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Development of a Photoacoustic Formaldehyde Monitor

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Key indoor air quality pollutant formaldehyde (H_2CO) is tracked on International Space Station (ISS) using passive badges returned to the ground periodically for analysis. The process is time-consuming both in preparation and for analysis upon return 6-12 months later. Badges also require precious crew time for deploy, retrieval and stow. As NASA's focus in space exploration shifts to the Moon and Mars, archival sample return becomes increasingly impractical, so the aim of this project is to develop a highly reliable real-time analyzer for H_2CO at low concentrations with data downlinked. Potential sources of H_2CO include materials off gassing, use of formalin as a tissue fixative in biological payloads and overheating of acetal polymers. The Spacecraft Maximum Allowable Concentration (SMAC) for H_2CO in air is 100 ppb for exposures of 7 days or longer. ISS concentrations of H_2CO are running only 10 - 30 ppb in the recent several years but have spiked as high as 60 ppb. Gateway real time monitoring requirements for H_2CO call for a range of 8 - 138 ppb. For this project, a concentration range of 5 - 500 ppb H_2CO is targeted. The core tunable diode laser spectroscopy (TDLS) technology used for this project was developed by Vista Photonics through the NASA and US Navy Small Business Innovation Research (SBIR) programs. Monitors based on TDLS have been demonstrated on ISS, trialed on a nuclear submarine and are being certified as portable Anomaly Gas Analyzers (AGA) for both ISS and Orion. Initially, direct absorption TDLS was used exclusively in these devices. The H_2CO target concentration, however, is low ppb, and a longer wavelength is required, so a photoacoustic spectroscopy (PAS) technique was adapted, where the laser excitation is detected by a sensitive microphone vs. a conventional photodetector. This paper will discuss the results of NASA-JSC laboratory testing of a prototype PAS based formaldehyde in air monitor and briefly discuss next steps.

Nomenclature

AGA = Anomaly Gas Analyzer
HALO = Habitation and Logistics Outpost
ISS = International Space Station
MGM = Multi Gas Monitor
PFM = Photoacoustic Formaldehyde Monitor
RH = Relative Humidity
SM = Service Module of ISS Russian Segment
T90 = Time for signal to reach 90% response
VOC = Volatile Organic Compound
ATCM = Atmosphere Trace Contaminant Monitor
H_2CO = Formaldehyde
LOQ = Limit of Quantitation
PAS = Photoacoustic Spectroscopy
ppb = parts per billion concentration
SBIR = Small Business Innovation Research
SMAC = Spacecraft Max Allowable Concentration
TDLS = Tunable Diode Laser Spectroscopy

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I. Introduction

NASA's strategy for monitoring the quality of spacecraft cabin air include the means to measure formaldehyde (H_2CO). Historically, dating back to Space Shuttle, this has been accomplished by means of commercial passive sampling badges that absorb H_2CO and are returned to a ground laboratory for analysis. Currently on ISS, the Formaldehyde Monitor Kit badges are deployed every 45 days for approximately 48 hours, then sealed up for return weeks or months later. This archival technique is fine for the well characterized and "aged" ISS but not for destinations beyond low Earth orbit and not for advanced spacecraft and habitats with increasing autonomy. H_2CO is one of the key terrestrial indoor air pollutants with wide public awareness [1], thus the efforts to improve technology for real-time monitoring would have significant terrestrial spin-off potential.

Formaldehyde is one of a couple dozen volatile organic compounds (VOCs) that are closely tracked in manned spacecraft for crew health/toxicology reasons because the allowable limit is quite low and incidence is persistent. From a health perspective, H_2CO can cause sensory irritation at relatively low levels. This endpoint serves as the basis for NASA Spaceflight Maximum Allowable Concentrations (SMACs) [2] at durations from 7 to 1000 days; this reflects the understanding that formaldehyde's irritating properties are a function of its concentration instead of accumulating intake over time. H_2CO is also challenging to monitor at these low concentrations.

H_2CO data from the passive badges deployed in the US Lab and Russian Service Module (SM) over the years is tracked and trended, and it figures prominently in the increment-by-increment assessment of ISS air quality. The last 2 years of available ISS data (Figure 1) indicates a fairly low concentration range, 7 – 20 ppb, never approaching the 100 ppb SMAC limit. Normally US segment and Russian Segment data track in parallel with US Lab data running 8-15 ppb higher than SM, probably because the Russian regenerable trace contaminant control system is more efficient at controlling H_2CO than the US trace contaminant control system, mainly due to higher air flow rate [3]. Figure 2 depicts the data from an early period of ISS operation where US Lab and SM results diverged, and this was eventually determined to be caused by intermodule ventilation impeded by debris in a duct. Although H_2CO has trended downward over the years (Figure 1), it still contributes significantly to the overall T value of the cabin atmosphere, where T is the summation of each key pollutant concentration divided by its own long term SMAC. Normally, the T value of ISS atmosphere is less than 0.6. An H_2CO concentration of 20 ppb adds 0.2 to the overall T value, which is quite a significant contribution from a single compound! The ISS Medical Operations Requirements Document [4] states "The atmosphere is considered acceptable if the T-value for each type of toxic effect is ≤ 1 when using acceptable-risk exposure limits"—that is, the long term SMAC limits.

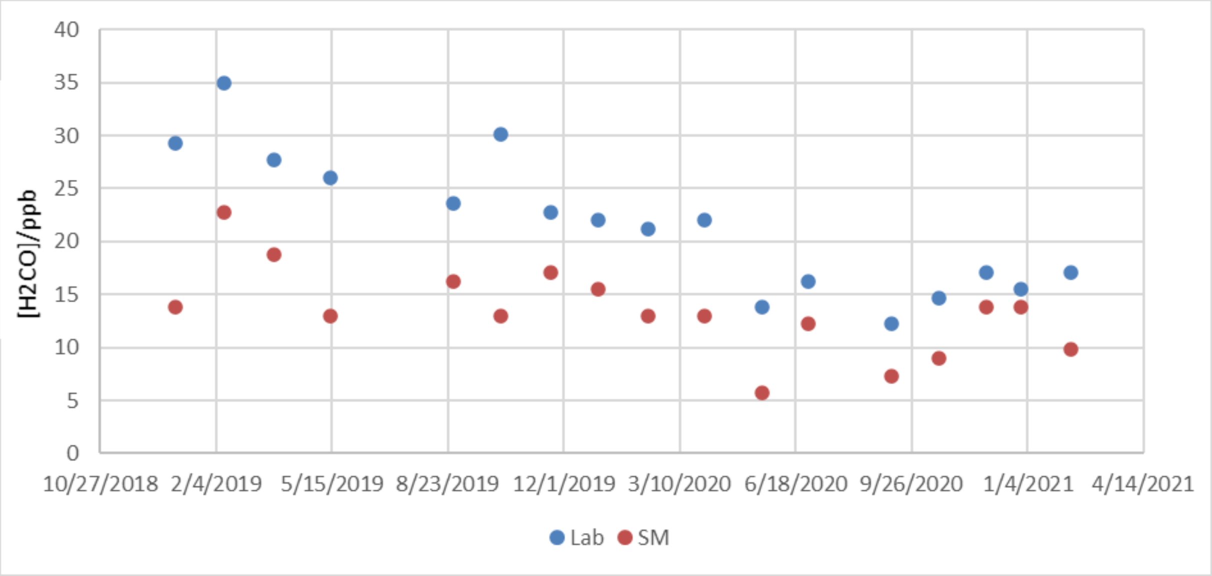

Figure 1. Recent H_2CO data from passive samplers deployed in US Lab & Service Module (SM)

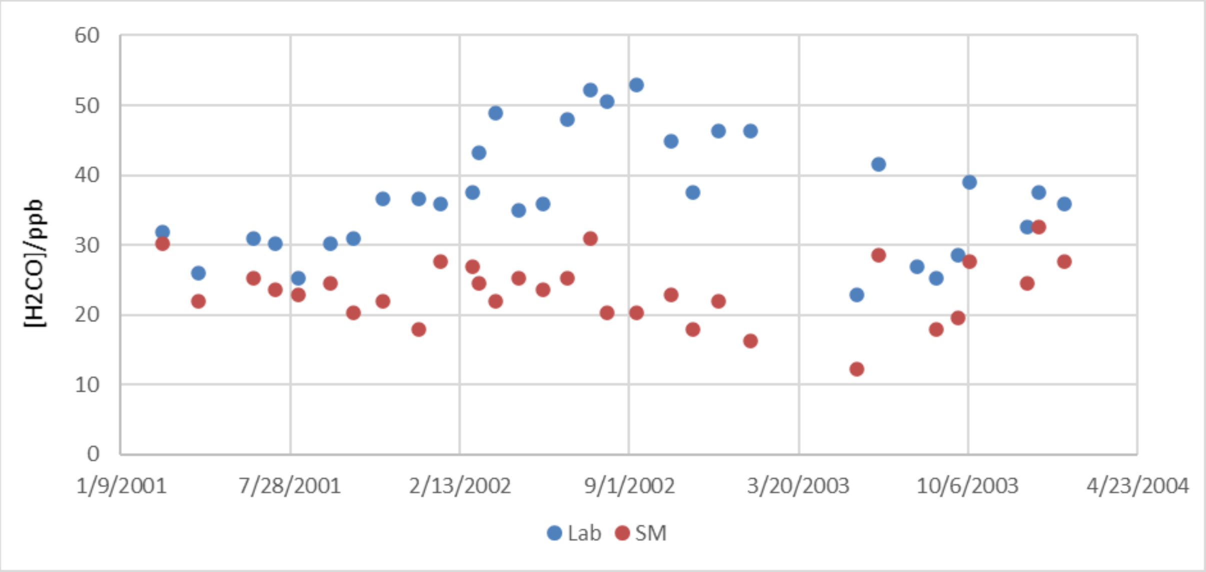

Figure 2. Early ISS H_2CO measurements via passive sampler in US Lab and Service Module (SM) showing the divergence between Lab and SM traced to a clogged ventilation duct that lasted over a year.

A. Commercial Formaldehyde Monitors

Regarding H_2CO measurement tools in the commercial market, there are a few different types, from low end colorimetric sorbent test papers, to handheld colorimetric devices to high end bench top laboratory units. In commercial environmental labs, methods typically involve trapping H_2CO via sorbent tube followed by liquid elution and liquid chromatography [5], or impingement method followed by visible spectrometry [6], both of which are quite labor intensive and require significant consumables. Inexpensive handheld colorimetric devices may be adequate for field work where estimates are acceptable, but they also require consumables with limited shelf-life. Conventional Draeger tubes are not able to detect H_2CO in the range [7] observed on ISS, without ancillary equipment and very high volumes of air pulled through the tube, thereby degrading accuracy. The unique application of spaceflight generally calls for a reasonably accurate automated device with low power draw, small footprint, low mass, high sensitivity and high reliability—characteristics not yet found in a single commercial device.

B. Specifying a Formaldehyde Monitor for Flight

A broad spectrum Atmosphere Trace Contaminant Monitor (ATCM) is in the early stages of development for NASA's Lunar Gateway Habitation and Logistics Outpost (HALO), and includes H_2CO as one of 23 target VOCs. The ATCM baseline requirements document [8] calls for analysis and "reporting the chemical contaminant Formaldehyde from a minimum of 0.01 to at least a maximum of 0.17 mg/m^3.", that is, from 8 to 138 ppb or higher. H_2CO will likely need to be monitored separately from the other VOCs. Standard temperature and pressure is assumed for verification. The wide concentration range covers both the current ISS scenario and somewhat beyond the long term SMAC of 100 ppb. Considering ISS experience and the fact that Gateway vehicles and habitats will be highly constrained, we estimated the following analytical and physical goals or draft requirements for a H_2CO monitor: Concentration range: 5 to 500 ppb; Accuracy +/- 25%; Mass: 1 Kg; Volume: 2.5 L; Power: 5 W. For this prototype phase, cabin environmental parameters will be limited to ISS like conditions, including atmospheric pressure (1 atm), temperature (20-25 °C) and relative humidity (RH, 25-40 %).

C. Development Progress to Date

Previous work in Tunable Diode Laser Spectroscopy (TDLS) by Vista and NASA-Johnson Space Center includes combustion product monitors for ground studies [9], a 2 year technology demonstration of a Multi-Gas Monitor (MGM) on ISS that measured oxygen, carbon dioxide, ammonia and water vapor [10], a 90 day US Navy submarine sea trial of the MGM [11], expansion of MGM gases to include 4 combustion products in the Anomaly Gas Analyzer (AGA) [12], and unique combustion product monitors prepared for the large fire demonstration "Saffire" flight experiment [13]. The core technology of the MGM is wavelength modulated absorption spectroscopy, using one diode laser per gas and a pathlength enhanced gas cell. For AGA, the combustion gases required the addition of a 2nd type of spectroscopy—photoacoustic, where, instead of a conventional photodetector, a sensitive microphone is used.

D. Photoacoustic Spectroscopy

The choice of photoacoustic spectroscopy (PAS) for H_2CO detection is driven by several considerations [14]. First, photodetectors at the target absorption wavelength are not very sensitive and have small surface areas. The small detector surface area limits performance in Vista's typical implementation approach to TDLS, which employs path length enhancement. The path length enhancement approach itself is, likewise, hindered at the target wavelength. In contrast, microphone performance is invariant with wavelength. The microphone detects a consequence of the optical absorption, namely the generated sound, and not the laser power itself. Secondly, the optical power available to diode lasers at the target wavelength, about 20 mW, favors PAS for low ppb concentration detection. Generally, for comparing PAS to TDLS, every mW of optical power in PAS equates to one meter path length in TDLS. Thus, an enhancement cell with 20 meter path length would be required to out-perform PAS in this application. While such enhancement cells do exist, they introduce a host of other issues for use in space flight.

PAS depends on detecting the sound generated by absorption of optical power by the target analyte. This sound has to be higher amplitude than the natural background sound experienced by the sensor. The background sound includes the typical environmental noise caused by local activity, flow noise caused by the gaseous sample stream flow near the microphone, and intrinsic electronic noise in the microphone itself. In practice, local environmental noise is typically the driver in establishing the limit-of-quantitation. The PAS sample cell volume is only a few cm^3, allowing for low sample flows that do not create excess background noise over the natural environment. The instruments are generally sensitive to a sharp, impulsive, strike or sound clap that can briefly overwhelm the microphones but typically settle back down in a few seconds.

A suite of prototype PAS instruments was delivered to the US Navy for evaluation towards possible use on submarines. The instruments are poised to be tested as part of an air quality monitoring system in this closed environment. The prototypes were designed to analyze for H_2CO, acrolein, carbon monoxide, ammonia, nitrogen dioxide, nitric oxide, and various refrigerants. This project allowed Vista to target and demonstrate the optimal wavelength for detection of H_2CO that provided both high sensitivity and selectivity. An early version of the US Navy H_2CO monitor (Figure 3-left) passed through the JSC laboratory for gross calibration, and the results looked favorable. This triggered new tasks on an existing Phase 3 SBIR contract at NASA-JSC to procure the correct diode laser and then to build a prototype Photoacoustic Formaldehyde Monitor (PFM) (Figure 3-right).

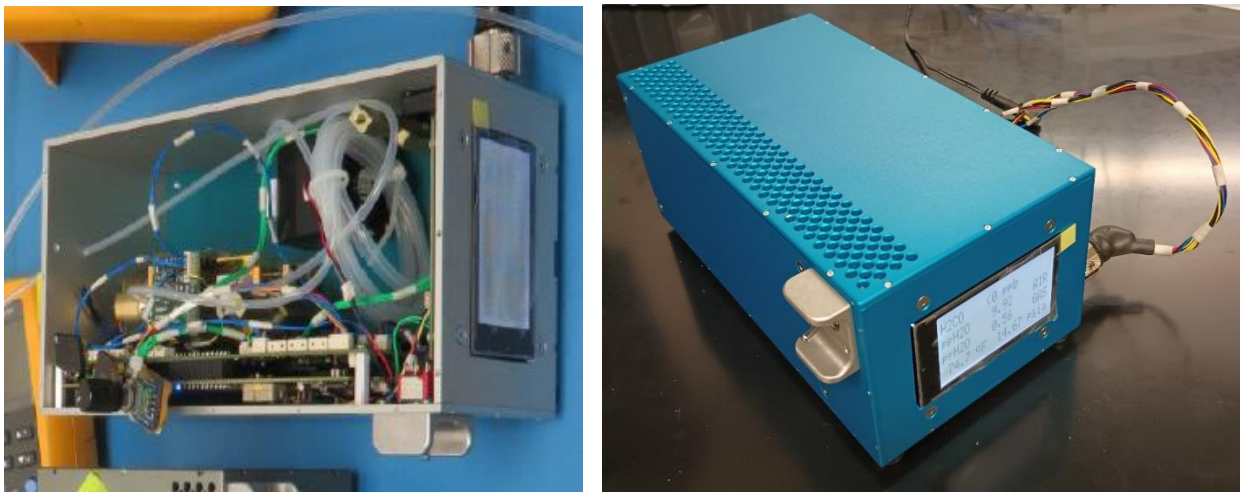

Figure 3. Early breadboard version of a photoacoustic formaldehyde monitor (PFM, left) and the prototype PFM as delivered to NASA-JSC (right).

II. Experimental

The H_2CO generation and delivery system setup is shown in Figure 4. Plumbing connections were made using standard Teflon tubing and stainless steel fittings. A polycarbonate chamber was installed between the H_2CO generation system and the PFM to ensure mixing and to eliminate flow noise that could affect the photoacoustic measurement. The PFM utilizes a low-flow pump or fan to introduce sample into the photoacoustic cell from the chamber. Interfering acoustic noise is created if the pump/fan is connected directly to a T-fitting in the exposure gas stream when high flow rates (> 5 liter per minute) are generated. These measures ensure the set up is not significantly different from deployment on a spacecraft, where ambient air is drawn in from the open cabin via the internal PFM fan. A calibrated temperature and humidity probe was installed in one of the chamber access ports. Samples were collected for independent measurements of the H_2CO concentrations using a pump and impinger (Figure 4). An outlet located in the chamber lid is where excess flow exhausts into the fume hood. In addition to the permeation tube gas generator, certified gas standards in pressurized cylinders were ordered from Linde Gas & Equipment Inc. in 1000 ppb and 5000 ppb concentrations (with 5 month shelf-life). The concentrations were checked via the wet chemical method and used as high end calibrants and check standards, plumbed in and diluted with zero air before the humidity bubbler, so that the method of exposure to the PFM was identical to the permeation tube gas generator. Regarding humidification, the ISS humidity is normally 10,000-12,000 ppm water or about 40-48% relative humidity at 21°C and 1 atm.

In addition to exposing the PFM to a sequence of increasing H_2CO concentrations at a constant humidity (~40% RH) which forms the basis of calibration, a series of gas challenges were conducted to assess the performance of the PFM. Table 1 prescribes pertinent challenges, some of which were completed and presented here (gray highlights).

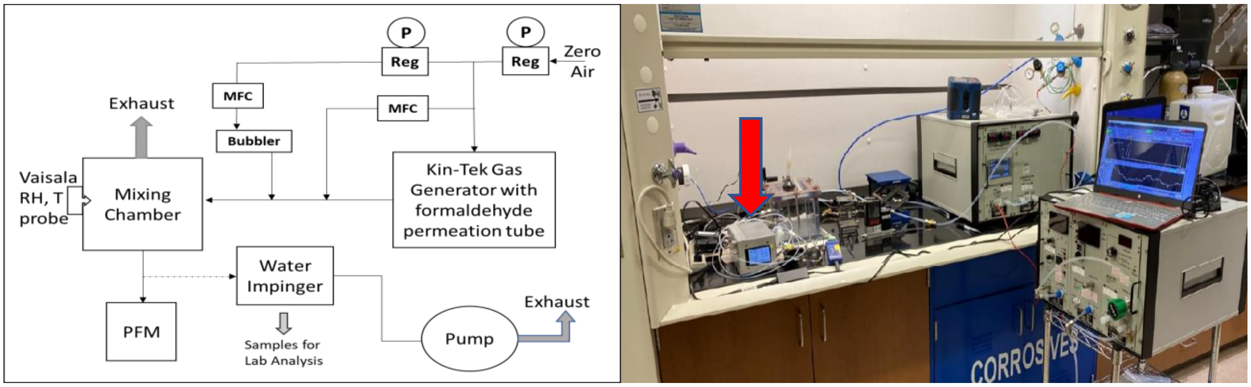

Figure 4. Gas system schematic (left) for presenting humidified H_2CO to PFM. MFC, mass flow controller; Reg is pressure (P) regulator. The Kin-Tek gas generator and associated equipment with test article (breadboard PFM indicated by red arrow) in fume hood (right).

Table 1. Challenge tests to assess performance of the prototype monitor

Test	Description
PFM Stabilization Time	From cold start, find duration required to achieve stable baseline
Effect of Humidity	At a constant H_2CO, vary the relative humidity, see how signal varies
Accuracy Test	Once calibrated, test unit against known standards, various levels
Response & Recovery Times	Assess time to stable reading when H_2CO concentration changes from zero to a mid level concentration, and from a mid level to low concentration. This is a standard test for field analytical equipment.
Precision Test	Repeated exposures to same concentration during a day with analysis
Method Detection Limit	Perform standard EPA style detection limit study/statistical analysis
Potential Interfering Compounds	Test against ISS levels of methane, CO_2, key organic compounds
O_2/N_2 ratio sensitivity test	Determine if small changes in atmosphere composition affects signal
Long-Term Exposure	Run for several days at a constant H_2CO to assess noise levels and drift

III. Results

Figure 5 shows the performance of the breadboard system with maximum averaging as the permeation oven is allowed to cool down to a temperature providing an ultimate concentration of about 50 ppb. Because this demonstrator was meant to be compared to the present H_2CO "badges" used on ISS, the accuracy and limit-of-quantitation (LOQ) were also determined with the maximum averaging presently available to the system. The badges are exposed for 48 hours on ISS and then returned for analysis. The longest averaging available at present to the H_2CO sensor provides a T90 response time of 15 minutes (time required for the sensor to reach 90% of steady state response). Noise at 1 sigma standard deviation in the steady state is about 1 ppb at the 50 ppb asymptote. SMAC for H_2CO (100 ppb) for durations of 7 to 1000 days is indicated for reference.

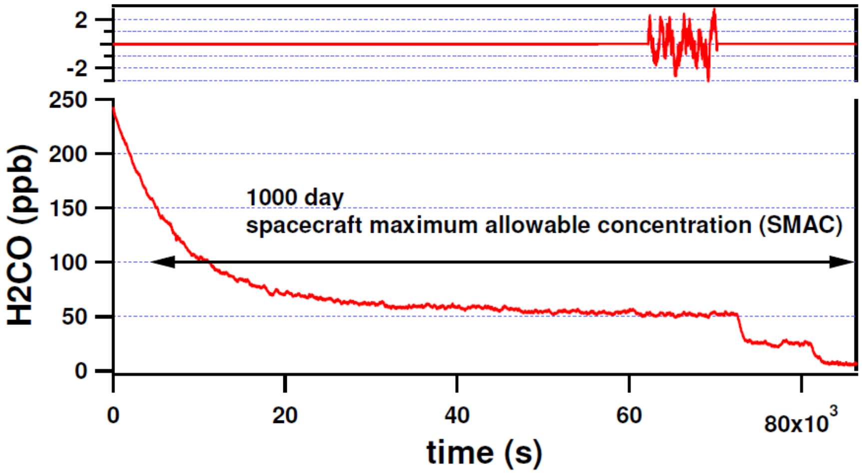

Figure 5. Breadboard H_2CO monitor exposed overnight to 50 ppb humidified stream of H_2CO showing quite low noise. Based on analysis of the signal-to-noise ratio, the detection limit could be as low as 5 ppb. Note that the exposure concentration was intentionally halved at about 72000 sec and reduced again about 82000 sec.

For accuracy, a factor of 3X standard deviation is commonly used leading to a measurement accuracy of about 3 ppb. The LOQ is typically defined as 10X the standard deviation. This places the LOQ at 10 ppb with the 15 minute response time. It is notable that these values are determined with dry H_2CO, which is not reflective of the ISS cabin environment (always humidified). Photoacoustic sensors can be sensitive to an effect known as kinetic cooling, which can cause the calibration to be dependent on other gases in the diluent blend, notably water vapor. Figure 6 shows a humidity dependence of the reported H_2CO concentration at 250 ppb. Dry H_2CO was determined by the sensor to be around 270 ppb. However, increasing humidity amplified the sensor reading up to about 30 % RH where increasing humidity gave little change in the reading of 430 ppb (factor of 1.6 times). Operating the sensor in an environment where the RH is always greater than 30 %, allows for this calibration factor to be used. Because the water vapor increases the PAS signal from H_2CO but does not increase noise, the LOQ seems to improve by this factor. The LOQ is about 6 ppb H_2CO when the RH is 30% or more.

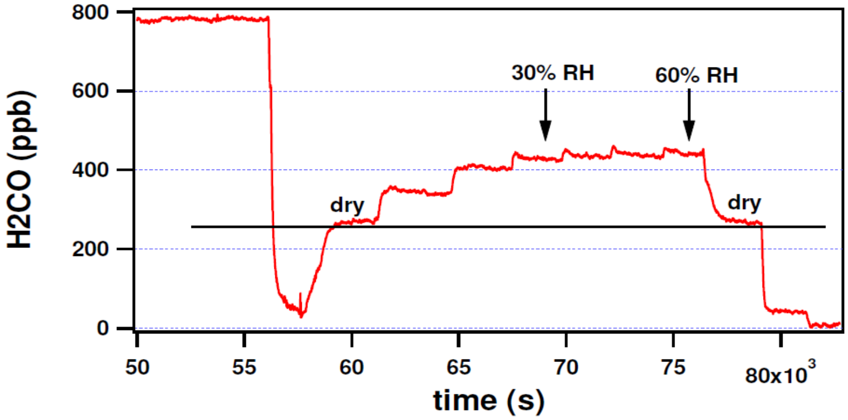

Figure 6. Breadboard PFM response to varying humidity at a constant H_2CO concentration

IV. Conclusion

A prototype photoacoustic formaldehyde monitor (PFM) was developed by Vista Photonics Inc with NASA funding. The unit was calibrated and challenge tested at NASA-Johnson Space Center under conditions representing the ISS cabin atmosphere. Results show the unit has quite a wide range of detection, with a low detectable limit of 6 ppb at modest humidity, and an upper limit of at least ~800 ppb (likely much higher). To optimize signal to noise, an integration time of 15 minutes was applied. Sensitivity of the photoacoustic measurement to humidity was confirmed. Relative humidity (RH) must be measured simultaneously with H_2CO and be included in the calibration algorithm. Alternative means to ensure that the RH in the air pulled into the PFM PAS cell remains above 30% should be explored. The state of the hardware is fairly advanced, but work on cross sensitivity, pressure and temperature dependence remains to be completed. With each significant refinement step, all of the tests listed in Table 1 will be performed to characterize the performance. This capability could fill a gap in our environmental monitoring preparedness for exploration vehicles and habitats.

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