

Evaluation of a Humidity Insensitive Sorbent-Based Air Sampling System

A. Flanagan^{1*}, D. Braithwaite², T.S. Topham², G.E. Bingham² and O. Monje³

¹Limerick Institute of Technology, Limerick, Ireland

²Space Dynamics Laboratory, Logan UT, USA

³Dynamac Corporation, Kennedy Space Center, FL, USA

* Email address: Aisling.O.Flanagan@nasa.gov

Abstract

Optimum plant growth in controlled environment chambers is generally attained at high relative humidities (60-75%). However, humid environments can interfere with air sampling methods utilizing thermally desorbing compounds to monitor volatile organic compounds (VOCs) in plant chambers. Co-adsorption of water vapor may interfere with quantitative analysis by decreasing the adsorptive capacity of the sorbent or reduce recoveries due to gas chromatographic artifacts. The objective of this study is to evaluate the performance of a sorbent-based air sampler designed specifically to minimize the effects of humidity. The sampling system was challenged with plant-produced VOCs at 70% relative humidity. The air sampler was used to monitor the air quality of radish plants growing in low mass plant chambers.

Introduction

Sampling of volatile organic compounds (VOCs) in spacecraft cabin air is needed for ensuring that crew health is not threatened when the concentrations of these VOCs exceed the Spacecraft Maximum Allowable Concentrations (SMACs). VOCs are produced by crew metabolism, in-flight operations, and off-gassing from hardware components (Limero et al., 2005). Sampling systems like the Grab Sampling Containers (GSC) has been used on ISS and Shuttle, while the Solid Sorbent Air Sampler (SSAS) has been used on Mir and ISS. Recently, a Dual Sorbent Tube system has been used on ISS because of reduced masses and volumes allotted for the sampling devices (Limero et al., 2005).

The SSAS and DST systems have made use of thermally regenerable adsorbents to trap VOCs in orbit, store them during return to Earth, and allow subsequent quantification using analytical methods. These adsorbents provide a time-integrated sample of cabin air because they are typically acquired over a 24h period (Limero et al., 2005). The adsorbents considered for use in DSTs include Tenax Ta, Carbotrap/Carboxen 569, Tenax TA/Carbosieve S111, and Tenax-Ta/Carboxen 569 (Matney et al., 2000). The optimum adsorbent trap composition was chosen based on the highest overall recovery of a 10-component gas mixture in both dry and humid conditions.

Studies for sampling plant produced VOCs (e.g. ethylene, acetone, and ethanol) from high humidity environments (60-80%) in plant growth chambers have found that water vapour can interfere with the trapping of VOCs by Carbosieve S111, a thermally regenerable adsorbent used for C2-C4 compounds (Monje et al., 2005). Unlike Tenax TA, C molecular sieves (e.g. Carbosieve S111 and Carboxen 569) were found to co-adsorb 15-25% by weight of water, which decreased their adsorptive capacity causing a decrease in breakthrough volume (Helmig and Vierling, 1995; Monje et al., 2007). A technique for minimizing the effects of humidity is to heat the sorbent filter tube by several degrees above air temperature while sampling the atmosphere (Karbiwiyk et al., 2002).

The goals of this study were:

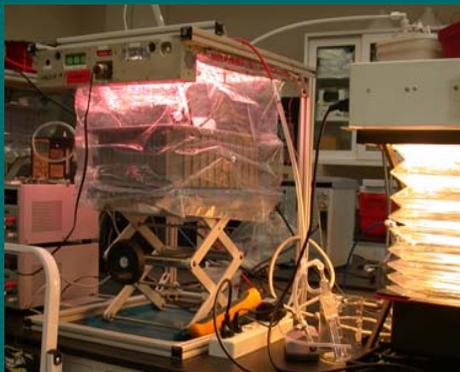
- Develop the methodology to test sorbent-based sampling techniques.
- Evaluate the performance of a sorbent-based air sampling prototype that heats the air during sampling.
- Test the hypothesis that heating the tube will increase the adsorptive capacity of ethanol onto Carbosieve S111 when used in high humidity environments.



Above view of the STS unit, showing the control circuit board, and the sorbent tube within the tube holder (right).



Figure 2. The sampling apparatus consisted of a tube connected to a valve, in turn connected to a 60ml syringe, and then to a 1L Tedlar bag.



The experimental set-up, (from left to right) The SKC Airchek Sampler, the Low Mass Veggie Chamber, the EtOH Impinger, and the STS.

Materials & Methods

Chamber Sampling Procedure. The ethanol concentration of a sealed low mass Veggie chamber (Orbitec, Madison, WI) was increased by bubbling air through an impinger containing 15% EtOH/H₂O (Fig. 1). Plant transpiration and soil evaporation maintained a high relative humidity (70-75%) in the chamber. Chamber temperature was measured to be 25°C±2°C. Chamber air was sampled through tubes using two air samplers. Chamber ethanol concentration was monitored periodically using a custom-made sampling apparatus (Fig. 2).

Commercial Adsorbent – Carbosieve S111 is a carbon molecular sieve with 60/80 mesh size, a packing density of 0.76 g/ml, and a surface area of 820 m²/g. Carbosieve S111 was found to be a very effective adsorbent for ethanol (Monje et al., 2007), which is a major functional class of spacecraft TCs. The adsorbent tubes (4mm diameter) were packed with 100 mg of Carbosieve S111. It has been found that humid samples breakthrough sooner, on Carbosieve S111, adsorbing less volume of VOC. When the humidity levels were lowered, or the tube was kept dry, the compound adsorbed VOC in larger amounts (Monje et al., 2007).

Sorption Tube System (STS) Sampler. The STS (Space Dynamics Lab, Logan, UT) is a programmable air sampler designed to sample a predetermined volume air (Fig. 3). The user interface (Sopware) sets the desired the sample volume, the number of pump intervals, and the sampling flow, as well as start and end times. As opposed to commercially available units, the STS controls of the temperature of the sorbent tube during sampling. It achieves this through the sorbent-packed tube being fitted into a heater (Fig. 4), controlled by two sensors; one monitoring the ambient air temperature, the other the temperature of the sorption tube. The unit also has a user-friendly user interface system.

The Control Air Sampling Unit. An SKC Airchek Sampler, Model 244-PCXR8, was used in this evaluation, as a representation of the commercially available air sampling units. It is possible with this unit, to pre-set a delayed start, as well as to control the pump flow, and duration of the sampling period. This unit applies no heat to the sorption tube.

Desorption Efficacy - The amount of ethanol (measured in µmol) adsorbed in the tubes was determined by desorbing the tube with a Short Path Thermal Desorption System (Model TD-4, Scientific Instruments; Ringoes, NJ). Desorption was conducted at 200 °C for 30 minutes using ultrapure He purge gas at ~10 mL/min. A custom receptacle was added to allow the tubes to be desorbed into evacuated 1L bags. An Electronic Control Unit controls the TD-4 and allows automated operation including automatic injection, timed desorption, and temperature ramping of heater block.

The purged gas was collected in a 1L Tedlar bag and the amount of ethanol in the tube was measured using a GC/FID. This method allowed detection of large concentrations of ethanol in a single desorption event.

Gas Concentration Analysis - Gas concentration from atmospheric samples, and from sorbent desorption samples were determined with the analytical gas chromatograph methods described in Monje et al. (2005). The ethanol elution peaks were integrated and the area was used to determine the concentration of ethanol in the samples. Sample concentration was calculated by comparing the area of the samples to the reference area and concentration. The total concentration of ethanol in the desorption samples was calculated from the recorded flow rate, volume and areas measured by the gas chromatograph, (GC), (Hewlett Packard 6890).

Sorption Tube Regeneration - The sorption tubes were cleaned overnight in a Desorption Tube Conditioning System (Model TD-6, Scientific Instruments; Ringoes, NJ) oven at 300 °C using ultrapure He purge gas at 4 mL/min. No loss of adsorptive capacity was ever detected after numerous (>10) adsorption / regeneration.

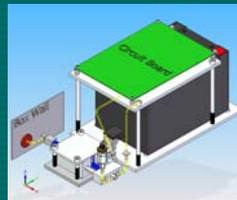


Figure 3, schematic of the Sorption Tube Unit. The main unit components are the tube sleeve (with heater), flow controller, control circuit board, and 12V battery.

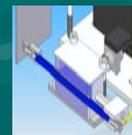


Figure 4, bisected view of the STS's tube sleeve, where the heater is located.

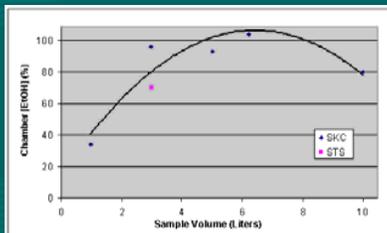


Figure 5, Concentrations measured at ambient temperature.

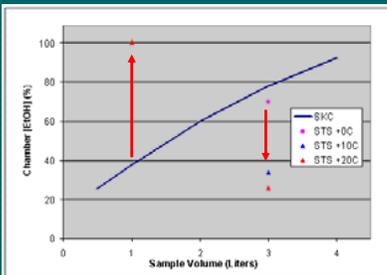


Figure 6, Concentrations measured with and without heating

Results & Discussion

The unheated, control SKC Airchek adsorbent tubes needed to sample up to 6L of air to capture enough ethanol to measure 100% of the chamber ethanol concentration (Fig. 5). At lower volumes, the sampler underestimated the chamber concentration by up to 60%, while at volumes greater than 6L the chamber concentration was also underestimated, probably because the sorbent began to elute VOC from the tube, comparable to when breakthrough volumes are exceeded in Carbosieve S111 at high humidities. The unheated STS gave similar results to the SKC Airchek sampler. When 3L of chamber air was sampled using the STS, the measured 70% of the actual VOC concentration, while the SKC measured 80% (Fig. 5).

When an adsorbent tube is heated, two events occur: 1; water co-adsorption is reduced; 2; thermal desorption of the VOCs adsorbed onto the sorbent bed may occur. Warmer air can hold more water, thus the heated tube prevents water vapor from condensing inside the adsorbent tube, reducing co-adsorption (Karbiwiyk et al., 2002). Evidence of reduced water adsorption was observed after tubes were desorbed into Tedlar bags with the TD-4. The tubes that had been heated showed no water droplets, while the control, unheated tubes, had visible water droplets in the bag.

The STS measured a chamber concentration of 100% when 1L of chamber air was sampled and when it was heated to +20°C above air temperature (Fig. 6). The unheated SKC control tube measured only 40% at the same sampling volume. Thus, it appears that heating diminished the sampling volume (eg. from 6L to 1L) needed to measure chamber concentration accurately by reducing water vapor that might have been co-adsorbed onto the adsorbent. However, at a larger sampling volume (3L) heating did not have the same effect. Heating the STS tube to 10°C above air temperature (Fig. 6) decreased its estimate of chamber concentration to 34%, and a further reduction (to 25%) was observed when the tube was heated to 20°C above ambient air temperature. This loss of VOC may be due to thermal desorption of the tube during sampling.

Conclusion

It can be surmised from the findings of this evaluation, that the benefit of heating the adsorbent tube while sampling, reduces the sampling volume required to accurately measure the atmospheric VOC concentration.

References

- T. Limero, S. Beck, P. Cheng, and V. de Vera, 2005. Study of Long-Term Compound Stability in Dual Sorbent Tubes. SAE Paper 2005-01-3093
- M. L. Matney, S. W. Beck, T. F. Limero, J. T. James, 2000. Multisorbent Tubes for Collecting Volatile Organic Compounds in Spacecraft Air. AIAA 61-69-75
- O. Monje, J.T. Richards, I. Erraso, T.P. Griffin, K.C. Anderson, J.C. Sager, 2005. Designing a reusable ethylene filter cartridge for plant hardware: Characterization of thermally desorbing compounds. SAE Paper 2005-01-2953
- D. Helmig, and L. Vierling, 1995. Water adsorption capacity of the adsorbents Tenax TA, Tenax GR, Carbotrap, Carbotrap C, Carbosieve S111, and Carboxen 569 and Water Management Techniques for the Atmospheric Sampling of Volatile Organic Trace Gases. Anal. Chem. 67:4380-4386
- C. Karbiwiyk, C. Mills, D. Helmig, J. Birks, 2002. Minimization of Water Vapor Interference in the Analysis of Non-Methane Volatile Organic Compounds by Solid Adsorbent Sampling. Journal of Chromatography A, 958: 219-229
- O. Monje, J. Catechis, J.C. Sager, 2007. Effects of Relative Humidity on the Adsorption of Dichloromethane by Carbosieve S111.

Acknowledgements

I want to thank Dr. Oscar Monje for his mentorship and support during this research. This work was supported by the Exploration Life Support and the ISS Research Projects of the Exploration Systems Mission Directorate, NASA. I would also like to express my gratitude to FAS, Ireland who selected me to participate in the FAS Science Challenge Internship programme, and Dynamac Corporation who have partnered with this programme, providing internship opportunities.

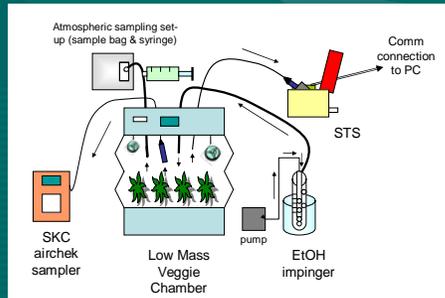


Figure 1, the schematic of the main components and set up of the experimental apparatus.