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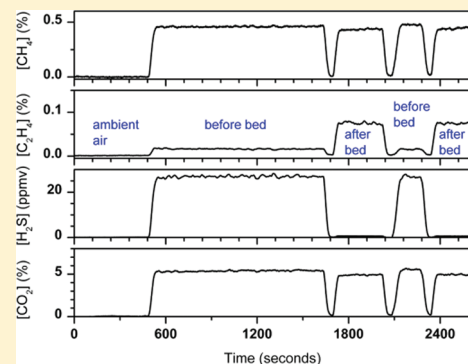
Rapid, Online Quantification of H₂S in JP-8 Fuel Reformate Using Near-Infrared Cavity-Enhanced Laser Absorption Spectroscopy

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ABSTRACT: One of the key challenges in reforming military fuels for use with fuel cells is their high sulfur content, which can poison the fuel cell anodes. Sulfur-tolerant fuel reformers can convert this sulfur into H₂S and then use a desulfurizing bed to remove it prior to the fuel cell. In order to optimize and verify this desulfurization process, a gas-phase sulfur analyzer is required to measure H₂S at low concentrations (<1 ppm_v) in the presence of other reforming gases (e.g., 25–30% H₂, 10–15% H₂O, 15% CO, 5% CO₂, 35–40% N₂, and trace amounts of light hydrocarbons). In this work, we utilize near-infrared cavity-enhanced optical absorption spectroscopy (off-axis ICOS) to quantify H₂S in a JP-8 fuel reformer product stream. The sensor provides rapid (2 s), highly precise (± 0.1 ppm_v) measurements of H₂S in reformat gases over a wide dynamic range (0–1000 ppm_v) with a low detection limit ($3\sigma = \pm 0.09$ ppm_v in 1 s) and minimal cross-interferences from other present species. It simultaneously quantifies CO₂ ($\pm 0.2\%$), CH₄ (± 150 ppm_v), C₂H₄ (± 30 ppm_v), and H₂O (± 300 ppm_v) in the reformed gas for a better characterization of the fuel reforming process. Other potential applications of this technology include measurement of coal syngas and H₂S in natural gas. By including additional near-infrared, distributive feedback diode lasers, the instrument can also be extended to other reformat species, including CO and H₂.



There is considerable interest in developing cleaner, more efficient fuel sources for next-generation power generators. One promising source that leverages the existing fossil fuel infrastructure involves generating hydrogen via the reformation of petroleum (e.g., diesel, gasoline, kerosene, and military logistic fuels) or gasification of coal (e.g., coal syngas). This hydrogen can then be used by fuel cells to generate electricity with very high efficiencies, approaching 60%.¹ The U.S. military is also interested in utilizing fuel cells because of their portability, quiet operation, and minimal detectable emissions. For these applications, one approach is to use military logistic fuels (e.g., JP-8), because of their widespread availability in the battlefield, to fuel solid oxide fuel cells (SOFCs).

One of the key challenges in using military fuels (or coal syngas) is their high sulfur content. This sulfur can severely poison the reforming catalysts,² and extensive research has focused on developing improved, sulfur-tolerant catalytic materials,³ reforming methods,⁴ pretreatments,⁵ and fuel desulfurization techniques.⁶ For example, one promising reforming method involves using a metal-mesh coated with a catalyst to improve heat and mass transfer via autothermal reforming (ATR).⁷ This methodology has been demonstrated to withstand high-sulfur content fuels (~ 400 ppm_w) for long run times (1000 h) and primarily converts the sulfur content of the fuel to H₂S. Under typical reactor operating conditions, the total sulfur concentration in the reformed gas (i.e., H₂S, COS) is approximately 10% of the liquid fuel sulfur content due to dilution and molar expansion. Both H₂S and COS damage the anode materials of most SOFCs,^{8,9} and a sulfur sorbing

bed is required between the fuel reformer and SOFC to reduce the sulfur levels (typically to below 1 ppm_v). The lifetime of the desulfurizer bed depends on the sulfur content of the fuel and the size of the bed and is typically targeted for ~ 1000 h on JP-8 with 100 ppm_w sulfur. These beds require periodic replacement or regeneration to prevent H₂S breakthrough.

In order to optimize and verify the desulfurization process, and avoid fuel cell stack exposure to sulfur, a gas-phase sulfur sensor is required to measure H₂S at low concentrations (<1 ppm_v) in the presence of other reforming gases (e.g., 25–30% H₂, 10–15% H₂O, 15% CO, 5% CO₂, 35–40% N₂, and trace amounts of light hydrocarbons). Currently, most gas-phase sulfur sensors are based on ultraviolet absorption or semiconductor metal oxide films. The former technique is widely used in industry, but, because of interfering UV absorptions from high-levels of CO₂, it is not well-suited for fuel reforming applications. The latter technology relies on using a doped metal oxide film (e.g., SnO₂ doped with CuO, AgO, Ag, and ZrO) that is deposited onto a glass substrate.¹⁰ When H₂S adsorbs onto the film and reacts with the substrate, the electronic resistance of the film changes. These sensors have several advantages including a very small form factor (e.g., chip-based), low detection limits (e.g., subppm_v for recent micromachined sensors¹¹), and ability to work at high temperatures. Moreover, recent advances using smaller dopants and

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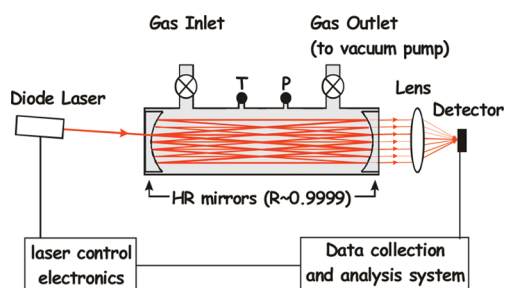


Figure 1. Schematic diagram of the off-axis integrated cavity output spectroscopy (off-axis ICOS) technique.

thinner films have reduced the detector response and recovery times to less than 20 and 60 s respectively. However, these sensors still have several limitations that make them nonideal for JP-8 reformate analysis. Foremost, these detectors exhibit substantial cross-interferences from water vapor and CO, which are prevalent in the reformate gas stream. Moreover, the response of semiconductor metal oxides to H₂S is highly nonlinear, and they typically provide accurate results over a small dynamic range (e.g., 0–10 ppm_v H₂S).¹¹

In this work, we utilize near-infrared cavity-enhanced optical absorption spectroscopy to quantify H₂S in a JP-8 fuel reformate stream. The sensor provides rapid (2 s), highly precise (± 0.1 ppm_v) measurements of H₂S in the reformer product gases over a wide dynamic range (0–1000 ppm_v) with a low detection limit ($3\sigma = \pm 0.09$ ppm_v in 1 s). The utilization of a chemometric data analysis algorithm minimizes H₂S measurement errors from interfering absorptions of other present species. It also simultaneously quantifies CO₂ ($\pm 0.2\%$), CH₄ (± 150 ppm_v), C₂H₄ (± 30 ppm_v), and H₂O (± 300 ppm_v) in the reformed gas for a better characterization of the fuel reforming process with high precision.

METHODS

Off-Axis ICOS Analyzer. We have utilized a cavity-enhanced optical absorption spectroscopy termed off-axis integrated cavity output spectroscopy (off-axis ICOS) to simultaneously quantify H₂S, CO₂, CH₄, C₂H₄, and H₂O using near-infrared optical transitions. The technique, illustrated in Figure 1, has been described elsewhere,¹² and only a brief overview will be provided below. A temperature-controlled, tunable, distributive-feedback (DFB) diode laser operating near 1.590 μm was coupled into a 28 cm long high-finesse optical cavity consisting of two highly reflective mirrors ($R \sim 99.995\%$ as determined by cavity ringdown spectroscopy¹³) that provided an effective optical path length of 5.6 km. Light transmitting through the cavity was focused onto a highly amplified InGaAs detector. A diaphragm pump continuously flowed gas through the cavity at 0.5–1.0 L/min, and a proportional solenoid valve retained the pressure inside the cavity at 80 Torr, assuring good absorption peak contrast.

The laser frequency was repeatedly tuned over 20 GHz to span over H₂S, CO₂, CH₄, C₂H₄, and H₂O molecular absorption features (Figure 2). Each scan required 5 ms (e.g., 200 Hz laser tuning), and 200 transmission spectra (1 s) were averaged to achieve a sufficient signal-to-noise ratio on the H₂S absorption feature. The averaged spectra were stored for off-line, chemometric data analysis.

Chemometric Data Analysis. The gas mixture resulting from JP-8 fuel reforming contains many compounds including N₂, H₂,

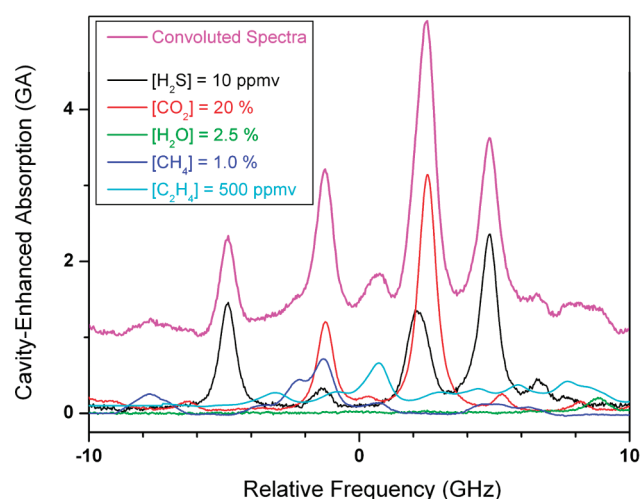


Figure 2. Measured basis sets of known concentrations of H₂S, CO₂, H₂O, CH₄, and C₂H₄ in air for the chemometric fitting routine. The measured cavity-enhanced absorption spectra of the constituents are linearly weighted to determine the convolved spectrum of the mixture. The y-axis is the cavity gain factor, G , multiplied by the single pass absorption, A . The former is given by $G = (R/(1 - R))$ where R is the mirror reflectivity.

CO, H₂O, CO₂, CH₄, H₂S, C₂H₄, and other small hydrocarbons. Some of these gases (e.g., N₂, H₂, CO, and trace levels of larger hydrocarbons) do not have appreciable optical absorptions near 1.59 μm . The other gases (e.g., H₂S, CO₂, CH₄, C₂H₄, and H₂O), however, do absorb in the probed spectral region, and the data analysis routine must be able to simultaneously fit several absorbing species. A chemometric data analysis routine^{14,15} was employed to analyze the complex measured absorption spectra. This routine has been described in detail elsewhere,¹⁶ and only a brief overview will be provided below. In this model, the total per-pass absorption spectrum, $A(\nu)$, is expressed as a weighted sum of the absorption spectra of the mixture components:

$$A(\nu) = c_0 A_0(\nu) + c_1 A_1(\nu) + c_2 A_2(\nu) + \dots$$

where ν is the laser frequency, c_n is the coefficient that corresponds to the concentration of the n th species, and $A_n(\nu)$ is the absorption spectrum of the n th species in the absence of other interfering gases. These absorption spectra were empirically determined by filling the cavity with certified concentrations of mixture components diluted in dry air and measuring the cavity-enhanced absorption spectra shown in Figure 2. Note that the spectra were taken under similar conditions (e.g., sample concentration, pressure, and gas temperature in the cavity) to extractively sampled JP-8 reformate gases. The H₂S, CO₂, and H₂O spectra all have discrete absorption features that consist of a multitude of Voigt profiles. Conversely, the CH₄ and C₂H₄ absorption spectra consist of much broader features that result from the blending of many adjacent absorption lines. Nitrogen (N₂), hydrogen (H₂), and carbon monoxide (CO) have no absorption features in this scan region. Note that, in this spectral region, the absorption spectra of most of these compounds (e.g., H₂S, CH₄, and C₂H₄) are poorly characterized in terms of line strengths, absorption frequencies, and ground-state energy levels. The chemometric data analysis strategy avoids having to characterize each of these and instead empirically includes the entire spectrum for a specific compound. However, the unknown

Table 1. Validation of the Chemometric Data Analysis Routine^a

	gas blend no. 1		gas blend no. 2		gas blend no. 3	
	actual	measured	actual	measured	actual	measured
H ₂ S (ppm _v)	0.47	0.58 ± 0.01	1.34	1.42 ± 0.01	0.46	0.55 ± 0.02
CO ₂ (%)	13.3	12.95 ± 0.03	13.3	13.02 ± 0.03	17.8	17.65 ± 0.02

^a Due to the uncertainty of the mass flow controlling system, the uncertainty for the actual concentrations for each species is typically ±2%.

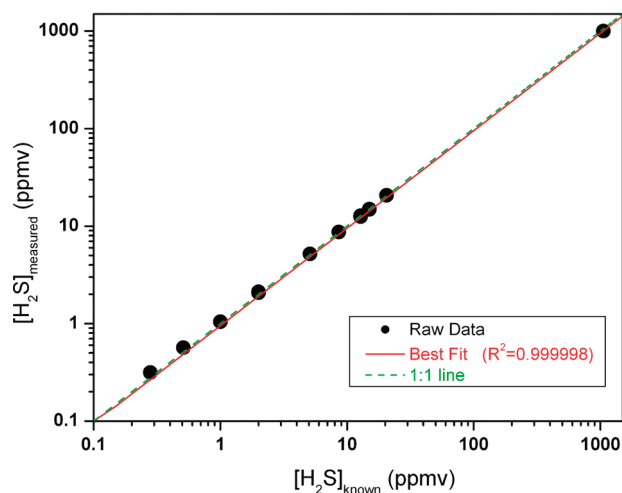


Figure 3. Linearity measurements for H₂S with the off-axis ICOS sensor. The sample was diluted from a cylinder with 1054 ppm_v H₂S in N₂ with mass flow controllers (MFC) and demonstrates the instrument's very wide dynamic range.

mixture must be measured under similar conditions (e.g., temperature and pressure) to that of the basis sets.

The absorption spectrum and chemometric data fit are also shown in Figure 2. The analysis strategy was validated by synthesizing three gas mixtures of low concentration H₂S blended with >15% CO₂, and ~2% H₂O, which represent typical gas mixtures in JP-8 fuel reformat stream. The analysis results are presented in Table 1. The measurements of H₂S and CO₂ are consistent with expectations to 100 ppb_v and ~0.3% respectively. Since the same gas bottles were used to develop the chemometric model and make the gas blends, this test does not provide a true measure of accuracy but instead demonstrates that the chemometric algorithm can distinguish components with minimal cross-interferences. Note that the uncertainty of the mass flow controlling system for each species is approximately ±2% (1σ).

RESULTS AND DISCUSSION

Laboratory Measurements. The accuracy, precision, linearity, dynamic range, detection limit, time response, and zero drift of the sensor were determined by repeated, long-term measurements of certified gas standards and manufactured gas blends. Foremost, a 1054 ppm_v H₂S/N₂ gravimetric standard was accurately (±1%) diluted with N₂ to produce H₂S concentrations ranging from 0–1054 ppm_v. Figure 3 indicates that the sensor is highly linear ($R^2 = 0.999998$) over this very wide dynamic range. The measured value of H₂S is typically accurate to within 0.1 ppm_v of the true value from 0–10 ppm_v. The slight positive offset at low H₂S levels

may be due to inaccuracies in the dilution of a concentrated standard, and more dilute standards can be employed in the future to further calibrate the instrument at low concentrations. Similar experiments were performed using controlled dilutions of a gravimetric CO₂ standard (20%/air), and a measurement precision of ±0.2% (1σ in 1 s) was empirically determined. For CH₄ and C₂H₄, basis sets were produced from mixtures containing 9980 ppm_v/N₂ and 500 ppm_v/N₂, respectively. The analyzer was not tested on controlled dilutions of these gases, and the measurement accuracy for these species was not verified; however, the measurement signal-to-noise ratio suggests a precision ±150 ppm_v and ±30 ppm_v for CH₄ and C₂H₄ (1σ in 1 s). A dewpoint generator was used to vary H₂O levels from 0–22 000 ppm_v in dry air, providing a measurement precision of ±300 ppm_v. These precisions are limited by signal-to-noise ratio of the cavity-enhanced absorption signal and associated parameters (e.g., temperature, pressure, and effective optical path length). Note that, because single gravimetric gas standards were sequentially diluted, the accuracy of the instrument for single components is limited to the ±1% accuracy of the standard.

The stability and precision of the sensor under the relevant sample conditions was determined by measuring a 0.08 ppm_v H₂S, 19.5% CO₂, and 2.5% H₂O gas blend for 3200 s before switching the sample to the ambient air (H₂S ~ 0 ppm_v). The measured data and resultant Allan deviation plot (Figure 4a) demonstrate an analyzer precision of ±13 ppb_v H₂S in 1 s (1σ) and improved precision with increased measurement time up to 200 s, where a measurement precision of ±2 ppb_v H₂S is achieved. The instrument's time response is mainly limited by the flow rate at which gas is transferred through the measurement cell (e.g., pump speed). For the gas cell (~380 cm³) and pump (11 SLPM) used in these laboratory studies, the 1/e time response of the analyzer was determined to be 2.1 s (Figure 4b) by rapidly (<0.1 s) switching the inlet from a 4.2 ppm_v H₂S standard to dry air. In the JP-8 fuel reformer studies presented below, a smaller pump (5 SLPM) was employed to avoid disrupting the reformer gas flow, increasing the instrument response time to ~4 s. Likewise, a large scroll pump (600 SLPM) could also be used to decrease the response time to <0.05 s for flux measurements or rapid industrial process control.

H₂S degrades in the presence of stainless steel. This degradation rate was determined to be 20 h (1/e) by trapping a 1 ppm_v H₂S sample in the cell and making continuous measurements over 28 h. Thus, the loss due to H₂S degradation is negligible during the first 400 s of measurement (<0.5%).

Measurements in a JP-8 Fuel Reformer. The sensor was interfaced to a 5 kW (thermal) autothermal fuel reformer (Precision Combustion, Incorporated) using standard 1/8 in. Swagelok connections. Sample gas was pulled from the reformer exhaust by a small diaphragm pump in the analyzer. An "open-split" configuration with a low flow rate assured that ambient air was not entrained in the sampled gas. The sample was passed through a chiller to remove water vapor to a dewpoint of <8 °C

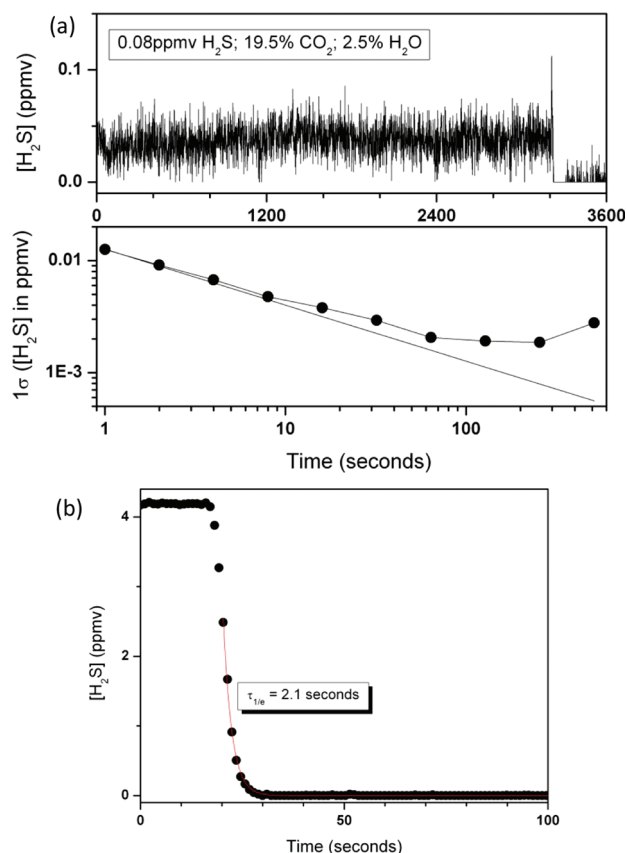


Figure 4. (a) A ~1-h measurement of ~0.08 ppm_v H₂S blended with 19.5% CO₂ and 2.5% H₂O before the sample was switched to the room air. The results prove that the sensor has high stability, high precision (<15 ppb_v at 1 s average), and high sensitivity (<80 ppb_v). Note that the Allan deviation plot does not include the room air measurements and that the sample concentration is below the stated accuracy of the analyzer (± 0.1 ppm_v). (b) With the flow rate of 11 SLPm/min, the sensor has a 1/e response time of ~2.1 s.

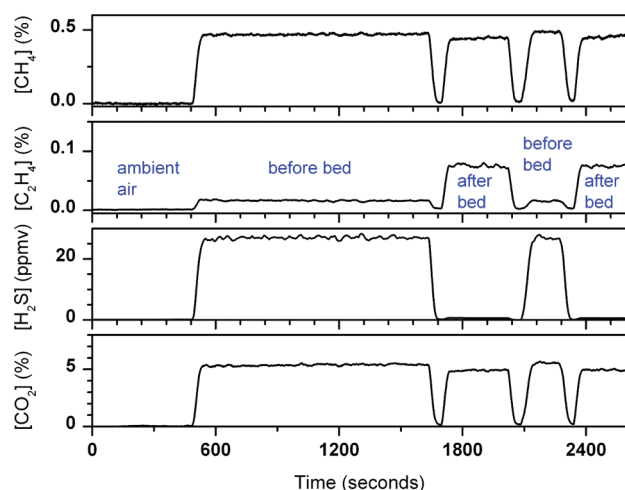


Figure 5. An example of in situ measurements of the product stream from a running JP-8 fuel reformer by off-axis ICOS. There are three different gases sampled as indicated in the figure: 1, ambient air only; 2, gas samples before entering the desulfurizing bed; 3, gas samples after leaving the desulfurizing bed. The gas samples were also measured with micro-GC for the comparison between two different sensors.

Table 2. Comparison between Measurements Made in the JP-8 Fuel Reformer Product Stream by Off-Axis ICOS and Micro-GC

	before desulfurizer bed		after desulfurizer bed	
	off-axis ICOS	GC	off-axis ICOS	GC
H ₂ S (ppm _v)	27.00 \pm 0.42	—	0.63 \pm 0.02	—
CO ₂ (%)	5.42 \pm 0.06	5.8 \pm 0.1	4.92 \pm 0.04	5.1 \pm 0.1
CH ₄ (%)	0.460 \pm 0.005	0.38 \pm 0.01	0.435 \pm 0.005	0.42 \pm 0.01
C ₂ H ₄ (ppm _v)	164 \pm 8	84 \pm 13	760 \pm 23	243 \pm 10
H ₂ O (%)	0.71 \pm 0.01	—	0.83 \pm 0.01	—
C ₂ H ₆ (ppm _v)	—	240 \pm 10	—	329 \pm 4
C ₃ H ₆ (ppm _v)	—	17 \pm 1	—	23 \pm 1
H ₂ (%)	—	29.2 \pm 0.2	—	28.6 \pm 0.1
N ₂ (%)	—	45.4 \pm 0.2	—	45.6 \pm 0.1
CO (%)	—	19.3 \pm 0.2	—	20.2 \pm 0.1

(corresponding to <1.08% of water). The instrument exhaust was directed through an open-split to a micro gas chromatography (micro-GC) instrument (Agilent Series 3000) to measure the dominant reformat gases and trace hydrocarbons (e.g., H₂, N₂, CO, CO₂, CH₄, C₂H₆, and C₂H₄). The reformer was operated on 360 ppm_w sulfur JP-8 at a 5 kW fuel input. Fuel, water, and air were flowed at 7 g/min, 8.1 mL/min, and 26.7 slpm, respectively. The oxygen-to-carbon and steam-to-carbon ratios were 0.93 and 0.90, respectively.

Typical measured data is shown in Figure 5 and presented in Table 2. In this run, the measurement point was repeatedly switched between ambient air, and upstream and downstream of the desulfurizer bed. As expected, the ambient air measurements had very low concentrations of all reformat species (e.g., H₂S < 0.1 ppm_v) except water vapor (~1%, consistent with the indoor absolute humidity). Upstream of the desulfurizer bed, the H₂S level approached 27.00 \pm 0.42 ppm_v (1 σ). The H₂S value is consistent with the expected sulfur concentration in the gas phase after dilution and molar expansion based upon using 360 ppm_w sulfur from the JP-8. In order to close the sulfur balance, a detection and quantification of COS is required and will be further studied in other efforts. The measured CH₄ and CO₂ levels were 4600 \pm 50 ppm_v and 5.42 \pm 0.06%, respectively, in good agreement with the micro-GC results of 3800 \pm 100 ppm_v and 5.8 \pm 0.1%, respectively, obtained via parallel GC measurement at the same time. Finally, the off-axis ICOS analyzer measured a C₂H₄ concentration of 165 \pm 8 ppm_v, whereas the GC measured a C₂H₄ concentration of 84 \pm 13 ppm_v. The source of this discrepancy is still uncertain and may be due to inaccuracy of the off-axis ICOS analyzer, cross-interferences between C₂H₄ and other broadband absorbers in the off-axis ICOS analyzer, or interferences between C₂ species in the GC. Downstream of the desulfurizer bed, the sensor measured 0.63 \pm 0.02 ppm_v H₂S, 4350 \pm 50 ppm_v CH₄, 4.92 \pm 0.04% CO₂, and 760 \pm 23 ppm_v C₂H₄. These measurements are in good agreement with the expected or GC-measured values of <1 ppm_v H₂S, 4200 \pm 100 ppm_v CH₄, and 5.1 \pm 0.1% CO₂. Again, the GC-measured C₂H₄ concentration of 243 \pm 10 ppm_v differs from the off-axis ICOS analyzer. The analyzer clearly indicates the efficiency of the desulfurizer bed in removing H₂S to a concentration sufficient for most SOFCs. Note that the GC did not provide water concentrations, and thus comparable H₂O data was not available.

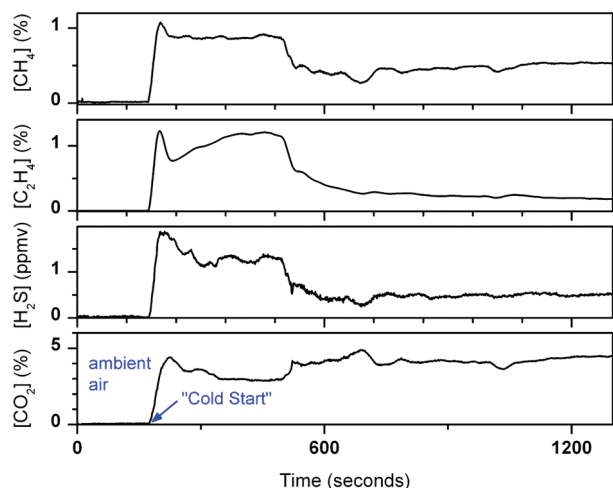


Figure 6. An example of in situ monitoring of H_2S , CO_2 , CH_4 and C_2H_4 during the cold-start of a JP-8 fuel reformer by off-axis ICOS. During the cold-start, the concentrations of H_2S , C_2H_4 , and CH_4 are much higher than before the reformer is warmed (~ 600 s).

One of the benefits of using the laser-based sensor over traditional GC measurements is the measurement time response (e.g., <5 s versus >60 s). This faster response allows for the sensor to quantify transient behavior in the fuel reformer (e.g., initial reactor start-up). In order to demonstrate this feature, the fuel reformer was allowed to cool to room temperature and measurements were made downstream of the desulfurizer bed as the reformer lighted-off and warmed up to its steady operational temperature. The data (Figure 6) show that, initially, H_2S levels downstream of the desulfurizing bed approach ~ 1.9 ppm, when the unit is first activated, but rapidly (<5 min) decrease to <0.5 ppm, despite the large upstream values (e.g., 27 ppm), suggesting that the desulfurizer bed is very efficient at removing H_2S even during the reactor start-up period. Moreover, CH_4 and C_2H_4 approach 9000–10000 ppmv during the warm-up transient. These high levels may be important to specific fuel reforming applications, where coking can limit efficiencies.

CONCLUSION

We have demonstrated the accurate, rapid quantification of H_2S , along with CO_2 , CH_4 , C_2H_4 , and H_2O in a JP-8 fuel reformat stream using off-axis ICOS. This sensor can be used to actively monitor desulfurizers and optimize the fuel reforming process. Additionally, by making measurements before the desulfurizing bed, the analyzer can be used to gauge the sulfur content of fuels. Other potential applications of this technology include measurement of coal syngas and H_2S in natural gas. Proximate H_2S features near $1.578\ \mu\text{m}$ have substantially weaker, interfering CH_4 absorptions, and preliminary work has shown that these absorptions can be used to quantify low levels (<1 ppm) of H_2S in pure CH_4 . By including additional near-infrared DFB diode lasers, the instrument can also be extended to other reformat species, including CO and H_2 .¹⁷

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