

Portable 4.6 μm Laser Absorption Spectrometer for Carbon Monoxide Monitoring and Fire Detection

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The air quality aboard manned spacecraft must be continuously monitored to ensure crew safety and identify equipment malfunctions. In particular, accurate real-time monitoring of carbon monoxide (CO) levels helps to prevent chronic exposure and can also provide early detection of combustion-related hazards. For long-duration missions, environmental monitoring grows in importance, but the mass and volume of monitoring instruments must be minimized. Furthermore, environmental analysis beyond low-Earth orbit must be performed *in-situ*, as sample return becomes impractical. Due to their small size, low power draw, and performance reliability, semiconductor-laser-based absorption spectrometers are viable candidates for this purpose. To reduce instrument form factor and complexity, the emission wavelength of the laser source should coincide with strong fundamental absorption lines of the target gases, which occur in the 3 to 5 μm wavelength range for most combustion products of interest, thereby reducing the absorption path length required for low-level concentration measurements. To address the needs of current and future NASA missions, we have developed a prototype absorption spectrometer using a semiconductor quantum cascade laser source operating near 4.6 μm that can be used to detect low concentrations of CO with a compact single-pass absorption cell. In this study, we present the design of the prototype instrument and report on measurements of CO emissions from the combustion of a variety of aerospace plastics.

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Nomenclature

QC	=	quantum cascade
CW	=	continuous wave
DFB	=	distributed feedback (laser)
TELS	=	Tunable Environmental Laser Spectrometer
2f	=	second harmonic (detection)
FPGA	=	field-programmable gate array
DC	=	direct current

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TEC	=	thermoelectric cooler
MCT	=	mercury cadmium telluride
PTFE	=	polytetrafluoroethylene
PVC	=	polyvinyl chloride
CO	=	carbon monoxide
CO ₂	=	carbon dioxide
H ₂ O	=	water (vapor)
N ₂ O	=	nitrous oxide
ppmv	=	part per million by volume
ppbv	=	part per billion by volume

I. Introduction

As part of the Advanced Exploration Systems Program, NASA supports the development of compact, low-power fire detection platforms and environmental monitoring systems for the International Space Station and future missions, with the goal of tracking concentrations of particulates, acid gases, and other airborne hazards.¹ Within the Spacecraft Fire Safety Demonstration project, we have developed a laser absorption spectrometer operating at wavelengths near 4.6 μm that can be used to detect small concentrations of CO without interference from CO₂, H₂O, or other gases normally present in habitable environments. The laser absorption spectrometer enables continuous monitoring of CO levels in order to avoid chronic exposure,² but the instrument also provides fast response for quickly identifying exposure related to immediate combustion-related hazards and equipment malfunctions.

Many fundamental rotational-vibration CO absorption lines exist in the spectral region between 4.5 and 4.8 μm , but interference from H₂O and N₂O leaves a narrow window between 4.59 and 4.61 μm (2170 to 2180 cm^{-1} wavenumbers) with CO lines exhibiting near ideal absorption characteristics. The relative strength of these absorption lines allows for significant on-resonance attenuation of light over interaction distances of just a few centimeters at atmospheric pressure, which enables the implementation of compact absorption spectrometers designed to quantitatively determine CO concentration.^{3,4} However, targeting this narrow spectral window in the mid-infrared regime introduces several unique instrument requirements. In recent years, many components, including high-performance detectors and passive optics, have become readily available in the 4 to 5 μm range; however, the limiting component for realizing deployable mid-infrared absorption spectrometers has been the light source, which must conform to mass and power requirements and produce emission at the desired wavelength with a high degree accuracy and stability.

Semiconductor-based QC lasers are capable of producing light at wavelengths near 4.6 μm , and frequency-selective elements can be used to isolate a single longitudinal laser mode for spectrally pure emission with linewidth comparable to typical gas absorption lines.⁵ Furthermore, compared with alternative solid-state laser technologies, QC lasers can be made compact and power-efficient, with CW power conversion efficiencies as high as 10% or more and form factors limited only by the packaging volume required for dissipation of waste heat.⁶ Lasers operating near the wavelengths required for CO detection are commercially available, although with relatively lower wall-plug efficiencies and significant power requirements. Recent research-level advances in QC laser technology indicate the availability of further optimized sources within the next few years.^{7,8}

In this work, we report on the development of a prototype portable Tunable Environmental Laser Spectrometer (TELS) instrument based on a QC laser source operating near 4.6 μm for detection of CO. Our instrument employs a 25-cm single-pass absorption cell and second-harmonic (2f) detection, and it is designed for 0.1 ppm precision and measurement response time on the order of 1 s. The prototype TELS instrument was qualified using an environmental test chamber at the NASA White Sands Test Facility, and we report high-temperature CO emissions data for several materials used aboard manned spacecraft, including PTFE, PVC, Nomex, Kapton, and polymer mixtures. We find that QC-laser-based absorption spectroscopy enables accurate long-term tracking of dangerous levels of ambient CO without the need for recalibration or replacement of consumable components, which recommends the technology as a viable platform for future spacecraft environmental monitoring instruments.

II. Instrument Design

The rotational-vibrational line spectrum of CO is most intense between 4.5 and 4.8 μm (approximately 2100 to 2200 cm^{-1} wavenumbers), enabling maximum optical interaction in a compact single-pass cell using sources in that wavelength range. As shown in Fig. 1(a), the strongest R-branch absorption lines occur near 2175 cm^{-1} and also coincide with a transparency window absent of strong H₂O and N₂O lines. However, the commercial distributed-

feedback (DFB) QC laser source acquired for this work (Hamamatsu Photonics) was limited to a few nanometers of tuning near $4.57\ \mu\text{m}$ ($2190\ \text{cm}^{-1}$). As indicated in Fig. 1(a), the target CO absorption line within the tuning range of the laser is still within a factor of two of the most intense R-branch lines and does not interfere with strong H_2O lines. Nevertheless, N_2O lines could become problematic for gas mixtures with comparable concentrations of CO and N_2O , but in typical ambient conditions, where N_2O levels are below 1 ppmv, CO can be unambiguously identified at levels relevant to spacecraft safety (concentrations greater than 1 ppmv).

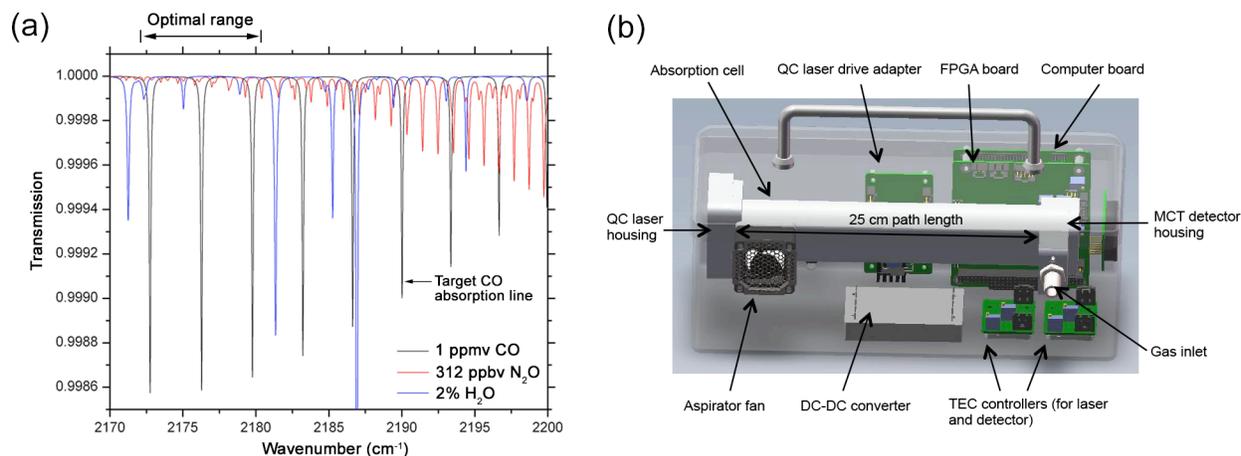


Figure 1. (a) Transmission over a 25-cm path length calculated for standard temperature and pressure with the indicated concentrations of CO, H_2O , and N_2O . The TELS instrument operates by scanning the QC laser wavelength across the indicated target CO absorption line. (b) Schematic of the TELS instrument, which uses a QC laser source operating near $4.57\ \mu\text{m}$ and a 25-cm single-pass absorption cell to measure ambient CO concentration.

A schematic view of the prototype TELS instrument appears in Fig. 1(b), showing the single-pass 25-cm absorption cell and the housings for the thermoelectrically cooled QC laser source and HgCdTe (MCT) infrared detector (Vigo System). Dedicated electronics are used to control the temperature and input power of the source and detector, and the ambient temperature and pressure are recorded with on-board sensors. For normal ambient monitoring, gases from the surrounding environment are drawn through the gas inlet using an aspirator fan at the opposite end of the cell; however, for the prototype testing described in Sec. III, a hose fitting was attached to back of the instrument housing to enable closed-loop gas sampling from an enclosed environmental chamber.

The laser absorption spectrometer instrument measures CO by scanning the laser wavelength across the target absorption line and measuring the amplitude of the CO absorption feature using second-harmonic (2f) detection. A linearly increasing current ramp is applied to the QC laser in order to tune the laser wavelength across the target absorption line. In addition to the DC signal, a small-amplitude sinusoidal current modulation is applied to the laser at a frequency of 31.2 kHz.

After collimation using an integrated lens, light passing through the gas cell is collected by the detector and demodulated at 62.4 kHz, using a custom-programmed FPGA board to extract the 2f detector response. For relatively low concentrations (below approximately 100 ppmv), the amplitude of the 2f peak is proportional to the CO concentration with a linear scaling factor determined from reference gas measurements. At higher concentrations, nonlinearities from Beer's law effects ($\sim 5\%$ error at 100 ppmv) and direct line broadening result in underestimation of the CO concentration when extracted from the 2f amplitude. In this case, the direct absorption spectrum can be used to corroborate (or correct) the CO concentration using the integrated area under the absorption peak; however, this requires background correction, accomplished by fitting a polynomial to the DC detector response. For the experiments described in Sec. IV, we extracted CO concentrations only from the 2f amplitude, since even the highest estimated CO levels were on the order of 100 ppmv.

The functional TELS instrument prototype is shown in Fig. 2. The ambient pressure and temperature are displayed on an integrated readout along with the scan parameters used to extract the CO concentration. These data are logged on an internal flash memory card and can also be read out in real-time using a serial connection to an external computer. The complete DC and 2f spectra are also recorded in memory for post-processing and analysis.

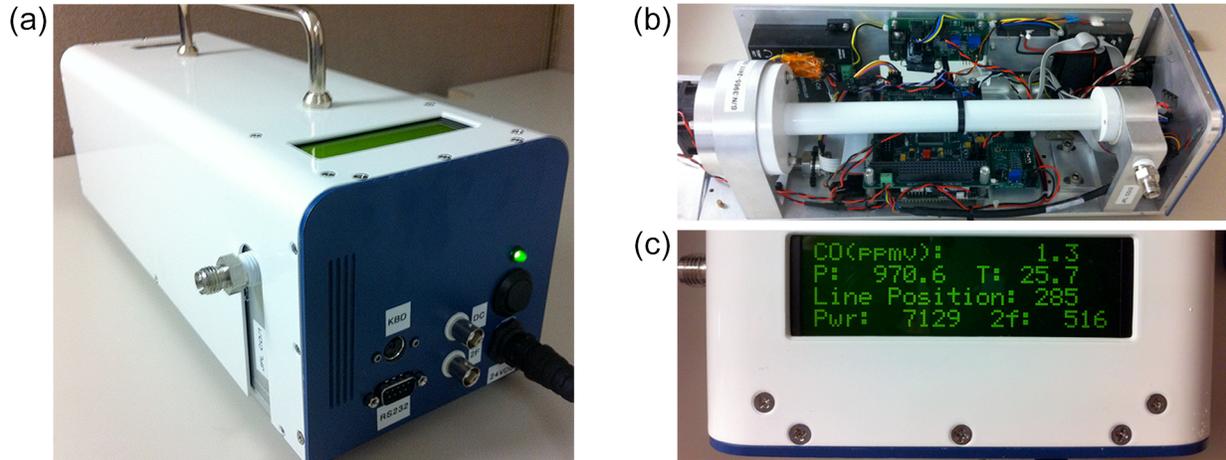


Figure 2. (a) Photograph of the operational TELS instrument prototype. (b) Removing the instrument cover reveals the absorption cell and related electronics. (c) The readout displays the CO concentration and relevant measurement parameters, including the ambient pressure in mbar and the temperature in °C. Over the course of a measurement, this information and complete absorption spectra are also recorded on an internal memory card.

Representative DC and 2f spectra from the TELS instrument are shown in Fig. 3, corresponding to a series of scans with varying CO levels in air. As the QC laser current is swept over a period of 200 ms, the DC detector signal increases, as expected, due to the increasing laser power; however, the laser power begins to saturate due to the increasing internal temperature of the laser and nonlinear detector response. Also, due to a low-pass filter, the modulated component of the drive current is not readily visible in the DC scans, but the peak appears flattened in the vicinity of the CO absorption feature. The 2f absorption feature is relatively insensitive to the nonlinearity in the DC spectrum, but small spurious peaks are generated by Fabry-Perot interference of light reflected between the collimating lens and the windows of the laser and detector packages. These peaks ultimately limit the lower detection limit of the instrument by obscuring the signature of the CO absorption line at low CO concentrations, although they can be minimized by improving the antireflective coatings on the gas cell optics. Note that each 2f spectrum is extracted in real-time from the preceding DC spectrum, and the spectra are recorded sequentially in memory, as displayed in left-hand panels of Fig. 3.

Detailed plots of DC and 2f spectra are indicated in Fig. 3 by the green and orange boxes, respectively, corresponding to a single scan collected while flowing a reference gas containing 100 ± 5 ppmv CO in air at a rate of 1 L/min. The upper right-hand panel shows the CO concentration extracted from the 2f peak amplitude during a continuous calibration run, during which the absorption cell was exposed to both 50 and 100 ppmv CO reference gases (Mine Safety Applications). For all measurements reported here, each concentration value was obtained from an average of five scans, resulting in time resolution on the order of 1 s. Due to the interference fringes from the gas cell optics, the lower detection limit is observed to be just below 5 ppmv (e.g., at t_1). The reference measurements (e.g., at t_2 and t_3) indicate accuracy to within 10%, which is correctable using the previously mentioned scaling factor. The stability of the reference measurements over a period of several minutes during exposure to the reference gases indicates a high level of precision (within 1 ppmv).

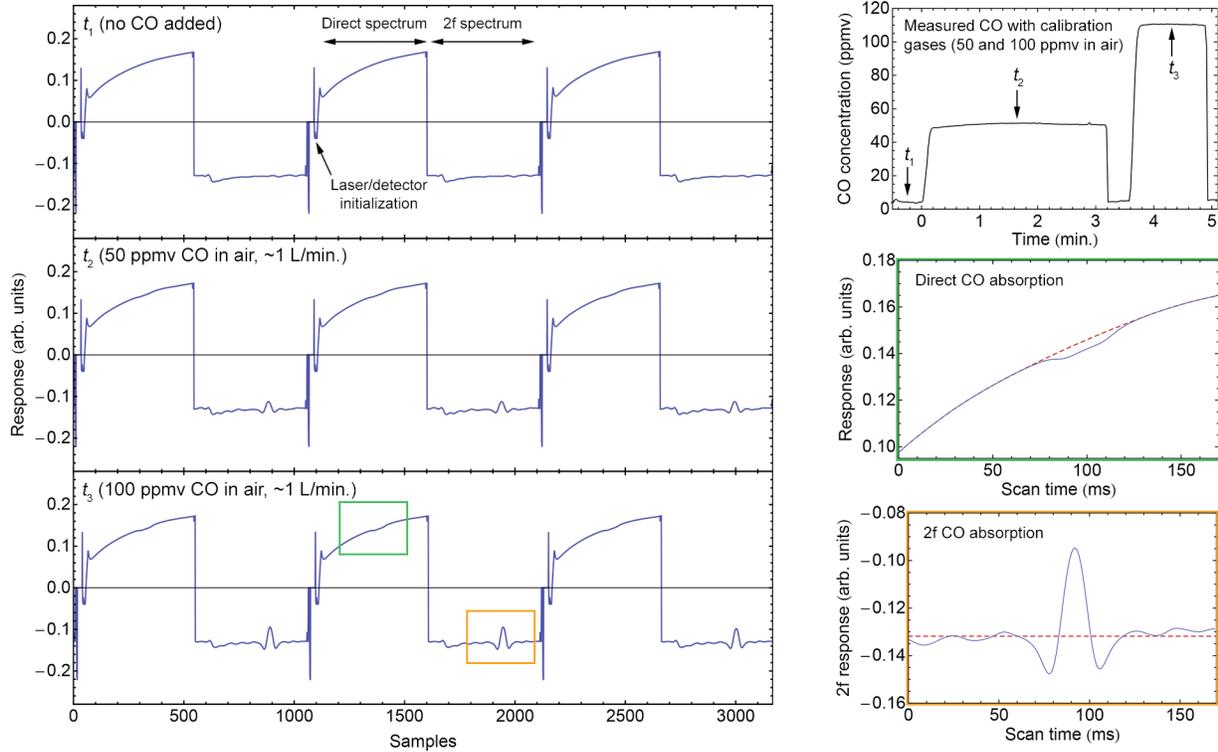


Figure 3. Measured direct (DC) and $2f$ spectra at varying CO concentrations. The direct detector response is shown after low-pass filtering, which removes the small amplitude modulation of the laser drive signal. The appended $2f$ spectrum is used to extract CO concentration. The $2f$ peak amplitude is proportional to CO concentration at low levels, and the minimum detection level is limited by interference fringes caused by reflections from the lens and windows of the laser and detector packages in the absorption cell.

III. Prototype Instrument Testing

The prototype TELS instrument was used to measure CO emissions from several aerospace plastics commonly used aboard spacecraft, including PTFE (white Teflon), PVC, Nomex, Kapton, wire insulation, and polymer-impregnated circuit board. At the NASA White Sands Test Facility, the instrument was attached externally to an enclosed environmental chamber with a total volume of approximately 600 L that had been outfitted with a high-temperature smoke generator. The smoke generator was constructed from a quartz tube wrapped with resistive coils and driven using a standard temperature controller to a maximum temperature of 640 °C. Standardized 0.5 g samples composed of shavings from the test materials were placed in the smoke generator and heated in air within the enclosed chamber. Tube liners were used to avoid cross-contamination between different material tests. After reaching maximum temperature, a mixing fan was activated inside the chamber, and the chamber was kept sealed for several minutes before being safely vented through the laboratory exhaust system. A photograph of the environmental chamber is shown in Fig. 4 (a), and photographs of the smoke generator operating at maximum temperature are shown in Fig. 4(b) for two different test materials.

To interface the TELS instrument with the environmental chamber, 0.25-in.-diameter vinyl tubing was used to connect a gas-line feedthrough on the chamber to the inlet of the instrument absorption cell. A recirculation pump was attached to a hose on the opposite end of the absorption cell, and the pump exhaust was returned to the chamber using an additional feedthrough, as shown schematically in Fig. 4(d). Over the course of each test, the TELS instrument was operated continuously while spectra and CO concentrations were logged. Reference electrochemical sensors (Dräger) were placed inside the chamber to monitor concentrations of CO and various other combustion products of interest.

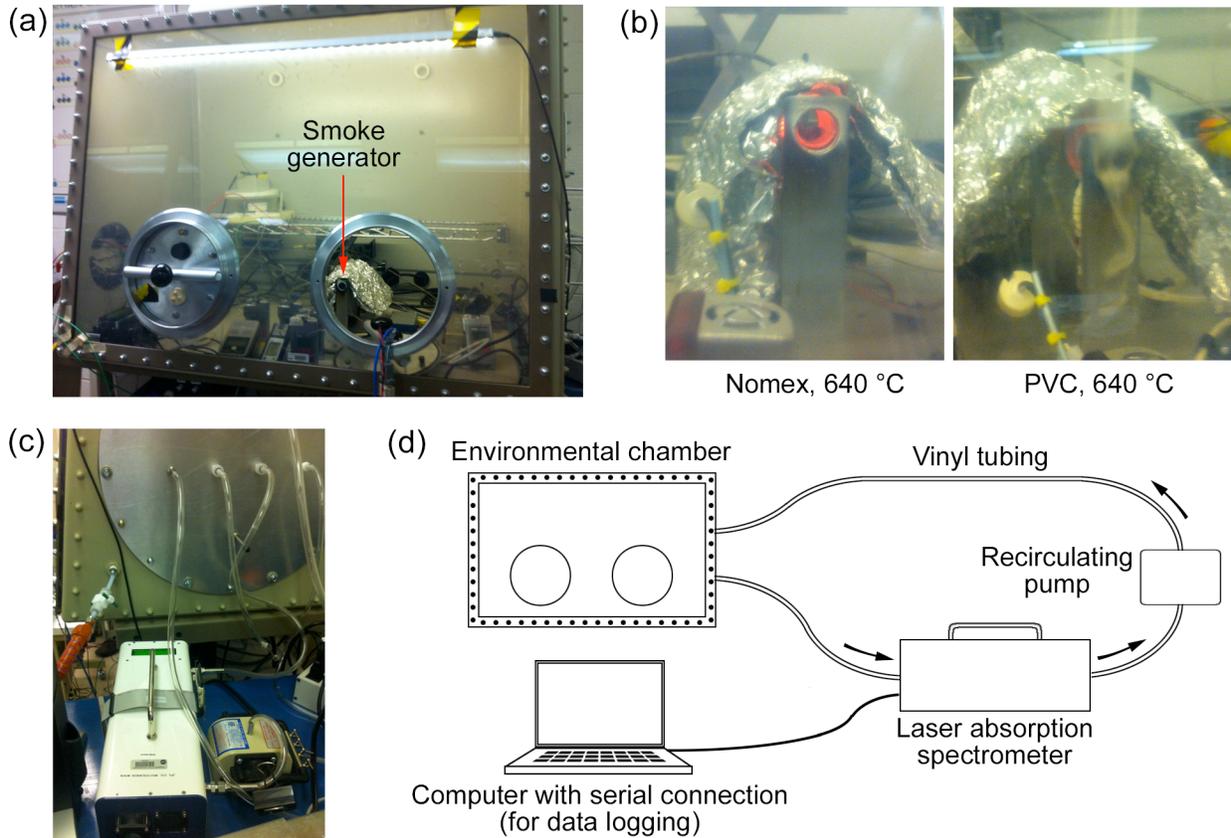


Figure 4. (a) Photograph of the environmental test chamber at the NASA White Sands Test Facility. The chamber is shown between tests with one of the ports unsealed to allow access to the smoke generator. (b) The smoke generator after being heated to a maximum temperature of 640 °C, shown with both Nomex and PVC samples. (c) The TELS instrument and recirculation pump interfaced with the environmental chamber. (d) Layout of the test setup for measuring CO emissions from materials heated inside the environmental chamber.

IV. Measurement of CO Emissions

Measured CO emissions from PVC are plotted as a function of time in Fig. 5(a). This representative data set shows the CO concentration prior to heating (ambient laboratory conditions), during the turbulent heating period as the smoke generator reaches its maximum temperature of 640 °C, and during the gradual decay in CO levels after the mixing fan is activated and the smoke generator begins to cool. We note that the measured CO concentration is relatively stable once the mixing fan is activated, indicating that the large variations in CO level during the heating period are due to actual inhomogeneities in the chamber environment rather than instrument noise. We also note that the time resolution of the TELS instrument enables precise tracking of these dynamic changes. Even with the external interface to the environmental chamber using vinyl tubing, the instrument output indicates elevated CO levels within a few seconds of the heater being activated.

Figure 5(b) shows the distribution of measured CO emissions for all of the high-temperature tests conducted, with each material subjected to the same heating conditions. In each case, the CO concentration was taken as the average value during the initial 30 s after the mixing fan was activated. Only PTFE produced CO levels that were close to the lower detection limit of the TELS instrument, while all other materials showed significantly elevated levels of CO. Measured CO concentrations from the reference electrochemical sensors placed inside the environmental chamber (not shown) were in qualitative agreement with the CO levels for the various materials but consistently 25% to 35% higher than the levels measured by the TELS instrument. This can possibly be attributed to the external measurement configuration used with the TELS instrument, which could have resulted in the loss of CO through small leaks in the tubing or in the absorption cell itself. This underestimation could also arise, in part, from nonlinearities resulting from Beer's law or CO absorption line broadening, both of which can be corrected with software modifications and more extensive testing.

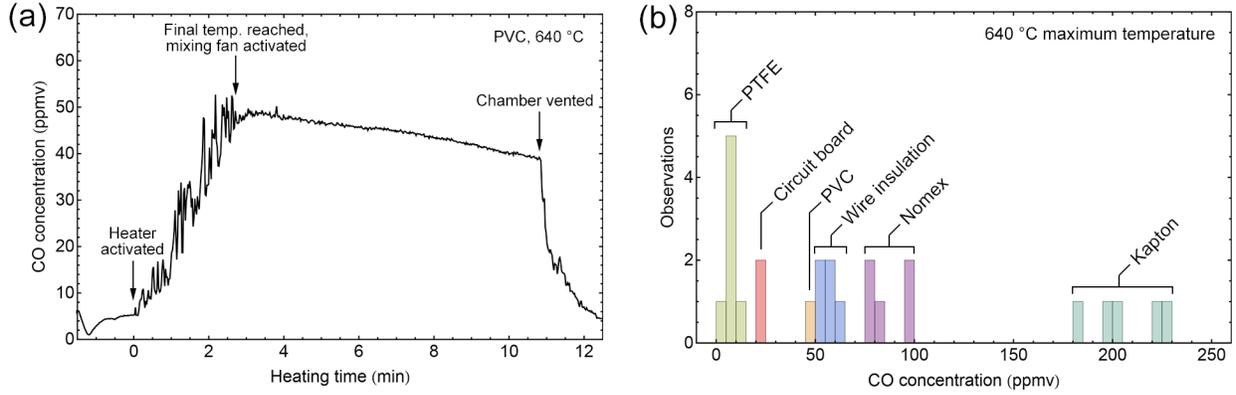


Figure 5. (a) CO emissions measured over time using the TELS instrument for a PVC sample heated to a maximum temperature of 640 °C. The CO level varies significantly during the initial heating period but becomes stable after the mixing fan is activated. (b) Distribution of CO emissions measured by the TELS instrument for various materials, each subjected to the same heating process. The observed CO concentration is taken as the average value over the first 30 s after the mixing fan is activated.

One material, polymer-impregnated circuit board, was tested at different maximum temperatures, and CO emissions profiles for each temperature are shown in Fig. 6(a). In each case, the CO level continued to rise slightly for a few minutes after the smoke generator began to cool and the mixing fan was activated, indicating that the combustion reaction might have been oxygen-limited, and unburned material continued to smolder even with decreasing temperature. Figure 6(b) shows the average measured CO concentration during the 30 s after the mixing fan was activated for two runs at each maximum temperature. While the average CO concentration (denoted with the dashed line) increases monotonically, significantly elevated levels of CO were measured even at the lower temperatures.

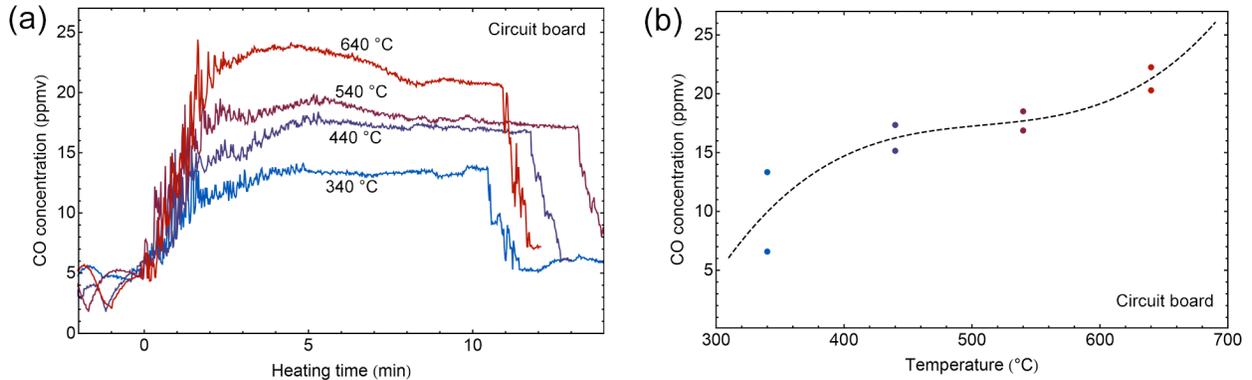


Figure 6. (a) CO concentrations measured over time for polymer-impregnated circuit board heated to different maximum temperatures. Two tests were completed at each temperature, but, for clarity, only the traces that produced the most CO at each temperature are shown. (b) Maximum CO concentrations for each run. The dashed line is a spline fit to the average concentration at each temperature.

V. Conclusion

We have designed and built a prototype portable absorption spectrometer for monitoring CO levels using a single-frequency QC laser source operating near 4.6 μm . The instrument uses 2f detection to extract CO concentration from a fundamental rotational-vibrational CO absorption line, enabling accurate low-level measurements with a compact 25-cm single-pass absorption cell. The instrument was successfully used to monitor CO emissions from heated polymer samples in an environmental test chamber at the NASA White Sands Test Facility, and further development is expected to advance the instrument as a viable technology for on-board spacecraft safety monitoring.

Acknowledgments

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