IN-LAB RAPID ANALYTICAL DETECTION OF LUNAR VOLATILES BY UNIVERSAL GAS ANALYZER WITH COMPARISON TO GC-MS SYSTEM. Saunab Ghosh[1], Ernest K. Lewis[2], Cecilia L. Amick[1], Christopher L. Harris[1], Crystal A. Mantilla[1], Kimberly K. Allums-Spencer[3], Jeremy W. Boyce[4], and Francis M. McCubbin[4]

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Introduction: The drive to collect samples from Permanently Shadowed Regions (PSRs) [1] on the lunar surface is largely based upon the volatiles observed during the LCROSS mission [2]. Advanced curation and allocation techniques under cold conditions are critical to the successful scientific analysis of these returned samples [3]. The rapid detection of important volatiles in returned extraterrestrial samples by a standalone analytical device is an area of intense research interest in our group and the Planetary Exploration & Astromaterials Research Laboratory (PEARL) facility, and this work is relevant to both the future study of samples returned from PSRs and icy regolith simulants for research and curation purposes.

In this context, we discuss in-lab procedures and experimental results for rapid qualitative analysis of the major volatiles detected by the LCROSS (water, H_2S, NH_3, CO_2, and CH_3OH) by a Universal Gas Analyzer (UGA) system, which is equipped with a quadrupole mass spectrometer [4]. The instrument performance was evaluated by measuring the isotopic ratios of known gases (e.g., atmospheric ^{40}Ar to ^{36}Ar). Finally, cross comparisons were made between the UGA and a Trace-1310/ISQ-7000 (ThermoFisher Scientific), Gas Chromatography-Mass Spectrometry (GC-MS) system to develop a robust analytical technique by comparing mass spectral data for H_2S headspace samples. This is a step towards gas analysis using both instruments to characterize the same sample aliquots, in series.

Background: The Stanford Research Systems benchtop UGA 300 instrument is equipped with a quadrupole mass spectrometer and is configured for several types of gaseous chemical analyses [4]. The inlet line continuously samples gases at low flow rates (several milliliters per minute) through a capillary limiting the intake pressure, making the instrument ideal for online analysis of volatiles and room air around atmospheric pressure. Moreover, the current UGA system can detect a change in composition at the inlet in ~200 milliseconds. A complete spectrum is acquired (for a range of 1-100 amu) in under 45 sec with masses measured at rates up to 25 msec per point [4]. This system provides quick upstream analytical data that can be cross-compared to results obtained by our GC-MS system, which essentially uses mass spectrometry for the detection of chemical compounds.

Sample Preparation: A small volume (2-4 mL) of an analyte solution was taken in a 10 mL glass vial and sealed with a crimped cap and purged with ultra-high purity Ar or N_2 gas to displace room air from the top. The headspace samples were scanned by the UGA instrument at analog (Fig 1), histogram (Fig. 2), and pressure vs. time modes (Fig. 4). The isotopic abundance ratio for ^{40}Ar-to-^{36}Ar was estimated by averaging background corrected signal intensity vs. time scans, focused on the mass-to-charge ratios (m/z) 40 and 36 respectively. For signal background correction, corresponding partial pressure focused on the (m/z) 37, was subtracted from each data point.

Results and Discussions: In this work, we have investigated the applicability of the UGA system by qualitative analysis of a series of volatiles measured individually.

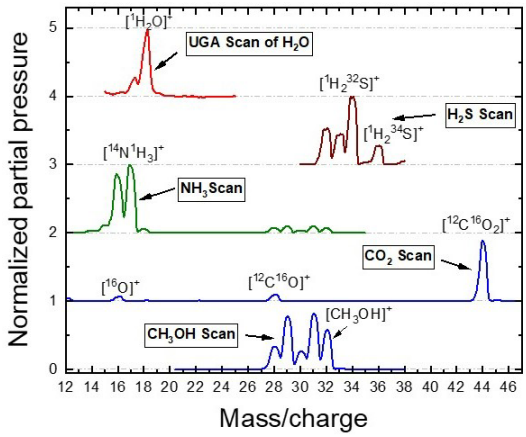

Figure 1. UGA mass spectral scan (partial pressure vs. mass/charge) for a set of five headspace vapor samples. Spectra are normalized and vertically offset for clarity. Molecular and fragment ion peaks (in some cases) are labeled. Spectral regions responsible for each sample are shown.

Figure 1 demonstrates a set of vertically offset spectra for the partial pressures measured as a function of mass-to-charge (m/z) ratios for five volatile samples. The average acquisition time for each spectrum was less than a minute. Therefore, the UGA system is ideal for

quick identification of gas species evolving from volatile-containing samples. For the cross-comparison, an H_2S headspace sample was analyzed by a Trace-1310/ISQ-7000 GC-MS system. The resulting mass spectrum was compared with previously measured UGA histogram scan data (Fig. 2). In both cases, major peak positions were the same, however, the intensities of fragment ions ($[^1H^{32}S]^+$ and $[^{32}S]^+$) were higher for the UGA, suggesting that the fragment ionization process is stronger in the UGA.

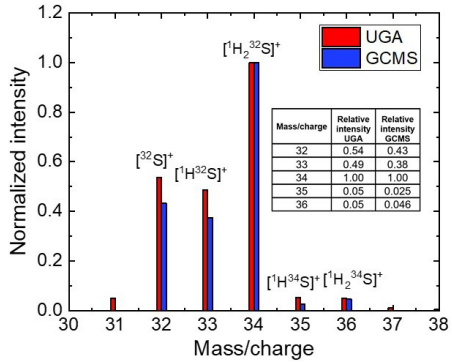

Figure 2. Cross mass-spectral comparison of H_2S headspace samples measured by a UGA (red) and a GC-MS system (blue). Inset table lists relative peak intensities of molecular and fragment ions measured by the UGA and GC-MS system.

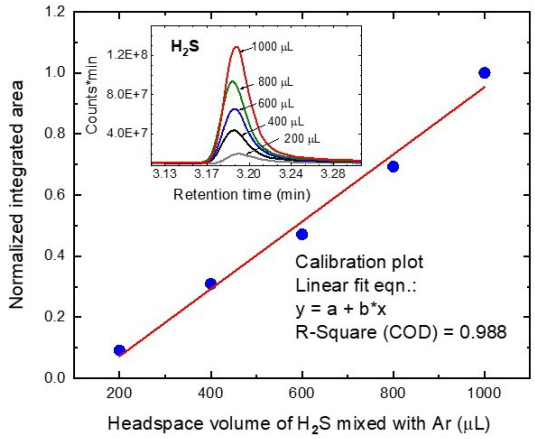

Figure 3. (Inset) GC-MS chromatograms for a set of 5 samples containing incremental volumes of 0.4% H_2S (in water) vapor headspace samples (200-1000 µL) mixed with Ar. The normalized integrated areas are utilized to draw a calibration plot (with a linear fit).

To investigate how the integrated area under each chromatogram varies with the headspace sample volume, a set of five H_2S headspace samples with increasing volumes was analyzed by the GC-MS system (Fig. 3, inset). A small volume (e.g., 200 to 1000 µL) of H_2S/H_2O vapor was extracted from a capped 20 mL stock sample vial containing ~5 mL of 0.4% H_2S in water by a gas-tight syringe and added to a 20 mL vial filled with argon and analyzed by the GC-MS system. Finally, the UGA detector sensitivity was evaluated by calculating the atmospheric ^{40}Ar-to-^{36}Ar isotopic abundance ratio in room air. Figure 4a shows a background corrected partial pressure vs. time scan, focused on the atomic mass 40; the equivalent plot for ^{36}Ar is not shown. Additionally, the calculated ^{40}Ar-to-^{36}Ar isotopic abundance ratios over time plot is shown by Figure 4b. The average $^{40}Ar/^{36}Ar$ ratio is 306 ± 13 (2σ). This calculated abundance ratio agrees with the canonical ratio of 298.56 [5] and the ratio obtained by the GC-MS system ($^{40}Ar/^{36}Ar \approx 303$ for a UHP grade Ar sample).

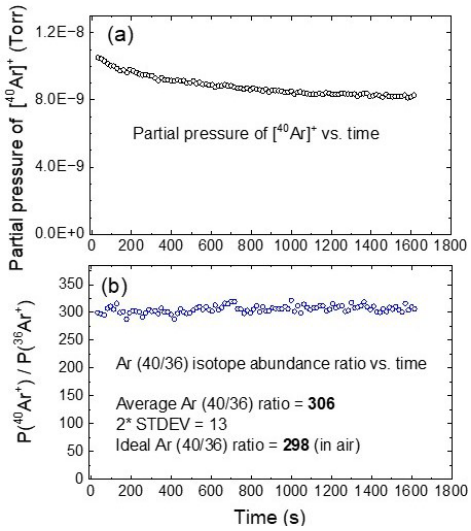

Figure 4. (a) Partial pressure (background corrected) vs. time scan of atmospheric ^{40}Ar in air. The mass-to-charge ratio for scanning was set at 40 to monitor $[^{40}Ar]^+$ species. (b) The $^{40}Ar/^{36}Ar$ isotopic abundance ratios vs. scanning time. Important values are shown.

Conclusions: The benchtop UGA system is a valuable analytical tool for the detection of volatiles from volatile-rich lunar samples. The rapid scanning capability and impressive detection sensitivity prove its worthiness as an essential and economical device for advanced geochemical and curation applications. In addition, cross comparisons with the GC-MS system provide important bridges into advanced curatorial efforts into the future.

References: [1] Bickel, V. T., et al. (2021) *Nat Commun 12*, 5607. [2] Colaprete, A., et al. (2010) *Science 330,* 463-468. [3] McCubbin, F. M., et al. (2019) Advanced Curation of Astromaterials for Planetary Science. *Space Sci Rev 215*, 48. [4] Operation Manual and Programming Reference. (2018) Universal gas Analyzers, Stanford Research Systems. [5] Lee, J. Y., et al. (2006) *Geochimica et Cosmochimica Acta 70,* 4507–4512.