Compact Multi-Channel Infrared Laser Absorption Spectrometer for Spacecraft Fire Safety Monitoring

Ryan M. Briggs,[1] Mathieu Fradet,[2] Clifford Frez,[3] and Siamak Forouhar[4]
Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109, USA

Randy D. May[5]
Port City Instruments, Wilmington, NC 28411, USA

We report on the design of a six-channel tunable laser absorption spectroscopy instrument for measuring ambient gas-phase concentrations of CO, HCl, HCN, HF, CO_2, and O_2 in spacecraft environments. Monitoring of these compounds can provide early warning detection of fire events while also indicating what materials have been exposed to heating. Continued post-fire monitoring of these hazardous gases can also facilitate safe and effective cleanup. The sensor is a miniaturized version of a five-channel prototype that was previously validated in ground-based oxidative pyrolysis tests. Here, we describe absorption line selection and theoretical detection limits for a sensor with reduced absorption pathlengths for each detection channel, which allows for a substantial reduction in overall instrument footprint. Ultimately, the new instrument is designed to be used in fire safety tests conducted by NASA, where various materials will undergo oxidative pyrolysis in an unmanned spacecraft returning from low Earth orbit.

© 2016 California Institute of Technology. Government sponsorship acknowledged.

Nomenclature

TLAS	=	tunable laser absorption spectrometer
CO	=	carbon monoxide
CO_2	=	carbon dioxide
O_2	=	oxygen (gas)
HCN	=	hydrogen cyanide (gas)
HCl	=	hydrogen chloride (gas)
HF	=	hydrogen fluoride (gas)
SMAC	=	Spacecraft Maximum Allowable Concentration
H_2O	=	water (vapor)
ppm	=	part per million (by volume)
FPGA	=	field-programmable gate array
2f	=	second harmonic (detection)
DC	=	direct current
PVC	=	polyvinyl chloride
AWG	=	American wire gauge
DFB	=	distributed feedback (laser)
QC	=	quantum cascade (laser)
IC	=	interband cascade (laser)

[1] Microdevices Engineer, JPL Microdevices Laboratory, Mail Stop 302-222.
[2] Microdevices Engineer, JPL Microdevices Laboratory, Mail Stop 302-205A.
[3] Microdevices Engineer, JPL Microdevices Laboratory, Mail Stop 302-205E.
[4] Deputy Director, JPL Microdevices Laboratory, Mail Stop 302-227.
[5] President, Port City Instruments, LLC.

I. Introduction

As future human spaceflight missions occur over longer durations and greater distances from Earth, spacecraft safety systems must be developed with the capability for long-term accuracy, stability, and maintenance-free operation. Monitoring of combustion products is important for early detection of accidental fires as well as evaluation of air quality following a fire event.[1,2] Currently, electrochemical sensors (Industrial Scientific CSA-CP) are used on the International Space Station for monitoring CO, CO_2, O_2, and HCN – gases that are generated or consumed during oxidative pyrolysis of various polymers. These sensors are portable and consume little power; however, they require periodic maintenance and calibration, and are generally inoperable following exposure to vacuum. In contrast, tunable laser absorption spectroscopy (TLAS) sensors can selectively detect gases at low concentrations over a wide range of total pressure[3,4] and, depending on component reliability, can operate for thousands of hours without maintenance or calibration.

We recently reported the development and testing of a five-channel TLAS sensor designed to continuously monitor ambient concentrations of CO, HCl, HCN, HF, and CO_2,[5] with low-level detection limits below the standard Spacecraft Maximum Allowable Concentrations (SMACs).[6] To achieve maximum sensitivity with a relatively compact two-pass absorption cell configuration, this sensor used a dedicated single-mode mid-infrared laser for each gas, with each laser wavelength selected to overlap strong absorption lines while avoiding interference from other gases found in human-occupied spacecraft environments. Figure 1 shows the absorption line strength of the target molecules at near- to mid-infrared frequencies. Absorption lines of H_2O, the main interfering gas in this regime, are also shown. Due to the more than order-of-magnitude greater line strength of the fundamental lines in the mid-infrared regime compared with overtone absorption lines at higher frequencies, the target gases can be unambiguously detected at part-per-million (ppm) levels near standard pressure over a relatively short optical pathlength. Using current tuning to sweep the emission wavelength of each laser across the target molecular absorption line, the TLAS instrument measured both on- and off-line absorption. As reported in Ref. 5, each TLAS sensor channel was calibrated over a broad range of concentration using reference gases. The instrument was then used to monitor emissions generated by heating several relevant spacecraft materials in an enclosed test chamber.

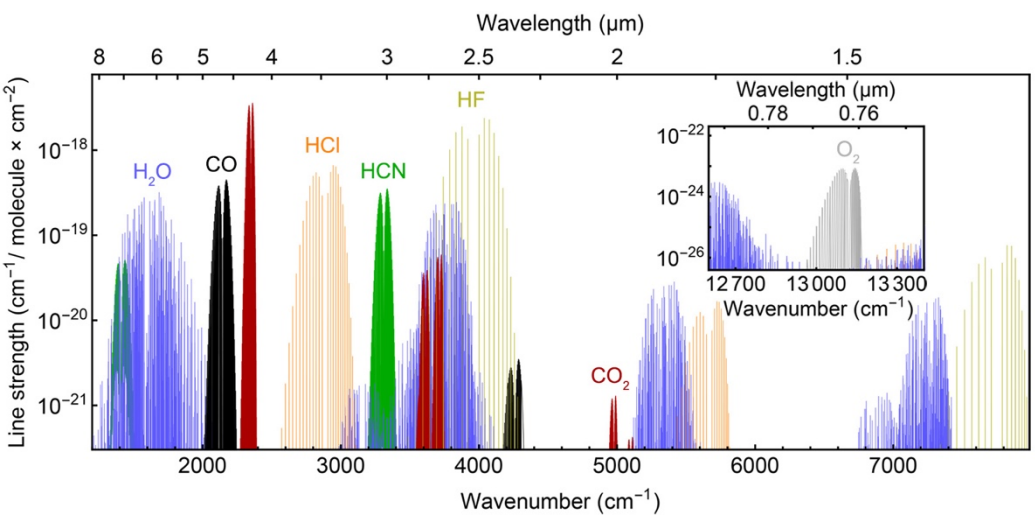

Figure 1. *Absorption lines of H_2O and the six gases targeted by the TLAS combustion product sensor in the near- to mid-infrared wavelength range. (Line strengths were obtained from the HITRAN Database.)*

Here, we report on the development of a next-generation sensor based on the same principles of operation but optimized for reduced volume and power consumption. In addition to the five species targeted by the first TLAS instrument, the new sensor is designed to measure O_2 concentrations near ambient levels. We focus specifically on the design of the absorption cell based on refined requirements for minimum detection levels of each target gas as well as findings from testing the first instrument.

II. Instrument Design

The multi-channel TLAS instruments described here are based on an open-cell configuration, where measurements are collected at the same pressure and temperature as the surrounding environment. The previous five-channel

instrument is shown in Fig. 2(a). Five lasers and five detectors were mounted to a single heat-sink assembly positioned 25 cm from a mirror bank, forming a 50-cm two-pass optical path. The concentrations of the target gases were determined by current-tuning the emission wavelength of each laser across each target absorption line with a scan period of 200 ms. Five separate FPGA boards supplied current to the lasers and recorded the corresponding detector response. A linear current ramp was applied to each laser with an additional small-amplitude sinusoidal current modulation, with a small frequency offset on each channel to avoid crosstalk. The detector signals were demodulated at twice the modulation frequency, producing the second-harmonic (2f) line shape of the target absorption feature.[7] The quasi-DC response was also recorded after passing the signal through a low-pass filter. The 2f and DC spectra from each channel, along with the on-board pressure and temperature sensor readings, were then transmitted by a data acquisition board to a computer for processing.

For the testing reported in Ref. 5, the 2f amplitude was used with total pressure and temperature corrections to determine the concentration of each target gas. As an example of the performance of the first-generation multi-channel TLAS instrument, Fig. 2(b) shows the measured concentrations of the target gases as a function of time during a pyrolysis test with a polymer mixture. A combination of Kapton film, PVC-insulated 24 AWG electrical wire, and M22759 insulated 10 AWG electrical wire were heated in an alumina boat inside a tube furnace from 200 to 640 °C over a period of 360 s, and air was used to push the emissions into a 326 L chamber where the TLAS instrument was located. After the measured gas concentrations reached a maximum, the chamber was vented. As expected for this fuel mixture, all gases except HCN were detected above the minimum concentration.

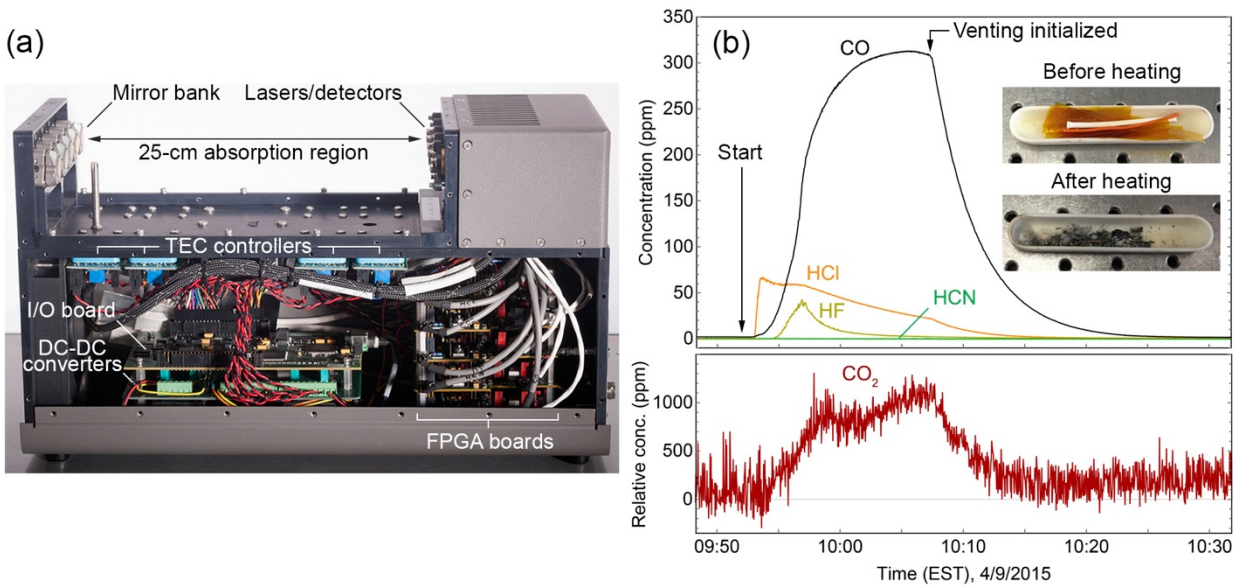

Figure 2. *(a) Photograph of the first-generation five-channel TLAS instrument capable of simultaneously measuring CO, HCl, HCN, HF, and CO_2 with a two-pass 50-cm-long optical path (more detailed information can be found in Ref. 5). (b) Combustion product concentrations measured over time during heating of a 2-g mixture of Kapton film and PVC- and fluoropolymer-insulted wire to a temperature of 640 °C in air. The CO_2 concentration is plotted as the value relative to the baseline level measured prior to heating the fuel sample, and the insets show photographs of the fuel mixture before and after heating.*

While the the first-generation instrument meets performance targets for combustion product monitoring, we are currently building a more compact next-generation instrument. The approach is primarily to combine the functionality of the individual FPGA control boards from the first-generation instrument in a single multi-function control board and also to minimize the size of the optical head, which is the main focus of the modeling described in this paper. The optical head, which includes the lasers and detectors for each TLAS channel, largely defines the overall instrument footprint.

Given the line strength and minimum detection limit for each target gas, the line-center absorption relative to off-line transmission for each laser wavelength can be calculated, as described in detail in the next section. Based on the observed performance of the first-generation instrument, we assume a minimum resolvable line-center absorption of 10^{-4} using 2f detection. It will be shown that the detection limit can be reached, with a significant margin, using a 10-

cm optical path by accessing the strong mid-infrared lines for CO, HCl, HCN, and HF. The same laser technologies implemented in the five-channel prototype sensor are to be used again in the new design: A low-power-consumption distributed feedback (DFB) quantum cascade (QC) laser for the longest-wavelength CO channel, an interband cascade (IC) DFB laser for the HCl channel, and type-I interband DFB lasers for the HCN and HF channels. For CO_2 and O_2, which have a significantly higher minimum detection requirement, the instrument will use single-mode DFB lasers targeting weaker lines in the near-infrared regime with a 1.7-m pathlength multi-pass absorption cell design. A rendering of the new instrument is shown in Fig. 3, where the critical absorption cell length of 10 cm is indicated.

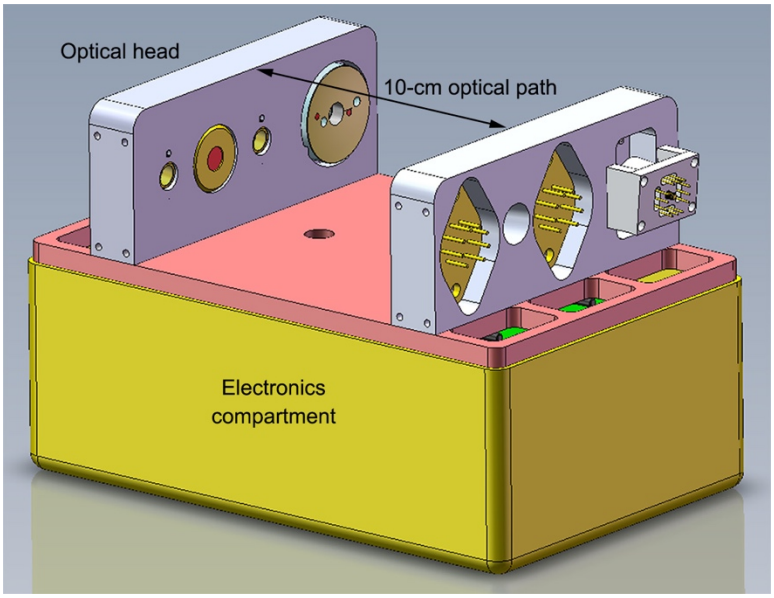

Figure 3. *Rendering of the compact next-generation TLAS instrument for combustion product monitoring. The long-wavelength channels (CO, HCl, HCN, and HF) utilize a 10-cm single-pass optical path, while the near-infrared channels (CO_2 and O_2) utilize a 1.7-m pathlength multi-pass cell configuration.*

III. Absorption Line Selection

Minimum detection level requirements were established for the next-generation TLAS sensor based on published SMACs for each toxic gas. In all cases, the target minimum detection limit is at or below the 24 h exposure level. For CO, the minimum detection limit is significantly below human exposure limits because of the importance of low-level CO detection as an early indicator of fire-related hazards. For O_2, a minimum detection limit of 15% is targeted since lower levels are not expected in habitable environments (O_2 levels will also be monitored on spacecraft by other instruments as a major environmental constituent).

Table 1 outlines the target performance range and optimal absorption wavelength for each of the six gases to be detected by the TLAS sensor. For each channel, the relative on-line absorption is calculated assuming standard temperature and pressure using data from the HITRAN Database. For O_2, the strongest absorption lines in the near- to mid-infrared regime correspond to electronic transitions occurring near 760 nm wavelength. For this channel, a multi-pass cell configuration is used to extend the optical pathlength to 1.7 m. This is less for sensitivity at the relatively large minimum O_2 concentration of 15%, where the line-center absorption is more than two orders of magnitude higher than the expected instrument detection limit, and more to ensure better than 1% accuracy for concentration measurements. Near the target wavelength, there is no appreciable absorption from interfering gases, including H_2O.

For the CO_2 detection channel, the instrument will target the relatively weak absorption lines near 2 μm wavelength while utilizing the same multi-pass cell as the O_2 channel. The strongest absorption lines are free from H_2O interference, and with an optical pathlength of 1.7 m, the measurement accuracy is expected to be better than 100 ppm. We note that CO_2 has negligible toxicity at levels below 0.1%; however, as described in Ref. 5, it is difficult to reliably monitor CO_2 concentration in normal conditions if the minimum detection level is comparable to ambient levels. Ultimately, the enhanced CO_2 sensitivity compared with the first-generation TLAS instrument, which had a CO_2 detection limit of 300 ppm, will enable better baseline tracking.

For each of the highly toxic gases, CO, HCl, HF, and HCN, the calculated line-center absorption for an optical pathlength of 10 cm is several times greater than the expected instrument detection limit at the target minimum concentration. In all cases, the most significant interfering gas is H_2O. Figure 4 shows the calculated transmission spectra near the target wavelength for each target compound of the TLAS sensor. The transmission is shown for the target minimum concentration for each gas and along with the transmission calculated for 2% H_2O, which is near the maximum H_2O concentration expected in a human-occupied environment (100% relative humidity at room temperature).

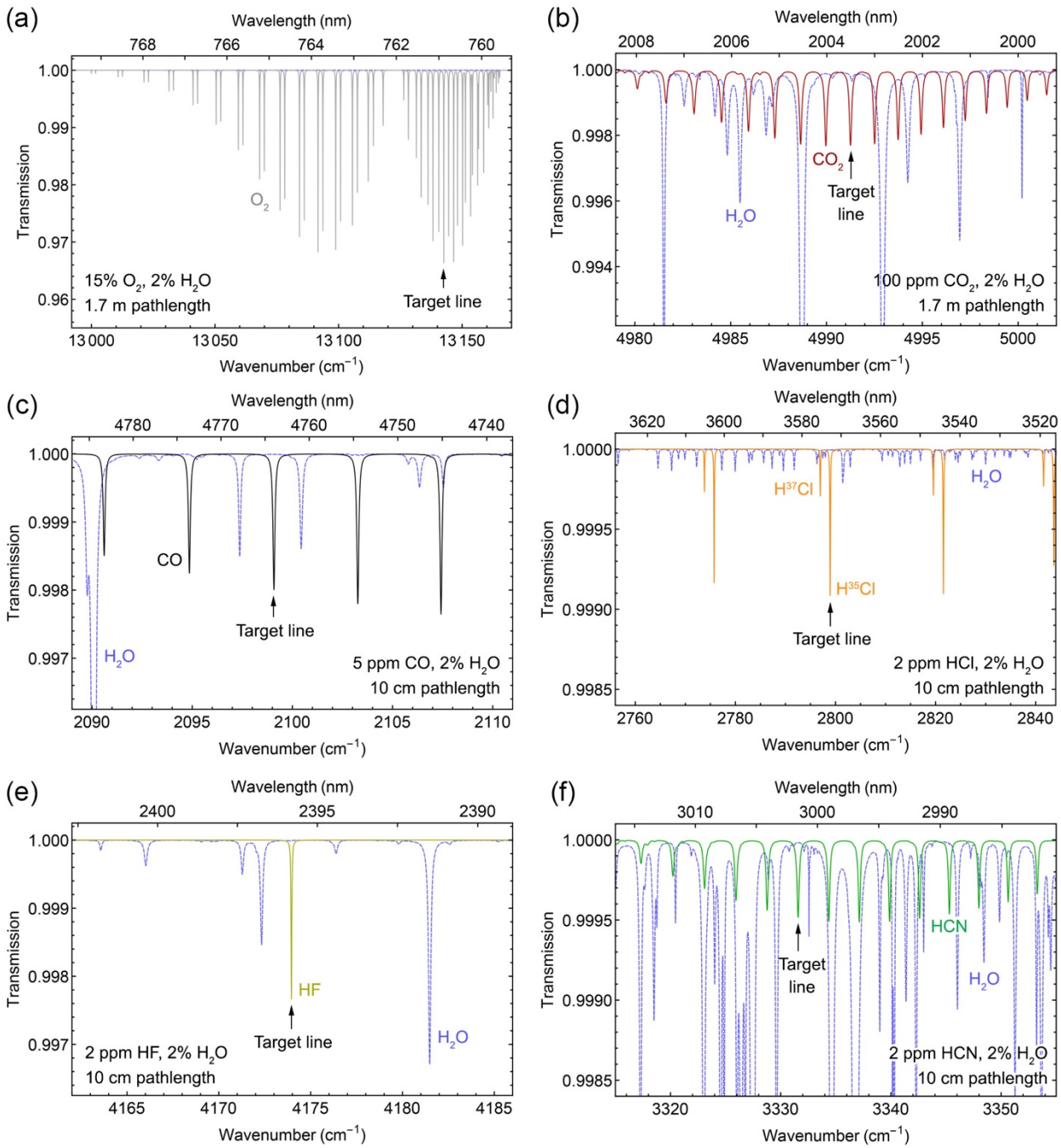

Figure 4. *Calculated transmission spectra for the six gases targeted by the next-generation TLAS combustion product sensor. The spectra were calculated at standard temperature and pressure assuming the indicated pathlengths. Transmission spectra are also plotted for H_2O, which is the primary interfering gas for each compound near the target absorption wavelength.*

Table 1. *Target range, absorption wavelength, optical pathlength, and calculated relative on-resonance absorption for each channel of the next-generation TLAS combustion product sensor. The on-line absorption values are for standard temperature and pressure and are to be compared to the instrument detection limit of 10^{-4}. The SMACs for toxic gases are taken from Ref. 6.*

Gas	Spacecraft Maximum Allowable Concentrations (SMACs)	Target performance range	Target wavelength	Optical pathlength	Relative line-center absorption at minimum detection level ($x10^{-4}$)
O_2	--	15 – 50%	760.9 nm	1.7 m	336.9
CO_2	1 h: 2% 24 h: 1.3% 7 d: 0.7% 30+ d: 0.7%	> 100 ppm	2003.5 nm	1.7 m	23.1
CO	1 h: 425 ppm 24 h: 100 ppm 7 d: 55 ppm 30+ d: 15 ppm	5 – 1,000 ppm	4764.0 nm	10 cm	20.0
HCl	1 h: 5 ppm 24 h: 2 ppm 7 d: 1 ppm 30+ d: 1 ppm	2 – 50 ppm	3572.8 nm	10 cm	9.2
HF	1 h: 5 ppm 24 h: 2.5 ppm 7 d: 1 ppm 30+ d: 1 ppm	2 – 50 ppm	2395.8 nm	10 cm	23.4
HCN	1 h: 8 ppm 24 h: 4 ppm 7 d: 1 ppm 30+ d: 1 ppm	2 – 50 ppm	3001.5 nm	10 cm	4.8

IV. Conclusion

We have detailed the optical design of a multi-channel laser absorption spectrometer designed to selectively measure the concentrations of gases related to accidental fires aboard spacecraft. The sensor measures CO_2, CO, HCl, HF, and HCN down to levels at or below the 24-h human exposure limit for human-occupied spacecraft environments and also measures O_2 at ambient levels. The instrument is a more compact version of a five-channel sensor that has been previously validated in ground tests through exposure to calibration gases as well as emissions from oxidative pyrolysis of common spacecraft materials. Spectral absorption calculations show that the new instrument design, with a significantly smaller optical head, will be capable of measuring all six target gases without crosstalk or interference from H_2O absorption, and the minimum detection level for each gas can be measured well above the instrument detection limit that was observed for the first-generation instrument. Looking ahead, this new compact optical configuration will be implemented and flight qualified for future spacecraft fire safety experiments.

Acknowledgments

This work was performed at the Jet Propulsion Laboratory (JPL), operated by the California Institute of Technology, under contract with the National Aeronautics and Space Administration. We thank M. E. Meyer, G. M. Berger, and G. A. Ruff at NASA Glenn Research Center, P. S. Mudgett at NASA Johnson Space Center, and N. Toomarian, M. R. Darrach, and D. J. Eisenman at JPL for their valuable technical input. We also gratefully acknowledge critical support from J. Joshi and the NASA Life Support Systems Project under the Advanced Exploration Systems Program.

References

[1] Ruff, G. A., Greenberg, P. S., Mudgett, P. D., Hornung, S. D., Pilgrim, J. S., and Vakhtin, A. B., "Towards the Identification of Chemical Markers for Spacecraft Post-fire Cleanup," 41st International Conference on Environmental Systems, American Institute of Aeronautics and Astronautics (AIAA), Portland, Oregon, 17-21 July, 2011.

[2] Meyer, M. E., Mudgett, P. D., Hornung, S. D., McClure, M. B., Pilgrim, J. S., Bryg, V., Ruff, G. A., and Hunter, G., "Materials Combustion Testing and Combustion Product Sensor Evaluations in FY12," 43rd International Conference on Environmental Systems, American Institute of Aeronautics and Astronautics (AIAA), Vail, Colorado, 14-18 July, 2013.

[3] Webster, C. R., May, R. D., Trimble, C. A., Chave, R. G., and Kendall, J., "Aircraft (ER-2) laser infrared absorption spectrometer (ALIAS) for *in-situ* stratospheric measurements of HCI, N_2O, CH_4, NO_2, and HNO_3," *Applied Optics*, Vol. 33, No. 3,1994, pp. 454-472.

[4] Kosterev, A., Wysocki, G., Bakhirkin, Y., So, S., Lewicki, R., Fraser, M., Tittel, F., and Curl, R. F., "Application of quantum cascade lasers to trace gas analysis," *Applied Physics B*, Vol. 90, No. 2, 2008, pp. 165-176.

[5] Briggs, R. M., Frez, C. E., Forouhar, S., May, R. D., and Ruff, G. A., "Qualification of a multi-channel infrared laser absorption spectrometer for monitoring CO, HCl, HCN, HF, and CO_2 aboard manned spacecraft," 45th International Conference on Environmental Systems, American Institute of Aeronautics and Astronautics (AIAA), Bellevue, Washington, 12-16 July, 2015.

[6] Committee on Spacecraft Exposure Guidelines, Committee on Toxicology, National Research Council, *Spacecraft Maximum Allowable Concentrations for Selected Airborne Contaminants*, Vol. 5, The National Academies Press, Washington, DC, 2008, pp. 125-142.

[7] May, R. D. and Webster, "Data processing and calibration for tunable diode laser harmonic absorption spectrometers," *Journal of Quantitative Spectroscopy and Radiative Transfer*, Vol. 49, No. 4,1993, pp. 335-347.