

On-Orbit Measurements of the ISS Atmosphere by the Vehicle Cabin Atmosphere Monitor

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We report on trace gas and major atmospheric constituents results obtained by the Vehicle Cabin Atmosphere Monitor (VCAM) during operations aboard the International Space Station (ISS). VCAM is an autonomous environmental monitor based on a miniature gas chromatograph/mass spectrometer. It was flown to the ISS on shuttle mission STS-131 and commenced operations on 6/10/10. VCAM provides measurements of ppb-to-ppm levels of volatile trace-gas constituents, and of the atmospheric major constituents (nitrogen, oxygen, argon, and carbon dioxide) in a space vehicle or station. It is designed to operate autonomously and maintenance-free, approximately once per day, with a self-contained gas supply sufficient for a one-year lifetime. VCAM is designed to detect and identify 90% of the target compounds at their 180-day Spacecraft Maximum Allowable Concentration levels.

Nomenclature

<i>AMP</i>	= Atomic and Molecular Physics Group
<i>DU</i>	= Development Unit
<i>ECLSS</i>	= Environmental Control and Life Support System
<i>GC/DMS</i>	= Gas Chromatograph/Differential Mobility Spectrometer
<i>GC/MS</i>	= Gas Chromatograph/Mass Spectrometer
<i>HOSC</i>	= Huntsville Operations Support Center
<i>IFM</i>	= In Flight Maintenance
<i>ISS</i>	= International Space Station
<i>JPL</i>	= Jet Propulsion Laboratory
<i>JSC</i>	= Johnson Space Flight Center

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<i>LDHF</i>	= Long Duration Human Spaceflight
<i>MCA</i>	= Major Constituents Analyzer
<i>MSFC</i>	= Marshall Space Flight Center
<i>MCE</i>	= Monitor and Control Electronics
<i>MPLM</i>	= Multi-Purpose Logistics Module
<i>NCO</i>	= Numerically-Controlled Oscillator
<i>NIST</i>	= National Institute of Science and Technology
<i>ORU</i>	= Orbital Replacement Unit
<i>PC</i>	= Preconcentrator
<i>PFU</i>	= Protoflight Unit
<i>PE</i>	= Processor Electronics
<i>rf</i>	= Radiofrequency
<i>RSD</i>	= Relative Standard Deviation
<i>SMAC</i>	= Spacecraft Maximum Allowable Concentration
<i>STD0</i>	= Station Detailed Test Objective
<i>TG</i>	= Trace Gas
<i>TReK</i>	= Telescience Research Kit
<i>VCAM</i>	= Vehicle Cabin Atmosphere Monitor
<i>VOA</i>	= Volatile Organic Analyzer
<i>VOCs</i>	= Volatile Organic Compounds

I. Introduction

The characterization of the cabin atmosphere for trace chemicals and the major constituents is vitally important to safeguard astronaut health during long duration human flight (LDHF). Analytical measurements of these types when performed terrestrially typically use gas chromatograph mass spectrometers (GC/MSs). GC/MSs have been indispensable in robotic exploration of the solar system where these instruments are powerful tools for identifying atomic, molecular, and biological species, and their abundances, in plasmas, complex atmospheres, liquids, or on surfaces. On the International Space Station (ISS) there have been many types of sensors for the detection and identification of atmospheric constituents, such as a magnetic sector mass spectrometer in the Major Constituents Analyzer¹ (MCA), a quadrupole MS for medical monitoring (breath analysis)², a gas chromatograph differential ion-mobility spectrometer (GC/IMS and GC/DMS)³⁻⁵ for trace volatile organic compounds (VOCs), a Fourier transform infrared spectrometer⁶, a variety of solid-state detectors for CO and combustion products⁷, and Draeger tubes for hydrazine detection in airlocks. There would be a significant savings in mass, volume, power and cost -- with no loss in performance -- if some of these sensors could be replaced by a single, miniature GC/MS instrument. A successful environmental monitor must operate autonomously, providing accurate and precise results in the complex ISS cabin environment while satisfying all requirements for sensitivity, identification (of both known and unexpected chemical targets), dynamic range, and instrument mass-volume-power. Examination of the chemicals on the Spacecraft Maximum Allowable Concentration (SMAC) target list illustrates the analytical difficulty of the task. Given the variety and concentrations of these chemicals, coupled with the potential for unexpected and unknown chemical releases into the LDHF environment, a GC/MS appears to be the best instrument to address these requirements. It is the standard instrument for analysis of chemicals in terrestrial and planetary environments. A description of the VCAM GC/MS approach was presented earlier.⁸⁻¹⁰ The results presented here summarize VCAM's analytical performance during its first year of operation as both a trace-gas and major atmospheric constituents analyzer aboard the ISS.

II. Description of VCAM

Shown in Fig. 1 is a schematic diagram of VCAM. The air is typically sampled at the VCAM location. One can also analyze at other locations within the ISS by collecting a sample at the remote location with an evacuated sample bag. For the analysis of cabin air for VOCs, VCAM operates in its TG mode where air (either *in-situ*, or using the sample bag) is sampled through a filtered inlet and adsorbed onto a PC module. After adsorption, the residual air is purged and VOCs are thermally desorbed from the PC in a low flow of helium directed through the GC microinjector. At the peak of the chemical thermal-desorption profile the microinjector captures approximately 20 μl of the stream into the sample loop. This portion is compressed by the pressure of the GC carrier gas, and is injected onto the head of the GC column. The GC elution stream is directed into the center of a Paul ion-trap mass spectrometer. There, a pulsed beam of electrons ionizes the analytes. The resultant ions are then mass-analyzed by

the Paul trap in its so-called selective mass-instability mode: the RF amplitude is swept linearly in time, and the ionized species are “walked” off the edge of the Paul trap stability region. The mass/charge-selected ions are ejected onto the front cone of a channel-type electron multiplier, and the mass spectrum stored. The Paul trap electrodes are coated with an inert silanizing layer. Together with an internal halogen bulb which maintains the mass spectrometer at approximately 100C during operation, these ensure surface cleanliness. The PCGC, microinjector, heaters, valves, sample pump, and Paul trap sequencing is controlled by the onboard Monitor and Control Electronics (MCE) and Processor Electronics (PE). The mass spectra are analyzed either autonomously onboard, or the data transmitted to ground and analyzed. In addition to the TG Mode, VCAM has a second operating path called the MCA mode. Identical plumbing and Paul trap are used for species analysis in this second mode. Here, cabin air is introduced directly into the microinjector and subsequent GC column, bypassing the PC. In this mode three of the major cabin-air constituents (N₂, O₂, and CO₂), as well as Ar, are identified and monitored. This provides dissimilar redundancy to the magnetic sector-based Major Constituents Analyzer already aboard ISS.

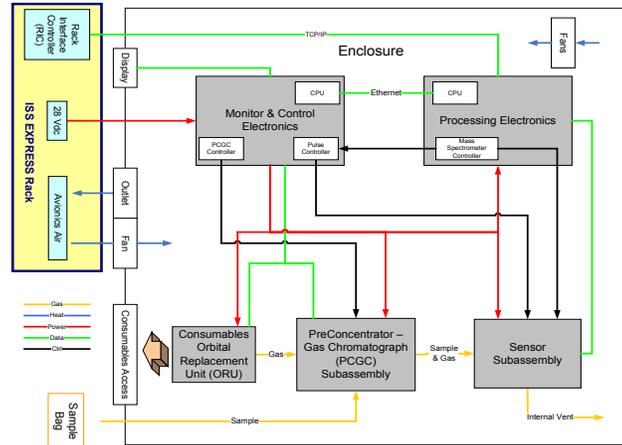


Figure 1. Schematic Representation of the VCAM Subassemblies. The Paul ion trap is contained in the high-vacuum Sensor Subassembly Module. The calibration and He carrier gases are part of the Consumables ORU.

A photograph of the VCAM PFU is shown in Fig. 2. Its mass is 25.2 kg (without consumables) and uses 140 W (peak) and 100 W (nominal) power as derived from the EXPRESS 28V rack. Gas consumables sufficient for one year of operational life comprise the orbital replacement unit (ORU). Its mass is 5.1 kg. The consumable gases are contained in two tanks: one of pure helium used as the GC carrier gas, and the other of a calibrant gas mixture (acetone, perfluoropropane, and fluorobenzene in He) used to verify the GC and MS performance (*e.g.*, mass range, mass resolution, and mass cross-talk). Cooling is by means of forced air supplied from the ISS avionics air-cooling loop; circulation through the VCAM interior is by a pair of internal fans. The VCAM sub-assemblies and packaging were not optimized for volume as they occupy the standard 64.4 liter EXPRESS rack module. Downlink data communication is through the ISS medium-rate data link, buffered onto the ISS high-rate outage recorder and telemetered to Earth. The data are routed through the White Sands and Huntsville Operations Support Center (HOSC), and then through the internet to JPL where they are presented *via* the Telescience Research Kit (TReK). Uplink for on-orbit commanding is *via* the inverse path. When necessary, new PFU instrument sequences are first tested on the VCAM Development Unit (DU). The DU is a form-fit-function duplicate of the PFU. Once operation is confirmed the

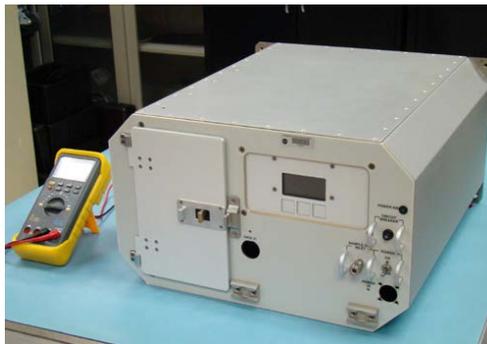


Figure 2. Photograph of the VCAM Protoflight Unit. Not shown is the Orbital Replacement Unit (ORU) comprising the helium GC carrier gas and calibrant gas.

sequence is uploaded via TReK to the PFU on board ISS. Typical measurement operations for trace gas or major constituents are not performed *via* direct ground commanding, but by uploading a schedule for automated measurements several days in advance.

Following successful completion of the validation in 8/09, the PFU was delivered to Kennedy Space Center (9/09) and packed into the Leonardo MPLM (2/10). A brilliant, pre-dawn launch of VCAM aboard STS-131 to the ISS occurred on 4/5/10. On 4/12/10 the PFU was installed into the Locker #8 of EXPRESS Rack #2. After initial checkout and startup procedures were completed, the PFU commenced regular cabin-air measurements on 6/6/10. Typical PFU operations since that date have been to perform 3-7 trace VOC and two MCA measurements per week. As part of VCAM's on-orbit validation, VCAM is performing co-temporal and co-spatial measurements with Grab-Sample Container (GSC) acquisitions made by the crew. A large number of GSCs were returned to earth on STS-133 and will be analyzed by the JSC toxicology personnel with their GC/MS laboratory instrument. When completed, a comparison of the two results will become the basis of gauging VCAM's accuracy and precision. Whenever possible, TG measurements were also scheduled co-temporally with those performed by the STDO GC/DMS currently in the Destiny laboratory.

Future developments for VCAM are directed along two paths. The first is to include water-quality monitoring by addition of a water-extraction subassembly that is homogeneous with VCAM's modular design. The second path is to continue the development towards subassemblies having yet lower mass, volume and power. Electronics developments include miniaturization of conventional power supplies to chip size; miniaturization of the RF NCO electronics card to chip size; and use of carbon nanotube arrays to effect ionization of the analytes within the trap.

III. VCAM Measurements

A. Measurements of Trace Volatile Organic Compounds in the ISS Atmosphere

For trace VOC analysis the targeted SMAC species are divided into three priority classes: *Priority 1* species (nine total) including ethanol, acetone, dichloromethane, and perfluoropropane; *Priority 2* (16 total) including benzene, C5-C8 alkanes and C3-C8 aldehydes; and *Priority 3* (12 total) including 2-butanone, freon-11, and freon-12. Summarized in Table 1 are the 32 chemical species and their associated concentration ranges over which VCAM was required to operate autonomously. An extensive validation program completed in September 2009 confirmed that the PFU met or exceeded all requirements for identification (> 90%), quantization accuracy (< 40%), and 24-hour precision (< 20%). Upon initiation of VCAM operations it was apparent that the normal concentrations of many of trace organic species in the ISS atmosphere were actually much lower relative to originally-specified VCAM requirements. On 7/2/10, about one month into operations, a halogen lamp that heats the Paul ion trap mass spectrometer ceased nominal operations. In order to extend the PFU quantization limits down to the characteristic ISS concentration levels and recalibrate for operations without the bulb heater, a series of additional measurements were executed using both the PFU and laboratory DU. Two recalibration methods were employed. The first used an extrapolation of the existing high concentration instrument response curves, generated in the 2009 Validation test program, down to lower concentrations. The second employed testing, on the DU, cocktails of the required SMAC chemicals at ISS-like concentrations. These new response curves were then used with the PFU. The two methods were in excellent agreement and yielded only modest increases in the quantization error. Longer term, in order to recover nominal instrument performance, a patch cable to ISS was wired and tested that when installed would allow a backup halogen heater bulb to be energized. The patch cable was delivered to ISS on STS-133. The astronauts are scheduled to install it in May, 2011. Summarized in Table 1 are the extended concentration detection limits for operations with and without the MS heater. The two measurement conditions have similar limits of detection, but measurements performed without the MS heater are unable to detect several chemicals at the concentrations typically found in the ISS atmosphere (*e.g.*, the siloxanes and 2-butanone).

Shown in Figure 3 are examples of ion chromatograms normally obtained for TG measurements of the ISS atmosphere when the MS heater is energized (Fig. 3 bottom) or not energized (Fig. 3 top). It is evident from the plots that measurements performed without the MS heater exhibit significant tailing in the polar-species elution peaks. This is due to the polar species absorbing and desorbing from the MS interior surfaces, a phenomenon often seen in terrestrial ion trap mass spectrometry. Some species, such as 1-butanol, although readily detected and quantified when the MS heater was operational became undetectable without the MS heater at concentrations typically found in the ISS atmosphere. Because of the good chromatographic separation, in most cases the tailing had little impact on

analytical performance, but the tailing did cause obscuration of some minor peaks. For example, acetone tailing obscured the minor ethyl acetate and 2-butanone peaks. The tailing also led to co-elutions between ethanol and 2-propanol, both present at relatively high concentrations. Although 2-propanol and ethyl acetate were readily identified as persistent compounds in the cabin atmosphere, the data analysis was unable to provide an accurate quantization. Following tests performed on the DU using ISS-like cocktails of chemicals, it is expected that after the spare bulb is energized the PFU will regain analytical performance for many chemicals (Table 1, Column 3).

It is significant to note that a large number of chemical species that were *not* part of the original VCAM requirements list have been detected in the ISS atmosphere. Using the standard NIST MS database and the properties of the VCAM GC column these additional species were readily identified, highlighting the advantages of a GC/MS instrument for analyzing atmospheres with *unknown* target species. Some minor peaks have two or three possible identifications. It is expected that discussions with JSC toxicology personnel will resolve ambiguities. Summarized in Table 2 is a list of the additional, non-targeted chemicals that have been detected as persistent or intermittent constituents of the ISS atmosphere. As yet no ground tests have been performed using these chemicals to accurately determine their ISS concentrations, but an upper bound of approximately 0.05 mg/m^3 (10 ppb) can be assigned. Trending graphs for the persistent compounds detected in TG measurements of the ISS atmosphere are shown in Figures 4-13. Not shown is a graph for the trending of furan concentration. Furan is always detected in TG measurements, but its concentration is consistently below 1 ppb (0.003 mg/m^3), at the limits of quantization.

Performance results were presented in January 2011 to technical team members from the VCAM project, the ISS Program, NASA Environmental Health, NASA HQ, and an independent technical referee for evaluation. At that time only a preliminary assessment of VCAM performance could be made using the results obtained from mini-GSCs analyzed by the JSC Toxicology Group from GSC samples collected on 9/15/10, 10/14/10, and 11/24/10. VCAM TG measurements performed co-temporally and co-spatially with the mini-GSC samples identified a total of 24 compounds in the ISS atmosphere, 11 of which were on the SMAC target list. There was very good agreement when compared to species and concentrations in the three mini-GSC sampling events. The only exception was non-detection of ethyl acetate during the 9/15/2010 event. Analysis for ethyl acetate was hampered by the VCAM MS heater being non-operational during this period. For the 11 VCAM target compounds that allowed comparison with mini-GSC quantitative results, eight were found to be within $\pm 40\%$ of the discrete concentrations reported for the mini-GSC analysis, with discrepancies for isoprene, ethanol, limonene, and perfluoropropane. When the backlog of archival GSCs returned on STS-133 have been analyzed, a comprehensive comparison to VCAM results will be performed and results published.

B. Measurement of the Major Constituents in ISS Atmosphere

Also performed during VCAM's operational period were autonomous measurements of the major constituents of the ISS atmosphere. On average, these measurements were scheduled to be performed twice per week and when possible, during major ISS docking events with ATV, HTV, and shuttle. In the major constituents mode of operation, pulses of cabin atmosphere bypass the GC and are directly injected into the MS. The trapped ions are then mass analyzed at the nominal rate of 50 Hz. The instantaneous ratios of the ion intensities of the N_2^+ , O_2^+ , CO_2^+ , and Ar^+ mass lines are then used to derive the partial pressures of these species. Equivalent measurements are also performed on board ISS by the Major Constituents Analyzer (MCA), an operational element of the ISS Environmental Control and Life Support System (ECLSS). The MCA is a magnetic sector mass spectrometer mounted in the US Destiny Laboratory Module. The MCA monitors the six major atmospheric constituents N_2 , O_2 , H_2 , CO_2 , CH_4 , and H_2O . Graphs showing the VCAM and MCA partial-pressure measurements of the major constituents are shown in Figs 14-17. There is excellent agreement between MCA and VCAM results: both sets of data track the major trending events with an accuracy in the VCAM data equivalent to that of the operational MCA instrument.

IV. Conclusions

A preliminary comparison indicates that VCAM is returning excellent qualitative results and good quantitative results for 11 compounds for which direct comparisons can be made to discrete concentrations reported from three mini-GSC samples. The VCAM instrument is returning excellent qualitative results on target compounds; and good quantitative results in spite of the MS heater failure. This demonstrates an operational flexibility beyond that expected for an instrument of its class. VCAM has been evaluated to be a viable part of the overall technical solution

to cabin-atmospheric monitoring for long-term human exploration. Qualitative major constituents analysis and trending as compared to the ISS MCA is excellent. This capability makes the VCAM a valuable backup to the ISS MCA for cabin-atmosphere major constituent analysis. Continued development of VCAM toward improved quantitative performance and component reliability is highly recommended and should receive priority by NASA and ISS Program technology development organizations. VCAM demonstration on board the ISS will be continued as consumables and funding permit. Priority will be given to returning regular-sized GSC canisters for comparison to VCAM results for the time period 6/10-12/10; as well as more recently acquired samples through STS-133/ULF5 return. Efforts should be made to return the VCAM ISS to Earth post-flight evaluation.

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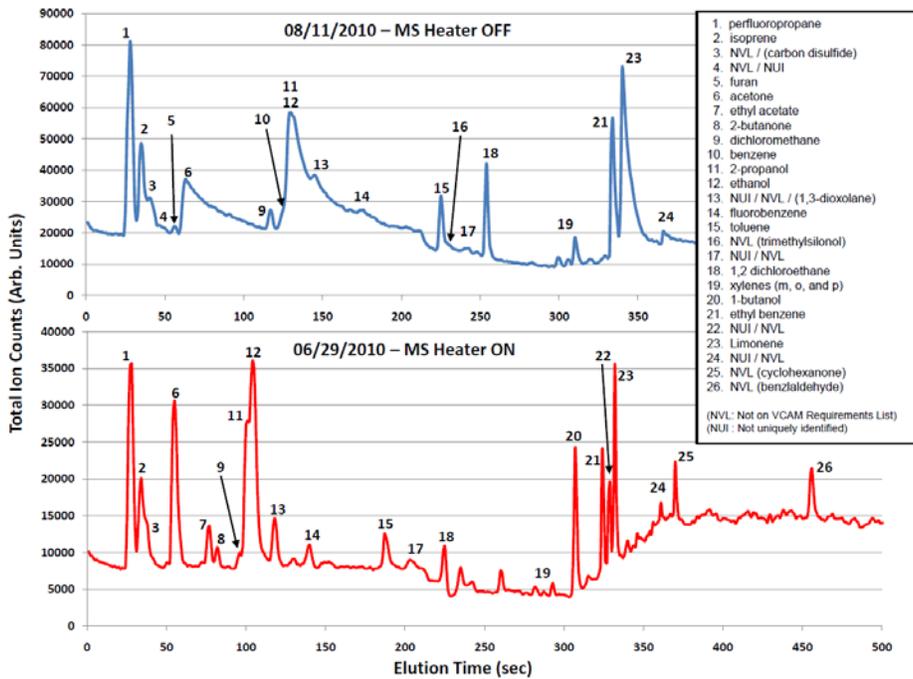


Figure 3. Total Ion Chromatograms Obtained During VCAM ISS Trace Gas Measurements. Examples of ion chromatograms obtained during TG measurements of the ISS atmosphere when the MS heater was off (top) on [8/8/August 8, 2010](#). Also shown is the ion chromatogram obtained with the MS heater on (bottom) on [6/29/June 29, 2010](#). The chemical identification of the elution peaks is obtained by matching the peak number to the chemicals listed in the text box [inset](#) on the right.

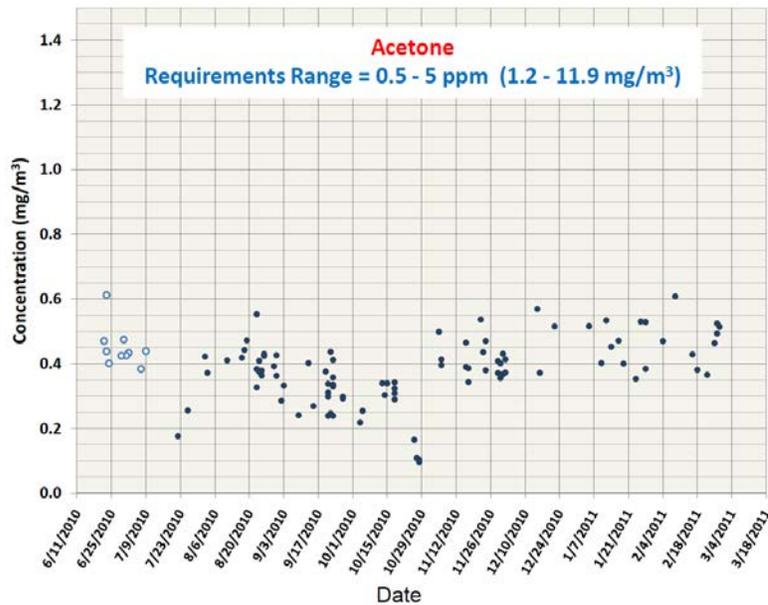


Figure 4. Acetone Concentration in the ISS Atmosphere Obtained from VCAM TG Measurements. Data [is-arc](#) for PFU measurements obtained with MS heater ON (open circle) and MS Heater OFF (closed circles). Absolute error in the acetone concentration is approximately 70% and the concentration precision (repeatability) over any 24-hour span is less than 20%.

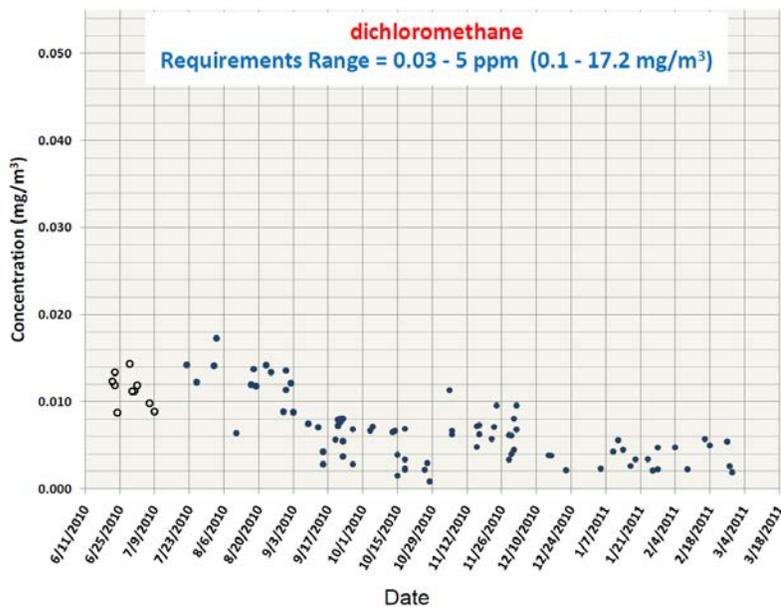


Figure 5. Dichloromethane Concentration in the ISS Atmosphere Obtained from VCAM TG Measurements. Data [is-arc](#) for PFU measurements obtained with MS heater ON (open circle) and MS Heater OFF (closed circles). Absolute error in the dichloromethane concentration is approximately 60% and the concentration precision (repeatability) over any 24-hour span is less than 20%.

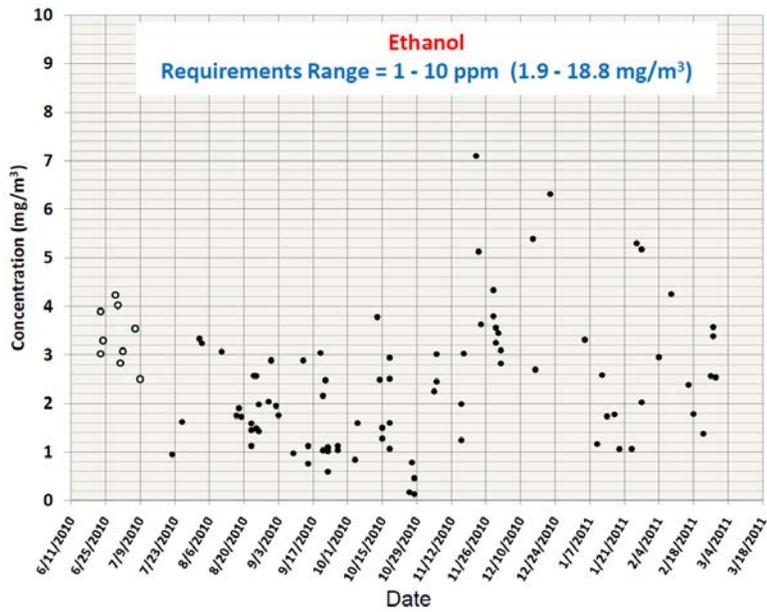


Figure 6. Ethanol Concentration in the ISS Atmosphere Obtained from VCAM TG Measurements. Data [is are](#) for PFU measurements obtained with MS heater ON (open circle) and MS Heater OFF (closed circles). Absolute error in the ethanol concentration is approximately 70% and the concentration precision (repeatability) over any 24-hour span is less than 20%.

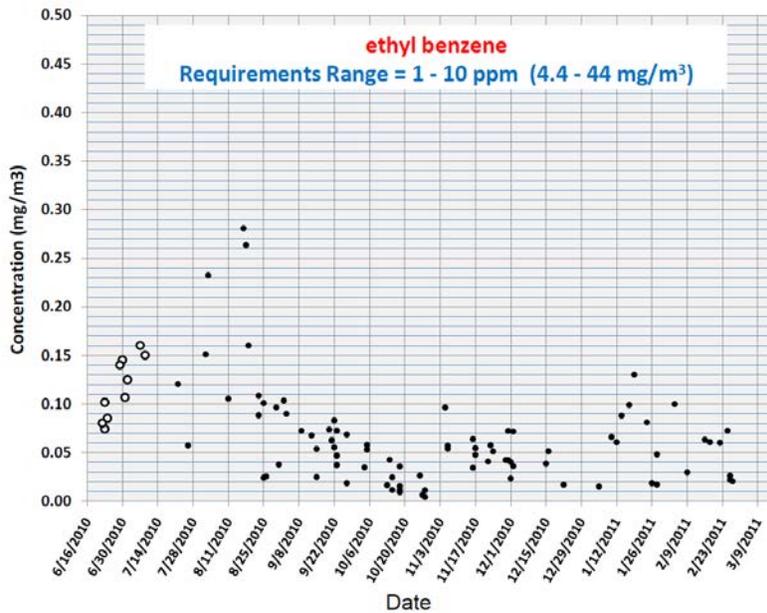


Figure 7. Acetone Concentration in the ISS Atmosphere Obtained from VCAM TG Measurements. Data [is are](#) for PFU measurements obtained with MS heater ON (open circle) and MS Heater OFF (closed circles). Absolute error in the ethyl-benzene concentration is approximately 80% and the concentration precision (repeatability) over any 24-hour span is less than 20%.

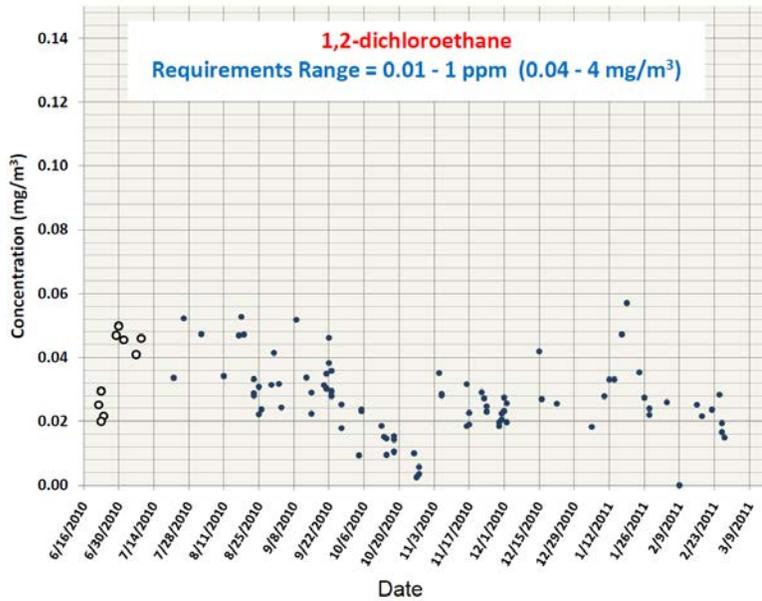


Figure 8. 1,2-Dichloroethane Concentration in the ISS Atmosphere Obtained from VCAM TG Measurements. Data ~~is~~ are for PFU measurements obtained with MS heater ON (open circle) and MS Heater OFF (closed circles). Absolute error in the 1,2-dichloroethane concentration is approximately 70% and the concentration precision (repeatability) over any 24-hour span is less than 20%.

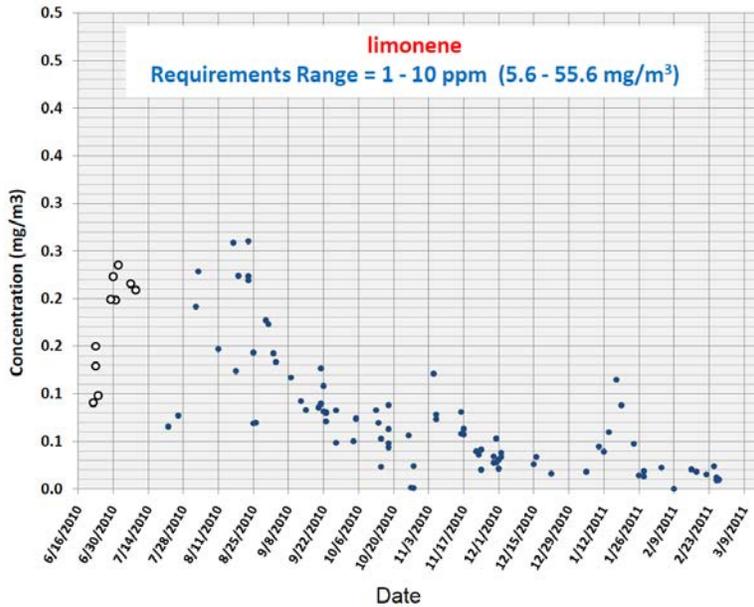


Figure 9. Limonene Concentration in the ISS Atmosphere Obtained from VCAM TG Measurements. ~~Data is~~ Data are for PFU measurements obtained with MS heater ON (open circle) and MS Heater OFF (closed circles). Absolute error in the limonene concentration is approximately 180% and the concentration precision (repeatability) over any 24-hour span is less than 20%.

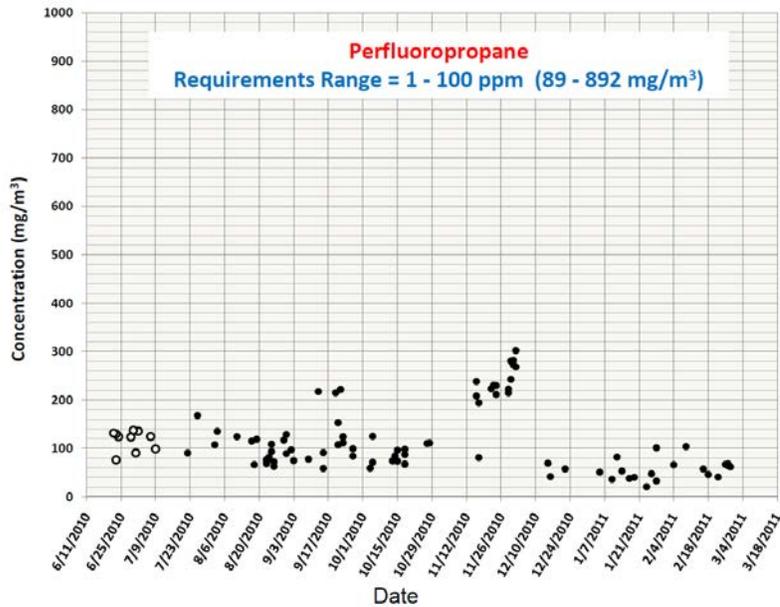


Figure 10. Perfluoropropane Concentration in the ISS Atmosphere Obtained from VCAM TG Measurements. Data is [is-arc](#) for PFU measurements obtained with MS heater ON (open circle) and MS Heater OFF (closed circles). Absolute error in the perfluoropropane concentration is approximately 120% and the concentration precision (repeatability) over any 24-hour span is less than 20%.

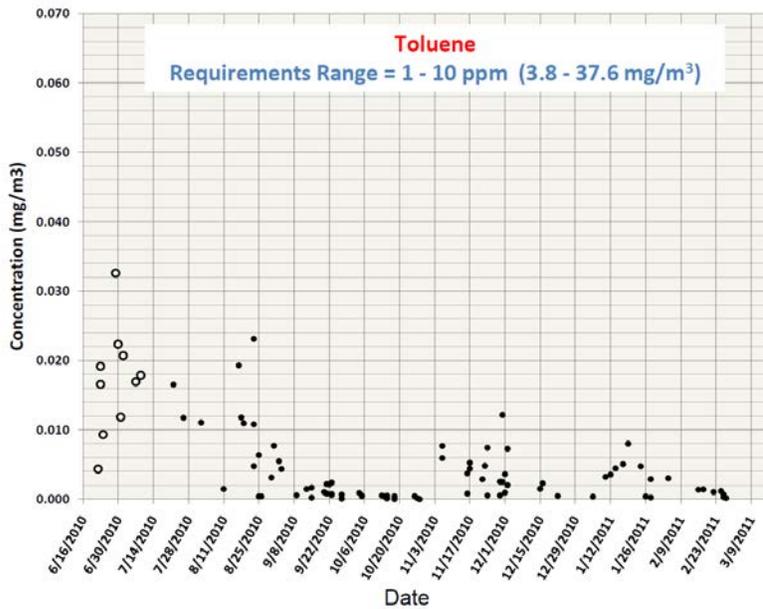


Figure 11. Toluene Concentration in the ISS Atmosphere Obtained from VCAM TG Measurements. Data is [is-arc](#) for PFU measurements obtained with MS heater ON (open circle) and MS Heater OFF (closed circles). Absolute error in the dichloromethane concentration is approximately 100% and the concentration precision (repeatability) over any 24-hour span is less than 20%.

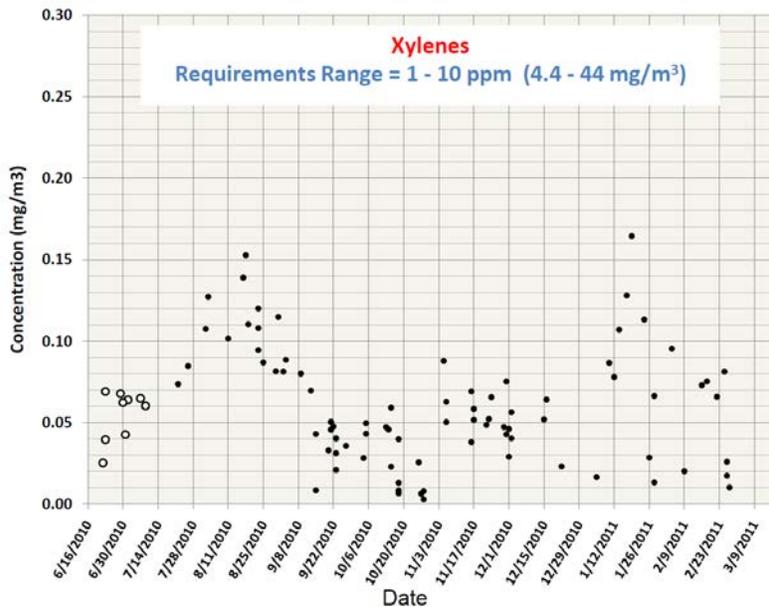


Figure 12. Xylenes (*o*-, *m*-, *p*- and *p*-) Concentration in the ISS Atmosphere Obtained from VCAM TG Measurements. Data is are for PFU measurements obtained with MS heater ON (open circle) and MS Heater OFF (closed circles). Absolute error in the xylenes concentration is approximately 100% and the concentration precision (repeatability) over any 24-hour span is less than 20%.

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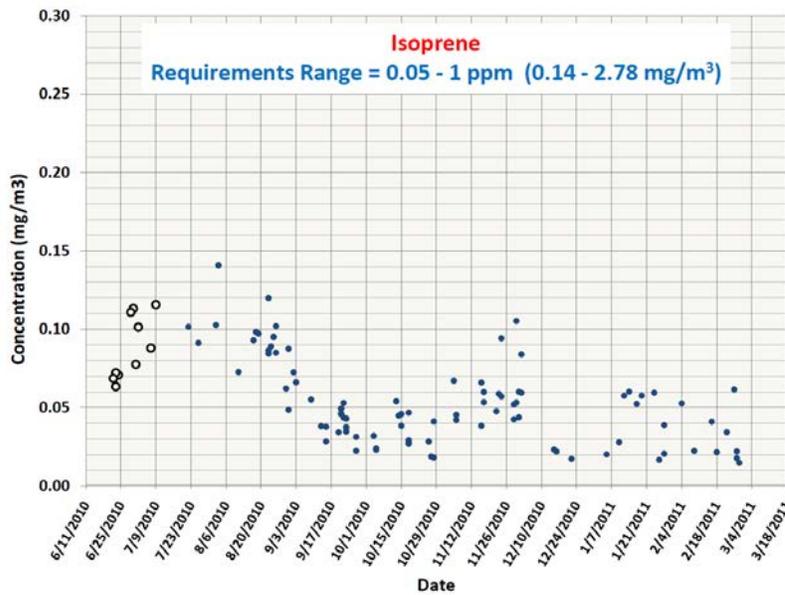


Figure 13. Xylene (*m*-, *o*- and *p*-) Isoprene Concentration in the ISS Atmosphere Obtained from VCAM TG Measurements. Data is are for PFU measurements obtained with MS heater ON (open circle) and MS Heater OFF (closed circles). Absolute error in the isoprene concentration is approximately 50% and the concentration precision (repeatability) over any 24-hour span is less than 20%.

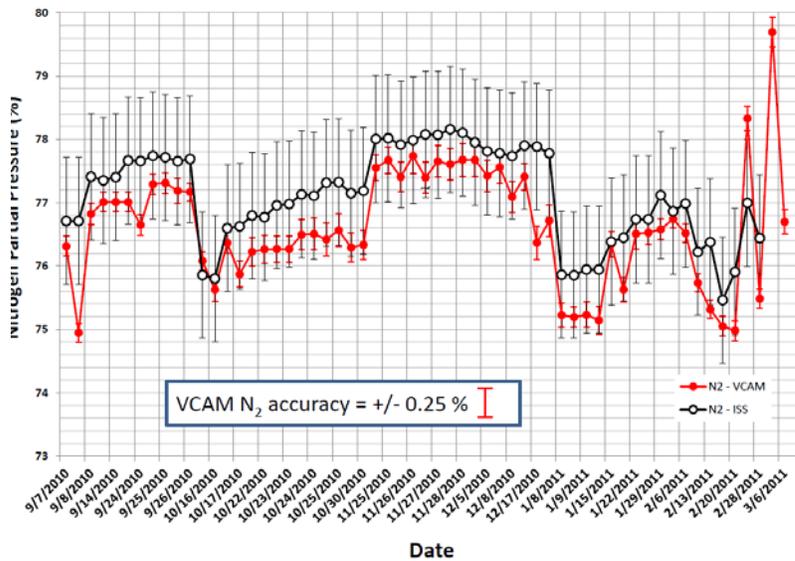


Figure 14. Nitrogen Partial Pressure- in the ISS Atmosphere Obtained from VCAM -Major Constituents Measurements. Data [is are](#) for VCAM PFU measurements (closed circles) and those obtained from the MCA (open circles). VCAM's absolute error in the partial pressure of nitrogen is approximately $\pm 0.25\%$.

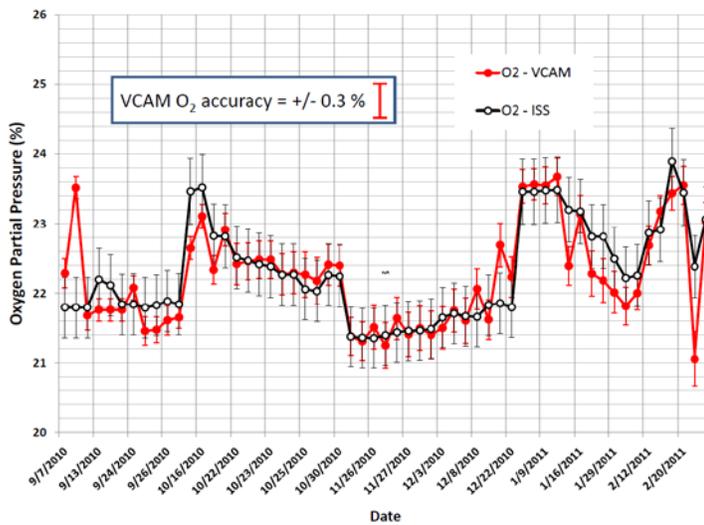


Figure 15. Oxygen Partial Pressure- in the ISS Atmosphere Obtained from VCAM -Major Constituents Measurements. Data [is are](#) for VCAM PFU measurements (closed red circles) and those obtained from the MCA (open circles). VCAM's absolute error in the partial pressure of oxygen is approximately $\pm 0.3\%$.

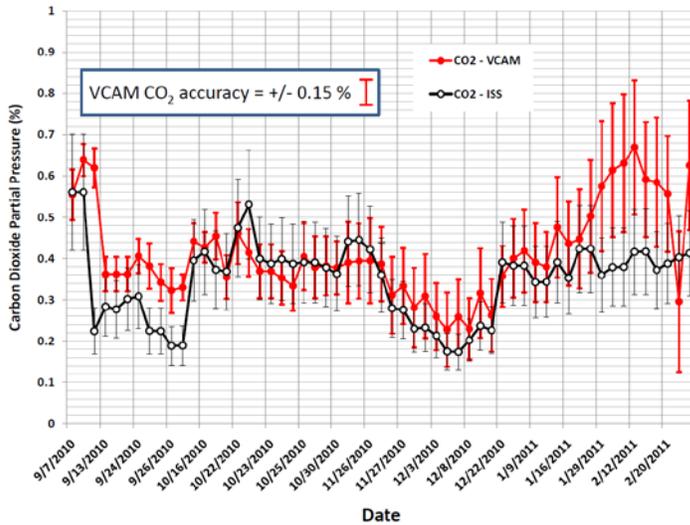


Figure 16. Carbon Dioxide Partial Pressure– in the ISS Atmosphere Obtained from VCAM– Major Constituents Measurements. Data [is are](#) for VCAM PFU measurements (closed circles) and those obtained from the MCA (open circles). VCAM’s absolute error in the partial pressure of carbon dioxide is approximately $\pm 0.15\%$.

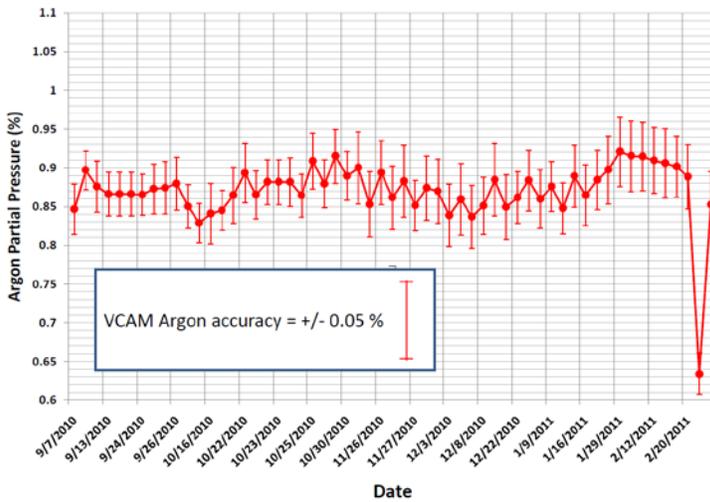


Figure 17. Argon Pressure– in the ISS Atmosphere Obtained from VCAM– Major Constituents Measurements. Data [is are](#) for VCAM PFU measurements where the absolute error in the partial pressure of argon is approximately $\pm 0.05\%$. [Argon is not a targeted species in the MCA, and hence no MCA data are available.](#)