A Miniaturized Gas Correlation Radiometer for Mapping Multiple Trace Gases in the Martian Atmosphere

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Introduction:

We present preliminary results in the development of a miniaturized gas correlation radiometer (GCR) for column trace gas measurements in the Martian atmosphere. The GCR is designed as an orbiting instrument appropriate for missions such as the ESA-NASA 2016 Orbiter-Carrier developed by the Joint Instrument Definition Team (JIDT) [1] and will be capable of mapping multiple gases for identifying active regions on the Mars surface.

Gas correlation radiometry is a mature sensing technology on Earth [2,3], and with successful miniaturization, it holds promise for trace gas measurements in the Martian atmosphere. The component that most impacts the size of a gas correlation radiometer is the gas correlation cell – the pathlength of which affects the sensitivity of the instrument. Based on a comparison with an Earth orbiting CO₂ gascorrelation instrument [4], replacement of the 10 meter multipass cell with hollow waveguide of equivalent pathlength reduces the cell mass from ~150 kg to ~0.5 kg, and reduces the volume from 1.9 m x 1.3 m x 0.86 m to a small bundle of fiber coils approximately 1 meter in diameter by 0.05 m in height (mass and volume reductions of >99%).

Here we show methane (CH₄) and formaldehyde (CH₂O) measurements from our prototype GCR that implements a lightweight, 1 mm inner diameter hollow waveguide as the gas correlation cell. This modular instrument technique can be expanded to include measurements of additional species of interest including water vapor (H₂O), deuterated water (HDO), nitrous oxide (N₂O), hydrogen sulfide (H₂S), methanol (CH₃OH), and sulfur dioxide (SO₂), as well as carbon dioxide (CO₂) for a simultaneous measure of mass balance.

GCR Development:

The passive GCR instrument measures the mole fraction of a trace gas through its absorption of sunlight in the 3.5 μ m region. For the orbital instrument, sunlight passes through the Martian atmosphere, reflects on the planet's surface, passes through the atmosphere again, and enters the GCR on the satellite platform. In the lab, sunlight is simulated with a silicon carbide lamp, and a range trace gas concentrations are produced in a 2 meter infrared gas cell. A schematic of the lab set-up is shown in Figure 1. The lamp and 2 meter gas cell are shown at the upper



Figure 1. GCR lab configuration. Hollow waveguides replace conventional gas correlation cells - resulting in significant mass and volume savings.

left. The GCR instrument is shown within the dashed line. Light that has undergone absorption by the trace gas is focused, modulated with an optical chopper, and re-collimated. Light then passes through a narrow bandpass filter at a wavelength that selects absorption features of the trace gas while minimizing interference from other spectral features. In the current set-up, the bandpass filters for both methane and formaldehyde sub-instruments are in the 3.5 μ m region. Unlike instruments that measure absorption using laser light (and measure absorption by a single rotational absorption feature), the GCR measures the absorption in a group of absorption features defined by the narrow bandpass filter. Considerations for selecting the exact wavelength region of the band-



Figure 2. GCR prototype instrument. The current design of the instrument will be modified to merge multiple gas instruments into a single consolidated package.

pass filter is discussed in the next section. After passing through the narrow bandpass filter, light is split into two channels with a pellicle beamsplitter.

In the first channel, a sample of the trace gas is enclosed in a 1 mm inner diameter, 3 meter long hollow waveguide that is used as a spectral filter. This channel blocks atmospheric absorption by this gas and is sensitive to changes in solar flux but not to changes in the trace gas.

The second channel has an equivalent, but evacuated hollow waveguide that is more sensitive to changes in atmospheric absorption than to changes in flux. The ratio of these channels is sensitive to changes in absorption but not to changes in solar flux. Use of duplicate hollow core fibers (filled and evacuated) reduces etalon and fringing effects in the ratio. Light from these channels is then focused onto HgCdTe detectors. Signals are processed through lock-in amplifiers referenced to the frequency of the chopped signals.

Formaldehyde Measurement Results:

The bandpass filter used in the formaldehyde instrument is centered at approximately $3.62 \ \mu\text{m}$. Figure 3 shows an FTIR scan of the bandpass filter (dashed line) with a simulated prefilter bandpass (solid line) overlaid on formaldehyde absorption features in P branch of the a1 band centered at $3.594 \ \mu\text{m}$ (2782.5 cm⁻¹).



Figure 3. The GCR measures absorption of multiple formaldehyde lines as defined by the bandpass filter.

This off-the-shelf bandpass filter is not the optimal wavelength range (it includes some interfering features) but is adequate for this proof-of-principal instrument. A future custom bandpass filter will select formaldehyde lines and minimize contributions from interfering absorption features.

In these measurements, the channel 1 waveguide was filled with 31.8 ppm formaldehyde in a balance of nitrogen for a total waveguide pressure of 1 atm (760 torr). Maintaining the waveguide pressure at atmospheric pressure reduced the likelihood of longterm contamination of air into the waveguide.

To track the sensitivity of the instrument to changes in the formaldehyde concentration, the 2 meter absorption cell (located at the front end of the instrument) was filled with concentrations ranging from 0 to 41.8 ppm formaldehyde in nitrogen while monitoring changes in the ratio of channel 2 to channel 1. Signals from both channels were recorded for an integration time of 1 second. Representative data from these experiments is shown in Figure 4. The linear regression of this data is shown as a solid line, and the square of the correlation coefficient is 0.995. Vertical error bars show the maximum standard deviation in three measurements for each data point.



Figure 4. GCR lab measurement of formaldehyde in the 2 meter infrared gas cell. This is equivalent to a \sim 30 ppb sensitivity to formaldehyde in the Martian atmosphere.

Assuming an average atmospheric pressure on Mars of \sim 7 millibars, two passes through the atmosphere at \sim 22.2 km, and a temperature of 210 K, the GCR in this preliminary configuration is sensitive to formaldehyde changes as low as 30 ppb.

The performance of a Mars orbiting GCR was simulated assuming a 3 meter long, 1000 micron inner diameter hollow-core fiber gas correlation cell, a 92.8 degree sun-synchronous orbit from 400 km with a horizontal sampling scale of 10 km x 10 km. The simulation generates a synthetic spectrum for reflected light containing spectral features from the HITRAN16 database.¹

The reflected solar flux signal received in the two channels of each sub-instrument (evacuated and gasfilled correlation cells) is calculated for light that has passed through the Martian atmosphere, reflected off the surface, and passed back up to the spacecraft. For each simulation, the total column of the species of interest is perturbed by 1% and the signals are recalculated. We compare the change in the ratio (filled cell to evacuated cell) caused by the perturbation to the detector noise of this ratio. The free parameters of the instrument design (filter bandpass, filter edge slopes, instrument FOV, etc.) are varied in an effort

¹ It should be noted that the HITRAN database is intended for evaluating absorption in the Earth's atmosphere and consequently, some bands found in the Martian atmosphere have been neglected or are incomplete in this database. However, it is still useful for initial performance simulations – as long as final spectral selections are not based on this alone.

to maximize the response to the species measured. Initial results indicate that for one second of averaging (3 km displacement along the satellite ground track), a detection limit of slightly better than 1 ppb is possible for formaldehyde. Preliminary lab results using less than optimal components (that were less expensive but adequate for this proof-of-principal prototype) nearly reach this target. Significant improvements in the sensitivity are anticipated with an improved optical design, a custom bandpass filter that can select absorption features with larger linestrengths, and optimized detectors.

Methane Measurement Results:

In the methane demonstrations, the channel 1 waveguide was filled with 1 atm (760 torr) of pure methane. The channel 2 waveguide remained evacuated. To test instrument sensitivity, the 2 meter infrared gas cell at the front of the instrument was filled with a low pressures of pure methane. Changes in the ratio are shown as a function of methane pressure in the 2 meter infrared cell in Figure 6. A change of 0.04 torr of methane is equivalent to an approximate change of 0.5 ppm methane in the Martian atmosphere.





For the methane instrument, the bandpass filter was also an off-the-shelf component. The wavelength range of the filter, centered at \sim 3.408 µm is shown in Figure 5. While this filter is adequate for demonstrating the functionality of the GCR instrument, it is not optimized for methane absorption features. A future bandpass filter will select a wavelength region that maximizes the number of large linestrength methane lines while minimizing absorption features from interfering trace gases.

Performance of the methane instrument in a Mars orbit was also simulated assuming a 3 meter long, 1000 micron inner diameter hollow-core fiber gas correlation cell, a 92.8 degree sun-synchronous orbit from 400 km with a horizontal sampling scale of 10 km x 10 km. Initial results indicate that for one second of averaging, a detection limit of 1 ppb is possible. A prefilter that includes methane lines with stronger linestrengths will significantly improve this result.



Figure 6. Sensitivity of GCR to changes in methane in 2 meter IR cell. This is equivalent to \sim 500 ppb change in methane.

Conclusions:

We have presented preliminary formaldehyde and methane measurements from a miniaturized gas correlation radiometer that implements hollow waveguides for gas correlation cells. Performance simulations that assume a 3 meter long, 1000 micron inner diameter hollow-core fiber gas correlation cell, a 92.8 degree sun-synchronous orbit from 400 km with a horizontal sampling scale of 10 km x 10 km indicate that a 1 ppb detection limit is possible for either formaldehyde or methane with one second of averaging. With non-optimized components, we have demonstrated an instrument sensitivity equivalent to ~30 ppb for formaldehyde, and ~500 ppb for methane. Custom bandpass filters are expected to significantly improve these promising early results.

References:

[1] Zurek, R. & Cicarro, A. Report to MEPAG on the ESA-NASA Joint Instrument

Definition Team (JIDT) for the Proposed 2016 Orbiter-Carrier. MEPAG meeting #31,

http://mepag.jpl.nasa.gov/meeting/jul-

09/JIDT_for_MEPAG.ppt (2009).

[2] Drummond, J. R. et al. Early Mission Planning for the MOPITT Instrument.

www.atmosp.physics.utoronto.ca/MOPITT/mission.pdf (1999).

[3] Liu, J., Drummond, J. R., Li, Q., Gille, J. C. & Ziskin, D. C. Satellite mapping of CO emission from forest fires in Northwest America using MOPIITT measurements. Remote Sensing of Environment 95, 502-516 (2005).

[4] Tolton, B. T., Hackett, J., Caldwell, D. & Miller, D. Strawman design for a gas-filter correlation radiometer satellite instrument to measure the atmospheric CO2 column. Proc. of SPIE 5543, 332-337 (2004).

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