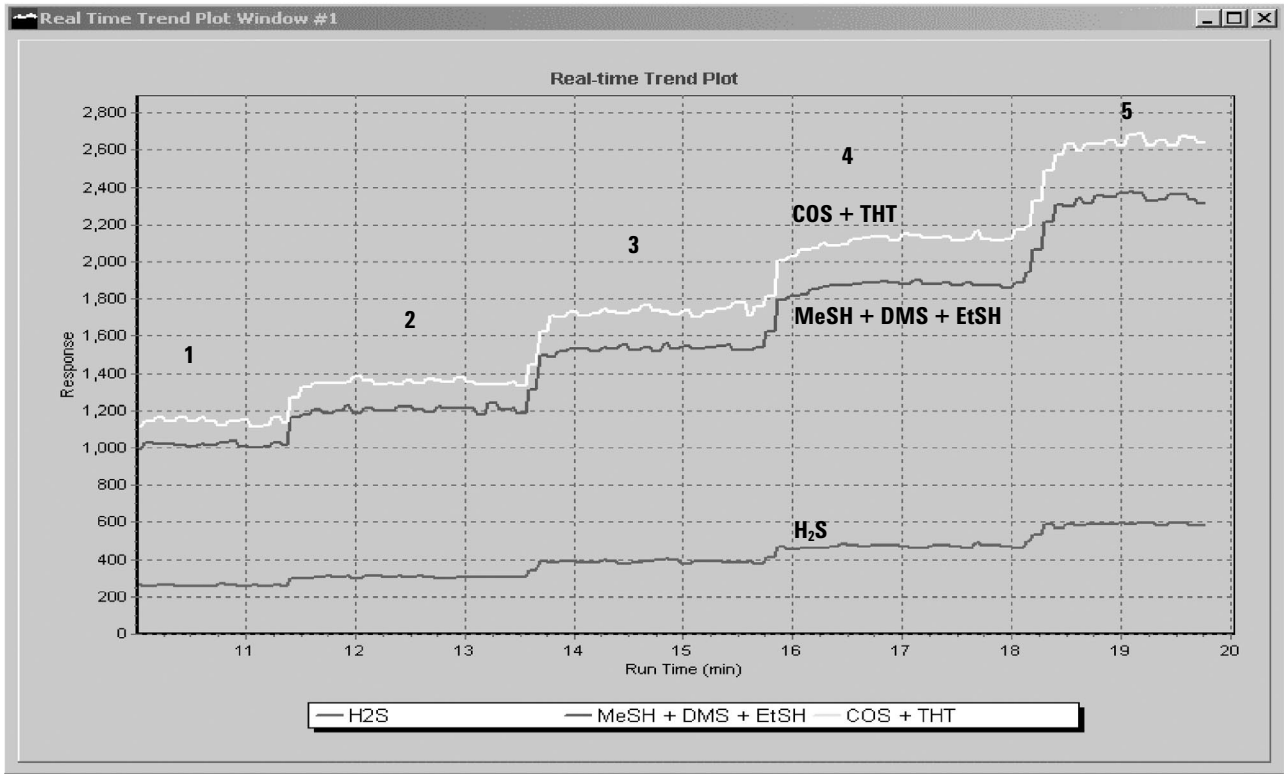

Figure 2. Real-time plot window of a five-step concentration run of sulfur compounds in helium. Table 3 shows concentrations for each step.

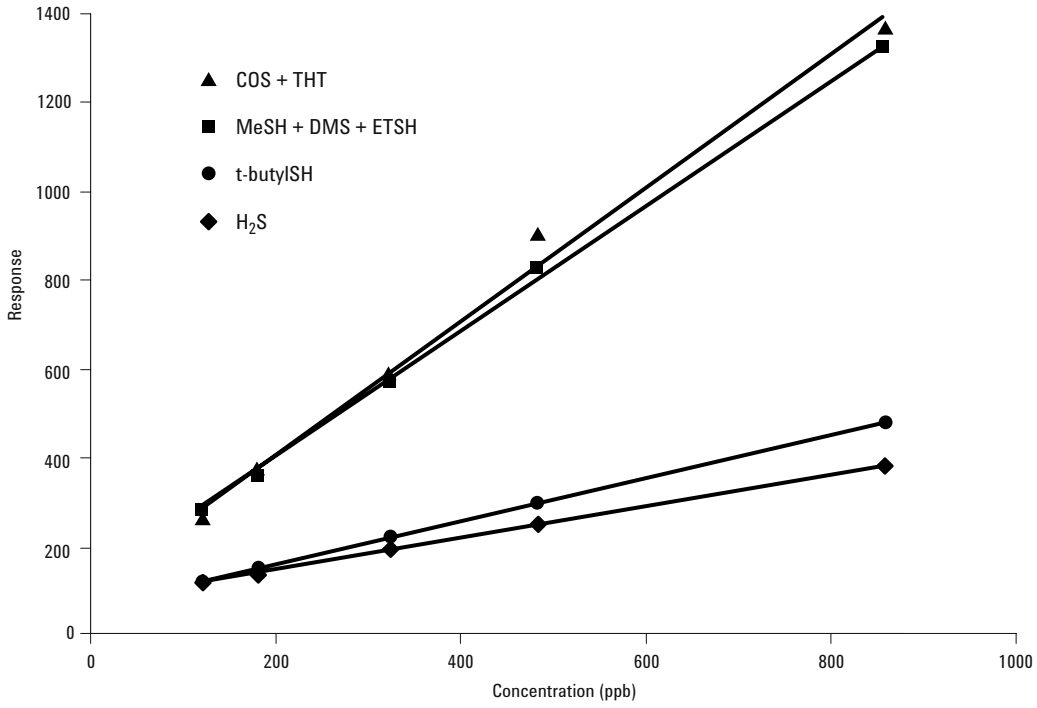

Figure 3. Calibration of selected sulfur compounds at the ppb level. SIM mode, 4000 ms dwell.

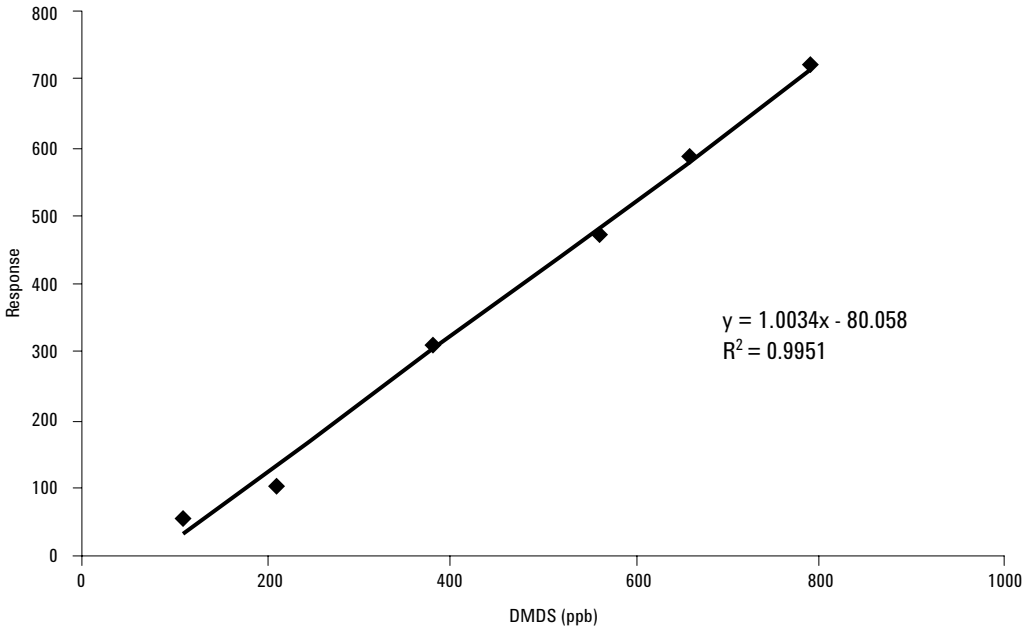

Figure 4. Dimethyl disulfide in helium at ppb levels.

Next, sulfur monitoring was evaluated in a fuel cell mix (50% H_2, 10% CO_2, 5% CH_4). Figure 5 shows a real-time plot of total sulfur (H_2S + MeSH + DMS + EtSH) in the fuel cell gas mixture at ppb levels. SIM mode was used, collecting data points every 45 seconds. Linearity was checked only in the ppm and ppb range because this is where most sulfur measurements are made. The intent was not to calibrate over the full dynamic range of the instrument, but rather to concentrate on impurity ranges that are likely to be encountered in real process monitoring situations. Calibration was accomplished with dynamic blending of the 5-ppm/component standard. Figure 6 shows an example of an H_2S calibration using the fuel cell mix as diluent. Due to its reactivity and adsorptivity, H_2S measurement at low levels is always challenging. The stainless steel sample path associated with the gas interface is apparently not adversely adsorbing H_2S that would adversely affect detection, or the continuous flow caused passivation.

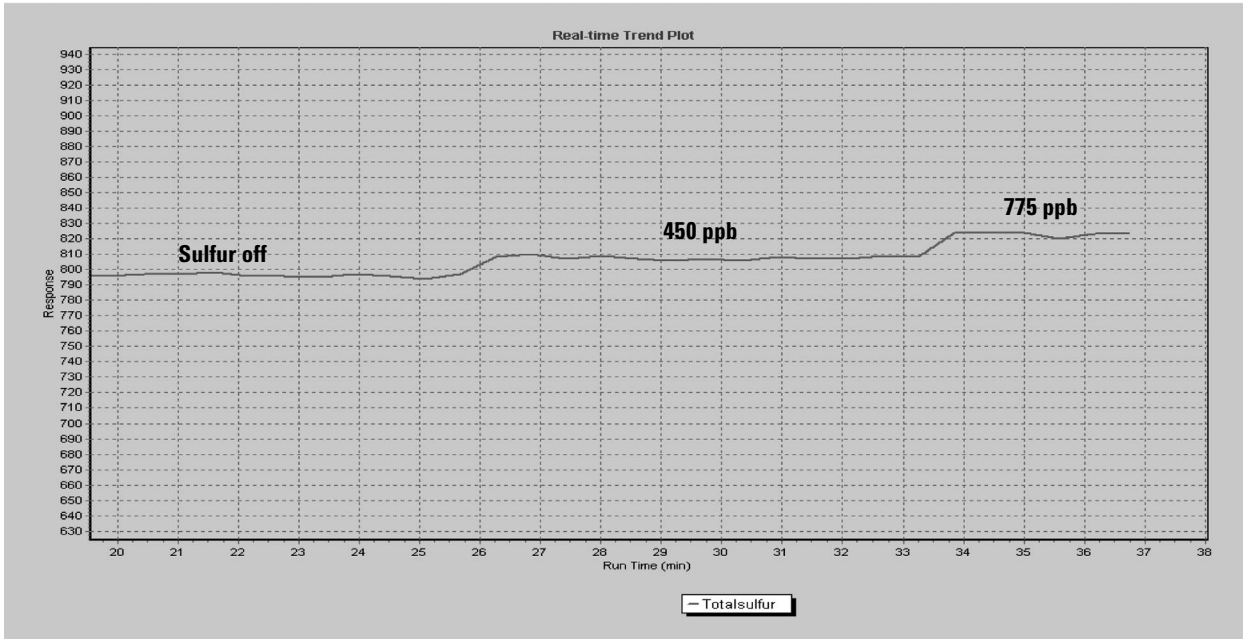

Figure 5. Monitoring sulfur at the ppb level in fuel cell gases.

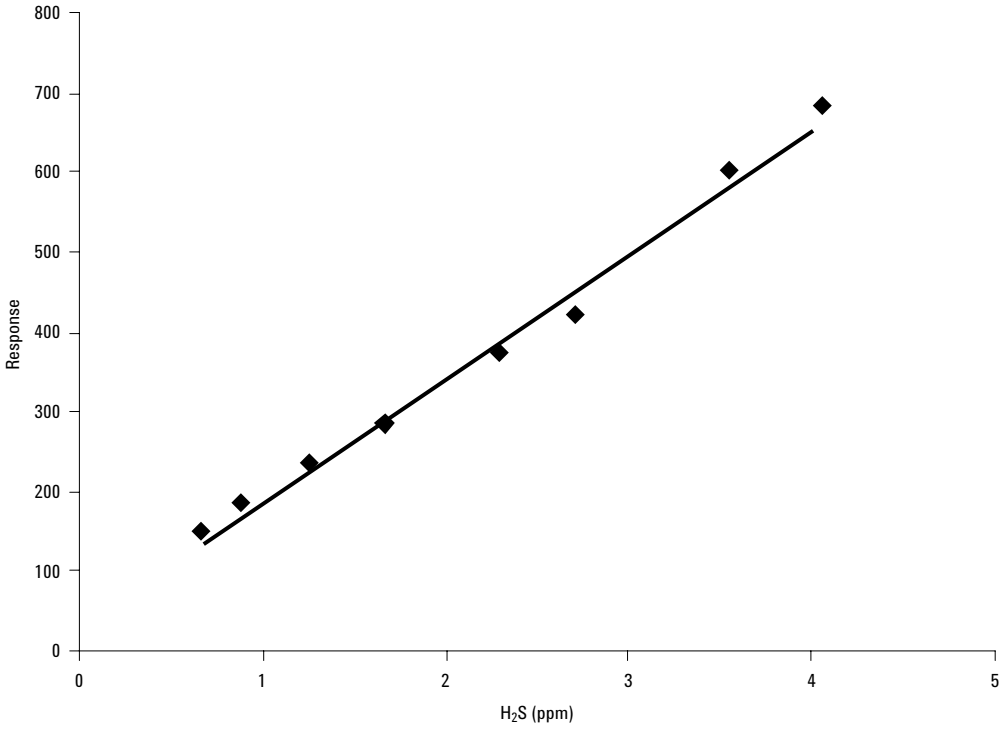

Figure 6. Calibration of hydrogen sulfide in a $H_2/CO_2/CH_4$ fuel cell mix.

High-hydrocarbon natural gas was the most complex matrix evaluated in this work. Most natural gas streams or reformed streams used to power fuel cells would most likely contain significantly less C2 to C5 hydrocarbons than found in the mixture used in this work, and as a result, even better detection limits for sulfur (than shown here) should be possible. Figure 7 shows a series of dilutions of the sulfur standard in natural gas. Ions monitored were 34, 47, and 60 for H_2S, mercaptans, and COS/THT, respectively. Concentrations were not step changed. Gradual changes were made as reflected in the plots showing a "bleed down" to the next level. Once a constant signal level was achieved, the next lower concentration was set as indicated. The H_2S concentration change from 600 ppb to 300 ppb is discernable, however, 300 ppb to 95 ppb is not. Concentration changes of 1.0 ppm to 285 ppb, and 700 ppb to 190 ppb can be easily seen for mercaptans (actually MeSH + DMS + EtSH + small contribution from THT), and COS + THT, respectively. Figure 8 shows a ppb- level calibration for ion 47 showing linearity, achieved by dynamic dilution of the sulfur standard in natural gas. Figure 9 shows a real-time plot of ion 60 (COS + THT) in natural gas at three concentrations.

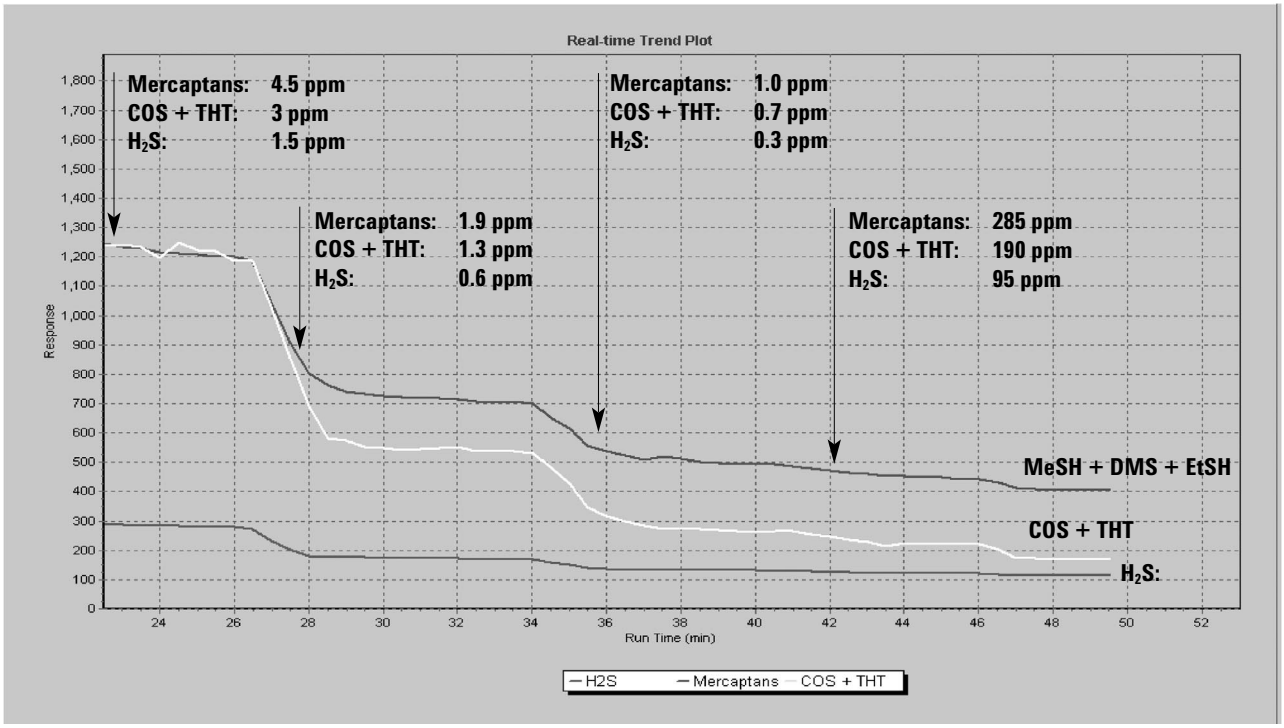

Figure 7. Real-time plot of sulfur compounds shows successive dilution in natural gas.

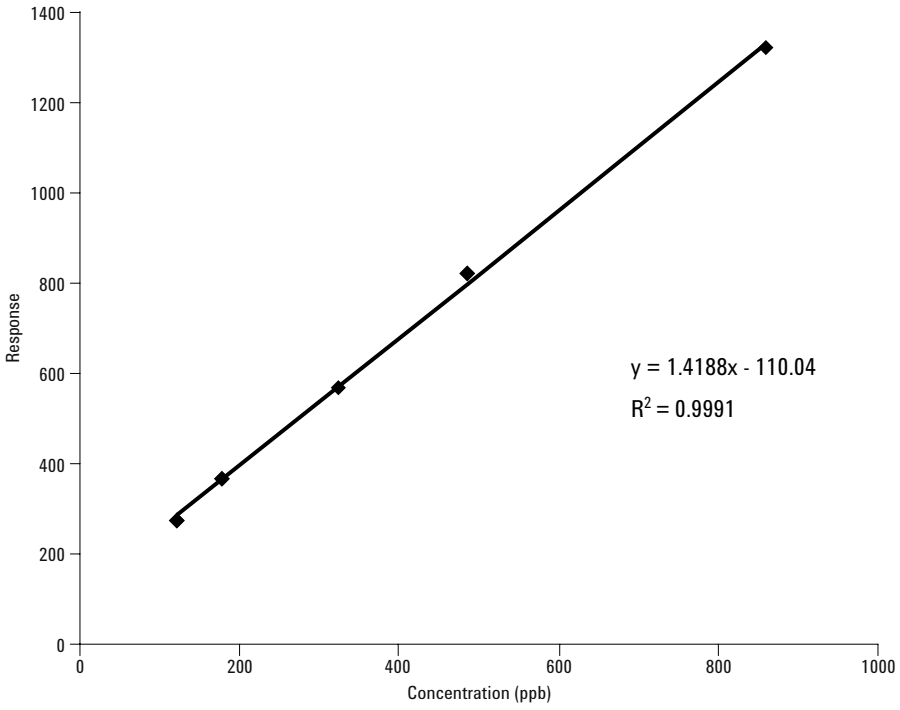

Figure 8. Calibration of ion 47 representing MeSH, EtSH, and DMS. Small contribution to ion 47 from THT also included.

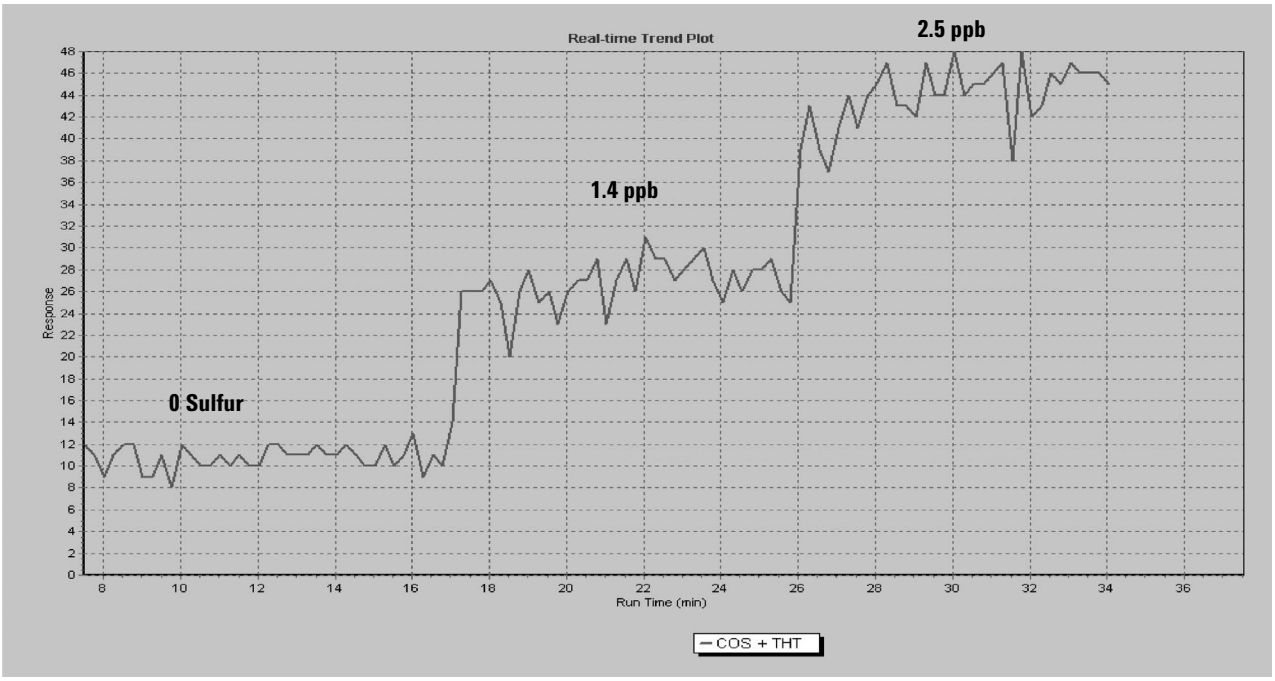

Figure 9. Real-time plot of ion 60. Data collected every 15 seconds in scan mode.

Background corrections

Background corrections may be useful when monitoring or quantifying impurities in gaseous streams. These are easily constructed in the calculation section of the RTGA method/edit section of the control software. In general, a defined signal can be treated in three ways with regards to background. These are: a) Use a defined signal mass response unmodified, b) Subtract out a constant (that is a response at defined impurity mass-produced by matrix alone), c) Subtract out a background ion that is representative of the background response from the matrix. RTGA background corrections can produce a signal that is a closer representation to the net analyte, (sulfur signal), especially with a continuously varying matrix. These corrections do not necessarily improve the signal-to-noise or detection limits. Actual detection limits are highly dependent on the matrix due to the complexity of fragmentation that occurs affecting ultimately the signal-to-noise ratio.

Conclusions

The Agilent 5000A RTGA is well suited to give detailed real-time qualitative and quantitative chemical impurity analysis of incoming fuels, processed fuels, and reformer output. Such information is of critical importance to fuel cell developers challenged with optimization of fuel clean-up processes and development of better catalytic materials throughout the fuel cell system. Impurities, such as hydrogen sulfide and common natural gas odorants, can be measured at ppb levels. Good linearity is seen for sulfur impurities in the concentration ranges of interest to the fuel cell industry. With response times as fast as 2 to 5 seconds, the system can monitor and capture rapid transients that could be missed by other monitoring equipment. The system should also prove useful in the evaluation of new anode materials and membrane electrode assemblies (MEAs).

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