PORTABLE MULTIGAS MONITORS FOR INTERNATIONAL SPACE STATION

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The Environmental Health System (EHS) on International Space Station (ISS) includes portable instruments to measure various cabin gases that acutely impact crew health. These hand-held devices measure oxygen, carbon dioxide, carbon monoxide, hydrogen chloride and hydrogen cyanide. The oxygen and carbon dioxide units also serve to back up key functions of the Major Constituent Analyzers. Wherever possible, commercial off-the-shelf (COTS) devices are employed by EHS to save development and sustaining costs. COTS hardware designed for general terrestrial applications however has limitations such as no pressure compensation, limited life of the active sensor, calibration drift, battery issues, unpredictable vendor support and obsolescence. The EHS fleet (inflight and ground inventory) of instruments is both aging and dwindling in number. With the retirement of the US Space Shuttle, maintenance of on-orbit equipment becomes all the more difficult. A project is underway to search for gas monitoring technology that is highly reliable and stable for years. Tunable Diode Laser Spectroscopy (TDLS) seems to be the front-runner technology, but generally is not yet commercially available in portable form. NASA has fostered the development of TDLS through the Small Business Innovative Research (SBIR) program. A number of gases of interest to the aerospace and submarine communities can be addressed by TDLS including the list mentioned above plus hydrogen fluoride, ammonia and water (humidity). There are several different forms of TDLS including photoacoustic and direct absorption spectroscopy using various multipass cell geometries. This paper describes the history of portable gas monitoring on NASA spacecraft and provides a status of the development of TDLS based instruments. Planned TDLS flight experiments on ISS could lead both to operational use on ISS and important roles in future Exploration spacecraft and habitats.

INTRODUCTION

Spacecraft like submarines are tightly closed inhabited vessels that require careful air quality control, materials control and monitoring as part of the strategy to protect and monitor the health of the crew. International Space Station (ISS) is a rather unique environment that is repressed periodically with fresh gases but has the potential for buildup of noxious compounds. Although the trace contaminant control system works to control VOCs, buildup of pollutants from off gassed materials and experiments is an ongoing concern. Malfunctioning equipment and overheated electronics produce various compounds some of which are toxic. From a fire safety and fire response standpoint, carbon monoxide (CO) is the first and foremost target gas for monitoring particularly as the atmosphere is recovering from an event (crew on masks). Current ISS requirements call for hand-held battery powered monitors for oxygen (O_2), carbon dioxide (CO_2), carbon monoxide (CO), hydrogen cyanide (HCN) and hydrogen chloride (HCl). Battery power is important both for portability and in case vehicle power is switched off/unavailable during contingencies. Currently, multiple commercial off-the-shelf (COTS) devices [1] are used to meet the requirements: (1) the Carbon Dioxide Monitor (CDM) depicted in Fig 1A is based on non-dispersive infrared detection and is a solid instrument with long life and pedigree. The CDM is used by the crew periodically to search for poorly ventilated areas, and in conjunction with payloads that may emit CO_2 such as SPHERES [2]. Because of reports of headaches from elevated CO_2, the CDM has been used to study CO_2 “clouds” in the vicinity of active crewmembers to try to correlate concentration and health affects [3,4]. (2) the Compound Specific Analyzer-Oxygen (CSA-O2) depicted in Fig 1B is an electrochemical sensor and is used in the airlock for Extravehicular Activity preparation as well as a backup to the vehicle Major Constituent Analyzer (MCA). The CSA-O2 is periodically calibrated inflight using a tank of qualified compressed air. (3) the Compound Specific Analyzer-Combustion Products (CSA-CP), depicted in Fig 1C, uses 4 different electrochemical sensors for O_2, CO, HCN, and HCl. The certified purposes of the device include checking fire ports via a detachable wand/pump to locate sources of smoke/”hot” odors and monitoring the scrubbing of the atmosphere after a fire while the crew has donned appropriate masks. The readout helps to determine when the crew can safely remove the masks, when comparing values to health standards (“mask doffing criteria”) for the 3 combustion products it measures. The crew also tends to use the CSA-CP to investigate off-nominal odors of any kind in the cabin to rule out combustion. That purpose provides an important “comfort factor” for both the crew and ground controllers. CSA-CP units are not first alert devices for fire detection, as they are not deployed and active full time.

Fig 1.Three hand-held instruments in use on ISS: (A) Carbon Dioxide Monitor, (B) CSA-O2 for oxygen; and (C) CSA-CP for combustion products CO, HCN, HCl. Each is about 5x3x2 inches and weighs 1.5 lbs.

There is also an instrument on ISS for broad spectrum volatile organic compounds (VOCs) in a larger yet portable configuration called the “Air Quality Monitor (AQM)”. AQM is a commercial development and is based on gas chromatography/differential mobility spectrometry [5]. The experimental and operational versions of the AQM are shown in Fig 2. The AQM’s power supply plugs into one of many available vehicle power outlets in the US Segment. The performance and data obtained to date on ISS is the subject of other papers at this conference [6].

Fig 2. Air Quality Monitor, based on gas chromatography/differential mobility spectrometry. (A) Experimental version of the AQM which has operated on ISS since 2009. (B) Operational version under development to be delivered to ISS in early 2013. Dimensions are approximately 10x6x5 inches. The unit weighs 6.6 lbs. Each unit will have an estimated 2 year life.

Unexpected Events that Potentially Affected ISS Air Quality

The purpose of the portable air quality monitoring hardware is reflected not only in the formal ISS air quality monitoring requirements [7] but also is rooted in historical considerations. Experience with unexpected events on spacecraft underscores the utility and necessity of instrumentation as part of the crew health care strategy. A partial list of unexpected events that occurred on ISS which may have impacted cabin air quality is provided in Table 1. Fortunately, only a few of the events were serious in nature, evolving combustion gases as measured by the CSA-CP. In the majority of cases in which the crew deployed the CSA-CP, however, the reported readings were all “zeros” or negligible. In certain cases, Grab Sample Containers (GSC) were used to collect a sample for ground analysis. In general, however, transient odors are difficult to capture, identify and quantify by any means. The ground laboratory has not had good success in identifying the source of transient odors based on analyzing GSC samples [8].

Table 1. Partial Record of Unexpected Events Affecting Spacecraft Cabin Air Quality

<u>Shuttle</u>

- Teflon sleeve pyrolyzed by electrical short (STS-28)
- Wire burnt beneath a humidifier (STS-6)
- LiOH dust escaped from CO2 removal canisters (several)
- Dust released from waste management system
- Combustion products from electronics pyrolysis in 2 data display units (STS-35)
- Formaldehyde pollution from pyrolysis of motor housing in a refrigerator (STS-40)
- Microbial production of methyl sulfides from liquid waste (STS-55)
- Airlock adapter coating strongly off-gassed during delivery to Mir (STS-89)

<u>Mir during the Shuttle-Mir Program</u>

- Frequent leaks of ethylene glycol from cooling loops into air
- Formaldehyde escaped containment from an experiment on Mir-18

- Oxygen candle fire produced thermal degradation products, e.g. benzene (Feb 97)
- Overheating BMP beds produced health threatening levels of CO (Feb 98)

International Space Station

- Crew sickened by rebreathe of exhaled air/CO2 due to poor ventilation in a work area (May 99)
- Freon 218 leaks from SM air conditioner (Apr 01 to Mar 02)
- High methanol in a sample of FGB air; exact source never determined (Aug 01)
- USOS METOX canister regeneration released many pollutants in air (Feb 02)
- Formaldehyde briefly exceeded long-term limits, when debris restricted ventilation (mid 02 to Feb 03)
- Strong solvent-like odor from Elektron oxygen generator after repair work (Mar 04)
- Odor from Service Module illumination light panel (Mar 05)
- Elektron O2 generator overheated; smoke & solvent smell; bushing smoldered; 7 ppm CO(Sep 06)
- Freon 218 (octafluoropropane) leaks from Service Module air conditioner during servicing (Apr 08)
- Report of smoke and odor from Russian galley (SRV-K); hot to touch; CO measured at 5 ppm (Oct 08)
- Japanese Experiment Module transient odor described as acetone or formaldehyde (Dec 08)
- Transient odors from Urine Processing Assembly in the US segment (Dec 08, Sep 10, Jul 11)
- 2nd report of smoke and odor from Russian galley (SRV-K); CO measured in 4-5 ppm range (Jul 09)
- US Lab thermal control aqueous fluid leak and odor from its orthophthalaldehyde biocide (Oct 09)
- Cargo vehicle HTV-1; crew headaches from odor; CSA-CP readings all zero; GSC collected (Sep-Oct 09)
- Rotten food smell from 35Progress cargo vehicle packed with trash; A2 scrubber deployed (Feb 10)
- Transient "funky", "locker room" odors reported in US Lab near Node 1; GSC collected (Oct 10)

Considerations for Replacement Multigas Monitor

The following are some of the factors being considered in the effort to research and replace the existing hand-held gas sensors for ISS:

1. Obsolescence. The hand-held equipment is obsolete—the current units are no longer supported by the manufacturer. The original certification for flight was completed in 1999. Units are supplied to ISS every 6 months, and remaining quantities on the ground are dwindling.

2. Box Count. The hand-held monitors tend to be used in pairs for redundancy. Also, as the photos above attest, the 3 monitors look very similar and could be confused during a contingency. One major objective in the development of the next generation hardware is to reduce the "box count" to reduce confusion and operational complexity for both the crew and ground teams. Ideally, a single hand-held instrument would be used to measure all contingency gases. The ultimate goal, naturally, is the realization of the "Tricorder" for all airborne target compounds.

3. Calibration life. Clock starts ticking on the useful life of electrochemical sensors immediately upon calibration. CSA-CP unit cannot be calibrated but can be zeroed in flight using the pump attachment and a special filter filled with Hopcalite which removes CO. Normally, calibrated units are delivered to the launch site then sit for a couple months awaiting integration and launch. Useful life on orbit is only 6 months. With Shuttle retirement, NASA's approach has changed from round trips to one way trips for

the hardware. This "build and burn" scenario translates to higher cost and pressure to replace hardware on a limited timescale.

4. Batteries. Currently, the crew monitors the battery status and calls down status periodically and with battery replacements (non rechargeable). Another objective of the replacement project is to simplify battery operations by building/certifying a recharging stand or use on-orbit rechargeable batteries. Thus, the new multigas unit would be like an emergency flashlight--- fully charged and ready at all times, with multiple units deployed in conspicuous places to respond optimally to contingencies.

5. Vehicle Aging: As the ISS vehicle ages, there are concerns about certain contingencies that could increase in probability, such as leakage of external coolant ammonia into the cabin via thin-walled heat exchangers. Currently there are Draeger tubes on board for approximating NH3 concentration ranges, but no continuous high fidelity monitor. EHS must be prepared with appropriate hardware to monitor any new target compounds related to aging and possible life extension of ISS beyond 2020.

Expert Panel Review of Technology

In September 2010, NASA-JSC, NASA-GRC and Jet Propulsion Laboratory jointly sponsored a Combustion Product Monitor Technology Evaluation Panel, consisting of outside experts from government agencies, universities and research organizations. The panel reviewed commercially available instruments and new technologies for measuring combustion gases and heard presentations from various vendors, small businesses and researchers. The outcome was a written report with recommendations to NASA on which technologies to pursue for the next generation instrumentation for ISS and Exploration. The executive summary states: "Overall, the panel identified laser absorption spectroscopy as the technology with the best prospects for reliable detection of combustion products in a 1-2 year horizon" and recommended side by side comparison testing in actual combustion environment on the ground [9].

Tunable Diode Laser Spectroscopy

The measurement of concentration by optical absorption is based on straightforward implementation of Beer's law,

$$\frac{I}{I_0} = \exp(-\alpha) \quad \text{and} \quad \alpha = S(T)g(v)n\ell = \sigma(v)n\ell$$

where I_0 is the light intensity incident on a gas sample, I is the transmitted intensity and α the absorbance. The absorbance is comprised of the absorption line strength S(T), the line shape function g(v), number density n in cm^{-3} and path length ℓ in cm. The line strength is a measure of how strongly light is absorbed and is a function of temperature but not pressure. The line shape function describes the wavelength dependence (v) of the absorption and depends on temperature, pressure and in some cases, the gas composition. The absorption cross section term $\sigma(v)$ is the product of S(T) and g(v) and has units of cm^2. In the low absorbance limit ($\alpha << 1$),

$$\frac{I_0 - I}{I_0} = \frac{\Delta I}{I_0} = \alpha$$

the fractional absorbance is linear with concentration. This method is a line-of-sight technique, so that the absorbances are always spatial integrals along the optical path. Since the quantity actually measured is the ratio of ΔI to I_0, the resulting concentration is independent of source intensity fluctuations and depends only on accurately-known parameters.

Optical absorption spectroscopy provides signal that is linear and quantitative in concentration of the absorbing species. As expressed by Beer's law, the signal is directly proportional to the concentration. Wavelength modulation spectroscopy (WMS) allows measurement of weak optical absorbance by shifting the detection band to high frequencies, where laser excess ($1/f$) noise is reduced, to achieve fractional absorption sensitivities near the shot-noise limit (10^{-8}) in the laboratory. Field measurements using WMS often attain minimum detection absorbances of 10^{-5} under extended operation. To implement WMS, a small sinusoidal modulation at frequency f is superimposed on the laser diode injection current causing modulation of the laser wavelength, because wavelength is tuned by changing the current. The amplitude of the current modulation is chosen so that the induced wavelength modulation is comparable to the width of the spectral feature under study. Absorption by the target gas converts the laser wavelength modulation to an amplitude modulation that induces AC components in the detector photocurrent. Phase-sensitive electronics are then used to demodulate the detector photocurrent at a selected harmonic, nf (typically, n = 2). By implementing this technique at sufficiently high frequencies, sensitivity can be improved over slower direct absorption measurements. Studies have shown that detection frequencies of a few kHz are often sufficient to achieve these objectives.

Repackaged Commercial Oxygen Monitor for ISS

The Vaisala oxygen monitor was selected for repackaging to replace the CSA-O2 chiefly for airlock EVA applications but also to back up the ISS Major Constituents Analyzers [10]. The Vaisala monitor, now marketed by SICK GmbH [11] as an oxygen transmitter for stack gases and other industrial uses, is shown in Fig 3A. The basis of measurement is direct absorption spectroscopy using tunable diode laser spectroscopy (TDLS) at 762 nm. After adding rechargeable battery power, modifying the programming for pressure compensation, hardening the case, and adding a handle, the product appears as shown in Fig 3B. Designed for a 10 year service life, this version is currently undergoing qualification at NASA-Johnson Space Center and the first units should arrive on ISS in mid 2012.

Integrating Sphere TDLS

Tunable diode laser spectroscopy, when implemented with wavelength modulation, is improved for gas sensing on spacecraft by combining the general technique with an integrating sphere sample cell and state-of-the-art digital electronics. An optical integrating sphere is used to take an optical source, including laser diodes and vertical cavity surface emitting lasers (VCSELs), and spread that optical power homogeneously over the sphere's interior surface. This is accomplished by multiple, near-Lambertian

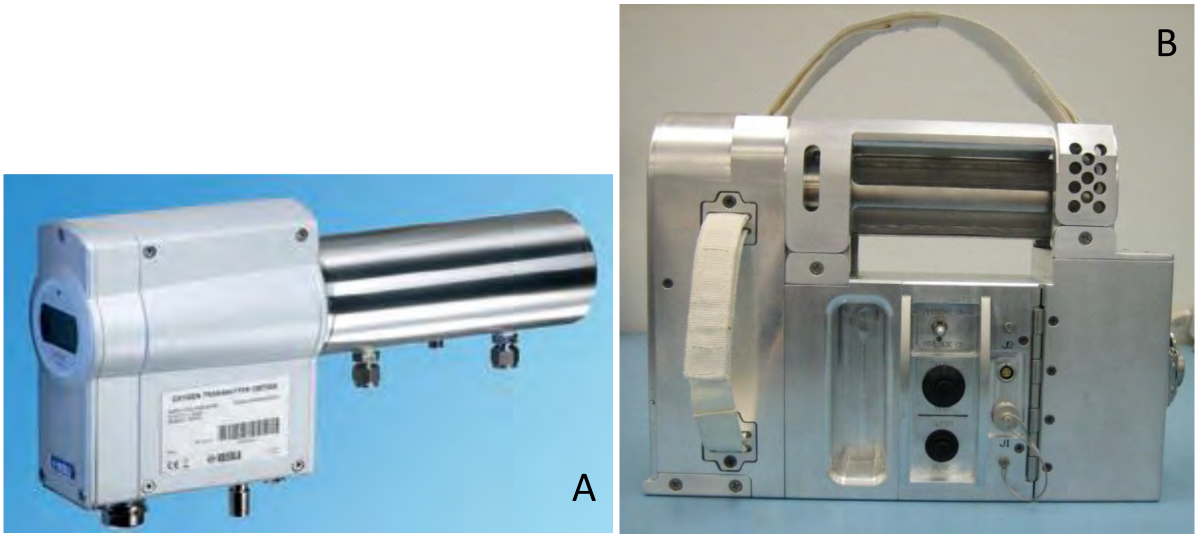

Fig 3. A. COTS Oxygen Transmitter monitor by SICK MAIHAK GmbH; B. Heavily repackaged, battery powered ISS Portable Oxygen Monitor (IPOM) is now undergoing qualification for flight. Dimensions are 11x8x3 inches and the mass is 10 lbs.

spheres offer nominal diffuse reflectivities of 0.99R (PTFE derivatives like Spectralon™) over an extremely broad wavelength range (350 nm to 1650 nm) with a useful range out to 2600 nm (R>0.95). These off-the-shelf spheres are available in a variety of sizes and costs. Vista Photonics has designed and developed a multi-faceted commercially-obtained integrating sphere specifically for accommodating multiple lasers and detectors for multiple gas detection on spacecraft. Photon flux incident on integrating spheres is amplified by the "sphere multiplier". The sphere multiplier is equivalent to the optical pathlength/power enhancement experienced by a traveling wave interferometer. In contrast to both traveling and standing wave build-up cavities, there are myriad optical paths traversed by rays within the integrating sphere. As a result, the integrating sphere does not introduce wavelength-dependent cavity build-up mode structure (etalon fringes) onto its gain spectrum. The sphere appears as a "white" path length amplifier. Because not every traversal of the integrating sphere passes through the sphere origin, the sphere multiplier does not return the exact path length enhancement of the device as it would for a Fabry-Perot cavity. The average chord length per traversal for the integrating sphere is 2/3 the sphere diameter. Thus, the average path length traversed by rays in the sphere is 2/3 the sphere diameter times the sphere multiplier. The real reflectivity is reduced from the nominal value by the presence of open apertures with no reflectivity. For the custom faceted spheres used for multiple gas detection the average path length varies between 100 and 250 cm depending on wavelength.

Multigas Monitor Development based on TDLS

The combination of these techniques has resulted in a multiple gas monitor with emerging spacecraft applications called the Optical Life Gas Analyzer (OLGA), Figure 4. OLGA measures four target gases: O_2, CO_2, ammonia (NH_3) and water vapor (relative humidity). The OLGA output data are generated at a rate of 0.149 Hz (once in every 6.7 s). The time constant (1/e) for signal averaging is 10 s. The measured concentrations are also displayed on an LCD, along with temperature and pressure. The data are also recorded on a compact flash memory card and can be uploaded to an external laptop computer via a serial interface. Each of the gases is detected with a dedicated wavelength-specific VCSEL while photodetectors for both infrared and visible ranges can be shared. The instrument cycles sequentially through the four gas measurements at a rate of 2 Hz. This work was done as a Phase 3 Small Business Innovative Research project followed up with a purchase of a development unit for evaluation [12].

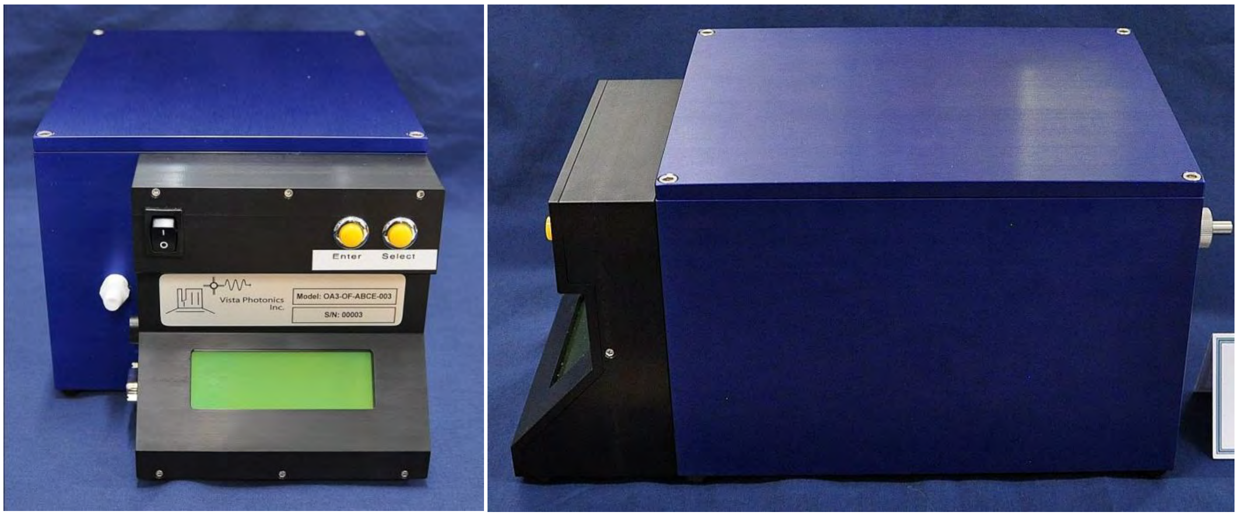

Fig 4. Optical Life Gas Analyzer (OLGA) evaluation unit, which is designed for vacuum backfilling, convenient for gas exposure testing. The unit is undergoing testing in the NASA-JSC Toxicology Lab. Dimensions are 8x7x5 inches. Mass varies with case requirements (see text).

Typical data are represented by the OLGA oxygen measurements. Figure 5 presents an example of an OLGA time-series oxygen data set acquired on 04/26/2011 at NASA Johnson Space Center. Figures 5 and 6 show the measured O_2concentration versus the set O_2 concentration based on the data obtained during the three day testing. The oxygen data show good accuracy and linearity. Statistical analysis of the residuals yields a standard deviation of $\pm$ 0.25%. This measurement uncertainty is about 3 times higher than normally obtained in long-term measurements using single certified gas mixtures (no flow mixing). At least two factors may have contributed to the additional uncertainties observed in these experiments. First, in some cases, because of the time constraints, dwell time was not long enough to allow the OLGA signal to level-off completely (the apparent response time in these experiments is determined by dilution/mixing time in the test chamber — the chamber volume is $\approx$ 11 liters, while the gas flow was $\leq$ 2 l/min). Another source of error can be the uncertainty in the set concentration created by the gas flow mixing system used in these experiments. Further, in the current version of the system the optical absorption signal is not corrected for temperature and laser power variations, which can significantly improve the measurement precision. Exposure plots similar to Fig 5 were measured for H_2O, CO_2 and NH_3. Detection limits and measurement precision for these gases are about 100 ppm, 20 ppm and 10 ppm, respectively. Other gases easily accommodated in the OLGA architecture include methane (CH_4) and hydrogen fluoride (HF), both of which could be important for the spacecraft cabin.

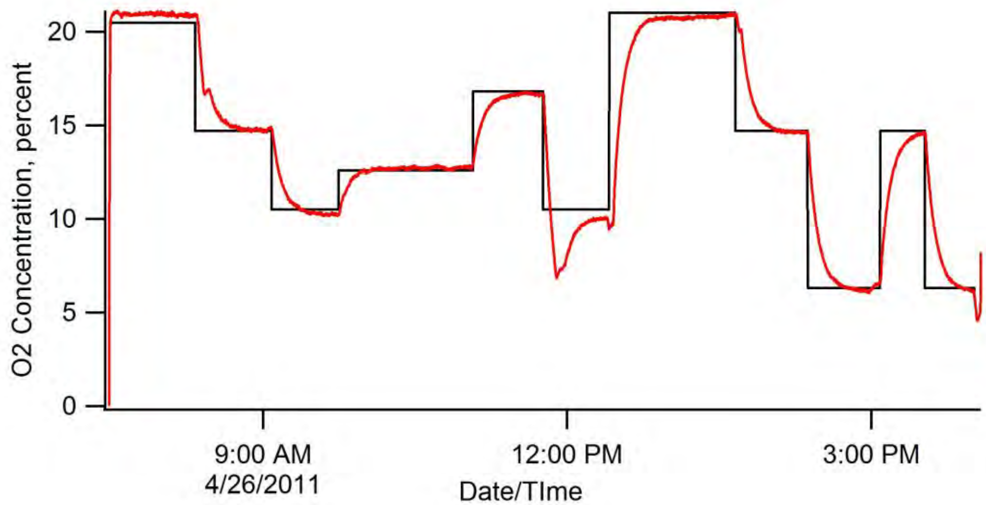

Fig 5. An example of a time-series data set obtained by acquiring the OLGA oxygen signal over about 8 hours on 04/26/2011. Black trace: feed concentration; red trace: OLGA measured [O_2].

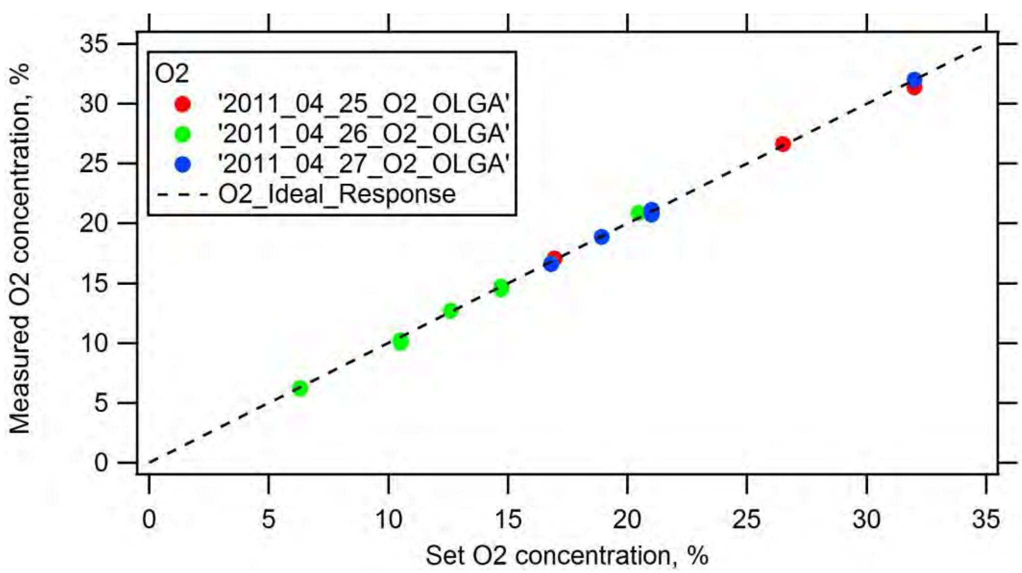

Fig 6. Measured [O_2] vs. set [O_2] at 760 Torr. Points of different colors show data obtained on 04/25/2011 (red), 04/26/2011 (green), and 04/27/2011 (blue). The dashed line shows the expected (ideal) response of the instrument, *i.e.*, zero offset and a slope of unity.

The OLGA architecture weighs between 1.0 and 3.5 kg depending on the type of enclosure employed. If an *in situ* sensor is required without being leak-tight, a low mass enclosure is sufficient. For vacuum operation, the enclosure pictured in Figure 4 is necessary but that incurs a higher mass penalty. The sensor draws 2.1 Watts at 6 VDC when running all four gases. A simple camcorder battery already in use on ISS is capable of powering OLGA for 8 hours. The sensor automatically powers itself down during a low battery condition. Preliminary results with an alternative digital electronics arrangement indicate the sensor volume can be reduced by a factor of two with no impact on performance. Alternatively, the new architecture would allow the enclosure shown in Figure 4 to accommodate up to 8 target gases.

Conclusions & Future Directions

Consistent with the recommendations of the Expert Panel, NASA plans to continue evaluation of Tunable Diode Laser Spectroscopy technologies for multiple simultaneous trace gas measurements for future human exploration. The initial 4 gas concept (OLGA) represents a platform on which other applications such as combustion products analysis can build. As VCSEL laser diodes in the mid-infrared become widely available, hand-held, battery-powered multigas monitoring devices will be realized for a broader range of gases. Testing of candidate devices is planned in realistic environments created in NASA facilities including White Sands Test Facility. Once validated on the ground, hardened versions of the technology can then be developed for flight demonstration on the International Space Station.

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